



Impact of Precipitation Physics on CMAQ Wet Deposition Predictions

Ashley Queen¹, Shiang-Yuh Wu², Srinath Krishnan¹, Yang Zhang¹, Jonathan Pleim³,
Shawn Roselle³, and Robert Gilliam³

¹North Carolina State University, Raleigh, NC

²Department of Environmental Quality, Richmond, VA

³Atmospheric Sciences Modeling Division, NOAA, Research Triangle Park, NC

Abstract

Precipitation aids the natural removal of atmospheric pollutants through the process of wet deposition. This process affects the ambient pollutant concentrations along with the amount and chemical composition of ground-level precipitation. Because of the direct linkage between meteorological conditions and types and amounts of atmospheric constituents in precipitation, an accurate representation of meteorological fields is vital for accurate simulations of wet deposition of chemical species by air quality models (AQMs). In this work, performance evaluation is conducted for both meteorological and chemical predictions for August and December 2002 using the Pennsylvania State University (PSU)/National Center for Atmospheric Research (NCAR) Mesoscale Model Generation 5 (MM5)-the U.S. EPA Community Multi-scale Air Quality (CMAQ) modeling system. To understand the uncertainties in simulating precipitation and wet deposition, the evaluation focuses on several most influential parameters including cloud fractions, precipitation, and mass concentrations and wet deposition amounts of sulfate, nitrate and ammonium. Results from the preliminary evaluation of the August baseline simulation show overpredictions of the precipitation, cloud fraction, and wet deposition amounts and underpredictions of the PM concentrations. The December baseline simulation results show overprediction of PM mass concentrations and wet deposition of NH_4^+ and NO_3^- , and both over and underprediction of SO_4^{2-} depending on the observations used in the model evaluation. Both precipitation and cloud fraction are underpredicted by MM5 in December. Sensitivity simulations of MM5 using an alternate cloud microphysics scheme are also performed. The preliminary evaluation of the sensitivity simulation for August 2002 shows an improved model performance for precipitation. Further analysis and additional sensitivity simulations are being conducted to identify major uncertainties in simulating precipitation with MM5 and wet deposition with CMAQ.

Introduction

Air pollution can cause adverse effects on human health and well-being. One control of the amount of atmospheric pollutants is their removal via natural processes. Clouds and precipitation play a critical role in the removal of atmospheric pollutants via wet deposition processes. These removal processes can proceed first with the cloud droplet formation via several mechanisms including heterogeneous nucleation (Iribarne and Cho, 1988; Hallberg et al., 1997; Andronache, 2004) and aerosol activation (Zhang et al., 2002); then with in-cloud scavenging by existing cloud droplets (Hallberg et al., 1997; Andronache, 2004); or below-cloud scavenging by falling precipitation (Andronache, 2004) or both. All of these processes influence the amount and composition of the ground-level rainwater. Therefore, an accurate representation of clouds, precipitation, and cloud scavenging processes is necessary for three-dimensional (3-D) air quality models to realistically simulate the removal of pollutants via wet deposition. An additional intricacy in accurately simulating wet deposition lies in the fact that it depends not only the aforementioned meteorological processes/parameters but also the ambient concentrations of depositing species in both the gas- and the particulate-phase, which are in turn affected by many atmospheric processes such as emissions, transport, gas and aqueous-phase chemistry, aerosol thermodynamics and dynamics, cloud processing of aerosols, as well as dry and wet removals. The model performance for wet deposition and associated uncertainties cannot be fully assessed without examining all these important aspects.

Recent studies have shown sensitivity of the simulated meteorological variables to cloud microphysics schemes (Gilmore et al., 2004; Medaglia et al., 2005). Different microphysical treatments in those schemes can directly affect simulated clouds, precipitation, and wet deposition amounts. The impact of the associated model errors in representing cloud microphysics on simulated wet deposition cannot be well

understood without assessing the appropriateness of those schemes and the importance of model biases in meteorological predictions relative to those in chemical predictions. The main objective of this work is to study major uncertainties in the simulated wet deposition amounts of ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}) using the Pennsylvania State University (PSU)/National Center for Atmospheric Research (NCAR) Mesoscale Model Generation 5 (MM5)-the U.S. EPA Community Multi-scale Air Quality (CMAQ) modeling system. This objective is achieved by first evaluating the impacts of cloud microphysics schemes used in MM5 on the predicted wet deposition amounts through influencing the simulated clouds and precipitation, and then by evaluating the impact of model biases in the simulated PM concentrations on the wet deposition predictions through influencing the amounts of PM available for wet removal. The two types of evaluations involve the use of observational data for meteorological variables such as cloud fractions and precipitation and chemical quantities such as mass concentrations and wet deposition amounts of PM species (e.g., NH_4^+ , NO_3^- , and SO_4^{2-}). As the first step, this study examines the performance of MM5/CMAQ with the default cloud microphysics scheme (i.e., the Reisner 1 scheme) in reproducing two meteorological parameters (i.e., cloud fractions and precipitation) and two chemical quantities (i.e., mass concentrations and wet deposition amounts) and the sensitivity of cloud fractions and precipitation to an alternate cloud microphysics scheme (i.e., the Reisner 2 scheme) used in MM5. Of particular interest to this study is the model performance on predicting the wet deposition of particulate species potentially affected by agricultural emissions of ammonia (NH_3), including NH_4^+ , NO_3^- , and SO_4^{2-} , due to the dominance of agricultural sources in the total NH_3 emissions in the simulation domain of interest (i.e., the state of North Carolina (NC)).

Methods

The study uses the MM5 version 3.7 simulation as input for CMAQ version 4.4. The MM5 simulations are conducted with four-dimensional data assimilation (FDDA) analysis. 3-D analysis nudging is performed for temperature and moisture aloft, and both 3-D and surface analysis nudging are conducted for wind fields. The meteorological output was translated for use in CMAQ by the Meteorology-Chemistry Interface Processor (MCIP). This modeling system is applied for two one-month simulations (August and December 2002) with a 4-km horizontal grid spacing over a domain covering most of NC and portions of the surrounding states. Figure 1 shows the modeling domain with a 4-km horizontal grid spacing and the locations of the measurement sites from all monitoring networks used in the model evaluation. The names of those sites and the associated networks are given in Table 1. The simulations are initialized using initial and boundary conditions generated from the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) 12-km MM5 and CMAQ simulations. No additional spinup is therefore conducted to reinitialize the 4-km simulations. For the baseline simulation, the modeling configurations are kept to be the same as those for the 12-km resolution simulations. For example, the CBM-IV mechanism is used to simulate gas-phase chemistry and the aero3 module is used to simulate aerosol dynamics in CMAQ. More details of model configurations can be found in the modeling protocol for the VISTAS Phase II regional haze modeling (Morris and Koo, 2004). It is important to note that at the 4-km grid resolution, the clouds from the MM5 cumulus parameterizations are not included in the CMAQ cloud module. This adjustment is made based on the assumption that the subgrid-scale clouds, which are parameterized in the cumulus schemes are resolved at 4-km (Roselle and Binkowski, 1999). The baseline CMAQ simulations use MM5 input files generated with the mixed phase (Reisner 1) microphysics scheme. Additional sensitivity simulations for both months are being completed with an alternative microphysics scheme (Reisner 2) that separately considers graupel and riming processes (Reisner et al., 1998).

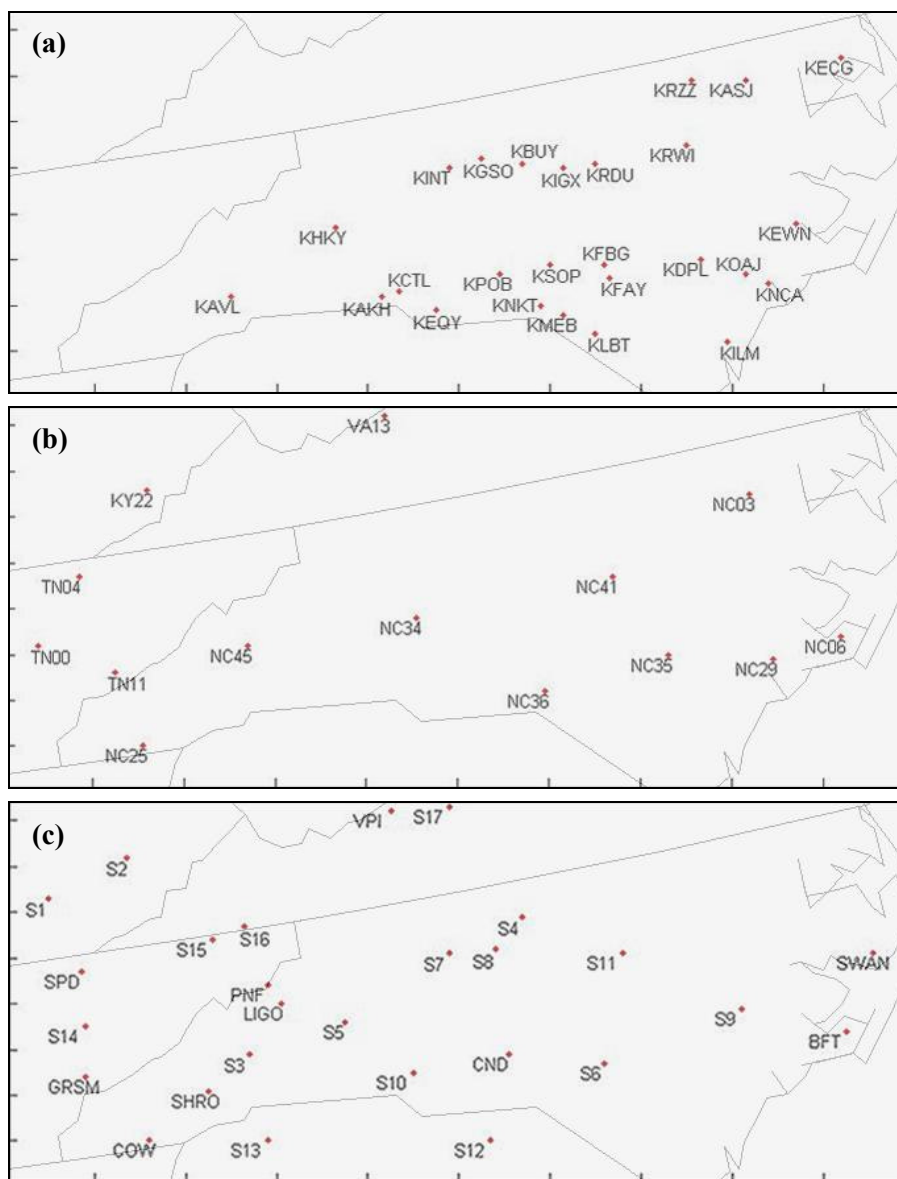


Figure 1. Modeling domain with a 4-km horizontal grid spacing and the locations of measurement sites from (a) ASOS/AWOS, (b) NADP, and (c) IMPROVE, STN, and CASTNet used in the model evaluation. The full names and locations of all measurement sites and their associated networks are given in Table 1.

The simulated fields that are evaluated include 8 parameters, namely, hourly cloud fraction, weekly total precipitation, weekly total wet deposition of NH_4^+ , NO_3^- , and SO_4^{2-} , and daily averaged particulate matter (PM) concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} . Observational data from six monitoring networks are used for model evaluation. These networks include the NC Automated Surface Observation Systems (ASOS), the Automated Weather Observing System (AWOS), the National Acid Deposition Program (NADP), the Clean Air Status and Trends Network (CASTNet), the Interagency Monitoring of Protected Visual Environments (IMPROVE), and the Speciated Trends Network (STN). Table 2 summarizes the total number of sites and sampling times of all observational data and their associated networks that are currently used in this study. The simulated hourly cloud fraction values taken from MCIP are compared with the ASOS and AWOS hourly observations. Only 26 total ASOS and AWOS sites out of a total of 60 NC sites are included in the model evaluation because of the availability of continuous datasets during

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August and December 2002. The remaining sites are excluded because of significant data missing. The weekly precipitation calculated from MCIP and the weekly wet deposition predicted by CMAQ are compared with the weekly NADP observations. Observational datasets from CASTNet, IMPROVE, and STN are used to evaluate model performance for concentrations of PM species in terms of statistical analyses, and temporal and spatial variations.

Table 1. The full names and locations of all 68 measurement sites and their associated networks.

Site ID	Site Name	Network	Latitude	Longitude
KAKH	Gastonia Municipal Airport	ASOS	35.2	-81.1
KAVL	Asheville Regional Airport	ASOS	35.4	-82.5
KBUY	Burlington Alamance Airport	ASOS	36.0	-79.5
KCTL	Douglas International Airport	ASOS	35.2	-80.9
KECG	Coast Guard Air Field	ASOS	36.3	-76.2
KEQY	Monroe Airport	ASOS	35.0	-80.6
KEWN	Craven County Airport	ASOS	35.1	-77.0
KFAY	Fayetteville Airport	ASOS	35.0	-78.9
KGSO	Greensboro Airport	ASOS	36.1	-79.9
KHKY	Hickory Airport	ASOS	35.7	-81.4
KIGX	Chapel Hill-Williams Airport	ASOS	35.9	-79.1
KILM	New Hanover County Airport	ASOS	34.3	-77.9
KINT	Smith Reynolds Airport	ASOS	36.1	-80.2
KLBT	Lumberton Municipal Airport	ASOS	34.6	-79.1
KMEB	Laurinburg-Maxton Airport	ASOS	34.8	-79.4
KRDU	Raleigh-Durham Airport	ASOS	35.9	-78.8
KRWI	Rocky Mount-Wilson Airport	ASOS	35.9	-77.9
KRZZ	Halifax County Airport	ASOS	36.4	-77.7
KASJ	Tri-County Airport	AWOS	36.3	-77.2
KDPL	Duplin County Airport	AWOS	35.0	-78.0
KFBG	Simmons Army Airfield	AWOS	35.1	-78.9
KNCA	New River MCAS	AWOS	34.7	-77.4
KNKT	Cherry Point MCAS	AWOS	34.9	-76.9
KOAJ	Albert Ellis Airport	AWOS	34.8	-77.6
KPOB	Pope AFB	AWOS	35.2	-79.0
KSOP	Moore County Airport	AWOS	35.2	-79.4
KY22	Lilley Cornett Woods	NADP	37.1	-83.0
NC03	Lewiston	NADP	36.1	-77.2
NC06	Beaufort	NADP	34.9	-76.6
NC25	Coweeta	NADP	35.1	-83.4
NC29	Hofmann Forest	NADP	34.9	-77.3
NC34	Piedmont Research Station	NADP	35.7	-80.6
NC35	Clinton Crops Research Station	NADP	35.0	-78.3
NC36	Jordan Creek	NADP	35.0	-79.5
NC41	Finley Farm	NADP	35.7	-78.7
NC45	Mt. Mitchell	NADP	35.7	-82.3
TN00	Walker Branch Watershed	NADP	36.0	-84.3
TN04	Speedwell	NADP	36.5	-83.8
TN11	Great Smoky Mountains National Park-Elkmont	NADP	35.7	-83.6
VA13	Horton's Station	NADP	37.3	-80.6

S1	21-125-0004	STN	37.1	-84.1
S2	21-193-0003	STN	37.3	-83.2
S3	37-021-0034	STN	35.6	-83.4
S4	37-033-0001	STN	36.3	-79.5
S5	37-035-0004	STN	35.7	-81.4
S6	37-051-0009	STN	35.0	-79.0
S7	37-067-0022	STN	36.1	-80.2
S8	37-081-0013	STN	36.1	-79.8
S9	37-107-0004	STN	35.2	-77.6
S10	37-119-0041	STN	35.2	-80.8
S11	37-183-0014	STN	35.9	-78.6
S12	45-025-0001	STN	34.6	-80.2
S13	45-045-0009	STN	34.9	-82.3
S14	47-093-1020	STN	36.0	-83.9
S15	47-163-1007	STN	36.5	-82.5
S16	51-520-0006	STN	36.6	-82.2
S17	51-770-0014	STN	37.3	-80.0
GRSM	Great Smoky Mountains NP	IMPROVE	35.6	-83.9
LIGO	Linville Gorge	IMPROVE	36.0	-81.9
SHRO	Shining Rock Wilderness	IMPROVE	35.4	-82.8
SWAN	Swanquarter	IMPROVE	35.5	-76.2
VPI	Horton Station	CASTNet	37.3	-80.6
COW	Coweeta	CASTNet	35.1	-83.4
PNF	Cranberry	CASTNet	36.1	-82.0
BFT	Beaufort	CASTNet	34.9	-76.6
SPD	Speedwell	CASTNet	36.5	-83.8
GRS	Great Smoky NP-Look Rock	CASTNet	35.6	-83.9
CND	Candor	CASTNet	35.3	-79.8

Given different sampling time resolutions for the observed variables, different time scales are used for comparison of simulated concentrations of PM species against those obtained from the three networks and for comparisons of simulated cloud fractions and precipitations. While the use of different time scales ensures statistical calculations paired with time and space for individual variable from individual network, it, however, creates difficulties and uncertainties in the cross-comparison of variables with inconsistent time scales from different networks. For example, the bias in predicting hourly cloud fractions from ASOS/AWOS is difficult to be linked to the bias in the predicted weekly total precipitation. Similarly, the bias in predicting 24-hr averaged concentrations of PM species (observed values are available every three days) from STN and IMPROVE is difficult to be interpreted to quantitatively indicate the bias associated with the weekly total amounts of PM species available for wet deposition amounts that are measured as a weekly total from NADP. While the hourly precipitation dataset from the national weather service (NWS) are being acquired and will permit a cross-comparison with hourly cloud fractions, we also calculate the monthly-averaged statistics to partially address this temporal inconsistency, in addition to statistics at different time scales. Lack of spatially-located datasets presents another limitation, also making the site-specific comparisons difficult. A careful interpretation of statistics obtained for different parameters at different sites is thus warranted. One approach to potentially address the spatial inhomogeneity is to perform additional evaluations (such as time series comparisons of different parameters and site-specific statistics) by grouping data from sites with similar site characteristics and/or within a distance of proximity (e.g., coastal vs. inland, rural vs. urban, upwind vs. downwind). Nevertheless, despite the sparseness or unavailability of collocated dataset for parameters paired up in space and time across all networks during the simulation period for the domain of interest, the cross-comparisons with different time scales and with monthly-averaged statistics may more or less provide qualitative (if not semi-quantitative or quantitative)

linkages among different parameters and may help identify critical data need for a more rigorous model evaluation.

Table 2. Observational datasets used for the model evaluation.

Network	Parameter/Species		Total Sites Evaluated	Sampling Period
ASOS/AWOS	MET	Cloud Fraction	26	Instantaneous hourly
NADP	MET	Precipitation	14	Weekly total
	WETDEP	NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻	14	Weekly total
CASTNet (mostly rural sites)	PM	NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻	7	Weekly average
STN (urban areas and towns)	PM	NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻	17	1 in 3 days; 24-hour average
IMPROVE (mostly remote sites)	PM	NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻	4	1 in 3 days; 24-hour average

The performance statistics calculated for all eight parameters include both the traditional measures such as the correlation coefficient (r), the mean bias (MB), the mean absolute gross error (MAGE), the root mean squared error (RMSE), the mean normalized bias (MNB), the mean normalized gross error (MNGE), the normalized mean bias (NMB), the normalized mean gross error (NMGE), the fractional bias (FB), and the fractional gross error (FGE) and the new statistical metrics developed by Yu et al. (2003) such as the mean normalized factor bias (MNFB), the mean normalized gross factor error (MNGFE), the normalized mean bias factor (NMBF), and the normalized mean error factor (NMEF). These metrics are calculated over the entire month for the entire domain based on individual observation-model data pairs for all eight parameters using observation time scales from each network. The use of observational data for the concentrations and wet deposition amounts of PM species from three different networks for separate statistical calculations provides a range of statistics for the three networks. In addition to evaluation at observation time scales, statistics are calculated for the monthly averaged observation-modeled data pairs for cloud fractions, precipitation, and wet deposition amount to reduce the influence of different sampling periods of raw data. Monthly-averaged statistics for PM concentrations are not evaluated, however, because of the relatively small number of sites from IMPROVE and CASTNet (4 and 7, respectively). For monthly statistics, all data pairs are averaged over the month at each individual site and the domain-wide statistics are then calculated from the monthly averages at all sites. Preliminary evaluation results with monthly-averaged statistics and those averaged at the observation time scales (i.e., hourly to weekly) are discussed in the following section.

Results and Discussions

Preliminary evaluation for the August baseline MM5 simulation shows that the simulated meteorological parameters are typically not in strong agreement with observed values. For example, the correlation of the simulated and observed weekly total precipitation amounts was weak with a correlation coefficient (r) value of 0.34 (0.39). Simulated and observed hourly cloud fractions during August are in better agreement with an r value of 0.49 (-0.10 for monthly-average). However, both meteorological parameters show moderate model overpredictions, with NMBs of 40.93% (40.95% for monthly-average) and 38.56% (37.71% for monthly-average) for precipitation and cloud fraction, respectively. Meanwhile, the baseline CMAQ simulation shows overall underpredictions for mass concentrations of all three PM species during the month of August with varying correlation coefficient values based on the location and network of the sites. Correlations between the predicted and observed values of PM mass concentrations of NH₄⁺ and SO₄²⁻ are relatively high with values for the three networks ranging from 0.61-0.81 and 0.51-0.86, respectively. Overall, CMAQ significantly overpredicts the weekly total wet deposition of all three species during August, with NMBs of 153.1% (154.7% for monthly-average) for NH₄⁺, 23.4% (26.1% for monthly-average) for NO₃⁻, and 363.5% (367.3% for monthly-average) for SO₄²⁻. The large values of NMB are due to large overpredictions of the wet deposition of NH₄⁺ and SO₄²⁻ during the first week of August, during which the observed values were small, but the modeled values were significantly higher. The model performance for the wet deposition amounts of NH₄⁺ varies both temporally and spatially with most sites having both over- and under-prediction during August. Wet deposition predictions of SO₄²⁻ are also highly variable; in some cases, especially those with low observed SO₄²⁻ values, the predictions are more than

twice the observed amounts. Although domain-wide statistics reflect overpredictions of NO_3^- wet deposition amounts, spatial variations do occur with some sites having modeled values that are 50% or less of the observed values. As shown above, small differences exist between the monthly NMBs and those with the observation time scales for precipitation, cloud fraction, and wet deposition amounts of all species and r for precipitation. However, the correlation between observed and modeled values of cloud fractions on an hourly basis is higher by a factor of 5 than that on a monthly-average basis. Examination of data pairs shows that monthly-averaged hourly simulated cloud fraction values for all sites range 0.42 to 0.50 compared to a range of 0.17 to 0.65 monthly-averaged hourly observed cloud fractions. Values for both observed and simulated individual cloud fraction range from 0.00 to 1.00. Thus, with a limited range of simulated values, the correlation coefficient for the monthly-average cloud fraction values is significantly smaller than that of the individual cloud fraction values.

The preliminary evaluation of the December baseline simulation shows overpredictions of both weekly precipitation and hourly cloud fraction. The calculated correlation coefficients for both parameters are better during this month than during August, with values of 0.52 and 0.36 for weekly total and monthly average precipitation, and 0.71 and 0.17 for hourly and monthly average hourly cloud fraction. The December CMAQ baseline simulation results show a weak correlation between simulated and observed wet deposition values, with values of r ranging from -0.06 to 0.25 for weekly total and -0.15 to 0.42 for monthly averaged wet deposition amount. Overpredictions of wet deposition amounts occur for all three species, with NMBs of 109.1% (111.4% for monthly average) for NH_4^+ , 109.3% (106.9% for monthly-average) for NO_3^- , and 66.9% (66.3% for monthly-average) for SO_4^{2-} . Correlation coefficients calculated using weekly total and monthly averaged values for both NO_3^- and SO_4^{2-} are similar, but differ largely for NH_4^+ r values (0.25 vs. 0.42, respectively). Observed and simulated PM mass concentrations have stronger correlations than those for wet deposition, with values of r from the three observational networks in the ranges of 0.51-0.64, 0.48-0.73, and 0.45-0.46 for NH_4^+ , NO_3^- , and SO_4^{2-} , respectively. Both NH_4^+ and NO_3^- are overpredicted during December, while either overprediction or underprediction may occur for SO_4^{2-} depending on the network. While the r values obtained with monthly average and the observation time scales (e.g., hourly or weekly total) for both cloud fraction and precipitation in December show larger difference than those in August, the NMBs for both evaluation methods remain very similar. The differences in statistics based on monthly averaged and weekly total are small for wet deposition amounts during December. Similar to the comparison for August, the largest difference in the statistical values calculated based on the two different time scales is found in the cloud fraction correlations. During December, correlation coefficients that are based on monthly averaged values for cloud fractions are nearly 5 times smaller than those based on hourly. Similar to results in August, the range of simulated values for the monthly-average cloud fraction (0.33-0.40) is much narrower than that of the simulated individual cloud fraction values (0.00-1.00). This shrinking in the range of simulated cloud fraction explains the large reduction in the correlation coefficient for monthly-average cloud fraction values.

A preliminary comparison between the MM5 baseline and sensitivity simulations for August 2002 has been conducted. Simulated total cloud fraction does not change significantly in the sensitivity simulation, because the cumulus cloud scheme is turned off in the 4-km simulation. The correlation coefficients based on hourly data remain similar for the sensitivity simulation with only a slight increase of the NMB from 38.6% to 39.1%. However, the sensitivity simulation with the Reisner 2 scheme does show significant improvement in the simulated precipitation during August, changing a moderate overprediction with an NMB of 40.9% in the baseline simulation to a slight underprediction with an NMB of -3% in the sensitivity simulation. The statistics based on monthly average and the observation time scales for the two parameters predicted by the sensitivity simulation are similar to those of the baseline simulation. NMBs for both precipitation and cloud fraction have only slight differences. However, correlation coefficients based on different time scales for both parameters are quite different. The values of r are 0.42 and 0.50 for weekly total precipitation and hourly cloud fraction, respectively while the values are 0.23 and -0.08, for monthly averaged precipitation and cloud fraction, respectively.

The baseline simulations for August and December will be further evaluated in terms of temporal and spatial variability. Further analysis is being conducted to understand mechanistically the differences between the MM5 baseline and the sensitivity simulation results using different cloud microphysics schemes. Sensitivity simulations of CMAQ for August (and December, if justified) will be conducted using the meteorological fields from the MM5 sensitivity simulations with the Reisner 2 microphysics scheme.

These results will then be compared with those from the baseline simulation to examine the impacts of alternate MM5 microphysics schemes on the wet deposition predictions by CMAQ. Additional diagnostic and sensitivity simulations may also be conducted to identify other possible reasons for differences between observed and simulated wet deposition amounts.

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Brickmaking in Agricultural Communities in Mexico: Distribution, Fuels Inventory, Emissions, and Effects on Animals and Plants

Miguel A. Rea¹; Ma. Eustolia Rodríguez-Muñoz¹; Miguel A. Rico-Rodríguez¹;
Ana Luz Anaya-Alonso¹ and David A. Grantz^{1,2}

¹Facultad de Química, Universidad Autónoma de Querétaro, Querétaro, Qro. MÉXICO

²Department of Botany and Plant Sciences and Air Pollution Research Center, University of California, Riverside, Kearney Agricultural Center, Parlier, CA USA

Abstract

Rural agricultural communities in the state of Queretaro (Qro.), in the central highlands of Mexico, are often sites of co-located industrial activities to supplement farm income. Notable among these are small-scale brickmaking operations, unlicensed and unregulated, highly contaminating, and located in close proximity to human habitations, field and permanent crops, and domesticated animals. Although small when considered individually, these industrial activities may dominate air quality degradation in these rural areas (Blackman, 2000). These brick kilns are characterized by inefficient combustion of extremely polluting fuels of many types. Similar situations exist in many developing countries, where brickmaking is well established as a significant source of hazardous gaseous and particulate pollutants. Areas of influence of individual brick kilns and of groups of kilns depend on transport and deposition characteristics of the emissions. Magnitudes and risks of exposure depend on the composition of emissions, the relative locations of sources and sensitive sinks, and access to the human food chain. These remain poorly characterized for these agricultural communities. Here we report a multi-scaled analysis of these problems. We have conducted a spatial analysis of the entire state of Queretaro, using GIS and GPS technologies, of the co-location of brick kilns, agricultural fields, exposed human populations, operator-reported fuel inventories, and brick making capacity. We have further characterized the small community of San Nicolas, Tequisquiapan, which exhibits a particularly dense and co-mingled distribution of kilns, crops and human dwellings, and represents 72% of the nearly 500 kilns in the state of Qro. Here we have defined wind patterns, established zones of influence of individual and aggregate sources, determined fuel inventories, and documented the spatial relationships among crop species, population densities and kiln locations. We have obtained photographic evidence of the density of plumes and samples of airborne and soil-deposited particles for gravimetric and chemical characterization. In this community we have determined some biological impacts of emissions on non-domesticated receptor mammals trapped in the wild (field mice: *Myotis spp*), by evaluation of genetic damage in peripheral blood cells using the micronucleus and comet assays. Further work is planned on deposition to vegetation and contamination of grain crops. Our results to date indicate that the human populations of these agricultural communities are at considerable risk of direct exposure to airborne contaminants, and that these contaminants are likely to enter the food chain through exposed crops and domesticated animals, potentially affecting urban populations. In these rural communities agricultural air quality is less impacted by traditional sources of agriculturally-sourced emissions than by co-located primary industries such as brickmaking. The results indicate that the emissions are biohazardous at current exposure levels. In the state of Queretaro, Mexico, approximately 200,000 rural inhabitants may be directly impacted.

Introduction

Agriculture and air quality exhibit many interactions, with effects in both directions. Agricultural communities have traditionally engaged in a variety of light industrial activities to supplement farm income. In these ways, the rural agricultural communities of the state of Querétaro, central highlands of Mexico, are typical. They are often sites of co-located, small-scale brickmaking operations situated in close proximity to human habitations, plantings of a variety of field and permanent crops, and domesticated animals cultivated for meat, milk, and wool.

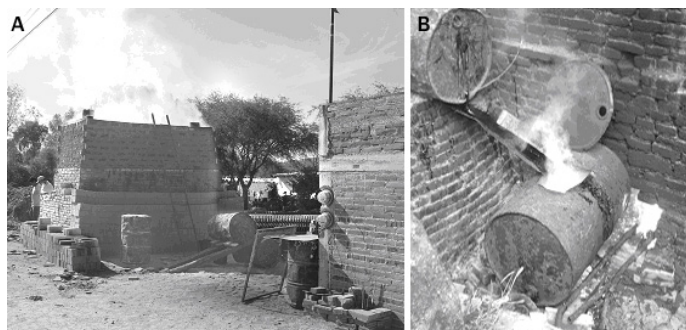


Figure 1. A) Typical co-location of brick kiln, fuel oil supply, and residential compound. B) The fuel feeding system and open hearth of a kiln in San Nicolas.

The brick-making installations provide a dominant source of income in some of these communities. The facilities and artisanal knowledge are handed down through the generations. The bricks are traditionally sun-dried then baked in kilns to produce the required mechanical strength and characteristic red color. A typical oven produces about 10,000 bricks per month, enough to construct about 3.5 typical (22.5 m^3) rooms. However, their copious ‘stack’ emissions to the air (Fig. 1A), their proximity to sensitive receptors, and the unknown nature of transport, deposition and chemical composition of the emissions, have raised serious questions about the sustainability of these agricultural-industrial-residential complexes.

The kilns are built of the locally-made bricks, measuring approximately 27 to 64 m^3 , with an open top some 1.5 -2.0 m above ground, and a base excavated some 1.5 -2.0 m below ground (Fig. 1B). An opening of approximately 50 x 50 cm at below ground level in one wall allows entry of air, and introduction of fuel and water through a locally constructed burner device that introduces a drip of liquid fuel and vaporized water. The burner consists of a piece of U-shaped iron pipe, with separate pressure fittings to allow entry of water and fuel. The water enters through a one-way valve, so that it becomes pressurized in the kiln and is injected alongside the fuel to disperse it throughout the firebox (bottom of Fig. 1B).



Figure 2. A field of grain sorghum nearing harvest in San Nicolas.

A typical brick kiln in the village of San Nicolas, Tequisquiapan, Querétaro is typical of this close association, with residential compounds at right and in the rear (Fig. 1A). Nearby are agricultural fields of sorghum (*Sorghum bicolor* L. (Moench)) and other seasonal crops (Fig. 2). With rough seed heads, the *Sorghum* seems likely to represent an efficient scavenger of particulate emissions.

The kilns are characterized by inefficient combustion of mixed and often extremely polluting fuels (Fig. 1B; Table 1). Liquid fuel may consist of fuel oil, recycled oil or industrial solvents. In other cases, solid fuel is loaded into the kiln, prior to loading the bricks, and manually through the lower opening during firing. Originally this solid fuel was wood, but in more recent industrial times, this has included a wide range of inexpensive, generally waste or recycled materials (Table 1), including garbage, construction waste, cloth and any other combustible that can be obtained economically.

Although there are regional technological differences in kiln design, similar situations exist in other areas of Mexico and in many developing countries, where brickmaking is well established as a significant source

of hazardous gaseous and particulate air pollutants. There has been considerable research into the emissions from similar kilns near the U.S.-Mexican border (TCEQ, 2000), the Indian subcontinent (Devkota and Neupane, 1994; CIDA, 2002), and elsewhere. It has been estimated that a Mexican brick kiln fired with wood emits to the environment approximately 390 kg of pollutants per firing, including NO_x (4.8 kg), CO (280 kg), particulate matter (45 kg) and volatile organic compounds (62 kg) (TCEQ, 2002). The number of brick kilns in Mexico is unknown, except for the reportedly 350 in the Texas-Mexico border (Blackman et al., 2000) and the data for Querétaro state reported below.

Table 1. The range of fuels used in the manufacture of bricks.

Recycled Oil
Fuel Oil
Filter cake from waste water treatment plants
Residual solids from municipal waste
Wax (natural and synthetic)
Used Tires
Plastic waste
Uncharacterized industrial waste from the local industry
Animal manure
Wood dust
Cloth (natural and synthetic fibers)
Construction debris
Refrigerator Insulation

There have been recent efforts (Marquez, 2001) to develop more efficient kilns with correspondingly reduced air emissions. At the present time, the MK kiln appears to be the most promising of these designs (Marquez, 2001); a 54% reduction of emissions has been demonstrated in some cases (TCEQ, 2002). A few models of such kilns are planned for installation in San Nicolas as a demonstration project.

Areas of influence of individual brick kilns and of groups of kilns depend on transport and deposition characteristics of the emissions. Magnitudes and risks of exposure depend on the relative locations of sources and sensitive target sinks, environmental transfer and access to the human food chain, and the chemical characteristics of the deposited emissions. These factors all remain poorly characterized for the agricultural communities of Querétaro, leaving the nature and magnitude of this environmental threat unknown.

The objective of the present preliminary study was to establish the first geospatially referenced inventory of brick making kilns in the state of Querétaro, along with associated information regarding the human and material resources that are devoted to this industry and current methods of kiln operation, including the actual mix of fuels being consumed. Additional objectives were to estimate the magnitude of air pollution and the biological impacts on animals, plants, and humans, and an assessment of the human population that is likely to be directly exposed. We present a multi-scaled analysis of these problems.

Methods

Geo-Referenced Inventory

A member of our team visited every brick kiln in the state of Querétaro, located its position by hand held GPS, and interviewed the brickmakers (owners or operators). These locations were plotted on a topographic map of the state (1:20,000) obtained from the National Institute of Statistics, Geography and Informatics (Instituto Nacional de Estadística, Geografía e Informática) using ArcView v. 3.2. Metadata were appended with additional site information. Population data were obtained from the Mexico National Census, 2000, and from the Mexican National Municipal Information System (INAFED, 2005).

Survey of Brickmaking Operations

A survey was developed, and delivered orally to the brickmakers at the time of each visit. Information was obtained regarding raw materials used, number and characteristics of persons employed, methods of production, kiln characteristics, production capacity, and self-identified health problems. Data averaging

and projections were based on all available survey data, though some respondents did not yield usable survey data.

Micrometeorological Measurements

Basic micrometeorological information was obtained for San Nicolas, the most important brickmaking village in Querétaro. Meteorological stations (Davis Instruments) were established at three points on the periphery of San Nicolas. Meteorological information was collected every 10 minutes. Wind roses were generated using the WRPLOT View v. 5.2.1 software (Lakes Environmental).

Biological Effects

Trapping of wild rodents. Sherman traps were placed in locations 0.1 –1 km from the periphery of San Nicolas in the direction E-SE to W to capture indigenous mice. The traps were left at the location for 24 hours to cover one period of darkness. Control mice were captured similarly, at the ecological reserve of El Tángano, Qro. Mice were anaesthetized at the site of capture with chloroform, and peripheral blood (50 ul) drawn under aseptic conditions from the lateral vein in the tail. Blood was immediately mixed with heparin to prevent coagulation. All mice were then released to the wild. The capture, handling of mice, and sample collection, were performed in a manner to minimize stress to the animal.

Micronuclei assay. Five micro liters of heparinized blood were extended on clean microscope slides. The slides were air dried (24 hr) and stained as reported by Salomone et al. (1980). Briefly, slides were fixed with absolute methanol (5 min), air dried (24 hr), stained with Giemsa stain (15 min), washed and stained with Harris Hematoxylin (10 min). After washing and air-drying, the slides were analyzed under the microscope (100x) and the number of micronuclei in 2,000 erythrocytes scored. Statistical significance between means was assessed using a t test.

Alkaline single cell-gel electrophoresis (comet) assay. DNA breaks were detected as described by Singh et al. (1988). Ten microliters of heparinized blood were mixed with phosphate buffered saline (1 ml), centrifuged (3000 rpm, 5 min) and the supernatant removed. The cell pellet was re-suspended in 300 µl of 0.5% low melting point (LMP) agarose at 37°C, and an aliquot (120 µl) was applied over a microscope slide coated with 1% normal melting point agarose. After solidification, a second layer (100 µl) of LMP agarose was applied. The cells were lysed (2.5M NaCl, 100mM EDTA, 1% triton x-100, 10% dimethyl sulfoxide, pH 10) at 4 °C for 1 h in the dark, exposed to alkaline conditions (300 mM NaOH, 200 mM EDTA pH 13) for 30 min, washed and electrophoresed (300 mA, 25 V) for 30 min using alkaline electrophoresis buffer (1300 mM NaOH, 200 mM EDTA pH 13). After electrophoresis, the slides were neutralized with Tris buffer (pH 7.5) and stained with ethidium bromide, and the overall comet length (CL) and comet head size (CHS) measured using a fluorescence microscope (Carl Zeiss 50HB). One hundred cells images were analyzed per mouse. Two microscope slides were used in every case to analyze one hundred cells. The comet tail length was calculated as the difference between the CL and the CHS. Cells were considered normal when comet tail length was within ±10% of CHS. The comet tails of exposed and control groups were compared using the Wilcoxon rank-sum test.

Results and Discussion

Queretaro, Statewide Scale

Kiln location. In the state of Querétaro there are currently 547 brick kilns (9% inactive) involved in the artisanal manufacture of red bricks (Fig. 3). Of these, 97.8% (535) are located in the villages or municipalities of Tequisquiapan (49.7%), San Juan del Rio (22.5%), Querétaro (15.4%) and El Marqués (10.2%). The rest (2.2%) are located in the municipalities of Pedro Escobedo (2%) and Ezequiel Montes (0.2%). The most important brickmaking community in the state is San Nicolás, a village within the municipality of Tequisquiapan. This community (Fig. 4) contains 251 kilns, 92% of the total number in Tequisquiapan and about 46% of the total number in the state. The corridor of 18 km between Tequisquiapan and San Juan del Rio (the communities of Bordo Blanco, San Nicolas, Vistha and San Pedro Ahuacatlan; Fig. 3) contains 72.2 % (395) of all brick kilns in the state of Queretaro.

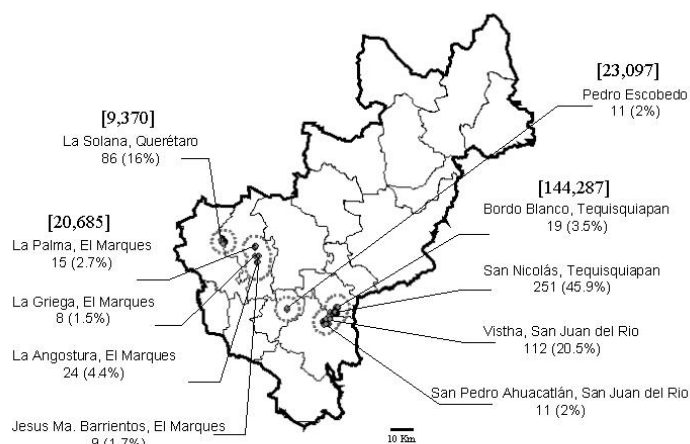


Figure 3. The location within the state of Queretaro of brick making kilns, along with the number and percentage of the total number of kilns, and the population living in a 5 km radius (dotted line).

Receptor co-location. Throughout the state of Queretaro, all brickmaking communities are located near or within centers of population, and along transportation corridors; 54.9 % and 45.1% of kilns are located within, and outside of, residential areas, respectively.

The potential for direct exposure and for dispersion by resuspension due to vehicular wake plumes is large. In and around the brickmaking communities of Queretaro state, approximately 197,500 persons are living within a radius of 5 km of a center of brick production (Table 2), approximately 144,300 in the San Juan del Rio-Tequisquiapan corridor. These local populations, including particularly the brickmaking personnel themselves, are likely to be exposed to toxic products of incomplete combustion, over prolonged periods of time.

There is an area of approximately 48,000 ha within a radius of 5 km of centers of brick production in the state (Table 2). Fifty percent of that area is used for irrigated agriculture, 33% for rain feed agriculture, and 3.8% for cultivated pasture. The rest (13%) is shrubland where animals roam freely. People, crops and domesticated animals constitute receptors of the emissions of brick kilns

Table 2. Receptors located within the 5 km estimated zone of influence of kilns in the state of Querétaro.

Receptor	Magnitude
Population (total)	197,500 persons
Land area (total)	48,339 ha
Irrigated agriculture	24,127 ha
Rain feed agriculture	16,057 ha
Crasicaul shrubland	5,596 ha
Subtropical shrubland	712 ha
Cultivated pasture	1,848 ha

Fuel inventory. The type of fuel used in the kilns varies seasonally, and according to the market. The fuel is generally a mix of available materials. Our survey results indicated (at one point in time) that 65 % of brickmakers self describe their fuel as fuel oil (n=194), 10.8% as recycled oil, 5.5% as a combination of fuel oil and wood, and 9.8% as other fuel (Table 3). There is evidence that in some cases these other fuels include hazardous waste. The fuel mix is tending toward fuel oil (combustoleo) but still consists in many

cases of whatever material, waste, or recycled product is available (Table 1). Large amounts of fuel are used in the artisanal manufacture of bricks. Although the amount varies depending on the type of fuel used, an average 1400 L of fuel oil is employed to manufacture 10,000 bricks. These large amounts are partly due to the inefficiency of the baking process.

Table 3. Resource utilization for manufacture of 10,000 bricks and self reported usage of fuels in the state of Querétaro.

Raw materials	N	Amount	Self-reported usage
Fuels			
Fuel Oil/Recycled Oil	6	1546 ± 413 L	6 (2%)
Recycled Oil	16	1304 ± 288 L	32 (10.8%)
Fuel Oil	31	1403 ± 313 L	194 (65%)
Recycled Oil / Wood	6	407 ± 159 / 2 ± 0.38 ton	17 (5.8%)
Wood	1	3 ton ± 0	17 (5.5%)
Other/ Unknown	--	Unknown	29 (9.8)
Constituents			
Clay plus sand	12	49 m ³ ± 0.9	
Water	4	~10,000 L	

San Nicolas, Tequisquiapan

At a finer scale we have characterized the small community of San Nicolas, Tequisquiapan, which exhibits a particularly dense and co-mingled distribution of kilns, crops and human dwellings. Here we have conducted a finer-grained spatial analysis, including zones of influence of individual sources, fuel inventories, crop speciation, and population densities within these zones, along with basic micrometeorological information to determine likely emissions transport and deposition patterns. In this community we have also obtained photographic evidence of the density of plumes.

In the case of San Nicolás, a community of 4,147 residents in an area of 283 km², most of the kilns are located within the domestic compounds of family residential complexes, within the heart of the community (Fig. 1A, 4).

The annual mean wind is predominately from the NE (Fig. 4). The seasonal variation in speed and direction are currently under evaluation.

Emissions

We have obtained samples of airborne and soil-deposited particles for gravimetric and chemical characterization (not shown), documenting elevated levels of polychlorinated biphenyls (PCB) in the ashes recovered from kilns in San Nicolas (Gómez et al. unpublished). The presence of polycyclic aromatic hydrocarbons (PAH) and chlorinated aromatic hydrocarbons (CAH), including dioxins and furans, is likely, given the types of products employed as fuel.

The persistence of CAHs in the environment and in organisms, their bioaccumulation through the food chain, and their toxicity depend on the specific chemical composition, particularly the number and position of chlorine atoms in the molecules (Geyer et al. 2002). The most biologically active, and thus toxic, CAHs are the planar molecules with chlorine in the four lateral positions. For example, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is the most toxic of the common CAHs.

In contrast to the PCBs, that were intentionally manufactured over a period of many years for industrial applications, dioxins and furans were not produced intentionally and are undesirable byproducts of bleaching in the paper industry, production of certain pesticides, and of a variety of incineration processes of municipal, hospital and toxic wastes (Fiedler 1996; Dyke et al. 1997). Their presence near fuel oil repositories in brickmaking communities suggests that they may be contaminants of the fuel itself, whereas their presence only in ash or aerial emissions could be equivocal, suggesting a possible byproduct of partial combustion during the brickmaking process itself.

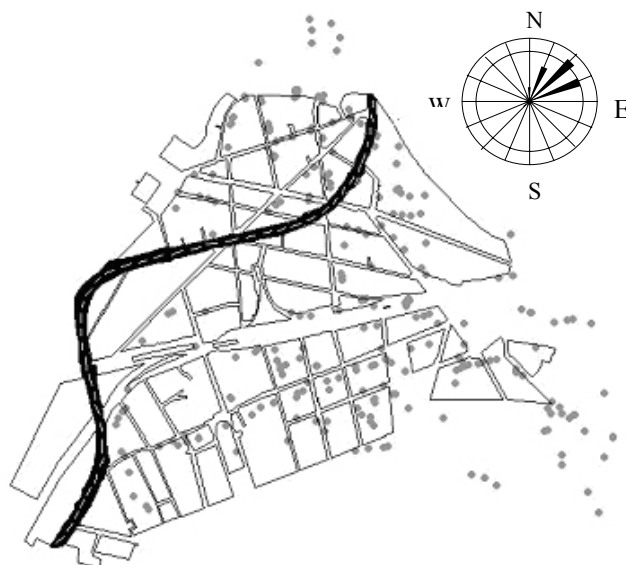


Figure 4. Map of the community of San Nicolás, Tequisquiapan, Qro. The points indicate the location of individual brick kilns. The dark line indicates Mexico Highway 120, a major intercity transportation corridor. The annual mean wind is predominately from the northeast.

The furans and PCBs exhibit physical and chemical properties, and environmental fates, similar to the dioxins, and are equally recalcitrant in the environment and similarly lipophilic. PCBs represent a family of 209 chlorinated compounds produced either intentionally or inadvertently, with no known source in the natural environment. A prominent former use of PCBs, due to their great stability and inertness, was in transformers and other electrical devices. Their environmental stability and toxicity led to their discontinued use, and to the generation of an illicit supply of waste transformer oil contaminated with PCBs. The CAHs also bioaccumulate and biomagnify, and exhibit considerable persistence in the environment.

Biological Effects

We have determined biological impacts of emissions on non-domesticated target mammals trapped in the wild (field mice: *Myotis spp*). We evaluated the frequency of micronuclei in peripheral erythrocytes and determined DNA breaks on peripheral lymphocytes assessed using the alkaline comet assay (Fig. 5). These assays are widely used to assess genetic damage *in vivo* and *in vitro* (Moller et al., 2000, Martin et al. 2005, Pitarque et al. 2002). Wild indigenous mice captured from San Nicolas (n=35) exhibited, on average, a seven-fold higher frequency of micronuclei than the control (n=10) group ($P < 0.05$; Fig. 5A). Similarly, 39.8% of cells of exposed animals (n=20) exhibited abnormal (tail > 10% of head) comets, as opposed to only 14.6% in the control (n=9) group. Furthermore, the average comet tail length for the exposed group averaged 8.3 μm , 1.7-fold longer than for the control ($P < 0.05$; Fig. 5B). These results suggest the presence of mutagenic compounds in the emissions of brick kilns.

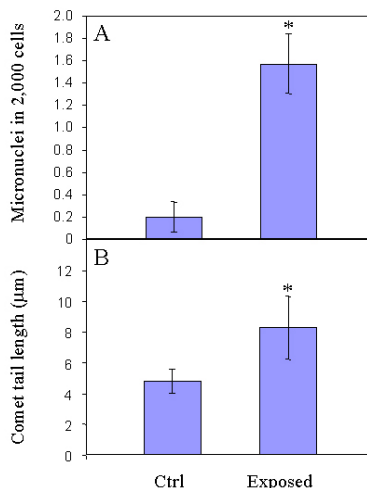


Figure 5. Biological effects. A) Micronuclei in peripheral red blood cells and B) Length of abnormal comet tails indicating DNA breaks in peripheral lymphocytes assessed by the alkaline comet assay.

Many of the compounds that are expected to be present in emissions from the brick ovens are powerful air toxics, causing considerable biological damage to organisms. Once HAHs are taken up by organisms, due to their low rates of metabolism, biodegradation and elimination, and high lipophilicity, the exposure to these compounds is cumulative, leading to persistent internal exposure from adipose tissue. It is estimated that the residence time (half-life of TCDD) in humans is approximately 8 years (Geyer et al. 2002).

Exposure to TCDD, for example, produces diverse effects including tumor generation and cancers, teratogenic effects, immunosuppression, atrophy of the thymus gland, hepatotoxicity, dermatological toxicity, endocrine disruption as well as reproductive disruption and death. (Safe 1993; Safe 1995; Denison and Heath-Pagliuso 1998; Bertazzi et al. 2001; Kerkvliet 2002).

Accidental exposure of humans to PCBs, and experimental studies with animals, demonstrate dermatological responses (chloracne), as well as immunosuppression, behavioral changes, and reproductive anomalies associated with endocrine disruption (Faqi et al. 1998; ATSDR 2000). Human exposure *in utero* has been demonstrated to cause negative effects in adulthood on production and vigor of sperm (Guo et al. 2000).

Future Plans

The deposition of particles to plant leaves and surrogate surfaces, their composition, and biological impacts on plants will be undertaken in the vicinity of the kilns. These data will extend the evidence of mammalian health hazards, to other components of the environment, and will investigate risks to the food chain.

Particles of kiln ash, and soil near these passive monitors will be collected as well. Suspended particles will be collected using polycarbonate Petri dishes and exposed horizontally for two weeks at 1 m above the ground, according to the method of Bytnerowicz et al. (1987) Leaves of tree species, and of marketable commodities (particularly ripening *Sorghum* heads, if available), will be collected nearby, according to the method of Freer-Smith et al. (1997). Petri dishes will be located in pairs. Half of the leaves and one of the petri dishes will be washed with dH₂O and the rinsate filtered for gravimetric determination of particulate load. The other half will be washed 3x in dichloromethane for characterization of surface deposited particles, followed by complete extraction of the leaves in dichloromethane to determine uptake into the tissues.

Effects on vegetation will be analyzed by evaluation of genotoxicity using *Tradescantia* pollen tetrads (Ma et al. 1994) and a pollen viability assay of plants growing in the vicinity of kilns (Micieta and Murin; 1996).

Conclusions

Our results indicate that the human populations of these agricultural communities are at considerable risk of direct exposure to airborne contaminants, and that these contaminants are likely to enter the food chain through exposed crops and domesticated animals, potentially affecting urban populations. The brickmaking industry of Querétaro state, Mexico, under current conditions of operation, poses a serious threat of environmental contamination with persistent organic pollutants, as well a threat of direct and indirect impacts on rural populations. The inefficiency of combustion and unregulated mix of questionable fuel substances contribute to emissions of toxic air pollutants, and also provide the most efficient avenues of mitigating the threat. In these rural communities agricultural air quality is less impacted by traditional sources of agriculturally-sourced emissions than by co-located primary industries such as brickmaking.

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Comparison of Models Used for the Calculation of National Ammonia Emission Inventories from Agriculture in Europe

B. Reidy^{1*}, U. Dämmgen², H. Döhler³, B. Eurich-Menden³, F.K. van Evert⁴, N.J. Hutchings⁵, H.H. Luesink⁶, H. Menzi¹, T.H. Misselbrook⁷, G.-J. Monteny⁸, J. Webb⁹

¹Swiss College of Agriculture, Laenggasse 85, CH-3052 Zollikofen, Switzerland

²Federal Agric. Res. Cent., Inst. of Agroecology, Bundesallee 50, 38116 Braunschweig, Germany

³Association for Technology and Structures in Agriculture (KTBL), Bartningstrasse 49, 64289 Darmstadt, Germany;

⁴Plant Research International, P.O. Box 16, 6700 AA Wageningen, The Netherlands

⁵Danish Institute of Agricultural Sciences, Research Centre Foulum, Tjele, Denmark

⁶LEI, P.O. Box 29703, 2502 LS The Hague, The Netherlands

⁷Inst. of Grassland and Env. Research, North Wyke, Okehampton, Devon EX20 2SB, UK

⁸Wageningen UR, Agrotech. and Food Innovations B.V., 6700 AA Wageningen, The Netherlands

⁹ADAS Research, Woodthorne, Wergs Road, Wolverhampton WV6 8TQ, UK

Abstract

Six mass-conservative N-flow models, used to calculate national ammonia (NH₃) emissions from agriculture in different European countries, were compared using standard data sets. Two scenarios were run (for dairy cattle and for pigs) with three different levels of model standardisation: a) standardised inputs to all models (FF scenario); b) standard N excretion, but national values for emission factors (FN scenario); c) national values for N excretion and emission factors (NN scenario). Results of the FF scenario showed very good agreement (following iterative modifications to some of the models) between models, indicating that the underlying N flows of the different models are highly comparable. Differences between models for the FN and NN scenarios could be explained by differences in national management practices and climate. The congruency exercise led to an improved harmonisation of the national models.

Introduction

The Gothenburg Protocol of the UN Convention on Long-range Transboundary Air Pollution (UNECE 1999) requires the reporting of national annual emissions of ammonia (NH₃). Accurate inventories of agricultural NH₃ emissions are required to calculate the total national emissions, since they commonly account for more than 80 % of the total emissions (EMEP 2005). To allow a co-ordinated implementation of the Protocol, different national inventories should be comparable; at present they are not.

A core group of emission inventory experts has therefore inaugurated the EAGER network (European Agricultural Gaseous Emissions Inventory Researchers Network), with the aims of achieving a detailed overview of the present best available inventory techniques, compiling and harmonizing the available knowledge on emission factors (EF) and initiating a new generation of emission inventories that satisfies protocol requirements. As a first step in summarizing the available knowledge, the objective of the work reported in this paper was to determine the degree to which results obtained with different NH₃ emission models currently used for inventory calculations agree, and to evaluate any larger disagreements.

Methods

The models used for the comparisons have been used in the framework of the national NH₃ emission inventory calculations and manure policy analyses in different countries of Europe (Table 1). The models all use a mass-conservative N-flow approach starting with a specific amount of nitrogen (N) excreted by a defined livestock category and simulate the total ammoniacal nitrogen (TAN) flow over the different stages of emissions (grazing, housing, manure storage and application). Ammonia emissions are generally calculated with EF, where the EF is the percentage of the respective TAN pool emitted. Emissions were compared for a dairy cattle and a pig scenario, with different levels of model standardizations. At a first level of comparison, the congruency of the underlying N flow was tested (FF scenario). For this purpose, the national specific N excretions rates, TAN contents and EFs were replaced by a set of standardised

values. At a second level of comparison, only the N excretion and TAN contents were standardised whereas the national EFs were used for the calculations (FN scenario). Finally, emissions were also calculated using the national N excretion rates, TAN contents and EFs (NN scenario).

Table 1. Models used in the comparisons.

Model	Country	Objectives of the model	Reference
DYNAMO	Switzerland	Estimation of the magnitude of NH ₃ losses at the farm and national level	Reidy and Menzi, 2006
DanAm	Denmark	Estimation of the magnitude of NH ₃ losses at the national level	Hutchings et al. 2001 ¹⁾
GAS-EM	Germany	Estimation of NH ₃ and other N losses at the national and district levels	Dämmgen et al. 2002 ²⁾
NARSES	United Kingdom	Estimation of the magnitude, spatial distribution and time course of agricultural NH ₃ emissions at the national level	Webb and Misselbrook 2004
MAM	Netherlands	Manure policy analyses and estimation of NH ₃ emissions at the farm and national level	Groenwold et al. 2002
FARMMIN	Netherlands	Ex-ante evaluation of the effect of management on profitability and nutrient losses	van Evert et al. 2003

¹⁾ An updated model fully based on the N-flow was used in this study.

²⁾ An updated model fully was used in this study.

Results and Discussion

Running the models with the defined livestock and manure management parameters and the standardised N excretion and EF (scenario FF) resulted in very similar estimates of the NH₃ emission for the respective emission stages as well as total emissions. This indicates that the underlying N flows of the different models are highly comparable. The small differences observed could largely be explained with slight modifications of the N flow, either related to an altered partitioning of the N deposited during grazing and housing or to the extent other N transformations are taken into account (e.g. mineralization or denitrification processes) in the different models. It is worthwhile mentioning that initial simulations of this scenario had shown greater differences between the models but that when investigated, these were found to be due to errors in logic or in programming.

Differences between the models were more pronounced when the emissions were calculated with national emission factors and/or national N excretion rates (FN and NN scenario). The variation in the calculated emissions was primarily the result of the distinct national emission factors and N excretion rates. Both parameters reflect the specific livestock and manure management systems of the different countries and can be explained by:

- Differences in N excretion that result from differences in feeding practice (e.g. the protein concentration in the diet) or from different production intensities (e.g. milk yield per cow, growth rate per pig).
- Variations in the types of animal housing, storage and technology used for field applications.
- Variations in animal management (e.g. duration of the grazing period)
- Climatic factors

The variations in the calculated emissions of the FN and NN scenarios are therefore real, fully valid and are the reason why emission inventories are most appropriately constructed at a scale that reflects the heterogeneity in agriculture and climate.

Conclusions

The models compared are generally well congruent and existing differences in the results obtained can mostly be explained by existing differences of natural conditions and farm management in the countries from which the models originate. The congruency exercise has led to a greater harmonization of the structure and function of the models tested, because the scientific debate necessary to understand the variation in results from the different models generated awareness and consensus concerning the importance of some processes (e.g. mineralization).

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DYNAMO: An Ammonia Emission Calculation Model and Its Application for the Swiss Ammonia Emission Inventory

Beat Reidy and Harald Menzi

Swiss College of Agriculture, Zollikofen, Switzerland

Abstract

Within the framework of the Gothenburg protocol member countries will have to regularly report in detail on the evolution ammonia emissions from agriculture. Present inventory approaches are generally not detailed enough to meet these requirements. A new emission inventory methodology has therefore been developed which is based on detailed survey data from farm and manure management and model calculations with an empirical mass flow model (DYNAMO). The calculations revealed that ammonia emissions from agriculture have decreased in Switzerland from 1990 to 2000 by approximately 20%. This change was primarily due to a substantial decrease in the livestock numbers and improved agricultural practices. The 2010 emission target of the Gothenburg protocol of a 13% reduction has therefore already been achieved.

Introduction

The Gothenburg Protocol will require member countries to regularly report on the evolution of ammonia emissions from agriculture. Existing emission inventory approaches are not sufficient to reproducibly detect relatively small changes of emissions (Stadelmann et al., 2006) because they are mainly based on expert assumptions and can only take into account farm management parameters to a very limited extent. For the calculation of a new Swiss ammonia emission inventory a new approach was therefore developed. It is based on emission calculations with an empirical model DYNAMO (**D**ynamic **A**mmonia Emission **M**odel) and on the results of a representative farm survey.

Methods

DYNAMO is an empirical mass-flow model following the N flow approach originally described by Menzi and Katz (1997) but with a widely extended set of farm management parameters. The model calculates emissions on the basis of the N-flow through the manure handling chain using emission factors in percent of the relevant amount of nitrogen present at each stage of emission. Considered emission stages include animal houses and hardstandings, manure storage and application, grazing, mineral fertilizer as well as crops and meadows. The model takes into account different animal categories and manure types and considers a series of different management practices relevant for ammonia emissions. Model input parameters on farm management were obtained from a questionnaire sent to 3880 farms. The stratified survey allowed the differentiation between nine regions (3 geographical regions x 3 altitude zones) and four farm types (Menzi and Reidy 2006). 1950 farms were eventually included in the emission calculations. The ammonia emissions for each of these farms were individually calculated with DYNAMO and the results up-scaled to the national level.

Results and Discussion

According to the ammonia emission inventory for the year 2000, agriculture is responsible for about 94% of the total anthropogenic emissions in Switzerland. Of the agricultural emissions, 88% originate from livestock production and manure management. Twelve percent of the emissions can be attributed to crop production, either to mineral fertilizer and sewage sludge application or to direct ammonia emissions from crops. With respect to livestock classes, the most important species are cattle and pigs, which contribute more than 90% of the emissions from animal production. In terms of emissions stages, 58% of the emissions result from manure application (Figure 1). Although the use of low emission application techniques (band application systems) has considerably increased in the last few years, still more than 85% of the slurry is spread with broadcasting systems as revealed by the survey. Primarily due to a strong increase in loose housing systems and the recent widespread introduction of hardstandings on cattle and pig

farms the contribution of livestock housing systems to the total emissions from livestock has increased since 1990 from 24 (Stadelmann et al., 1998) to 28%. The greatest part of the slurry is still stored in covered slurry tanks. Manure storage therefore contributes only 12% of the total emissions from livestock production and manure management.

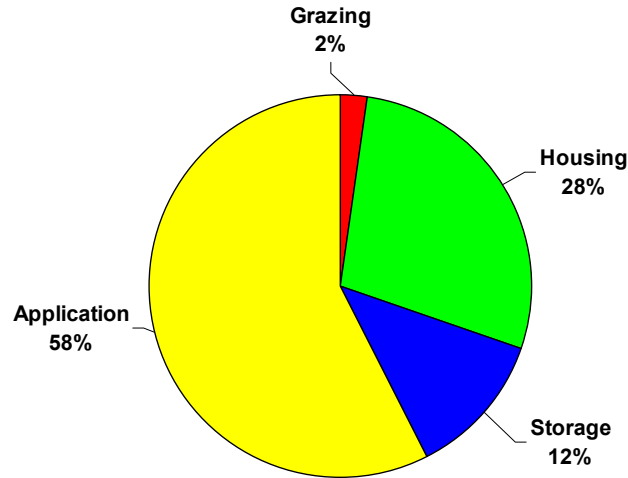


Figure 1. Contribution of each emission stage to the total ammonia emissions from livestock production and manure management in the year 2000.

Average annual $\text{NH}_3\text{-N}$ emissions per hectare agricultural area in the different regions ranged up to 38 kg. Maximum annual emissions of $60 \text{ kg ha}^{-1} \text{ NH}_3\text{-N}$ can be observed in the central and eastern part of Switzerland. In these regions average livestock densities of more than two livestock units per hectare agricultural area can frequently be observed.

Nevertheless, primarily thanks to a substantial reduction of the overall livestock numbers and improved agricultural practices the total emissions from agriculture decreased by about 20% since 1990. The 2010 emission reduction target of 13% of the Gothenburg protocol has therefore already been exceeded.

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Effect of Air Pollution on Crop Productivity in China: Application of an Agricultural Ecosystem Model (AEM)

Wei Ren, Hanqin Tian, and Mingliang Liu

Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, 100101, PR China.

Abstract

Evidence from field observation has shown that tropospheric ozone concentration in both urban and rural areas has increased significantly. Emissions of ozone precursors are expected to be double in the next 20 years in China and the levels of photo-oxidants may increase substantially. The individual mean values of related trace gases (NO, NO_x, SO₂ and CO) were much higher than that of background level. Strong seasonal variations of observed data in the sites were expounded with peaks in winter. To assess the effect of air pollution on crop productivity, we have developed the Agricultural Ecosystem Model (AEM), which fully couples crop growth processes and major biogeochemical cycles with hydrological cycles at a daily time step, especially adding air pollution (ozone, aerosol) effects on production processes. Our integrative assessment with the AEM suggests that elevated tropospheric ozone concentration has led to a significant decrease in the yield of four major grain crops (wheat, rice, corn and soybean). Of the four major grain crops, soybean yield is the most sensitive to elevated tropospheric ozone concentration, with a loss of more than 20%. Results drawn from our analysis imply that rising tropospheric ozone concentration could potentially influence China's capacity in feeding its growing population.



New Standards for Odour Emissions from Pig Facilities in Denmark

A. L. Riis

The National Committee for Pig Production, DANISH BACON & MEAT COUNCIL,
Copenhagen, Denmark

Abstract

The aim of this study was to determine the average odour emission from the most common pig facilities in Denmark during the summer in order to find new standards for odour emissions. The summer period was selected as odour emissions from finishing pigs was found to be highest during this period and is of great concern during public administration in the regulation of air pollutants.

To determine the odour emission from the nine most common categories of pig facilities in Denmark, 216 odour samples were collected. The nine categories of pig facilities were: dry sows kept in individual crates with partially slatted floors, dry sows kept loose, lactating sows kept in individual crates with partially or fully slatted floor, respectively, weaners kept in pens with partially or fully slatted floor, respectively, and finishers kept in pens with partially slatted, fully slatted or drained floor, respectively. Each category was represented by four intensive pig units, which all were mechanically ventilated. Odour samples were collected from each unit on three days with two samples per day. The samples were collected from the exhaust ventilation air in Tedlar[®] bags, and odour concentration was determined by an accredited odour laboratory. The ventilation rate of each house type was measured by a Fancom measuring fan.

The odour emission from dry sows did not differ significantly between the types of facility. This was also observed for weaners and therefore one number for odour emission is given for each of these stages of production. No difference was found between fully slatted floor and drained floor in finisher facilities. The odour emissions given in $\text{OU}_E \text{ s}^{-1} \text{ animal}^{-1}$ were 16 for dry sows, 72 for lactating sows with partially slatted floor, 100 for lactating sows with fully slatted floor, 7 for weaners, 19 for finishers with partially slatted floor and 29 for finishers with fully slatted or drained floor.

Furthermore, the ammonia concentration was measured in the exhaust ventilation air by Kitagawa Gas Detector Tubes at each odour sample. The ammonia emissions were 10.9, 13.4, 25.3, 0.1, 1.7, 4.6 and 6.2 $\text{g d}^{-1} \text{ animal}^{-1}$ for dry sows, lactating sows with partially slatted floor, lactating sows with fully slatted floor, weaners with partially slatted floor, weaners with fully slatted floor, finishers with partially slatted floor and finishers with fully slatted or drained floor.

Introduction

In cases concerning air pollution with odour from livestock buildings in Denmark, emission standards for odour based on measurements from German livestock buildings in the 1980s (Oldenburg, 1989) have been used so far. Consequently, there was an acute need for emission standards of odour measured in Danish livestock buildings in 2005. Therefore, as part of the Agreement on the Action Plan for the Aquatic Environment III 2005-2015 in Denmark (Danish Ministry of the Environment, 2004), new standards for odour emissions from livestock facilities were selected as an area that required research. The new standards for odour emissions will form part of a new odour guide from the Danish Ministry of the Environment.

Odour emissions from different categories of pig facilities have been measured in other countries (Mol and Ogink, 2002; Hayes et al., 2005; Gay et al., 2003; Lim et al., 2001; Zhu et al., 2000; Verdoes and Ogink, 1997), but not in Denmark.

The main aim of the present study was to determine the average odour emission from the most common pig facilities in Denmark during the summer in order to find new standards for odour emissions. The summer period was selected as odour emissions from finishing pigs was found to be highest during this period and is of great concern during public administration in the regulation of air pollutants. Secondly, the ammonia emissions from the pig facilities were determined at each odour sample. However, only the odour emissions found in this study are used for new regulation in Denmark.

Methods

The nine most common categories of pig facilities in Denmark were selected for this project. Each category was represented by four intensive pig units, which all were mechanically ventilated. The nine categories were:

- Dry sows kept in individual crates with partially slatted floor
- Dry sows kept loose
- Lactating sows kept in individual crates with partially slatted floor
- Lactating sows kept in individual crates with fully slatted floor
- Weaners kept in pens with partially slatted floor
- Weaners kept in pens with fully slatted floor
- Finishers kept in pens with partially slatted floor
- Finishers kept in pens with drained floor
- Finishers kept in pens with fully slatted floor.

Olfactometric odour samples were collected in each unit on three days with two samples per day. Samples were collected from the exhaust ventilation air in Tedlar[®] bags containing 30 L in compliance with European olfactometric standard EN:13725 (CEN, 2003). On each sampling day, the Tedlar[®] bags were filled with 0.7 L per minute between 12.00 and 1.00 pm for the first sample and after 1.30 pm for the second sample. A total of 216 olfactometric odour samples were collected in the summer period from June to October. Odour concentration was determined by an accredited olfactometric laboratory according to European olfactometric standard EN:13725 (CEN, 2003). For calculation of the odour emission, the ventilation rate in the pig facility for each odour sample was determined with a Fancom measuring fan (FarmTech a/s, Herlufmagle, Denmark).

To determine the average odour emission from a livestock facility in the summer, the outside temperature was preferred to be averagely 20 °C at sampling time to ensure maximum ventilation in the facilities. Typically, piglets are weaned at four to five weeks of age and therefore emissions of odour were measured 14 days after farrowing. The odour emission from weaners was measured at 19 kg since they are normally housed in the weaner facility from 7 to 30 kg. Finishers weighed averagely 65 kg when odour measurements took place. For dry sows, the production is continuously and therefore odour measurements were not planned for specific stages in the production period. At each sample day the numbers of pigs were counted and the average weight were estimated from weight at insertion, date of insertion and average daily gain.

In connection with each odour sample, the ammonia concentration was measured in the exhaust ventilation air by Kitagawa Gas Detector Tubes 105SD (Mikrolab, Aarhus, Denmark).

Data Analysis

Odour emission per animal was calculated as:

$$OU_E/s \text{ per animal} = \left(\frac{L \times Q}{W \times 3600} \right),$$

where L is the odour concentration, OU_E/m^3 ; Q is the ventilation rate, m^3/h ; and W is the total number of pigs in facility, no.

The ammonia emission was estimated by using the equation:

$$g \text{ NH}_3\text{-N/d per animal} = \left(\frac{M \times V \times Q \times 24}{R \times T \times 1000 \times W} \right),$$

where M is the mol weight of N, g/mol; V is the volume, ppm = ml/m^3 ; Q is the ventilation rate, m^3/h ; R is the gas constant, $0,0821 \text{ Lxatm/molxK}$; T is the temperature in Kelvin, K; and W is the number of pigs in facility, no.

The ammonia emissions and the logarithm transformed odour emissions were processed with an analysis of variance in the MIXED Procedure in SAS (SAS Inst. Inc., Cary, NC).

Results and Discussion

The average odour emissions per animal from the different pig facilities are presented in Table 1. In facilities for dry sows, no statistical difference was found in odour emission depending on whether sows were housed in individual crates or kept loose. However, in facilities for lactating sows, a tendency to lower odour emission was found, if farrowing crates had partially slatted floor compared with farrowing crates with fully slatted floor ($P=0.08$). The odour emission per animal from lactating sows in farrowing crates with partially slatted floor was 28 per cent lower compared with lactating sows in farrowing crates with fully slatted floor. For weaners, no statistical difference was found in odour emission depending on type of facility. Correspondingly, facilities for finishers did not reveal any difference in odour emission regardless of whether the pens had drained floor or fully slatted floor. However, a tendency to lower odour emission was found for finishers kept in pens with partially slatted floor compared with pens with fully slatted floor or drained floor, respectively ($P=0.09$). The odour emission from finishers kept in pens with partially slatted floor was 34 per cent lower compared with facilities for finishers with drained floor or fully slatted floor in pens.

Table 1. Odour emissions from different categories of pig facilities. The odour emissions are stated per animal and 5 per cent and 95 per cent quantiles are shown in brackets.

Category of pig facility	Number of observations	Odour emission, $\text{OU}_E \text{ s}^{-1} \text{ animal}^{-1}$ (5 per cent & 95 per cent quantiles)
Dry sows – Kept in individual crates or kept loose	48	16 (7 – 39)
Lactating sows – Kept in crates with partially slatted floor	24	72 (40 – 125)
Lactating sows – Kept in crates with fully slatted floor	24	100 (56 – 280)
Weaners – Kept in pens with partially slatted floor or fully slatted floor	48	7 (4 – 14)
Finishers – Kept in pens with partially slatted floor	24	19 (8 – 48)
Finishers – Kept in pens with drained or fully slatted floor	48	29 (13 – 78)

The connection between the observed odour emissions in the summer from different categories of pig facilities and an entire integrated production unit is illustrated in Figure 1. A unit that has a production capacity of 100 livestock units (approximately 100 sows plus finishers) where the farrowing crates for lactating sows have fully slatted floor and the pens for finishers have drained or fully slatted floor, the total odour emission will be 22.900 $\text{OU}_E/\text{second}$. However, if both the farrowing crates for lactating sows and the pens for finishers have partially slatted floor, the total odour emission will be reduced by 28 per cent, which corresponds to 16.600 $\text{OU}_E/\text{second}$. The figure illustrates that facilities for finishers account for more than 2/3 of the entire odour emission of an integrated production unit.

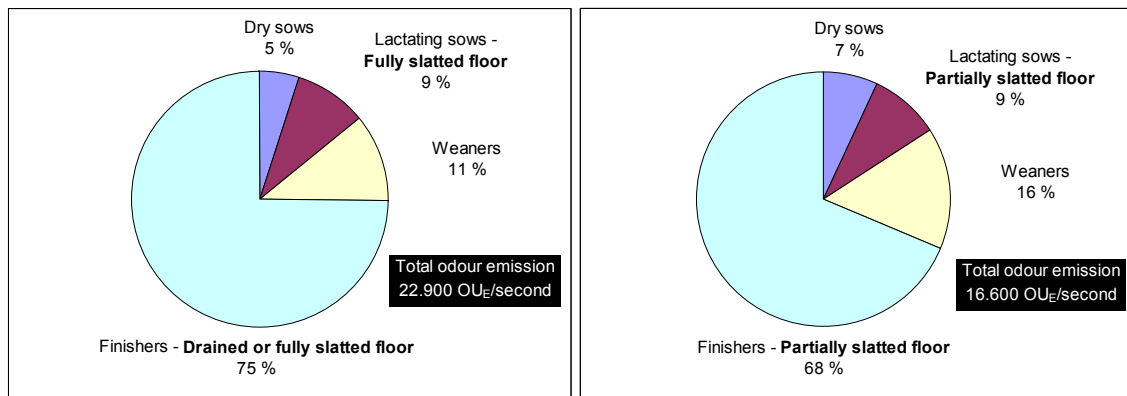


Figure 1. The figure to the left illustrates the distribution of odour emission in the summer from an integrated production unit with a capacity of 100 livestock units (approximately 100 sows plus finishers) where farrowing crates for lactating sows have fully slatted floor and pens for finishers consist of drained or fully slatted floor. The figure to the right illustrates the same distribution, but where both farrowing crates for lactating sows and pens for finishers have partially slatted floor.

The ammonia emissions from different categories of pig facilities are illustrated in Figure 2. No statistical difference was found in ammonia emission from dry sows regardless of whether they were housed in individual crates or kept loose. Correspondingly, no difference was found in ammonia emission from finishers regardless of whether the pens had drained floor or fully slatted floor. However, the ammonia emission was significantly lower from lactating sows in farrowing crates with partially slatted floor compared with crates with fully slatted floor ($P=0.01$). Also a significantly lower ammonia emission was found from weaners in pens with partially slatted floor compared with pens with fully slatted floor ($P=0.04$). In addition, the ammonia emission of finishers in pens with partially slatted floor was lower compared with pens with drained or fully slatted floor ($P=0.04$). Generally, the ammonia emission was higher per animal from dry and lactating sows compared with weaners and finishers.

Conclusions

In conclusion, the type of facility has a great impact on both odour and ammonia emissions from pig facilities in the summer. The odour emission per animal from lactating sows in farrowing crates with partially slatted floor was 28 per cent lower compared with the odour emission from lactating sows in farrowing crates with fully slatted floor. The odour emission per animal from finishers kept in pens with partially slatted floor was 34 per cent lower compared with facilities for finishers with drained or fully slatted floor in pens. Overall, the results illustrates that facilities for finishers account for more than 2/3 of the entire odour emission of an integrated production unit.

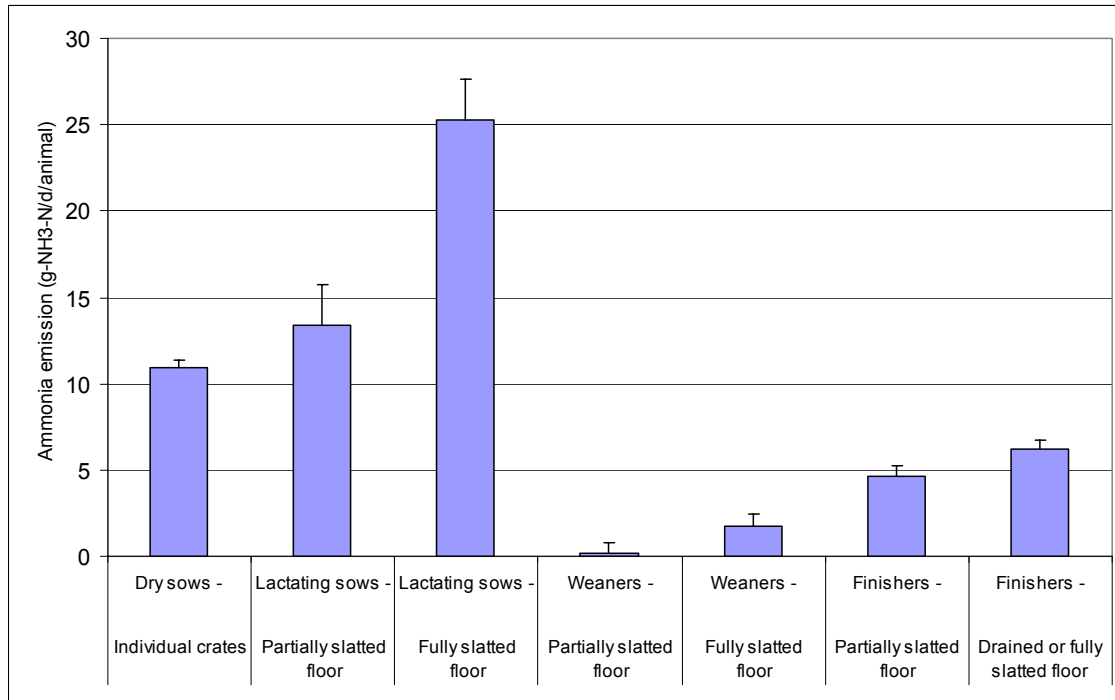


Figure 2. Ammonia emission from different categories of pig facilities measured at each odour sample in the summer period (June to October).

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A Simple Estimate of Nitrogen Deposition Across a Region of Variable Ammonia Emission Density

W.P. Robarge¹ and J.T. Walker²

¹North Carolina State University, Department of Soil Science, Raleigh, NC, USA, 27695-7619

²U.S. EPA, National Risk Management Research Laboratory,
Air Pollution Prevention and Control Division, Research Triangle Park, NC 27711

Abstract

Animal production in eastern North Carolina, particularly for swine and poultry, is centered primarily in six counties. Ammonia emission densities arising from animal production in these six counties ranges from > 5000 to 2000-3000 $\text{NH}_3\text{-N km}^{-2} \text{ yr}^{-1}$. The ammonia emission density for the remainder of eastern North Carolina declines steadily moving away from these six counties. The fate and transport of this emitted ammonia and its potential impacts on air quality and nutrient sensitive ecosystems within the state and along the coast is of major concern. We have followed a three-step approach in deriving a simple estimate of ammonia-N deposition across this region of variable ammonia emissions density. First, over 5 years of monitoring ambient ammonia chemistry in eastern North Carolina using annular denuder technology has yielded insight into the distribution of gaseous ammonia and fine particulate ammonium ($\text{PM}_{2.5}$) throughout the region. Yearly mean gaseous ammonia varies by a factor of 5 going from high to low regions of ammonia emissions. Fine particulate ammonium concentrations vary by a factor of 2 to 3. Both gaseous ammonia and fine particulate ammonium demonstrate seasonal differences in concentration, as does the association of fine particulate ammonium with chloride, nitrate and sulfate. Second, our knowledge of the atmospheric ammonia chemistry across the region, combined with micrometeorological studies of ammonia-N deposition to various vegetative canopies, is used to estimate dry deposition of ammonia-N. These estimates are combined with N wet deposition measurements from several National Atmospheric Deposition Program collectors located in eastern North Carolina. Together, these data yield an estimate of ammonia-N deposition across this region of variable ammonia emission density. This number is compared to the estimate of total ammonia-N emissions from animal production. Third, the estimate of ammonia-N deposition is contrasted to projections of N deposition in this region using multi-media computer models. This comparison is used to assess the need for further monitoring of ambient atmospheric ammonia chemistry in the region, and to determine to presence of possible error in the databases, such as the NADP data sets. This work is part of our continuing efforts to characterize ambient ammonia chemistry across eastern North Carolina and to predict changes in wet and dry deposition of nitrogen across the region with changes in density of animal production facilities and the imposition of alternative technologies to reduce ammonia emissions.

Introduction

During the past decade, much attention has been paid to the swine industry in North Carolina (NC) and its potential negative impacts on the environment (Aneja et al., 2001). Many of the specific criticisms against the industry have been centered on swine operations as concentrated sources of nitrogen (N) emissions. In the gas phase, these emissions occur primarily as ammonia (NH_3) that is released directly into the atmosphere. Release of the water-soluble phase (ammonium ion; NH_4^+) can occur when transported off site in runoff events or after conversion to nitrate (NO_3^-) in the soil. The amount of ammonia-N emitted from swine operations in NC has been the subject of considerable debate. As a consequence, most of the research effort in the state has been directed toward quantifying NH_3 emissions from the relatively large swine production facilities located predominately in eastern North Carolina (Aneja et al., 2001). Relatively little effort has been directed to measuring or estimating the amount of ammonia emitted from swine operations that is actually being deposited in the state. Published reports have focused primarily on wet deposition (Walker et al., 2000; Whitall and Paerl, 2001). The fate and transport of this emitted ammonia and its potential impacts on air quality and nutrient sensitive ecosystems within the state and along the coast is of major concern. Discussed here is a portion of our efforts to derive a simple estimate of

ammonia-N deposition derived from animal agriculture across this region of variable ammonia emissions density.

Ammonia Emission from Swine Operations

Figure 1 contains a schematic of a typical swine production facility in NC using a lagoon for waste treatment and land application for reuse of nutrients and disposal of excess water. Ammonia emissions can occur from each of the major components of this type of swine production facility. Ammonia emissions arise from the conversion of organic-N in urine and fecal matter into ammonium. This occurs on the floor of the housing units, within the pits underlying the houses, and within the lagoon. Conversion of organic-N is largely the result of microbial activity, which means that the rate of conversion to ammonium is temperature dependent. Temperature is considered a major controlling variable in regulating ammonia emissions from swine operations, thus emissions of ammonia (especially from lagoons and spray fields) are seasonal in nature (Visscher, et al., 2002).

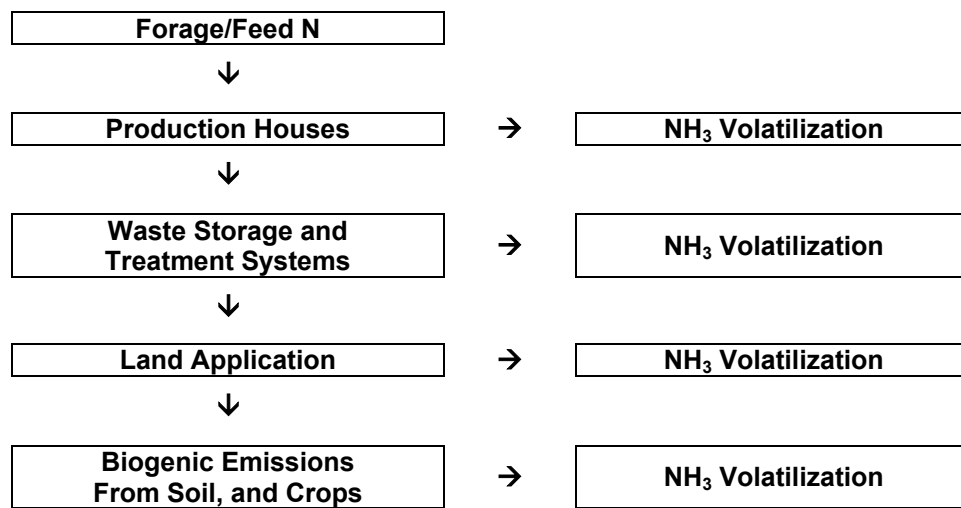


Figure 1. Major routes for ammonia emissions from a typical swine production facility in North Carolina. (Adapted from Aneja et al., 2001).

Recent estimates of emission factors published for swine operations in NC range from 7 +/- 2 kg NH₃-N yr⁻¹ hog⁻¹ (Doorn et al., 2002) to 5.4 kg NH₃-N yr⁻¹ per finished hog (Aneja, et al., 2003). (Note: NH₃-N means the units refer to the mass of N emitted as ammonia). Assuming a steady-state population of approximately 9.3 million swine in NC (the vast majority of which are finished hogs), this range in emission factors translates into a range of between 50,220,000 to 65,100,000 kg NH₃-N emitted per year from swine operations. In English units this range translates to 55,240 to 71,610 tons of NH₃-N per year. To put these numbers into proper perspective requires an estimate of the N excreted per year by the swine population in NC. Table 2 is an example calculation of the N excreted by the NC swine population in 1999: 102,000,000 kg of N. Contrasting the two sets of numbers suggests that between 50 to 64% of the N excreted by swine is emitted as ammonia. Doorn et al. (2002) reports an emission factor of 9 kg NH₃-N/yr per hog which would mean 83,700,000 kg (92,100 tons) or > 80% of N excreted is emitted as ammonia. This number seems unreasonably high given the N applied to crops as fixed by required nutrient management plans, and the accumulation of N in the sludge in lagoons.

Table 2. Estimate of N excreted from swine production in 1999 for North Carolina (Sources: W. Cherry, NC Pork Council; Dr. T. Van Kempen, formerly An. Sci., NCSU, Raleigh, NC; personal communications).

Swine Production	N Excretion Factor	N Excreted (lbs N)	N Excreted (kg N)
14,358,900 (market hogs)	14.8 lbs N per pig	212,500,000	96,300,000
3,000,000 (20-50 wt class; sent out of state)	4 lbs N per pig	12,000,000	5,400,000
TOTAL=			101,700,00

Nitrogen Deposition

Wet Deposition

In the United States, the composition of rainfall has been monitored since 1978 by the National Atmospheric Deposition Program (NADP), which is now part of the National Trends Network. North Carolina is fortunate to have 9 active NADP active collectors, one of which is in the center of Sampson County at the Clinton Horticultural Crops Research Station (latitude 35.0258, longitude -78.2783, elevation 41 m; NADP designation NC35). Another is located in Bertie County, just outside of Lewiston, NC at the Peanut Belt Research Station (latitude 36.1325, longitude -77.1708; elevation 22 m; NADP designation NC03). The Lewiston location is of significance because it is in a region with a fairly low density of swine operations, and is also downwind (located northeast) of the six counties in NC with the highest density of swine operations.

Summaries for the wet deposition of NH₄-N and NO₃-N for 1980 to 2002 for the Sampson County site (NC35) and the Bertie County site (NC03) are provided in Tables 3 and 4. The data have been converted to mass of N as the respective chemical species to allow summation of terms to estimate total inorganic N inputs (NH₄-N + NO₃-N) per year as well as to calculate the percent contribution to total inorganic N from NH₄-N. For the Sampson Co. site, there is an obvious increase in the wet deposition of NH₄-N beginning in 1995 (Table 4), which corresponds to the period of rapid increase (1989 – 1997) in the swine population in eastern NC. There is no corresponding increase in NO₃-N deposition, which appears to have remained constant for the past 22 years. There is no similar trend in the NH₄-N data from Bertie Co. (Table 3). The similarity in NO₃-N annual summaries between the two locations indicates that failure to not see an increase in NH₄-N annual deposition at the Bertie Co. site is not due to an artifact in total volume of rainfall measured between the two locations.

Table 3. Summary for wet deposition of NH₄-N and NO₃-N recorded by the National Atmospheric Deposition Program Collector (NC35) in Sampson Co., NC (mean +/- std. dev.).

Period	NH ₄ -N (kg N/ha)	NO ₃ -N (kg N/ha)	Total N (kg/ha)	% NH ₄ -N of Total N
1980-1989	1.52	2.26	3.77	40.0
	0.30	0.31	0.57	3.8
1998-2002	3.70	2.25	5.94	62.4
	0.40	0.41	0.77	2.5

The data in Tables 3 and 4 provide a number of insights as to the fate and transport of N from swine farms in eastern NC. First, as evident in the data summary for the years 1980-1989 for Sampson Co. (Table 3), and the data summary for the Bertie Co. site (Table 4), atmospheric deposition in general has been responsible for ~4 kg N ha⁻¹ (as NH₄-N and NO₃-N) across eastern NC since 1980, before there was a significant increase in the swine population or change in style of management. Of this amount, ~1.5 kg N ha⁻¹ yr⁻¹ has been in the form of NH₄-N. Second, in the region of the state with the highest density of swine operations, there has been an increase of NH₄-N deposition of ~2.2 kg N ha⁻¹, or roughly a doubling of the

NH₄-N deposition. This doubling is not evident at the Bertie Co. site nor is it present at other NADP sites in NC (data not shown). Third, since 1998, the amount of NH₄-N deposition at the Sampson Co. site has remained fairly constant, demonstrating no more variation in annual yearly totals than is evident for the period 1980-1989, or for comparable periods at the Bertie Co. site. This suggests that the source of NH₄-N influencing rainfall events in Sampson Co. has remained relatively constant since 1998. Whitall and Paerl (2001) monitored the composition of rainfall in the Neuse River Basin from 1996-1999 and concluded that counties with the highest density of swine operations, or counties immediately adjacent to these counties, did in fact experience an increase in the NH₄-N content of the measured rainfall. Counties within the basin that did not meet these criteria did not experience an increase in NH₄-N deposition.

Table 4. Summary for wet deposition of NH₄-N and NO₃-N recorded by the National Atmospheric Deposition Program Collector (NC03) in Bertie Co., NC (mean +/- std.dev.).

Period	NH ₄ -N (kg N/ha)	NO ₃ -N (kg N/ha)	Total N (kg/ha)	% NH ₄ -N of Total N
1980-1989	1.45	2.41	3.86	37.2
	0.42	0.35	0.68	5.7
1998-2002	1.77	2.23	4.00	44.3
	0.28	0.33	0.60	1.8

Dry Deposition

Dry deposition of ammonia is partly a function of the ambient atmospheric ammonia concentration. In 1998, the authors began monitoring ambient atmospheric concentrations of ammonia and ammonium-based aerosols in Sampson Co., NC at the Clinton Horticultural Crops Research Station using annular denuder technology (Robarge et al., 2002). In succeeding years, this effort was expanded to include other areas in eastern North Carolina (Walker et al., 2004), including the Bertie Co. location of NADP collector NC03 (Walker et al., 2006). Average NH₃ concentration from April, 2002 to October, 2003 at the Bertie Co. site was 1.05 µg m⁻³ as opposed to an average concentration of 5.59 µg m⁻³ measured in 2000 in Sampson Co. Mean gas concentrations were 0.30, 0.91, 0.43, and 3.17 µg m⁻³ for HCl, HNO₃, HONO, and SO₂, respectively during the same period and differed little from similar measurements made in Sampson Co. in 2000. These observations suggest that aside from NH₃, regional gas chemistry across eastern NC may be relatively constant in atmospheric composition at ground level. Average NH₄⁺ concentration at the Bertie Co. site was 0.74 µg m⁻³, and the total concentration of inorganic (NH₄⁺ + NO₃⁻ + SO₄⁼ + Cl⁻) particulate matter with an aerosol diameter < 2.5 µm (PM_{2.5}) was 4.88 µg m⁻³ from April 2002 to October 2003. These numbers are approximately half the values recorded in Sampson Co. in 2000 (1.76 µg m⁻³ for NH₄⁺ and 7.96 µg m⁻³ for NH₄⁺ + NO₃⁻ + SO₄⁼ + Cl⁻) (Walker et al., 2004). The relatively high concentrations of NH₃ observed at the Sampson Co. site are consistent with a relatively large source of ammonia-N emissions in the immediate region surrounding the site. The data are also consistent with the wet deposition data collected by NADP collector NC35 at the Sampson Co. site, and support the assumption of a gradient in dry deposition across eastern NC moving from areas with the highest density of ammonia emissions (> 5000 kg NH₃-N km⁻² yr⁻¹; Duplin and Sampson Co.) to the relatively lowest (500 to 750 kg NH₃-N km⁻² yr⁻¹, Bertie Co.).

A Simple Mass Balance for Emissions

The rainfall data from the NADP collector in Sampson Co., together with the extensive observations of ambient atmospheric ammonia and ammonium-based aerosol concentrations made at the same location using annular denuder technology, make a strong argument that a significant portion of the estimated 50,220,000 to 65,100,000 kg NH₃-N emitted per year from swine farms in NC is being deposited locally in the counties with the highest density of animal operations in the state. However, the question still remains of whether this enhanced amount of local deposition can account for the majority NH₃-N emitted. If not, then the rainfall data from other NADP collectors in the state, such as Bertie Co., NC, would suggest that the remaining NH₃-N emissions not deposited locally are in fact not being deposited in the remainder of eastern NC. The following is a simple mass balance calculation in an attempt to address this issue.

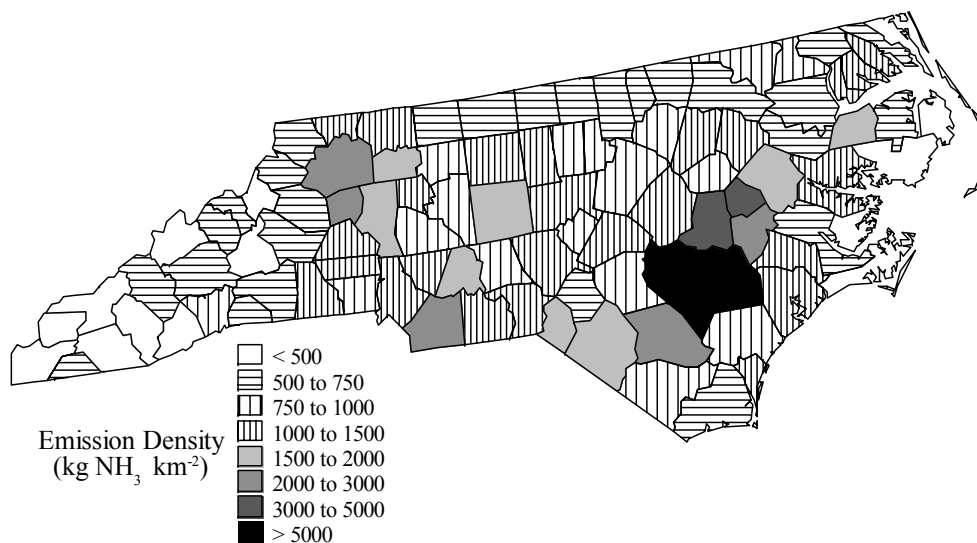


Figure 2. County-scale NH₃ emission density for North Carolina. Livestock activity data represent 2000 levels. All other activity data represent 1996 levels.

Figure 2 is a map of eastern NC highlighting the six counties with the highest density of swine operations in the state. For the simple mass balance calculation, the Coastal Plain region of the state was divided into two separate land areas – one area included the six counties with the highest density of animal operations (Bladen, Duplin, Green, Lenoir, Sampson and Wayne) and the other area included the remaining counties in the Coastal Plain. Note that the area with the six counties includes several of those observed by Whitall and Paerl (2001) to have relatively high amounts of NH₄-N wet deposition. According to NC Department of Environment and Natural Resources records, the six county region contains approximately 1700 registered swine operations, and approximately 70% of the swine produced in NC. Selecting an average value of 57,400,000 kg for total NH₃-N emissions from swine farms in the state yields an estimate of 40,200,000 kg of NH₃-N emitted per year by the six designated counties.

The designated six counties occupy a region of approximately 3,660,000 acres or 1,481,100 hectares. From Table 3, the *additional* NH₄-N observed in wet deposition at the Sampson Co. site for the period 1998-2002 averaged 2.2 kg NH₄-N ha⁻¹ yr⁻¹ (1998-2002 average corrected for the 1980-1989 average). Whitall and Paerl (2001) conducted similar calculations for their more limited three-year data set for the Neuse River Basin and derived *additional* NH₄-N estimates in wet deposition of 3-5 kg NH₄-N ha⁻¹ yr⁻¹. A value of 3.5 kg NH₄-N ha⁻¹ yr⁻¹ was selected for the purposes of this calculation, which yields a total of 5,184,000 kg NH₄-N (5700 tons of NH₄-N) in wet deposition of *additional* N. This is roughly only 13% of the total assumed emissions from the six county area. The remaining counties in the Coastal Plain occupy an area of approximately 11,280,000 acres or 4,563,300 hectares including the sound and estuaries. Of the remaining 30%, 25% of the swine produced in NC were assumed to be in this area and emit approximately 14,400,000 kg of NH₃-N per year. Reviewing the calculations in Table 4 indicates that the amount of *additional* NH₄-N detected by the NADP collector at the Bertie Co. site (downwind of the six-county area) was 0.8 to 0 kg NH₄-N ha⁻¹ yr⁻¹ depending your interpretation of the uncertainty associated with the average values. Assuming that NH₄-N deposition would taper off moving away from the six county region, a value of 1 kg NH₄-N ha⁻¹ yr⁻¹ was chosen for *additional* N in wet deposition, which yields a total of 4,563,300 kg NH₄-N (5000 tons of NH₄-N) in wet deposition of *additional* N. This is roughly 32% of the total assumed emissions from the remainder of the Coastal Plain region.

To complete the simple mass balance calculation for emissions requires an estimate of dry deposition within the two selected areas. It can be argued that dry deposition within the six county area would be enhanced due to the elevated levels of ambient ammonia and ammonium-based aerosol concentrations. As a first approximation, therefore, dry deposition was set equal to twice the wet deposition estimate of 3.5 kg NH₄-N ha⁻¹ yr⁻¹ of *additional* N, or 10,368,000 kg NH₄-N (11,400 tons of NH₄-N). This brings the

estimate of total *additional* N deposited in the six county area to 15,500,000 kg (17,100 tons), which only accounts for 38.5% of the estimated emissions of N from the swine farms in the six counties. For the remaining portion of the Coastal Plain, dry deposition was set equal to wet deposition, meaning that 64% of the emissions are accounted for in this area. Combining these estimates yields a total of 24,600,000 kg NH₄-N for the calculated *additional* N from both wet and dry deposition across the Coastal Plain of North Carolina. Depending on selection of the emissions factor, this sum only accounts for 38 to 49% of the estimated emissions for NH₃ from large-scale swine operations in eastern NC.

Conclusions

It is acknowledged that these calculations are only approximate and cannot differentiate from other agricultural sources of ammonia in eastern NC. However, emission inventories in the state indicate that swine production is the dominant source of ammonia emissions in this area, and that changes in swine density of production are the most consistent with observed changes in wet deposition chemistry. These calculations also reflect actual field observations that have been made in eastern NC during the past five years, as well as general rules of thumb that have been derived from deposition studies on various ecosystems. As such, the attempted simple mass balance calculation can only account for ~ 40 to 50% of the estimates NH₃ emissions from swine. The remaining emissions, if real, must be transported outside of the Coastal Plain, either West into central NC, along the East Coast, and/or East out to the Atlantic Ocean.

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Monitoring Ambient Ammonia Chemistry in an Agricultural Region with a Low Density of Animal Production

Wayne Robarge¹, John Walker², Arun Shendrikar³, and Hoke Kimball³

¹North Carolina State University, Department of Soil Science, Raleigh, NC, USA, 27695-7619

²U.S. EPA, National Risk Management Research Laboratory,
Air Pollution Prevention and Control Division, Research Triangle Park, NC 27711

³North Carolina Department of Environment and Natural Resources,
Division of Air Quality, Raleigh, NC 27626

Abstract

We present several years of ambient ammonia (NH_3), ammonium (NH_4^+), hydrochloric acid (HCl), chloride (Cl^-), nitric acid (HNO_3), nitrate (NO_3^-), nitrous acid (HONO), sulfur dioxide (SO_2), and sulfate (SO_4^{2-}) concentrations at a rural site in the Coastal Plain region of North Carolina. The site is located at the Peanut Belt Research Station (latitude 36.1325, longitude -77.1708; elevation 22 m) in Bertie Co., NC. The total NH_3 emission density of the county ranges from 500 to 750 $\text{kg NH}_3\text{-N km}^{-2} \text{ yr}^{-1}$, and the county itself is approximately 80 km northeast of the region with the highest density of ammonia emissions ($> 5000 \text{ kg NH}_3\text{-N km}^{-2} \text{ yr}^{-1}$; Duplin and Sampson Co.) in eastern North Carolina. Average NH_3 concentration from April, 2002 to October, 2003 was $1.05 \mu\text{g m}^{-3}$ as opposed to an average concentration of $5.59 \mu\text{g m}^{-3}$ measured in 2000 in Sampson Co. Mean gas concentrations were 0.30, 0.91, 0.43, and $3.17 \mu\text{g m}^{-3}$ for HCl, HNO_3 , HONO, and SO_2 , respectively during the same period and differed little from similar measurements made in Sampson Co. in 2000. These observations suggest that aside from ammonia, regional gas chemistry across eastern NC may be relatively constant in atmospheric composition at ground level. Average NH_4^+ concentration at the Bertie Co. site was $0.74 \mu\text{g m}^{-3}$, and the total concentration of inorganic ($\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-$) particulate matter with an aerosol diameter $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) was $4.88 \mu\text{g m}^{-3}$ from April 2002 to October 2003. These numbers are approximately half the values recorded in Sampson Co. in 2000 ($1.76 \mu\text{g m}^{-3}$ for NH_4^+ and $7.96 \mu\text{g m}^{-3}$ for $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-$). The cumulative frequency distributions for aerosol sulfate for Bertie Co. from 2002-2003 versus those from Sampson Co. in 2000 suggest that the measured difference in ammonium-based aerosol mass $< 2.5 \mu\text{m}$ between the two counties is due to differences in both sulfate and ammonium in the aerosol fraction. This work is part of our continuing efforts to characterize ambient ammonia chemistry across eastern North Carolina and to predict changes in wet and dry deposition of nitrogen across the region with changes in density of animal production facilities and the imposition of alternative technologies to reduce ammonia emissions.

Introduction

Loss of nitrogen through volatilization of ammonia (NH_3) from animal wastes represents a potential source of nitrogen loading via wet and dry deposition to surrounding terrestrial and aquatic ecosystems (Walker et al., 2000). This may be particularly true in eastern North Carolina (and especially in Sampson and Duplin counties) where there is a relatively high density of large-scale swine and poultry production facilities. Fate and transport of NH_3 emitted from effluent lagoons, housing units, or land application of animal wastes (effluent or litter) is dictated in part by the partitioning between ammonia and ammonium aerosols in the atmosphere. Ammonium aerosols form as a result of an acid-base reaction between NH_3 (a base) and acidic atmospheric species such as nitric acid (HNO_3), hydrochloric acid (HCl) or sulfur dioxide (SO_2). Ammonia has a relatively short residence time in the atmosphere, especially as compared to ammonium aerosols. Thus conversion of atmospheric NH_3 to ammonium aerosols favors transport of nitrogen lost by volatilization of NH_3 from animal wastes away from the immediate source area (such as portions of eastern North Carolina), enhancing the potential for its deposition in adjoining river basins or even across state boundaries.

Conversion of atmospheric NH_3 to ammonium aerosols also has broader implications for human health. In 1997, the U.S. EPA revised the national ambient air quality standard (NAAQS) for particulate matter (PM) to include specific rules for fine aerosol [$\text{PM}_{2.5}$ ($d_p < 2.5 \mu\text{m}$)] (US EPA, 1997). The revision set a standard of $15 \mu\text{g m}^{-3}$ for the 3-year average of annual arithmetic mean concentrations, and a 24-hour standard of 65

$\mu\text{g m}^{-3}$ based on the 3-year average of 98th percentile concentrations. In addition to adverse effects on human health, which form the basis for these standards, elevated atmospheric particulate concentrations degrade visibility and air quality in general.

The concentrations of NH_3 and ammonium aerosols in the atmosphere can be determined using annular denuder technology (Robarge et al., 2002). A denuder, in its most simple form, is a cylindrical tube coated with a reagent that selectively samples a specific gaseous component as air is drawn through the tube. Air is sucked through the denuder tubes, or series of tubes arranged in sequence and coated with different reagents, for a certain period of time and the sample volume is measured by a gas meter or estimated from the sample time and air flow, the later usually being controlled by a critical orifice. After sampling, the coating of the denuder is extracted and analyzed for the compound of interest. The coating used for a denuder tube is selected for the trace gases of interest, is stable under ambient temperature and changes in relative humidity, and is compatible with commonly used analytical techniques. Annular denuders represent an improvement over the basic cylindrical denuder tube design allowing for sampling at higher flow rates of air (Purdue, 1992). Due to their sampling rates, annular denuders can be adapted relatively easily for application in monitoring. They can also be readily adapted to other studies such as measuring dry deposition. Addition of a filter pack at the end of a series of annular denuder tubes allows the capture of fine particulates and aerosols that have been separated from the trace gases in the air flowing through the denuder tubes. Thus annular denuder technology, when properly configured, can provide a substantial amount of information about the concentrations of a number a trace gases in the atmosphere.

This project was designed to enhance the efforts already underway to monitor the atmospheric concentrations of ammonia gas and ammonium aerosols in eastern North Carolina. Specifically, annular denuder technology was selected to continue to provide daily (day/night 12 hour sampling periods) measurements of ambient ammonia/ammonium concentrations downwind (summer winds) of the relatively high density of large-scale animal production operations located in primarily Bladen, Duplin, Sampson and Wayne counties. These measurements compliment daily annular denuder measurements made in 1999 and 2000 at the Clinton Horticultural Crops Research Station (latitude 35.0258, longitude -78.2783, elevation 41 m) located in Sampson County. Presented in this paper are results for annular denuder data collected for the periods April 29, 2002 – August 4, 2002, and December 12, 2002 – October 12, 2003. Chemical analyses for the gaseous species has been completed and a summary of the data is included in this report together with previously published data from 1999 and 2000 (Robarge et al., 2002; Walker et al., 2004).

Methods

An annular denuder system (URG Corporation, Chapel Hill, NC) purchased was installed at the Peanut Belt Research Station (36.1325 degrees latitude, -77.1714 degrees longitude, elevation 22 meters) located North of Lewiston, North Carolina in Bertie County. The annular denuder system allows for 4 days (day and night cycles) of unattended operation. The computerized mass flow controller and associated mast to hold the annular denuder tubes were installed inside the fenced compound located near the headquarters building of the research station. This fenced in area also contains a National Atmospheric Deposition Program monitor (NC03) positioned at the research station. The research station is equipped with a fully functional weather station run by the State Climate Office of North Carolina.

The annular denuder system operated on 12-hour day- night cycles (0600 to 1800 hours day-cycle; 1800 to 0600 hours night-cycle), yielding 12-hour average concentrations. The system consisted of the following components: two 3-channel annular denuder tubes (30 mm x 242 mm length) coupled together to form one denuder tube combination, a total of 8 denuder tube combinations arranged in sequence along two 4-channel manifolds, two #30 aluminum Teflon coated cyclones (10 Lpm, < 2.5 micron cutoff) attached to each manifold, eight 2-stage Teflon filter packs with one attached to the bottom of each denuder tube combination, and a computerized sampling pump (8 channel) with accompanying mass flow controller. One of the annular denuder tubes in a denuder tube combination is coated with sodium carbonate and is used to trap acidic gases (HNO_2 , HNO_3 , HCl and SO_2). The second denuder tube in the denuder tube combination is coated with phosphorous acid and is used to trap NH_3 . The Teflon filter pack contains a 2 micron Teflon filter (47 mm diameter) followed by a 0.8 micron Nylon filter. The Teflon filter essentially traps all of the particulates and aerosols < 2.5 microns in size that pass through the preceding aluminum Teflon-coated cyclone and two annular denuder tubes (intake height set at 2.65 m). The second Nylon filter is necessary to ensure quantitative recovery of ammonium because of potential secondary reactions that

may occur on the Teflon filter. Use of the mass flow controllers allows precise control of air flow through the annular denuder tube assembly such that the total volume of air sampled is equal to the sampling period times the set flow-rate (typically 10 Lpm). The 8 channel sampling pump allowed unattended alternate day and night cycle sampling for a total of 4 days. During the initial sampling period (April 29, 2002 – August 4, 2002), the system was set to collect samples every other day. At the start of the second sampling period (December 12, 2002 – October 12, 2003), the sampling sequence was switched to four sequential days (Wednesday through Sunday) to facilitate maintenance of the site.

The annular denuder system was maintained by weekly trips to the research station from North Carolina State University at Raleigh, NC. These trips were typically made either Monday or Tuesday of the following week. Thus unexposed tubes were deployed for no longer than two days before start of sample collection (Wednesday 1800 hours), and recovered typically within one day following the end of a sampling session (Sunday 1800 hours). Flow rates were checked (BIOS DryCal DC-Lite Primary Flow Meter, Butler, NJ) bimonthly. The denuder tubes were color-coded using electrical tape to facilitate assembling the various denuder tube – filter pack combinations on site. The intake lines from the computerized mass flow controller were also color coded to ensure proper connection of denuder tube assemblies with proper position in the programmed sampling sequence. When assembled, the various color-coded tubes and connections provided a rapid visual check with a color chart carried by the field staff to ensure that all tubes were assembled and deployed properly.

Exposed annular denuder tubes were extracted within 24 hours of being returned to the research laboratory at North Carolina State University. The sample extracts and exposed filters were transferred to 20 mL plastic scintillation vials with screw cap (plastic liners) lids and stored at 4°C until analysis. All handling of the denuder tubes and filter packs (both in the field and in the laboratory) was done using gloves to minimize contamination, especially from chloride and sodium. Chemical analysis of extracted samples was performed by the Analytical Service Laboratory located in the Department of Soil Science, NCSU (Dr. W. Robarge, Supervisor). Standard colorimetric procedures were used to determine soluble NH₄-N and NO₃-N using a flow injection autoanalyzer (Lachat Model 8000 3-channel Autoanalyzer). Soluble Cl⁻, NO₂⁻ and SO₄⁼ were determined using ion chromatography (Dionex Model 500 and Model 160 Ion Chromatographs with autosamplers).

Results and Discussion

Gaseous Species

The summary statistics for HCl, HNO₃, HONO, NH₃ and SO₂ as measured by annular denuder technology at the Lewiston, NC site are provided in Table 1. Also provided for comparison purposes, are data for the same gaseous species measured at the Clinton Horticultural Crops Research Station in 1999 and 2000. For HCl, HNO₃, HONO and SO₂, the measured concentrations at the Lewiston site are very similar to those measured in the center of Sampson County in 1999 and 2000 (Robarge et al., 2002; Walker et al., 2004). The agreement in mean values and standard deviations is exceptionally close, even though the absolute number of observations above the corresponding detection limits is substantially less than the data set for the Clinton site. The difference in total number of observations probably also explains why the recorded 12-hour averaged maximum values for the four gases are all higher at the Clinton site. Even so, the maximum values between the Clinton and Lewiston site differ by less than an order of magnitude, suggesting that there is little difference in the ambient concentrations of these gases measured at Lewiston in 2002/2003 compared to the Clinton site in 2000.

Similarity between the Lewiston and Clinton sites is also demonstrated by comparing the cumulative frequency distribution of SO₂ (Figure 1). Eighty percent of the observations at both sites are less than 6 µg SO₂ m⁻³, although the overall distribution for the Lewiston data is shifted to lower concentrations. This shift amounts to a difference of roughly 1.0 µg SO₂ m⁻³ which may reflect some differences in local sources of SO₂, and/or differences in meteorology between years, since 2003 was a wet year compared to 2000.

Table 1. Summary statistics for atmospheric gases measured using annular denuder technology. Data for Lewiston site reflects two collection periods: April 29, 2002 to August 4, 2002, and December 12, 2002 to October 12, 2003. Data for Clinton site reflects collection period of January 1, 2000 to December 4, 2000.

Gaseous Species	Monitoring Site	N	Mean	S.D.	Min.	Max.
				---- ug/m ³ ----		
HCl	Clinton	1168	0.43	0.45	0.10	5.96
	Lewiston	327	0.30	0.24	0.01	2.17
HNO ₃	Clinton	1168	0.94	1.02	0.09	7.34
	Lewiston	365	0.91	0.86	0.13	6.07
HONO	Clinton	1168	0.43	0.58	0.67	4.10
	Lewiston	178	0.43	0.33	0.09	1.91
NH ₃	Clinton	1168	5.59	5.13	0.06	36.4
	Lewiston	454	1.05	0.69	0.03	3.6
SO ₂	Clinton	1168	3.90	3.71	0.05	33.0
	Lewiston	465	3.17	3.61	0.01	20.7

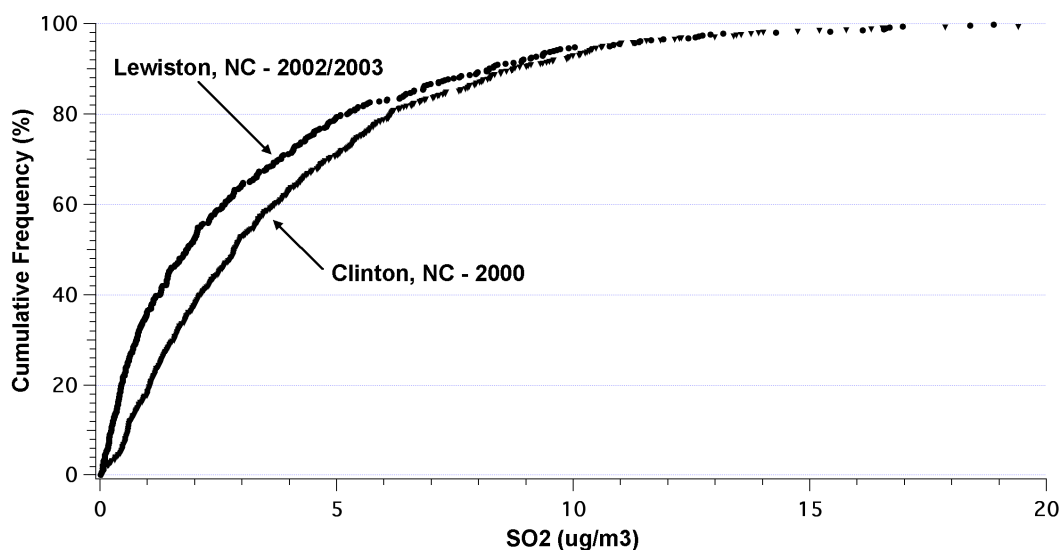


Figure 1. Cumulative frequency distribution for SO₂ measured using annular denuder technology at Lewiston, NC in 2002/2003 and Clinton, NC in 2000.

The only measured gaseous species using annular denuder technology that demonstrates a major difference in 12-hour average concentrations between the Lewiston and Clinton sites is ammonia. The mean concentrations vary by a factor of 5 (Table 1) and the observed maximum concentrations vary by a factor of 10. The difference in observed ammonia concentrations is even more striking when the cumulative frequencies for the observations from the two sites are compared (Figure 2). For the Lewiston site, 90% of the measured 12-hour average concentrations fall below 2 ug NH₃-N m⁻³, whereas almost 80% of the observations recorded at the Clinton site in 2000 are above 2 ug NH₃-N m⁻³. It is doubtful that this difference in gaseous ammonia concentrations can be attributed to differences in meteorology between 2000 and 2002/2003. Rather, the differences are consistent with differences in local source terms for ammonia emissions at these two locations. One logical explanation for differences in local source terms for

ammonia would be the differences in animal production densities in Sampson and compared to Bertie County. The total NH_3 emission density for Sampson County is $4800 \text{ kg NH}_3\text{-N km}^{-2} \text{ yr}^{-1}$. For Bertie County the NH_3 emissions density is $< 400 \text{ kg NH}_3\text{-N km}^{-2} \text{ yr}^{-1}$ which corresponds to a difference by a factor of approximately 10 and is consistent with the observed difference in 12-hour average ammonia concentrations (Table 1).

Ammonium-Based PM_{2.5}

The summary statistics for ammonium-based PM_{2.5} (NH_4Cl , NH_4NO_3 , NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$) as measured by annular denuder technology at the Lewiston, NC site are provided in Table 2. Also provided for comparison purposes, are data for the same aerosol species measured at the Clinton Horticultural Crops Research Station in 1999 and 2000. The data in Table 2 reflect the analyses completed for the samples obtained from the Lewiston site for the periods April 29, 2002 to August 4, 2002, and December 12, 2002 to May 18, 2003.

Based on the limited analyses completed to date, the 12-hour average concentrations of ammonium, nitrate and sulfate appear lower at the Lewiston site in 2002/2003 than at the Clinton site in 2000. This is especially true for ammonium and nitrate, which differ by a factor of 3 or more in both the calculated mean values and maximum values observed to date as compared to the 2000 Clinton dataset. The differences in sulfate concentrations between the two monitoring is less obvious, and could be due to the difference in total number of observations between the datasets. However, cumulative frequency plots of the sulfate data (Figure 3) suggests that there is in fact a consistent difference between the two datasets that would require a substantial shift in measured aerosol sulfate concentrations during the later part of the year at the Lewiston site in order to obtain parity in the mean values between the two sample populations. This would seem unlikely to happen. Indeed contrasting temporal plots of ammonium-based PM_{2.5} between the two samples sites (data not shown) suggests that the overall variation in aerosol concentration remains constant throughout the year and that the differences in ammonium-based PM_{2.5} concentrations between the Clinton site in 2000 and the Lewiston site in 2002/2003 will remain upon completion of the analyses of the remaining aerosol samples.

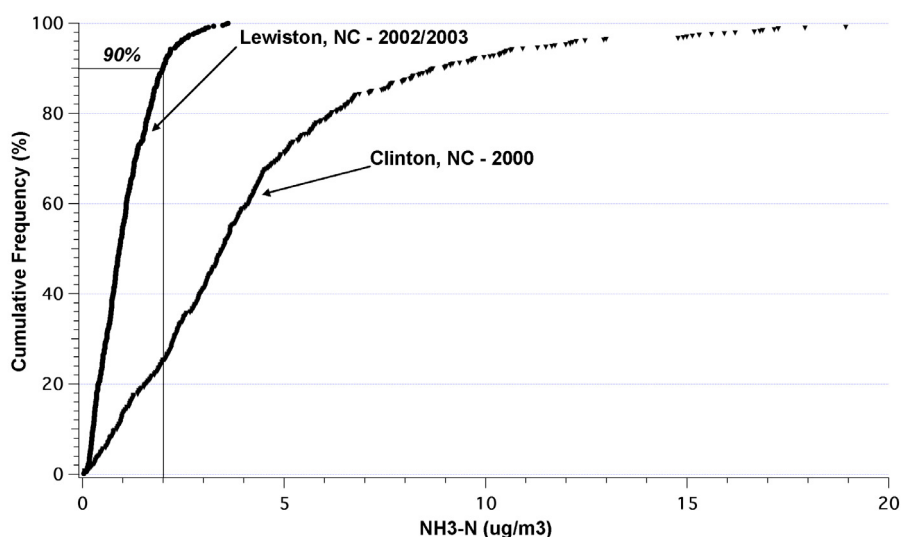


Figure 2. Cumulative frequency distribution for NH_3 measured using annular denuder technology at Lewiston, NC in 2002/2003 and Clinton, NC in 2000.

Table 2. Summary statistics for ammonium-based PM_{2.5} measured using annular denuder technology. Data for Lewiston site reflects two collection periods: April 29, 2002 to August 4, 2002, and December 12, 2002 to May 18, 2003. Data for Clinton site reflects collection period of January 1, 2000 to December 4, 2000.

Chemical Species	Monitoring Site	N	Mean	S.D.	Min.	Max.
				----- ug/m ³ -----		
Cl	Clinton	1100	0.07	0.11	0.02	1.67
	Lewiston	127	0.34	0.37	0.05	2.58
NH ₄	Clinton	1100	1.76	1.38	0.06	10.1
	Lewiston	288	0.74	0.68	0.05	3.85
NO ₃	Clinton	1100	1.91	2.05	0.09	23.0
	Lewiston	211	0.20	0.21	0.03	1.38
SO ₄	Clinton	1100	4.22	3.65	0.05	20.7
	Lewiston	288	3.60	2.77	0.33	20.6

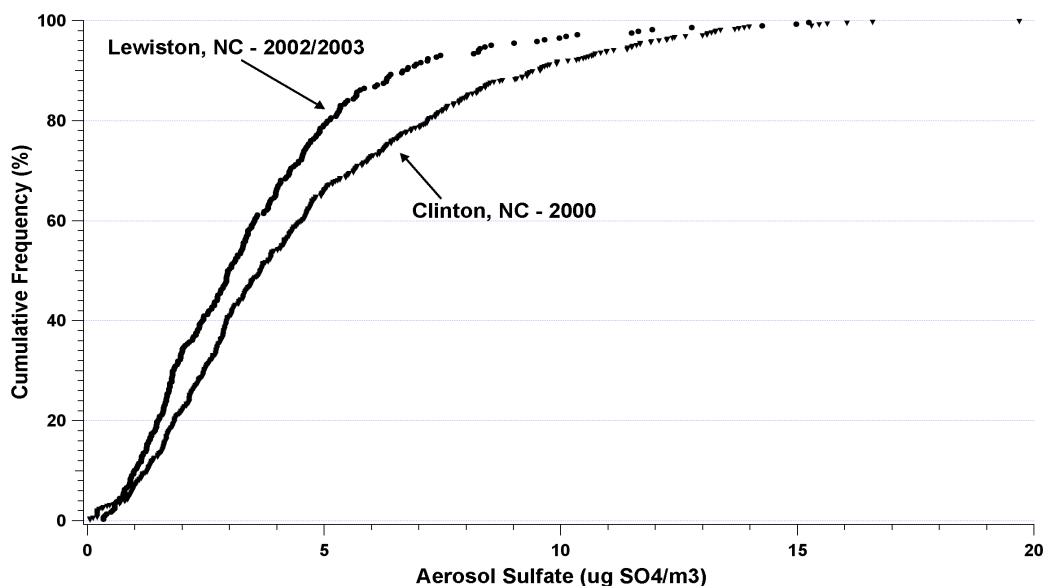


Figure 3. Cumulative frequency distribution for aerosol sulfate measured using annular denuder technology at Lewiston, NC in 2002/2003 and Clinton, NC in 2000.

Prior analysis of the annular denuder data collected at the Clinton site (Robarge et al., 2002; Walker et al., 2004) indicated that the average ammonium-based PM_{2.5} mass concentration for the 2-year period 1999-2000 is 8.0 (± 5.84) $\mu\text{g m}^{-3}$. On average, SO₄⁼, NO₃⁻, NH₄⁺, and Cl⁻ account for 53, 24, 22, and 1% of total ammonium-based PM_{2.5} mass. During both years, SO₄⁼ becomes the primary constituent during warm months. Nitrate concentrations are higher during colder months. Chloride appears not contribute significantly to PM_{2.5} at any time.

Given the results of studies which have investigated speciated PM_{2.5} in the eastern U.S. (U.S. EPA, 1996; Tolocka et al., 2001), it may be reasonable to assume that, on average, ammonium-based aerosol accounts for less than 53% of total PM_{2.5} mass. If this assumption is valid, the annual standard of 15 $\mu\text{g m}^{-3}$ may be routinely violated at the Clinton site, based on the observed 2-year average concentration (8.0 $\mu\text{g m}^{-3}$) and the distribution of daily values shown in Figure 8. During 2000, total PM_{2.5} concentrations at 17 sites

across the state of North Carolina ranged from 12.3 to 18.0 $\mu\text{g m}^{-3}$ (NCDENR, 2002). Total $\text{PM}_{2.5}$ annual mean concentrations in Duplin, Lenoir, and Wayne counties, which are also within the six-county agricultural region described earlier, were 13.1, 12.7, and 15.9 $\mu\text{g m}^{-3}$, respectively, during 2000 (NCDENR, 2002). To date, the ammonium-based $\text{PM}_{2.5}$ concentration collected at the Lewiston site averages 4.6 (± 3.4) $\mu\text{g m}^{-3}$. If the trends in measured ammonium-based $\text{PM}_{2.5}$ concentrations continue, it is unlikely that the $\text{PM}_{2.5}$ regulations will be violated at the Lewiston site.

Conclusions

The presence of excess NH_3 in the atmosphere influences the concentration and atmospheric chemistry of ammonium-based aerosol. At the Clinton site located in the center of Sampson County (estimated NH_3 emission density 4800 $\text{kg NH}_3\text{-N km}^{-2} \text{yr}^{-1}$) prior investigations have shown that the relatively high concentration of atmospheric NH_3 establishes the condition of acid-gas limited ammonium aerosol formation during all seasons; i.e. no obvious seasonal trends in total ammonium-based $\text{PM}_{2.5}$ mass. At the Clinton site, ammonium-based aerosol concentrations are likely to be more sensitive to SO_2 and NO_x emissions than NH_3 emissions (Walker et al., 2006). The Lewiston site being monitored in this project provides an important test of this hypothesis. Ambient ammonium concentrations are significantly reduced suggesting more dependence of ammonium-based $\text{PM}_{2.5}$ on ammonia emissions or transport of ammonia into the site. Continued monitoring at the Lewiston site will provide much needed data on ambient N-containing inorganic gas and aerosol concentrations leading to a better understanding of the impact of emissions of ammonia on local and regional air quality.

Acknowledgements

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Carbon Dioxide Efflux from Poultry Litter Applied Soils under Conventional and Conservation Tillage Systems in North Alabama

Tiffany Roberson^{1,2}, E.Z. Nyakatawa¹, K.C. Reddy¹, and R.L. Raper²

¹Alabama A & M University, Department of Plant and Soil Science, PO Box 1208, Normal, AL 35762.

²USDA-ARS, National Soil Dynamics Laboratory, 411 S. Donahue Drive, Auburn, AL 36832-5806.

Abstract

Elevated carbon dioxide (CO₂) levels from anthropogenic sources such as agriculture, use of fossil fuels, and deforestation pose problems such as global warming which can negatively impact natural ecosystems and food production. Intensive tillage can lead to C loss from agricultural soils. The objective of this study was to measure and document carbon dioxide loss and carbon storage in tilled and non-tilled cotton plots receiving poultry litter and ammonium nitrate as a nutrient source.

The atmosphere contained about 370 ppm CO₂ in 2002 as compared to about 280 ppm CO₂ before the industrial revolution (Brady and Weil, 2002) due to a phenomena known as global warming. It is speculated that future global CO₂ emissions to the atmosphere will increase from the current 7.4 billion tons of atmospheric carbon per year to about 26 billion tons per year by 2100 if major changes are not made in the way the world manages ecosystems and the way the world uses energy, particularly that from fossil fuels (Department of Energy, 2002). Agricultural ecosystems are important in the global context because of the large CO₂ flux to the atmosphere, and also because C storage in these systems can be sensitive to management practices such as tillage and cropping systems (West and Post, 2002). Soil conservation practices which can increase C levels include reduction in tillage such as use of mulch-tillage and no-tillage instead of conventional-tillage, planting cover crops such as winter rye [*Secale cereale* (L.)], and applying manures such as poultry litter (USDA Technical Note, 2001). Cover crops provide needed organic material which improves soil organic matter (Schertz and Kemper, 1994). Reddy et al. (2004) found that winter rye [*Secale cereale* (L.)] cover cropping increased surface residue cover by up to 35, 70, and 100% in CT, MT, and NT systems respectively. In addition to using conservation tillage, and growing cover crops, application of poultry litter can be used to increase soil carbon (Nyakatawa et al., 2001).

A field study to measure carbon dioxide efflux and C storage in tilled and non-tilled cotton [*Gossypium hirsutum* (L.)] plots receiving poultry litter as a nutrient source was conducted at the Tennessee Valley Research and Extension Center, Belle Mina, AL (34° 41' N, 86° 52' W) on a Decatur silt loam (clayey, kaolinitic thermic, Typic Paleudults) from 2003 to 2004. The treatments consisted of conventional-till, mulch-till and no-till tillage systems with winter rye [*Secale cereale* (L.)] cover cropping and ammonium nitrate and poultry litter sources of nitrogen. Conventional tillage was carried out using a moldboard plow in November and disking in April, followed by a field cultivator to prepare a smooth seedbed. In mulch tillage, a Lely rotary cultivator (Lely USA, Inc., Naples, FL) was used to destroy and partially incorporate crop residues to a depth of 5 to 7 cm in April before planting. No-tillage included planting directly into untilled soil using a Tye (Glascook Equipment and Sales, Veedersburg, IN) no-till planter. The winter rye cover crop variety 'Elbone' was planted in the fall and killed with glyphosphate herbicide about 7 d after flowering in the spring of 2003 and 2004. The time between killing of winter rye and cotton planting was about 6 wk each year to allow for total drying of residues. Ammonium nitrate was used at a single rate of 100 kg N ha⁻¹, the recommended N rate for cotton in the Tennessee Valley region. Poultry litter amounts necessary to supply 100 and 200 kg N ha⁻¹ were calculated for application each year based on the N content of the poultry litter. Soil CO₂ efflux was measured using the LI-COR 6400 IRGA (LI-COR, Lincoln, NE) system attached to a LI-09 soil chamber (LI-COR, Lincoln, NE) and polyvinyl chloride (PVC) soil collars.

In 2003, CO₂ efflux in CT plots which averaged 4.4 μmol m⁻² s⁻¹ was 16% and 63% significantly higher than in MT and NT respectively. In 2004, CO₂ efflux in mulch till which averaged 3.2 μmol m⁻² s⁻¹ was 14% and 33% greater than CT and NT respectively. In 2003, total carbon was 4% and 13% higher in NT than in CT and MT plots. In 2004, total carbon was 10% and 7% higher in NT than in CT and MT plots.

respectively. Plots receiving poultry litter released 18% more CO₂ than those receiving ammonium nitrate. Our study suggests that NT can reduce soil CO₂ emissions by 10.7 Mg CO₂ ha⁻¹ during the cotton growing season of about 130 days. In summary, practicing conservation tillage methods such as no-tillage and mulch-tillage in addition to using recommended rates of poultry litter as a nutrient source and leaving plant residues on the soil surface, helps to sequester carbon in cotton production systems. Conservation tillage reduced CO₂ release to the atmosphere, and thus will in the long term play a significant role in reducing CO₂ to the atmosphere. Conservation tillage practices which promote carbon sequestration serve a vital role in the storage and release of total carbon from soil.

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GHG Fluxes from Agriculture and Land-Use Change in Russia

A.A. Romanovskaya

Institute of Global Climate and Ecology, Moscow, Russia

Abstract

Anthropogenic emissions of methane (CH₄) and nitrous oxide (N₂O) in agriculture and flux of carbon dioxide (CO₂) on abandoned agricultural land of Russian Federation are considered for the period from 1990 to 2003. Domestic livestock (major contributor) and rice cultivation are sources for CH₄. In 1990, its release to the atmosphere was 4993.3 Gg. In 2003 it dropped to 2247.5 Gg. N₂O emissions were estimated from manure management systems and agricultural soils taking into consideration input of nitrogen with synthetic fertilizers, animal wastes, decomposition of crop residues left on fields and cultivation of histosols. Crop residues are the main N₂O source in national agriculture. In 1990 total estimated anthropogenic N₂O emissions from agriculture were 713.1 Gg. In 2003 it decreased to 46% of 1990 level (328.0 Gg). The decrease in CH₄ and N₂O emissions is mainly caused by reduction in number of agricultural animals and poultry, decline in the area of managed land and decreased fertilizer use in the country. CO₂ fluxes from the abandoned agricultural lands that were under natural regrowth over the territory of Russia were estimated as annual changes in soil carbon stocks. Total area of abandoned agricultural land is 25.4 millions ha. The RothC model was employed in the investigation of carbon dynamics in soils. Average annual net-emissions over the territory of abandoned lands was $2,1 \pm 1,8$ Tg C/yr in 1990-1999. CO₂ removal from the atmosphere by soils was $5,7 \pm 2,5$ Tg C/yr on average in 2000-2003.

Introduction

The increase of greenhouse gas atmospheric emissions due to anthropogenic impact results in global warming that may cause negative implications on human activities and the general biosphere functioning. Carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are the greenhouse gases whose human-induced emissions are subject to mandatory inventory under United Nations Framework Convention on Climate Change (UN FCCC, 1998). According to 1996 IPCC Revised Guidelines (IPCC, 1997) and Good Practice Guidance (IPCC, 2000), the agricultural sector is a source of anthropogenic CH₄ and N₂O emissions. Methane emissions come from enteric fermentation of domestic livestock, animal waste management systems (AWMS), and rice cultivation. Agricultural soils are considered the major anthropogenic source that accounts for more than 50% of global N₂O emission to the atmosphere (Khalil and Rasmussen, 1983; Bouwman et al., 2005). The intensity of N₂O formation and release to the atmosphere depends on content of soil nitrogen compounds. Input of organic (manure and human sewage) and mineral (synthetic) fertilizers, atmospheric deposition of nitrogen compounds of anthropogenic origin, decomposition of agricultural crop residues on fields, and cultivation of histosols rise nitrogen content in soil and consequently, increase N₂O emission from them (Bouwman et al., 2005; Mosier et al., 2005). Leaching and runoff of nitrogen compounds from fields induce subsequent formation of N₂O in groundwater, rivers and estuaries. These secondary sources are also associated to human activities in agricultural sector.

Soils play an important role in the global carbon cycle and can serve both as a sink and a source of carbon in the atmosphere. The organic carbon pool in the world soils is assessed at 1350 billion tons (Chapin and Matthews, 1994), which is equal to about 80% of the total pool of organic carbon in the terrestrial ecosystems, including vegetation (Land Use, 2000). The anthropogenic influences on soils affect the content of organic carbon and, thus, affect the global carbon balance in the biosphere. One of the main types of the anthropogenic influence on soils is related to the character of land use. For example, tree felling and plowing of virgin lands may result in a considerable loss of soil carbon and, hence, CO₂ release into the atmosphere, whereas the overgrowing of abandoned plowlands may lead to a gradual restoration of the soil humus pool and, thus, to carbon sequestration. In the 1990s, the global annual flux of carbon into the atmosphere under the impact of changes in the land use was equal to 2.2 ± 0.8 billion tons (Houghton, 2003). The main contribution to the carbon emission was due to forest cutting in tropical areas.

The aim of this work is to estimate anthropogenic emissions of CH₄ and N₂O from Russian agriculture and to study the changes in the total pool of organic carbon within the long-fallow lands of Russia for the period from 1990 to 2003.

Methods

The calculation of anthropogenic CH₄ and N₂O emissions was performed in accordance with Revised 1996 IPCC Guidelines (IPCC, 1997) and Good Practice Guidance (IPCC, 2000), and with the use of national statistical data (The Agricultural and Industry..., 1995; Agriculture in Russia, 1998, 2004). Methane emission from enteric fermentation and AWMS was estimated as a sum of emissions from particular animal categories and poultry, whereas the emission from rice cultivation is calculated for continuously flooded fields. Country-specific activity data on nitrogen content in manure and the split of various AWMS in Russia were derived to estimate N₂O emission from livestock categories. These are based on amount of nitrogen produced by domestic livestock and poultry as well as typical waste management practices applied within the country (Gytarsky et al, 2001). Default emission factors were applied to calculate N₂O and CH₄ emissions from enteric fermentation, AWMS and rice cultivation (IPCC, 1997; 2000). Country-specific emission factors were derived to estimate anthropogenic N₂O emission from the input of synthetic nitrogen fertilizers (Romanovskaya et al., 2001, 2002a, b). Nitrous oxide emissions from main types of cultivated soils (chernozems and soddy podzols) were estimated with the use of country specific emission factors (Romanovskaya *et al.*, 2001, 2002b). Calculations for other soils were made with the use of IPCC default emission factors. Nitrous oxide emissions from decomposition of agricultural crop residues (aboveground and underground) left on fields were also estimated with country-specific data on the amount of residues of various crops and their typical N content, including both N-fixing and non-N fixing crops (Romanovskaya et al., 2002a). The default IPCC methodology was applied to calculate emissions from cultivation of histosols in the country and indirect N₂O emissions in agriculture (IPCC, 1997; 2000).

To estimate changes of soil carbon pools within the abandoned lands the recently (after 1990) long-fallow lands of the Russian Federation are analyzed; in agreement with the Kyoto Protocol (Kyoto Protocol, 1998), the lands abandoned prior to 1990 are not considered, though some loss or accumulation of organic carbon may take place in them. Estimates of the areas of long-fallow lands were done on the basis of the official statistical data (The Agricultural and Industry..., 1995; Agriculture in Russia, 1998, 2004) via subtracting the area under croplands and annual fallow from the total area of arable land in separate regions. It was assumed that the soils that had not been plowed in 1990 remained in the fallow state afterwards, i.e., that the natural vegetation succession on them had a continuous character.

Changes in the reserves of organic carbon in the abandoned arable soils depend on the climatic parameters and the type of vegetation; these two factors dictate the annual input of organic remains into the soil and the rates of their decomposition, humification, and mineralization (Titlyanova, 1990; Chapin and Matthews, 1994; Orlov et al., 1996). The methods of mathematical modeling with due account for the entire set of parameters affecting the fate of soil organic carbon are usually applied to estimate the changes in the soil carbon pool. In our study, the RothC model was used (Coleman and Jenkinson, 1996; Jenkinson, 1990). This model was developed to simulate the soil carbon cycle in the cultivated soils. It is known that the properties and structural state of the formerly cultivated soils do not change much during the first two--three decades after the transfer of the former cropland into the category of long-fallow land. The initial input data of the model are the climatic data (the mean monthly temperature, precipitation, and evaporability), the soil properties (the initial content of organic carbon in the plow layer and the clay content in the soil), and the vegetation characteristics (the input of organic remains into the soil). This model makes it possible to calculate the soil organic carbon budget on a monthly basis; it can be used for long periods of forecasting. The models take into account four different pools of soil organic carbon: easily decomposable vegetation remains, difficulty decomposable vegetation remains, the microbial biomass, and the soil humus. The calculations are performed for each of these pools and for the pool of inert soil organic matter with high resistance to microbial decomposition.

In our calculations, the territory of Russia was subdivided into 40 regions with due account for the administrative division and for the similarity of soil and climatic conditions in the neighboring administrative regions (oblasts). Data on the monthly precipitation (mm) and temperature (°C) were obtained from the long-term records of weather stations (Reference Book on the Climate of the USSR, 1965; Hong-Kong Observatory, 2003) and averaged for the areas of particular regions. The climatic data

for the period from 1960 to 1990 were mainly obtained from the website of the Hong-Kong observatory (Hong-Kong Observatory, 2003). The evaporability was calculated by the Thornthwaite method (Thornthwaite, 1948) on the basis of data on the mean monthly temperatures.

Information on the reserves of humus in different types of Russian soils was taken from the database compiled by Bolotina (1976), which has the most detailed information on the humus content in the plow layer (0–20 cm) for different types of soils differentiated with respect to the character of the land use. The carbon content in the soil humus was assumed to be equal to 58% (Kononova, 1984). Using this value, the reserves of humus in the plow layer were recalculated into the reserves of organic carbon. The data on the humus content in the plow layer of different soils were linked to the map of the administrative division of Russia. The distribution of plowed areas by different types of soils in each of the administrative regions was obtained from the statistical information of the Ministry of Agriculture (Distribution of Agricultural Lands..., 1980). On this basis, the average humus content in the humus of plowed soils was calculated for all the regions.

The databases developed by Bolotina (1976) and Sokolov and Rozov (1976) contain generalized information on the texture of the arable soils in the former Soviet Union; a distinction is made between loamy sandy, loamy, and clayey soils. The average content of the physical clay fraction in these groups of soils can be obtained from (Golubev, 1970). In our work, the physical clay content in the loamy sandy soils is assumed to be equal to 15%; for the loamy podzolic soils, 35%; for the loamy steppe (chernozemic) soils, 40%; for the clayey podzolic soils, 65%; and for the clayey chernozems, 72.5%. Taking into account the areas occupied by different soil types in the croplands of particular administrative regions (Distribution of Agricultural Lands..., 1980), the average content of the physical clay fraction in the cultivated soils of the regions can be determined.

The model distinguishes between different groups of soil organic carbon. The inert pool of soil humus is difficultly decomposable and remains virtually stable for decades. Thus, this pool of soil humus was excluded from further calculations (Jenkinson, 1990). The initial data for the other structural components of the soil organic matter were calculated according to the methodology suggested by the authors of the model (Coleman and Jenkinson, 1996; Jenkinson, 1990). It was supposed that the organic matter of the plowed soils was in a quasiequilibrium state with the environment before the cessation of the plowing. To adjust the model, the reserves of organic carbon in the plow layer (0–20 cm) were calculated for long time periods (up to 10 000 years) with due account for the soil and climatic conditions of a given region and for the different values of the annual input of postharvest residues into the soil. The organic carbon content in the postharvest residues of major types of cultivated crops was determined according to the method of Levin (Levin, 1977; Romanovskaya et al., 2002a). The calculation of the initial pool of organic carbon in the active components of the soil organic matter (labile humus, microbial biomass, and plant remains) was stopped when the total organic carbon content predicted by the model reached the values corresponding to the average organic carbon content in the soils of a given region calculated on the basis of the work of Bolotina (1976). The difference between the values calculated by the model and the values calculated by us on the basis of published data was less than 0.01 t C/ha.

The dynamics of the input of plant remains into the soil after the cessation of crop growing depends on the type of vegetation succession taking place on the former cropland (Gusev, 1932; Nersesyan and Shur-Bagdasaryan, 1989; Snakin, 1992; Snytko et al., 1986, 1988; Turnagaev and Pestereva, 1976). The annual productivity of plant communities in the succession can be expressed in percent of the maximum productivity of meadow communities in the given region. In turn, the latter can be calculated on the basis of data by Bazilevich (1993). Information on the productivity of meadow herbs in the zones of the middle and southern taiga, mixed and broad-leaved forests, forest-steppes, and steppes, as well as in the mountainous regions, has been averaged for the particular zones and, then, for the particular regions distinguished in our study.

It can also be supposed that the annual phytomass production of herbs in the plant successions on the abandoned croplands (long-fallow lands) is approximately equal to the amount of the plant remains getting into the soil. This assumption suggests that the development of vegetation successions on the abandoned croplands follows the natural pattern. Haymaking, pasturing, grass burning, and other kinds of anthropogenic impacts on the vegetation of the abandoned croplands are not taken into account. The minimal influence of the latter factors on the character of the vegetation successions on the recently

abandoned croplands can be indirectly proved by the data on the bulk harvest of hay in Russia in the past decade. From 1990 to 2003, it decreased by 40% (The Agricultural and Industry..., 1995; Agriculture in Russia, 1998, 2004). Thus, we can conclude that no additional hayfields appeared in the country during this period.

Results and Discussion

Greenhouse gas emissions from agriculture in Russia are presented in the Table 1. In 1990 the total CO₂ equivalent emissions from agricultural sources estimated as high as 325.9 Tg. During the period from 1990 to 2003 the total agricultural emissions dropped on 54.3% and in 2003 agriculture provided not more of 148.9 Tg CO₂ eq. The decrease in CH₄ and N₂O emissions is mainly caused by reduction in number of agricultural animals and poultry, decline in the area of managed land and decreased fertilizer use due to political and economical changes in the country.

The trends of the major greenhouse gases in agriculture during the period from 1990 to 2003 are given on the figure 1. Both gases show constant decline in their emissions. In 1990, CH₄ release to the atmosphere was 4993.3 Gg. In 2003 it dropped to 2247.5 Gg. Total estimated anthropogenic N₂O emissions from agriculture were 713.1 Gg in 1990 and in 2003 it decreased to 46% of 1990 level (328.0 Gg).

Contributions of various category sources to the total agricultural emissions in the country are rather stable all over the whole period of estimations (Figure 2 and 3). Enteric fermentation is the priority source of methane emission in national agricultural sector. Methane release from enteric fermentation depends on type, age, weight productivity and diet of animals, as well as the orientation of their growing. Ruminant animals have the most intensive fermentation and consequently, CH₄ emission. Almost 87% of CH₄ emissions from enteric fermentation come from dairy and non-dairy cattle. CH₄ emission from AWMS is mainly produced by cattle and swine farms. Rice cultivation contributes to 2.5% of total methane emission from national agriculture.

Table 1. Greenhouse gas emissions in Russian agriculture, Gg/yr.

Gas: Category source	1990	1995	1996	1997	1998	1999	2000	2001	2002	2003
CH ₄ : Enteric fermentation	4376.2	3233.6	2951.5	2605.7	2334.1	2108.0	2067.6	2009.2	1991.6	1954.4
CH ₄ : Manure management	502.3	357.5	325.6	284.8	258.8	242.9	243.5	228.7	228.7	230.7
N ₂ O : Manure management	183.75	131.4	117.9	103.0	93.4	86.4	85.3	82.0	82.2	82.1
CH ₄ : Rice cultivation	114.8	68.4	68.8	60.4	58.4	69.2	70.0	61.6	59.6	62.4
N ₂ O: Direct emissions from agricultural soils	338.5	221.9	211.9	206.2	179.5	175.5	182.7	181.7	182.1	175.0
N ₂ O: Grazing of animals	29.1	20.8	18.7	16.3	14.6	13.2	12.9	12.6	12.6	12.5
N ₂ O: Indirect emissions from agricultural soils	161.8	88.6	80.7	72.6	65.1	58.7	61.8	59.0	60.1	58.5
Total GHG emission, Tg CO ₂ eq.	325.93	220.30	203.28	185.38	164.97	154.32	156.26	152.23	152.35	148.87

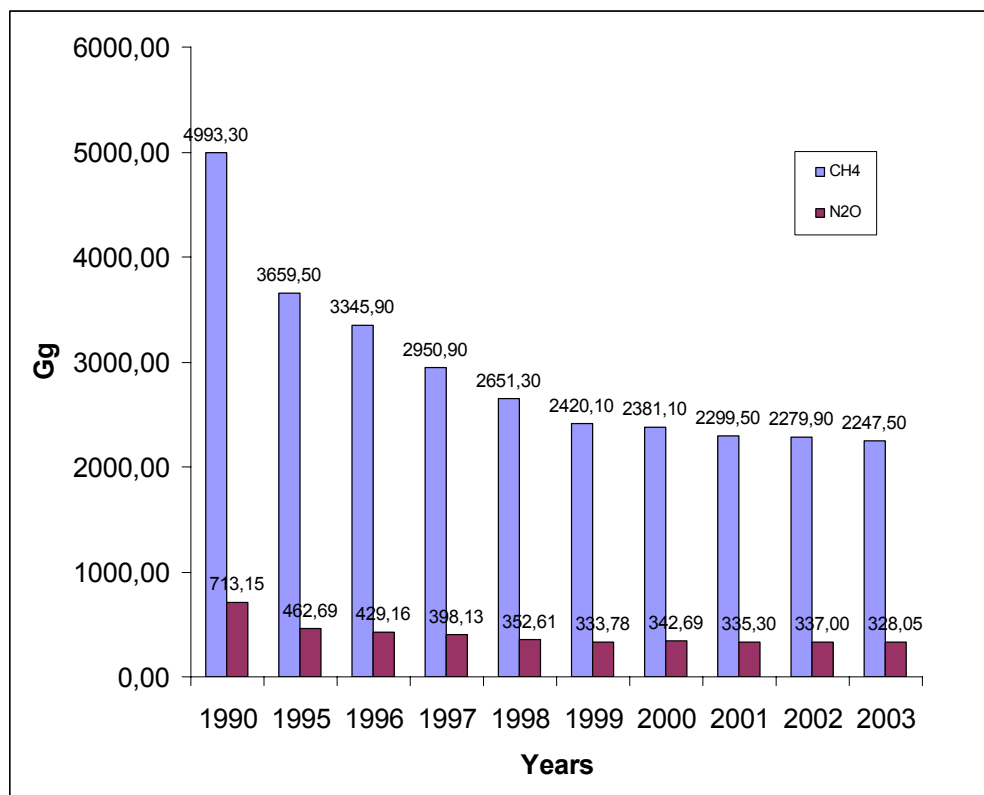


Figure 1. Trends of the methane and nitrous oxide emissions from agricultural sources.

N₂O emissions were estimated from manure management systems and agricultural soils taking into consideration input of nitrogen with synthetic fertilizers, animal wastes, decomposition of crop residues left on fields and cultivation of histosols. Crop residues are the main N₂O source in direct emissions from agricultural soils, contributing from 40% in 1990 up to 57% in 2003 to that category source. That corresponds to 13% and 21% contribution to the total agricultural emissions respectively (Figure 2 and 3). After 1990, the decrease in use of synthetic nitrogen fertilizers resulted in decrease of N₂O emission from this source and therefore its contribution. In 1990 the input of fertilizer nitrogen caused the release of 83 Gg N₂O. In 2003 emission dropped and became approximately 19.5% of the 1990 level (16 Gg N₂O).

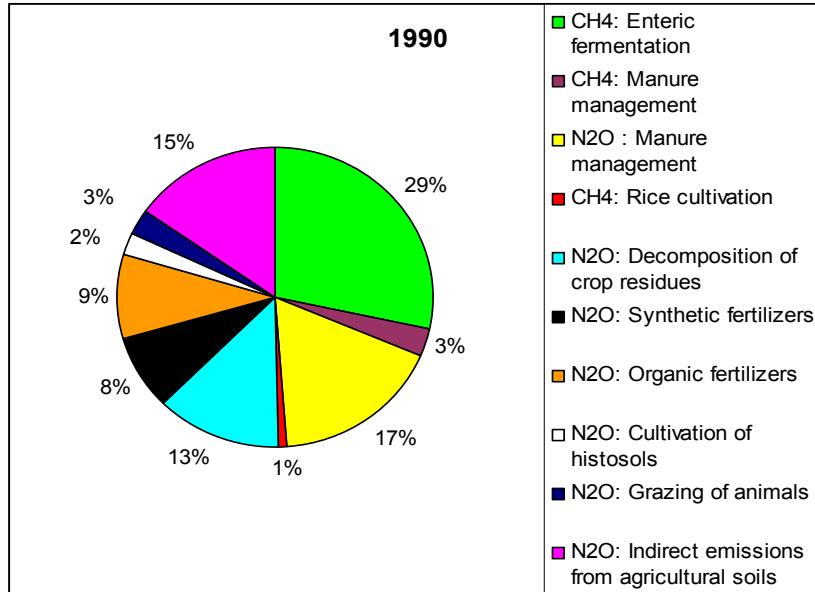


Figure 2. Contribution of different categories sources to the total GHG emissions from agriculture in 1990 (CO₂ eq.).

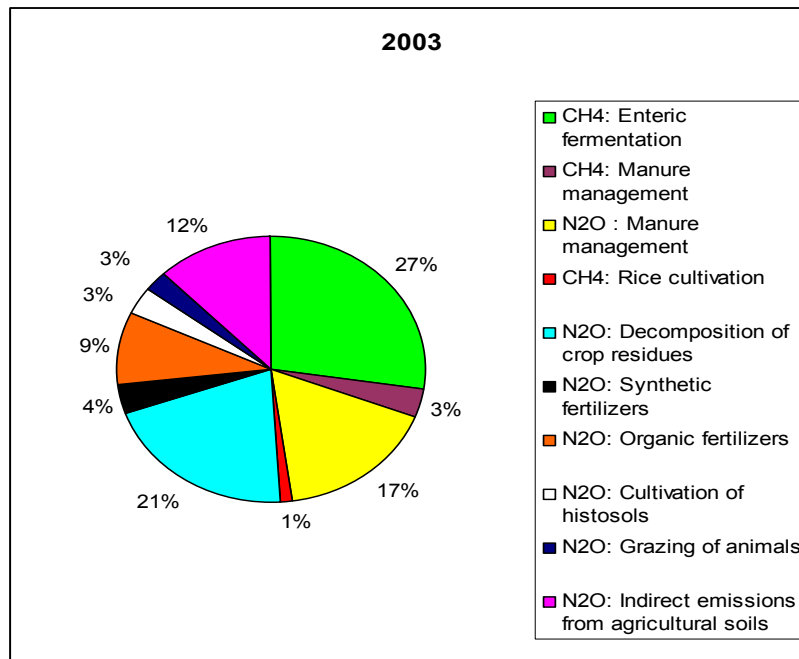


Figure 3. Contribution of different categories sources to the total GHG emissions from agriculture in 2003 (CO₂ eq.).

Soil Carbon in Abandoned Land

The results of our calculations indicate that the area of recently abandoned plowlands subjected to overgrowing with natural vegetation considerably increased in Russia from 1990 to 2003. In 1990, the total area of long-fallow lands comprised 0.5% of the total area of the cropland in Russia. In 2003, the area of long-fallow lands increased to 17.4% of the total area of the cropland, i.e., by almost 30 times. Overall, the area of abandoned cropland during these years reached 25.4 million ha.

The dynamics of the soil organic carbon on the abandoned croplands for some regions of Russia are shown in Fig. 4. In all of them, the general tendency is the same: during the first years after being abandoned, the former croplands lose organic carbon; then, as the vegetation succession leads to the development of more productive communities, the accumulation of organic carbon in the soils takes place. The rate of carbon accumulation may be higher than the rate of its loss during the first years. It should be noted that the rate of changes in the humus pool depends on the initial content of the organic carbon. In soils with an initially high humus content (e.g., in plowed soils of the central chernozemic zone and Western Siberia), these changes are relatively slow (Fig. 4). In contrast, in the low-humus soil, the dynamics of organic carbon upon the soil fallowing is more pronounced, especially in the zones with favorable climatic and vegetation conditions (e.g., in the plowed soils of Irkutsk oblast and Khabarovsk region). In Vologda oblast, the abandoned plowlands are overgrown with meadow vegetation of low productivity. Therefore, though the carbon accumulation in the soil begins on the third year of the succession, the rate of this process is relatively low. In general, the highest intensity of organic carbon accumulation in the overgrown soils of abandoned plowlands is the highest in the central region of Russia (up to 5.8 t C/ha per year) and in the Far East (up to 8 t C/ha per year), which is related to the high productivity of herbaceous biocenoses in the zones of mixed and broad-leaved forests. For the chernozemic regions of Russia, including Rostov oblast, Krasnodar region, and Stavropol region, the loss of organic carbon from the abandoned plowlands is especially significant. In 13 years, the total losses of soil organic carbon from the abandoned plowlands in these regions reached 4.8, 4.6, and 6.9 t C/ha. This is explained by the warm climate of these regions and, thus, the enhanced mineralization of the soil organic matter against the background of the low productivity of the secondary biocenoses in the dry steppe zone. The organic carbon accumulation in the abandoned and overgrown croplands in these regions begins in the ninth--tenth year after the beginning of the natural succession and proceeds at a low rate. Therefore, the net balance of carbon for the whole period under consideration (1990--2003) is negative in these regions.

Model estimations of the annual carbon flux in abandoned land during 1990-2003 shown on the Figure 5. Positive values on the figure 5 are emissions of CO₂ and negative values correspond to its sink. Before 1998 abandoned land in Russia loses soil carbon. Associated with ageing of soil after abandonment the annual plant production on unmanaged land is growing. That leads to the accumulation of the organic carbon in soils. Therefore after 1998 abandoned lands in Russia are responsible for net-sink of CO₂ with exception for 1999 then new large territories were abandoned as a result of economical crisis in 1998. Average annual net-emission over the territory of abandoned lands was 2.1 ± 1.8 Tg C/yr in 1990-1999. CO₂ removal from the atmosphere by soils was 5.7 ± 2.5 Tg C/yr on average in 2000-2003. As the largest territories of managed land were abandoned in southern regions of Russia, for those losses of soil carbon are typical, therefore, total balance of soil carbon on territory of abandoned lands in Russia during 1990-2003 shifted to emissions of 5.4 Tg C (19.8 Tg CO₂).

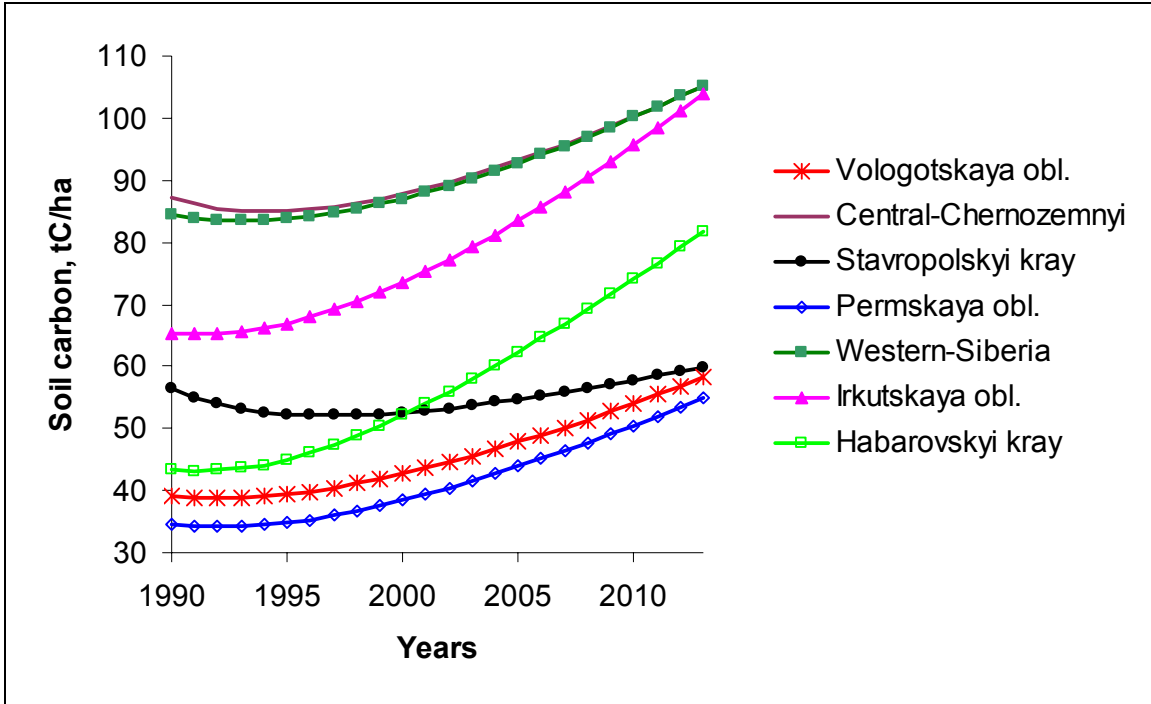


Figure 4. Dynamics of the soil organic carbon in abandoned land of some regions of Russia.

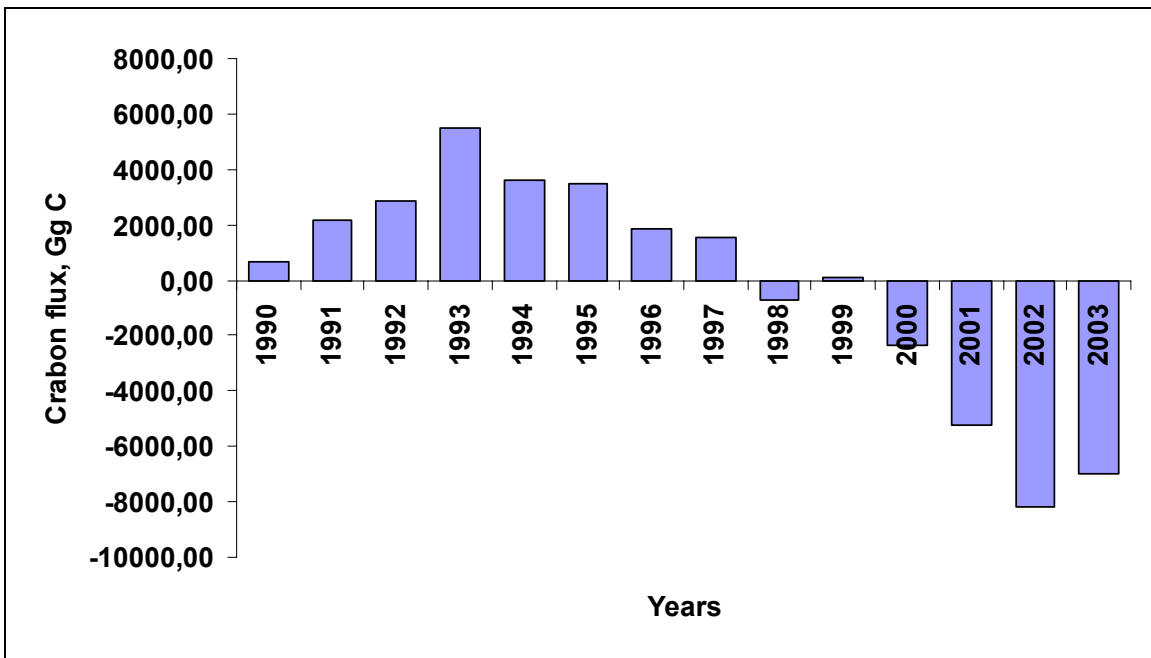


Figure 5. Annual flux of soil carbon on the territory of abandoned land in Russia.

At the same time, the current tendency in the dynamics of the soil organic carbon on the plowlands abandoned several years ago (Figs. 4) is directed towards its increased accumulation in the soils. It can be expected that this tendency will be preserved up to 2015--2020. Moreover, already in 2008--2012, when the obligations imposed by the Kyoto Protocol will come into force, the long-fallow soils in the Russian Federation will serve as a sink for carbon; it is expected that the pool of organic carbon in them will be

higher than that in 1990. In other words, the long-fallow lands of Russia can be considered as a sink for carbon in 2008--2012. More accurate estimates of the capacity of this sink should be made in the future.

Conclusions

Methane and Nitrous Oxide Emissions from Agriculture

- 1) Enteric fermentation of ruminant animals provides the major contribution to anthropogenic CH₄ emission in Russian agriculture. The animal waste management systems comprise for no more than 13% of sectoral methane emission. In 1990, Russian agriculture was a source of 4993 Gg of CH₄ that is 3% of its global emission from agriculture. Later the emission dropped and in 2003 it was 45% of the 1990 level (2247 Gg).
- 2) Agricultural soils are the major source of anthropogenic N₂O emission in Russia. Within the period from 1990 to 2003, crop residues contributed from 30% to 57% of direct emissions from agricultural soils. In 1990 total N₂O emission was 713 Gg. In 2003 the emission dropped and became no more than 46% of the 1990 level (328 Gg).
- 3) The decrease in methane and nitrous oxide emissions in Russian agriculture between 1990-2003 is associated with a reduced input of nitrogen fertilizers, decline of cultivated area and population of domestic livestock and poultry in agriculture.

Soil Carbon in Abandoned Land

- 1) The area of long-fallow lands in Russia considerably increased from 1990 to 2003. In total, the area of abandoned croplands transferred into the category of long-fallow lands in Russia during these 14 years reached 25.4 million ha.
- 2) The general tendency in dynamics of soil carbon in abandoned land of different regions of Russia is the same: during the first years after being abandoned, the former croplands lose organic carbon; then, as the vegetation succession leads to the development of more productive communities, the accumulation of organic carbon in the soils takes place. The rate of carbon accumulation may be higher than the rate of its loss during the first years. However, the rate of changes in the humus pool depends on the initial content of the organic carbon.
- 3) Average annual net-emission over the territory of abandoned lands was 2.1 ± 1.8 Tg C/yr in 1990-1999. CO₂ removal from the atmosphere by soils was 5.7 ± 2.5 Tg C/yr on average in 2000-2003. As the largest territories of managed land were abandoned in southern regions of Russia, for those losses of soil carbon are typical, therefore, total balance of soil carbon on territory of abandoned lands in Russia during 1990-2003 shifted to emissions of 5.4 Tg C (19.8 Tg CO₂).

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Nitrous Oxide Emissions from Denitrification in Swine Manure Treatment

Joe Rudek¹ and William L. Chameides²

¹Environmental Defense, Raleigh, NC

²Environmental Defense, New York, New York

Abstract

Alternative manure treatment technologies such as anaerobic digesters are effective in preventing losses of undesirable gases to the atmosphere during the mineralization of organics. Consequently, these treatments result in increased quantities of ammonia nitrogen in the treated liquid, relative to that remaining in a lagoon. Denitrification is often considered as a means to convert the ammonia nitrogen into a benign end product, N₂. The production of nitrous oxide as a byproduct of (nitrification and) denitrification may be an environmental concern given its high global warming potential.

Discussion

Decades ago the anaerobic lagoon was designed, at least in part, to protect groundwater from nitrate contamination during animal waste treatment. This protection was accomplished by enhancing ammonia volatilization into the atmosphere. At the time, emitting ammonia into the atmosphere seemed sensible, given concerns about nitrate. Unfortunately the large fluxes of ammonia from the lagoons has led to significant health risks and environmental impacts. As efforts to find alternative animal waste treatment technologies proceed, it would be prudent to consider the potential for similar unintentional impacts that might not be apparent today. One such concern is nitrous oxide loss as a result of denitrification. While nitrous oxide loss during denitrification is generally only a small percentage (less than 2%) of the nitrogen being processed, its very high global warming potential (310 times CO₂) means even a small percentage loss can have a significant climatic impact. Reductions in methane emission, also a goal of many alternative waste treatment systems, could partially offset the net global warming potential of nitrous oxide lost during waste treatment. However, the global warming potential of methane is 21 times CO₂, nearly 15 times less potent than nitrous oxide. The impact of potential nitrous oxide loss in the advent of widespread adoption of denitrification as part of an alternative swine waste treatment system will be evaluated. The offsets and tradeoffs of simultaneous methane and ammonia loss reductions relative to increased nitrous oxide emissions in alternative treatment systems will also be considered.



Ammonia Emission Fluxes from a Dairy: Stalls, Lagoons, and Slurry Application

Brian Rumburg¹, George H. Mount¹, Brian K. Lamb¹, Hal Westberg¹, Jenny Filipy¹, David Yonge², Kris Johnson³, Ron Kincaid³,

¹Laboratory for Atmospheric Research, Department of Civil & Environmental Engineering, Washington State University, Pullman, Washington, USA 99164-2910

²Center for Multiphase Environmental Research, Department of Civil & Environmental Engineering, Washington State University, Pullman, Washington, USA 99164-2910

³Department of Animal Sciences, Washington State University, Pullman, Washington, USA 99164-6310

Abstract

The effect of atmospheric ammonia (NH_3) emissions on the atmosphere, environment, and human health are not well understood due to a lack of information about emissions, transport, and fate. Ammonia in the atmosphere reacts to form fine aerosols which impact human health and its deposition has serious environmental impacts. Sulfate and nitrate in the atmosphere will react with NH_3 to form particulate matter less than 2.5 microns in aerodynamic diameter ($\text{PM}_{2.5}$) which is regulated by the Environmental Protection Agency (EPA). The largest anthropogenic source of atmospheric NH_3 is animal excreta. Dairy cows are the largest per animal emission source due to the large energy requirements of milk production. Short-path differential optical absorption spectroscopy (DOAS) was used to measure NH_3 concentrations, and an area source tracer ratio technique was used to calculate emission fluxes. Measurements were made from the housing area, waste lagoons, and sprinkler application. Emissions models were developed to understand the physical processes and local transport of NH_3 . Housing emission fluxes for the summer averaged $8.1 \pm 5.2 \text{ mg cow}^{-1} \text{ s}^{-1}$ at 18° C average temperature. The housing model had an error of $\pm 30\%$ when compared to measured concentrations. Lagoon emission fluxes ranged from $30 \mu\text{g m}^{-2} \text{ s}^{-1}$ at an air temperature of 11° C to $150 \mu\text{g m}^{-2} \text{ s}^{-1}$ at an air temperature of 27° C . The lagoon model had an error of $\pm 21\%$. Slurry application emissions from the sprinkler were 18% of the slurry ammonia-N concentration. The initial measured flux from the field was $47 \mu\text{g m}^{-2} \text{ s}^{-1}$ and this decreased to $17 \mu\text{g m}^{-2} \text{ s}^{-1}$ during the experiment due to slurry infiltration into the soil. Annual emissions based upon theoretical models estimate emissions to be $130 \text{ kg NH}_3 \text{ cow}^{-1}$.

Introduction

Ammonia emissions and the impact of atmospheric NH_3 on human health and the environment in the United States is not well understood due in part to a lack of measurement data from the major anthropogenic sources, waste from domesticated animals. The measurement of atmospheric NH_3 is difficult since it adheres to instrument inlet walls creating measurement artifacts. The United States Environmental Protection Agency (EPA) established a new standard for particulate matter with an aerodynamic diameter less than 2.5 microns ($\text{PM}_{2.5}$) in 1997. The passage of the $\text{PM}_{2.5}$ standard has led to interest in NH_3 emissions because NH_3 reacts with nitrate and sulfate species in the atmosphere to form $\text{PM}_{2.5}$. Current U.S. emission estimates are based upon European measurements where farming practices and regulations are different from the U.S., leading to possible errors in the current NH_3 emission estimates.

Most current emission estimates are annual estimates based upon a few measurements and do not reflect the influence of meteorology on emissions. Ammonia emissions vary seasonally due to the volatilization rate being temperature dependent. The production of NH_3 from the biological breakdown of organic N in animal waste is also temperature dependent. Cows produce the largest fraction of NH_3 globally, and of these, dairy cows have the largest per animal emissions due to their consumption of large amounts of protein for milk production. Emissions vary depending upon the housing, waste storage, and waste disposal methods.

The purpose of this work was to determine the total emissions of NH₃ from the milking dairy cows at the Washington State University (WSU) dairy and develop emissions algorithms for use in a regional air quality model. The emission sources measured include the housing area, waste lagoons, and waste application. This paper discusses the measurements of NH₃ emission fluxes and model results.

Methods

A series of concentration measurements and tracer experiments were conducted downwind of the milking cow housing, waste lagoons, and during sprinkler application of the waste at the WSU dairy from 2000 to 2004.

Instrumentation

Atmospheric NH₃ was measured using an open path differential optical absorption spectroscopy (DOAS) as described in Mount et al. (2002). The open-path method is advantageous because it does not suffer measurement problems due to NH₃ adhering to inlet walls. The instrument measures the photoabsorption of NH₃ in the mid-ultraviolet from 200 to 235 nm. The spectrograph is housed in a trailer along with the Xenon light source, collimating and collecting optics. Retro reflectors were used to direct the light beam to the collecting optics and then into the spectrograph. The spectrograph is a double crossed Czerny-Turner design with a silicon array diode detector. The instrument has a very high signal to noise ratio allowing high precision measurements as fast as every second. The detection limit is a few ppbv. For the experiment, spectra were co-added and recorded approximately every five minutes.

Tracer Ratio Flux Method

Fluxes from the dairy housing, waste lagoons, and waste application were measured using a tracer ratio technique. Sulfur hexafluoride (SF₆) was used as a tracer gas due to its low reactivity. The higher molecular weight of SF₆ compared to NH₃ has a negligible effect due to turbulent diffusion being the dominant transport mechanism (Kaharabata et al., 2000). The area source tracer ratio technique first discussed by Ludwig et al. (1983) was used to calculate the fluxes of NH₃. The method has been used to measure emissions of natural gas from urban areas (Lamb et al., 1995; Shorter et al., 1997), hydrocarbons from refinery waste impoundments (Howard et al., 1992), and greenhouse gases from cattle processing waste lagoons (Eklund, 1999). Tracer techniques have been shown to be in good agreement with other flux measurement techniques (Lamb et al., 1986). In this approach, a tracer is released as close as possible upwind of the area source, at a known rate and is measured downwind at the same location as the pollutant concentration from the area source. Knowing the tracer release rate and downwind concentrations it is possible to calculate the pollutant emission rate. The best conditions for tracer experiments are a steady wind so turbulence is the dominant dispersion mechanism and small σ_z so the tracer plume traverses the area source.

The equation for the concentration downwind of an infinite line source is the following

$$C_l = 2Q_l / (\sigma_z u (2\pi)^{1/2}) \quad (1)$$

where C_l is the line source concentration at ground level (g m^{-3}), Q_l is line source emission rate ($\text{g m}^{-1} \text{s}^{-1}$), σ_z is the vertical plume diffusion coefficient, and u is the wind speed (m s^{-1}). For this derivation the following assumption was made

$$\sigma_z = a x^b \quad (2)$$

where a and b are empirical coefficients and x is the distance of the emission source from the receptor.

For an area source the above equation can be integrated to yield:

$$C_A = 2Q_A (X_u^{(1-b)} - X_d^{(1-b)}) / (u a(1-b) (2\pi)^{1/2}) \quad \text{for } b \neq 1 \quad (3)$$

where C_A is the area source concentration at ground level (g m^{-3}), Q_A is the area source emission rate ($\text{g m}^{-2} \text{s}^{-1}$), X_u is the distance to upwind edge of area source (m) and X_d is the distance to downwind edge of area source (m).

The area source and line source equations can be combined to solve for the flux from the area source. The only unmeasured variable is b which can be estimated from the tracer measurements or taken from the literature.

$$Q_A = (C_A Q_l (1 - b)) / (C_l (X_u^{1-b} - X_d^{1-b}) x^b) \quad (4)$$

Tracer experiments were conducted during periods of high and steady winds to ensure that SF_6 and the NH_3 plume was being measured. During low wind speeds and times of high σ_0 the SF_6 and NH_3 plumes separated and the results were inconsistent.

The SF_6 line source was located at the upper edge of the area sources, the tubing had restrictors placed every 4 m. Sequential 30 minute average portable syringe samplers were placed along the instrument path. The syringes were analyzed using a HP 5880A gas chromatograph (Hewlett Packard, Palo Alto, CA), with standards from Scott-Marrin (Riverside, CA). Line source emission rates were measured using a Alltech Digital Flow Check (Alltech, Deerfield, IL) flow meter.

Washington State University Dairy

The WSU Knott Dairy Center is a research and commercial dairy that also serves as a teaching and research laboratory in addition to supplying milk for the WSU creamery. The milk from the dairy is processed on campus and sold as cheese; students manage and take care of their own small herd and research is conducted on diet, milk production, waste production and cow health. The WSU dairy is located 8 km south of Pullman, Washington U.S. (N 46° 43.8', W 117° 10.1'). It has approximately 175 Holstein milking cows, 35 dry cows, 130 heifers and 75 calves.

The milking cows are housed in three-sided freestall barns with concrete floors. Waste, which includes milking cow manure and urine, bedding and milking parlor wash water from the stalls, is scraped into pits daily. The pits are flushed with recycled wastewater and the wastewater goes to a solids separator where solids greater than 0.3 cm in diameter are removed. From the solids separator the wastewater goes to a high solids lagoon (250 m³) where additional solids are removed via gravity settling. The supernatant from the high solids lagoon goes to the low solids lagoon (9500 m³) where additional settling occurs. The low solids lagoon is used as the primary storage lagoon for waste from the dairy. Two additional lagoons (19000 m³) are used for long term storage of waste until the waste is applied to the surrounding grass fields in the late summer and early fall.

The milking cows are fed a diet of 26 kg of feed per day on a dry matter basis, the crude protein of the diet is 19%. The feed consists of alfalfa silage (25.6%), alfalfa hay (22.3%), concentrate (35.7%), wheat mill run (6.6%), and whole cottonseeds (9.9%). The cows consume 475 g day⁻¹ of K and 790 g day⁻¹ of N. The daily consumption of Na is estimated to be 83 g day⁻¹, but it varies as the cows have unlimited access to salt. The daily milk production for the herd averages about 41 kg cow⁻¹.

Results and Discussion

Housing Emissions

The average measured flux from the housing area was 8.1 ± 5.2 mg cow⁻¹ s⁻¹ at an average temperature of 18° C. A mechanistic model of emissions was developed based upon a model of cow urea excretions and the reactions of urea to form liquid NH_3 , and the volatilization rate from the liquid. The modeled concentrations had an error of $\pm 30\%$ compared to the measured concentrations. The model was most sensitive to changes in the pH. Emissions were highest during the summer with the maximum being about 80 kg NH_3 day⁻¹ during warm windy conditions. Total annual emissions from the housing is 7000 kg NH_3 (40 kg NH_3 cow⁻¹). A N mass balance of the housing area showed that maximum emissions would be 7900 kg NH_3 yr⁻¹ (Rumburg et al., 2006a).

Waste Storage Emissions

The NH_3 fluxes from the waste lagoons ranged from 30 to 150 $\mu\text{g m}^{-2} \text{s}^{-1}$ depending upon temperature. A theoretical emissions model was developed based upon the temperature dependence of the ammonia concentration in the lagoons, volatilization rate and pH partitioning of NH_3 and NH_4^+ in solution. The theoretical emissions model predicts the downwind concentrations of NH_3 best when using the air

temperature as opposed to the lagoon temperature. The normalized mean error of the model using the ambient air temperature as the lagoon temperature input was 21%. The model is very sensitive to changes in pH. The daily lagoon fluxes ranged from over 100 kg per day in the summer to 0 in the winter when the lagoons were frozen over. The annual emissions were calculated to be 9700 kg or (55 kg cow⁻¹ yr⁻¹) based upon dairy lagoon operating conditions (Rumburg et al., 2006b).

Waste Application Emissions

The dominant emissions from the slurry application with the "Big Gun" sprinkler were measured to be from the sprinkler itself, with 18% of the NH₃ in solution volatilizing. Initial emission from the field were 47 μg m² s⁻¹ which decreased to 17 μg m² s⁻¹ in four and a half hours. An empirical exponential function was fit to the emissions data to model the concentration of slurry at the soil surface, and a theoretical emissions model was developed based upon the infiltration of slurry into the soil and the subsequent reactions of NH₃ and NH₄⁺ in the soil complex. Volatilization from the soil is related to soil ammonia-N concentration, soil temperature and atmospheric convection at the soil surface. The total WSU dairy waste application emissions from the sprinkler is 4600 kg. The annual field emissions derived from the tracer experiment data are estimated to be 1300 kg. Total waste application emissions for the WSU dairy are approximately 5900 kg or 34 kg NH₃ per milking cow per year (Rumburg et al., 2005).

Conclusion

The annual per cow emissions from the housing, lagoons, and waste application is estimated to be 40, 55, and 34 kg NH₃ cow⁻¹ yr⁻¹, respectively. The total annual emissions from the WSU dairy is estimated to be 130 kg NH₃ cow⁻¹ yr⁻¹ which is significantly higher than the EPA NEI estimate of 38 kg NH₃ cow⁻¹ yr⁻¹ based upon European data (EPA, 2004). Differences in farming practices increased N excretions based upon higher milk production levels are most likely the reason for the large differences in emissions.

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Characterizing Ammonia Emissions from Potential Environmentally Superior Technologies for Hog Farms in Eastern North Carolina

I. C. Rumsey¹, V. P. Aneja¹, S. P. Arya¹, D-S. Kim¹, W.P. Robarge²,
D.Dickey³, L.S. Stefanski³, H. Semunegus¹, H.L. Arkinson¹, K.S. Bajwa¹, W.W. Stephens¹, S.B.
Goetz¹, L. Todd⁴, K. Mottus⁴, C.M. Williams⁵

¹Department of Marine, Earth and Atmospheric Sciences, North Carolina State University,
Raleigh, NC 27695-8208, USA

²Department of Soil Sciences, North Carolina State University, Raleigh, NC 27695-8208, USA

³Department of Statistics, North Carolina State University, Raleigh, NC 27695, USA

⁴Department of Environmental Science and Engineering, University of North Carolina-Chapel Hill,
Chapel Hill, NC 27599-7431, USA

⁵Animal and Poultry Waste Management Center, North Carolina State University,
Raleigh, NC 27695, USA

Abstract

Ammonia fluxes from anaerobic lagoons and hog houses at two conventional hog farms in eastern North Carolina were measured and analyzed to elucidate their temporal variability (seasonal and diurnal), and to derive regression relationships between ammonia flux and physico-chemical properties. These emissions are compared and contrasted with emissions from eleven (11) Environmentally Superior Technologies (EST's): (1) AHA Hunt farm- Sequencing Batch Reactor (SBR); (2) Barham farm – In-ground ambient temperature anaerobic digester/energy recovery/greenhouse vegetable production system; (3) Brown's of Carolina (BOC) Farm #93 – Upflow biofiltration system (EKOKAN) ; (4) Carrolls farm- Aerobic Blanket System (ABS); (5) Corbett #1, – Solids separation/gasification for energy and ash recovery centralized system (BEST); (6) Corbett # 2 farm – solid separation/ reciprocating water technology (ReCip); (7) Corbett #3,4- Solids separation/gasification for energy and ash recovery centralized system (BEST); (8) Goshen Ridge Farm- Solids separation/nitrification-denitrification/soluble phosphorus removal/solids processing system (Super Soils); (9) Harrells farm- Permeable Bio-cover System (PBS); (10) Howard farm – solid separation/ constructed wetlands; (11) Vestal farm- Recycling of Energy, Nutrients and Water System (RENEW). Measurements of ammonia flux were limited to two, two-week long periods, representing warm and cool seasons. A flow-through dynamic chamber system and two sets of open-path FTIR spectrometers measured continuously NH₃ fluxes from water holding structures and emissions from barns at the EST and conventional LST sites. For comparing the emissions from water holding structures at ESTs with those from lagoons at conventional sites under differing environmental conditions, a conventional statistical-observational model for lagoon NH₃ flux was developed, using multiple linear regression analysis of continuous NH₃ flux measurement data against the relevant environmental parameters measured at the two conventional farms, during two different seasons of year. Percentage reductions in NH₃ emissions from different components of the EST, as well as the whole farm were evaluated. These results were all normalized by the appropriate nitrogen excretion rate at the EST farm, as well as the appropriate conventional farm. This study shows that emissions were reduced by some ESTs under some of the environmental conditions. However, based on our evaluation results and analysis, and available information in the scientific literature, most of the evaluated alternative technologies may require additional technical modifications to be qualified as Environmentally Superior as defined by the NC Attorney Generals Agreements.

Introduction

Ammonia is the most biologically active reduced form of nitrogen, and is a very important alkaline constituent in the atmosphere. NH₃ is emitted by a large number of sources such as biomass burning, fossil fuel combustion, emissions from human excreta, soils and agricultural crops, synthetic fertilizers and animal waste (Oliver et al., 1996; Bouwman et al., 1997). In North Carolina, Hog waste releases an estimated 68,540 tons of nitrogen per year (Aneja et al., 1998). This relates to an increase in commercial

swine facilities since the 1960's, and particularly since 1980, where the hog population has increased from about 3 million to a present population of around 10 million. Ammonia reacts with a variety of acidic atmospheric species, namely nitric acid (HNO_3), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). These reactions result in the formation of ammonium aerosols, the majority of which are of the fine particle size ($<2.5 \mu\text{m}$). There are a variety of environmental consequences associated with the presence of atmospheric NH_3 and its deposition including soil acidification, aquatic eutrophication and fine particulate matter formation. In North Carolina, the main environmental consequence is the nutrient loading of coastal plain river systems (Aneja et al., 1998).

The conventional lagoon and spray technology (LST), is the current system used in North Carolina to manage hog waste. It consists of anaerobic lagoons to store hog waste (~98% liquid) and effluent from the lagoons is sprayed on surrounding crop fields as a nutrient source (Aneja et al. 2001). Four distinct components and associated processes at LST release NH_3 to the atmosphere: (1) production houses, (2) waste storage and treatment systems such as lagoons, (3) land application through injection or spraying, and (4) biogenic emissions from soils and crops (Aneja et al., 2001). The need for developing sustainable solutions for managing the hog waste problem is critical for shaping the future of hog farms in North Carolina. As a result of this, an agreement between the North Carolina Attorney General and several commercial hog farming companies was reached to develop environmentally superior technologies (ESTs) for swine facilities. Program OPEN (Odor, Pathogens, and Emissions of Nitrogen) is an integrated study of the emissions of ammonia, odor and odorants and pathogens from potential environmentally superior technologies for swine facilities. Program OPEN aims to evaluate the EST's at swine facilities to determine if they would be able to substantially reduce atmospheric emissions of NH_3 , pathogens and odor from their observed or estimated emissions from the conventional lagoon and spray technology used at selected LST hog farms (Moore farm and Stokes farm) in different (warm and cold) seasons or observation periods.

As part of Program OPEN, this study focuses on the emissions of NH_3 from the different components/processes involved in swine waste treatment, including hog houses, water-holding structures, and spray fields at eleven (11) potential EST sites: (1) AHA Hunt farm- Sequencing Batch Reactor (SBR); (2) Barham farm – In-ground ambient temperature anaerobic digester/energy recovery/greenhouse vegetable production system; (3) Brown's of Carolina (BOC) Farm #93 – Upflow biofiltration system (EKOKAN) ; (4) Carrolls farm- Aerobic Blanket System (ABS); (5) Corbett #1,- Solids separation/gasification for energy and ash recovery centralized system (BEST); (6) Corbett # 2 farm – solid separation/ reciprocating water technology (ReCip); (7) Corbett #3,4- Solids separation/gasification for energy and ash recovery centralized system (BEST); (8) Goshen Ridge Farm- Solids separation/nitrification-denitrification/soluble phosphorus removal/solids processing system (Super Soils); (9) Harrells farm- Permeable Bio-cover System (PBS); (10) Howard farm – solid separation/ constructed wetlands; (11) Vestal farm- Recycling of Energy, Nutrients and Water System (RENEW).

Methodology and Experimental Set-up at EST Sites

Ammonia flux measurements were made during two different seasons at two conventional (i.e. LST) and 15 EST swine farms in eastern North Carolina. Descriptions of the potential ESTs can be found on the website produced by the Air & Poultry Waste Management Center, NCSU, Raleigh, NC (A&PWMC, 2005. http://www.cals.ncsu.edu/waste_mgt/smithfield_projects/smithfieldsite.htm). NH_3 fluxes from water-holding structures and other area sources at the potential ESTs and conventional farms were measured by a dynamic flow-through chamber system. The emissions of NH_3 from hog houses at the potential EST and conventional farms were measured by using Open-Path Fourier Transform Infrared (OP-FTIR) spectroscopy. Emissions were normalized by nitrogen excretion rates, which were based on hog population and feed data. The percentage reduction of NH_3 emissions are calculated for the whole farm for each potential EST.

Approach to Evaluate Ammonia Emissions from Water-Holding Structures at EST Farms

At each environmentally superior technology and conventional site, the estimated ammonia emissions were limited to about two two-week periods, representing both a warm and a cold season. However, since measurements at different sites were made at different times of the year, environmental conditions are likely to be different at different sites, even during a representative warm or cold season. There is a need for

accounting for these differences in our relative comparisons of the various alternative and conventional technologies.

It is suggested that the estimated emissions from an environmentally superior technology for each measurement period be compared with the estimated emissions from conventional sites, after the later are adjusted for the average environmental parameters (most likely lagoon temperature and/or air temperature) observed at the former (EST) site. A rational basis for this adjustment for somewhat different environmental conditions could be the multiple regression model developed between ammonia emissions and measured environmental parameters at the two conventional sites. Such a comparison would not require highly uncertain extrapolations of emissions at EST sites beyond the two measurement periods. It would also provide sound basis for ranking the various ESTs based on their comparisons with conventional sites for each of the warm and cold seasons. An algorithmic flow diagram for the evaluation of NH₃ emissions from water holding structures at the EST farms is shown in Figure 1. Estimated ammonia emission from animal houses at a potential EST were compared to the estimated ammonia emissions from similar houses at a conventional farm (either Moore farm-tunnel ventilated, or Stokes farm-naturally ventilated), depending on the type of the house ventilation used at the EST farm, for the same season.

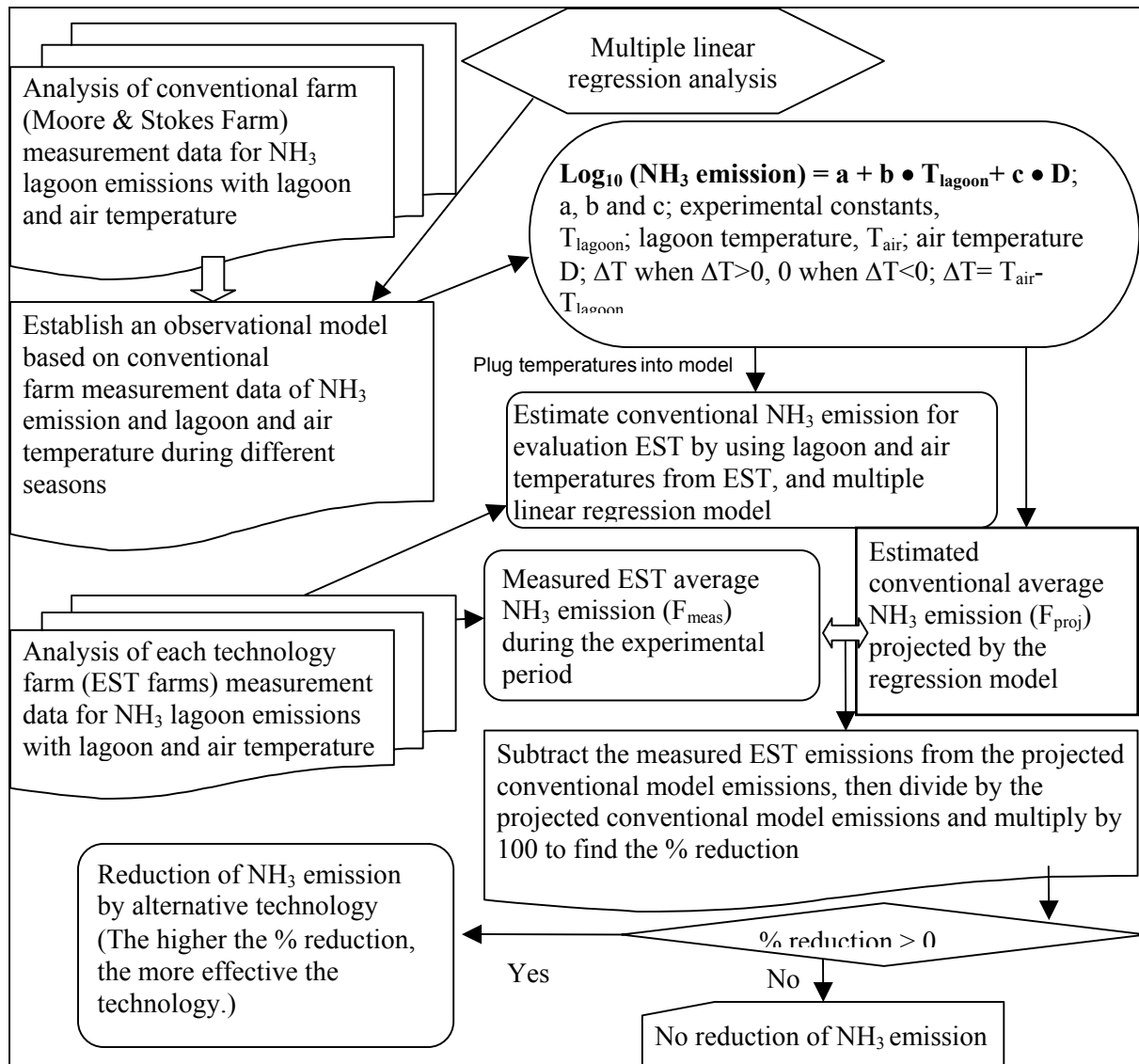


Figure 1. Algorithm flow chart for evaluation of Environmentally Superior Technology (EST) ammonia emissions from water-holding structures.

Results and Discussion

Nitrogen Excretion Rates Based on Animal Feeding

Animal weight, feed consumption and feed nutrient analysis data were used to estimate total nitrogen excretion rate produced at each experimental farm. Based on the nitrogen mass balance equation with given animal feed information (Table 1), nitrogen excretion rate (E) in unit of kg-N wk^{-1} (1000 kg-lw^{-1})¹ was determined using the following equation:

$$E = \frac{F_c \times N_f \times (1 - e_r)}{\bar{w}} \times 1000, \quad (1)$$

where F_c is the feed consumed ($\text{kg pig}^{-1} \text{ wk}^{-1}$), N_f is the fraction of nitrogen content in feed, e_r is the feed efficiency rate (ratio of average gain of nitrogen to nitrogen intake) [PigCHAMP, 1999], and \bar{w} is the average live animal weight (kg/pig). Nitrogen excretion at each farm was calculated in term of the same units as $\text{NH}_3\text{-N}$ emissions estimated from different components of the EST farm (e.g., lagoon, barns, etc) and shown in Table 1. All NH_3 emissions were normalized by nitrogen excretion rate (E) for the farm, and are called %E. Thus, %E represents the loss rate of ammonia from a source, as a percentage of N-excretion rate. A potential EST was evaluated by comparison of %E value from the EST (%E_{EST}) farm to %E value from a baseline conventional farm (%E_{CONV}), and percent reduction of $\text{NH}_3\text{-N}$ can be estimated as

$$\% \text{Reduction} = \frac{(\%E_{CONV} - \%E_{EST})}{\%E_{CONV}} \times 100 \quad (2)$$

Such percentage reductions can be estimated, separately for water holding structures, animal houses/barns, etc., as well as for the whole EST farm.

Multiple Regression Model for Lagoon NH_3 Flux Model Based on Conventional Farm Measurements

Two conventional farms were chosen for obtaining background measurements of NH_3 , and evaluating EST's. Measurements at the conventional farms were conducted by using the same methods as used at EST's in two different seasons, including the fall (September – October, 2002; and winter January – February, 2003) measurement campaigns. Relationship between NH_3 flux and lagoon temperature, pH and TKN, as well as certain environmental parameters were examined over a relatively wide range of lagoon temperatures ($\sim 2^\circ\text{C}$ to $\sim 35^\circ\text{C}$) and lagoon air temperature differences that were observed during the field campaigns of fall and winter months at both the conventional farms.

The multiple regression equation based on flux measurement data from two conventional farms is given by

$$\text{Log}_{10}F = 3.8655 + 0.04491(T_1) - 0.05946(D). \quad (3)$$

Here, F denotes the average $\text{NH}_3\text{-N}$ emission from the conventional lagoon in $\mu\text{g min}^{-1}/1000 \text{ kg-lw}$, T_1 is the lagoon temperature in $^\circ\text{C}$, and D is a hot-air variable that is equal to zero if lagoon is warmer than air, but is equal to $\Delta T = T_a - T_1$ when $T_a > T_1$ and T_a is air temperature in $^\circ\text{C}$ at 10m height. This regression model was used to estimate the projected $\text{NH}_3\text{-N}$ flux from lagoons at the LST baseline farms to compare with the measured $\text{NH}_3\text{-N}$ flux from water-holding structures at an EST site, for the average values of T_1 and D observed at the latter.

Table 1. The summary of animal weight, feed consumed, N-content and N-excretion at potential Environmentally Superior Technologies (ESTs) farms.

Farm Information	No. of pigs	Average pig weight (kg/pig)	Total pig weight (kg)	Feed consumed (kg/pig/wk)	N-content (%)	N-excretion (kgN/wk /1000kg-lw)
AHA Hunt						
Feb- Mar. 2004	10,909	59.2	645,813	13.97	2.38	4.08
Apr. 2004	12,106	66.1	800,206	14.46	2.34	3.29
Barham						
Apr. 2002	4,000	238.1	952,560	12.84	2.25 ^A /3.09 [†]	1.65
Nov. 2002	4,000	238.1	952,560	15.92	2.38 ^A /3.43 [†]	1.77
BOC # 93						
Apr. 2003	4,221	82.7	348,994	11.93	2.78	2.82
June. 2003	4,373	48.0	209,952	14.41	3.24	5.25
Carrolls						
Mar-Apr. 2004	6,332	59.2	374,854	12.89	2.56	3.90
June. 2004	6,095	59.7	363,872	13.21	2.67	4.13
Corbett # 1						
Oct. 2003	3,386	55.4	187,584	15.44	3.01	5.86
Dec. 2003	2,680	104.7	280,596	16.27	2.15	2.34
Corbett # 2						
Mar. 2003	1,249	98.5	123,054	16.27	2.76	3.19
June 2003	1,485	70.3	104,396	14.47	3.08	4.50
Corbett # 3,4						
Sep. 2003	3,620	106.8	386,616	12.74	2.03	1.69
Dec. 2003	4,122	76.3	314,509	8.98	2.49	2.05
Goshen Ridge						
Apr. 2003	3,519	93.4	328,675	17.03	2.67	3.41
Jan. 2004	3,814	61.9	235,972	14.67	2.42	4.02
Feb-Mar. 2004	3,138	99.8	313,172	16.18	2.49	2.83
Harrells						
Feb. 2004	2,071	110.3	228,431	18.62	2.26	2.67
Jun. 2004	2,417	86.5	209,071	16.25	2.06	2.71
Aug. 2004	2,615	50.9	133,103	12.61	2.98	5.17
Howard						
Jun. 2002	3,618	64.3	232,777	13.24	2.59	3.73
Dec. 2002	3,881	96.8	375,762	15.58	2.25	2.53
Vestal						
Mar. 2004	9,507	38.3	364,118	10.03	2.79	5.03
Aug. 2004	10,248	44.7	458,086	11.02	3.17	5.47

^AN-content of the feed in gestation houses; [†]N-content of the feed in farrowing houses.

NH₃ Emissions from Water-Holding Structures

Water-holding structures emissions from 11 EST farms (AHA Hunt, Barham, BOC #93, Carrolls, Corbett #1, Corbett # 2, Corbett # 3,4, Goshen Ridge, Harrells, Howard, and Vestal) were calculated from measurements of NH₃ flux from EST farms, water-holding structure surface area, and farm production data (number of pigs, average pig weight, and feed consumed) during two approximately two-week long measurement periods, representing both warm and cool seasons. Emissions at the EST's are normalized live animal weight in the units of kg-N/wk/1000kg-lw. Farm production data for the EST farms are given in Table 1. Total estimated emissions are presented in Table 2.

Total emissions (kg-N/1000kg-lw/wk), normalized for nitrogen excretion were calculated for each experimental period for each EST farm (see Table 2). The emissions for the cool season for all EST farms ranged from 0.02-0.25, with a mean value of 0.13. The emissions for the warm season for all EST farms ranged from 0.02-2.14, with a mean value of 0.48. For nine out of eleven farms the total emissions were higher in the warm season than the cold season, the exceptions were Corbett # 3,4 and Goshen Ridge. This suggests that the seasonal variability of meteorological parameters such as lagoon and air temperature are significant factors in influencing NH₃ from hog facilities.

NH₃ Emissions from Housing Units

During each two-week sampling period at the EST farm sites, FTIR measurements were conducted to measure the NH₃ flux from the ventilation systems at the hog houses. Hog houses employ two different types of ventilation systems, mechanical or tunnel ventilation and natural ventilation. At Barham, BOC # 93, Carrolls and Howard farm mechanical ventilation was employed. For AHA Hunt, Corbett # 1,2,3,4, Goshen Ridge, Harrells, and Vestal farm the hog houses had natural ventilation. For the mechanically ventilated hog houses, the OP-FTIR spectrometers were placed adjacent to the fans of the houses and the open-path beam was placed at the centerline of the fan opening. The operation of the fans (monitoring when they are on or off) was performed during the entire sampling period. NH₃ emissions from hog houses were estimated based on FTIR path averaged NH₃ concentration measurement. The average NH₃ emission from the hog houses was calculated by multiplying the 15 minute path-averaged concentrations of NH₃ (measured as ammonia mg/m³) across the midline of the fans exhausting the houses by the measured or factory calibrated fan rates (m³/min).

To calculate the average NH₃ flux from the naturally ventilated houses, air-flow measurements were made by sampling at one location along each of the four sections of the building on the upwind side while the OP-FTIR was deployed. Each location was sampled for 30-60 seconds and the high and low readings recorded for all four locations over a 5-7 minute period of time. The high and low wind velocity readings were used to calculate the average wind velocity. The curtain opening for each section was measured and the volume of air per second (ventilation rate) flowing through the upwind side of the barn was calculated as the sum of curtain openings times the average wind velocities for the four sections of the building. The net ammonia concentrations associated with emissions from the building were obtained by subtracting the upwind readings from the downwind readings using the OP-FTIR and then converting the difference to concentrations of ammonia. A moving average was then applied to the concentration data to reduce the effect of wind variations (times when the wind deviated from the predominate direction). Flux from the building was obtained by multiplying net ammonia concentration times the corresponding ventilation rate. The flux calculations were then normalized by the total live weight of swine in the house (1000 kg-lw).

Table 3 shows the overall averaged NH₃ emissions estimated by OP-FTIR measurements from the hog barns at 11 EST farms during the sampling periods. Higher emissions from the barns were experienced during the warm period at ten out of eleven EST farms, the exception being Barham farm.

Table 2. Estimated NH₃ emissions from water-holding structures at EST farms during the experimental periods.

Farm name and sampling period	Total emission/1000kg-lw (kg-N/1000kg-lw/wk)	Farm name and sampling period	Total emission/1000kg-lw (kg-N/1000kg-lw/wk)	Farm name and sampling period	Total emission/1000kg-lw (kg-N/1000kg-lw/wk)
AHA Hunt Feb-Mar. 2004	0.17	Corbett # 1 Oct. 2003	0.33	Goshen Ridge Feb-Mar. 2004	0.04
AHA Hunt Apr. 2004	0.56	Corbett # 1 Dec. 2003	0.12	Harrells Feb. 2004	0.07
Barham Apr. 2002	0.31	Corbett # 2 Mar. 2003	0.18	Harrells Jun. 2004	2.14
Barham Nov. 2002	0.07	Corbett # 2 June. 2003	0.35	Harrells Aug. 2004	1.55
BOC # 93 Apr. 2003	0.02	Corbett # 3,4 Sep. 2003	0.10	Howard Jun. 2002	1.2
BOC # 93 Jun. 2003	0.03	Corbett # 3,4 Dec. 2003	0.23	Howard Dec. 2002	0.25
Carrolls Mar-Apr. 2004	0.22	Goshen Ridge Apr. 2003	0.02	Vestal Mar. 2004	0.02
Carrolls June-July. 2004	0.23	Goshen Ridge Jan. 2004	-*	Vestal Aug. 2004	0.05

* Emissions from water-holding structures were not measured during this period.

Table 3. Estimated NH₃ emission from the hog houses at EST farms during the experimental periods (OP-FTIR measurements).

EST farms	Sampling periods	Barn emissions (kg-N/1000kg-lw/wk)
AHA Hunt	February-March, 2004	0.01
	April, 2004	0.71
Barham	April, 2002	0.34
	November, 2002	0.49
BOC # 93	April, 2003	0.57
	June, 2003	1.29
Carrolls	March-April, 2004	0.98
	June-July, 2004	1.15
Corbett # 1	October, 2003	0.16
	December, 2003	0.008
Corbett # 2	March, 2003	0.12
	June, 2003	0.49
Corbett # 3,4	September, 2003	0.48
	December, 2003	0.16
Goshen Ridge	April-May, 2003	0.72
	January, 2004	0.01
Harrells	January-February, 2004	0.05
	June, 2004	0.27
Howard	June, 2002	1.42
	December, 2002	0.85
Vestal	March, 2004	0.07
	August, 2004	0.75

Evaluation of Ammonia Emissions from EST Farms

In order to evaluate the potential percentage reduction of NH_3 emissions for the whole farm, both water-holding structures and barns were taken into consideration. To achieve this, potential EST emissions were compared to projected emissions at the conventional LST farms. The projected emissions from the LST farms were adjusted to the environmental conditions i.e. air and lagoon temperature, which have been determined to be statistically significant to ammonia emissions. The projected emissions from the barns are the measured emissions for the corresponding season from the two conventional farms, Moore and Stokes, respectively. Moore farm emissions are used to project emissions for farms with tunnel or forced ventilation. Stokes farm emissions are used to project emissions for farms with natural ventilation. To calculate the total % reduction, the sum of projected emissions and measured emissions are taken for the water-holding structures and barns are taken. These numbers are then used to calculate total % reduction using the same process that is applied individually for water-holding structures and barns.

Table 4 shows the $\%E_{\text{EST}}$, $\%E_{\text{CONV}}$ and the % reduction from the EST farms. Out of eleven farms, five show % reduction in NH_3 emissions for both experimental periods. The BEST technology employed at Corbett # 1 was the most successful of these, with a reduction of 71.8% in the warm season, and 66.0% in the cool season. The next largest % reduction was the ISSUES-RENEW system employed at Vestal farm with % reductions of 54.0 and 31.1 for cool and warm seasons, respectively. Other technologies that reduced ammonia emissions in both seasons included the EKOKAN technology at BOC # 93 farm, which had % reductions of 23.5 and 43.3 for the cool and warm seasons, respectively. Another technology with reductions in both seasons was the ISSUES-PBS, which was located at Carrolls farm. There was a small reduction of 8.1% in the cool season, and a larger reduction of 49.5% in the warm season. The ReCIP technology, which was employed at Corbett # 2 farm produced small reductions in both seasons, 20.9% in the cool season and 9.7% in the warm season.

Five technologies had mixed results, reducing emissions in one experimental period, but enhancing in the other. The largest variance in % reductions was the PCS technology located at Harrells farm. In the cool season there was a % reduction of 69.4, but in the warm season, there was a % reduction of -109.9. The Super Soils technology, which was located at Goshen Ridge farm also had a large variance in % reductions. A huge reduction of 98.5 % was calculated for the cool season, but for the warm season % reduction was -1.9. The Sequencing Batch Reactor employed at AHA Hunt farm was also moderately successful in the cool season with a % reduction of 67.2%, but emissions were slightly enhanced in the warm season (% reduction = -4.9). The BEST technology at Corbett # 3,4 showed the same seasonal pattern. % reduction values were 17.0 and -29.2 for the cool and warm seasons, respectively. The technology at Barham farm had a marginal reduction of 2.5 % in the cool season. In the warm season, emissions were enhanced with a % reduction of -11.9%.

The constructed wetlands at Howard farm was the only technology that showed enhancement of emissions in both seasons. The technology had % reduction values of -50.9 and -62.6, respectively.

Conclusions

Eleven potential ESTs were evaluated to determine if they would substantially reduce atmospheric emissions of ammonia at the swine facilities from their estimated emissions from the conventional lagoon and spray technology used at selected LST hog farms in two different experimental periods. Five out of eleven potential ESTs showed % reduction in NH_3 emissions for both periods. The BEST technology employed at Corbett # 1 had the highest % reductions of 71.8% and 66.0% for the warm and cool seasons, respectively.

Table 4. % E_{EST}, %E_{CONV} and % reduction values from the EST farms during the experimental periods

EST Farms	Sampling Periods	Emission Sources	%E _{EST}	% E _{EST} (WHS + house)	%E _{CONV}	% E _{CONV} (lagoon + house)	% reduction
AHA Hunt farm	Feb-Mar ,04	WHS	4.2	4.4	3.4	13.4	67.2
		house	0.2		10.0		
	Apr,04	WHS	17.0	36.5	24.8	34.8	-4.9
		house	19.5		10.0		
Barham farm	April -02	WHS	18.8	39.4	11.3	35.2	-11.9
		house	20.6		23.9		
	Nov-02	WHS	4.0	31.7	9.7	32.5	2.5
		house	27.7		22.8		
BOC # 93	Apr,03	WHS	8.2	28.4	14.3	37.1	23.5
		house	20.2		22.8		
	Jun,03	WHS	11.0	35.6	38.9	62.8	43.3
		house	24.6		23.9		
Carrolls farm	Mar-Apr,04	WHS	5.6	30.7	10.6	33.4	8.1
		house	25.1		22.8		
	Jun-Jul,04	WHS	5.6	33.4	42.2	66.1	49.5
		house	27.8		23.9		
Corbett # 1 farm	Oct,03	WHS	5.6	8.3	19.4	29.4	71.8
		house	2.7		10.0		
	Dec,03	WHS	5.1	5.4	5.9	15.9	66.0
		house	0.3		10.0		
Corbett # 2 farm	Mar-03	WHS	11.0	14.8	8.7	18.7	20.9
		house	3.8		10.0		
	Jun-03	WHS	18.0	28.9	22.0	32.0	9.7
		house	10.9		10.0		
Corbett # 3,4 farm	Sep,03	WHS	13.6	42.0	22.5	32.5	-29.2
		house	28.4		10.0		
	Dec,03	WHS	4.9	12.7	5.3	15.3	17.0
		house	7.8		10.0		
Goshen Ridge	Apr-May,03	WHS	0.6	21.7	11.3	21.3	-1.9
		house	21.1		10.0		
	Feb-Mar ,04 Jan, 04	WHS	0.1	0.3	9.7	19.7	98.5
		house	0.2		10.0		
Harrells	Jan-Feb ,04	WHS	2.6	4.5	4.7	14.7	69.4
		house	1.9		10.0		
	Jun,04	WHS	79.0	89.0	32.4	42.4	-109.9
		house	10.0		10.0		
August,04	WHS	30.0	-	29.6			
	house						
Howard farm	Jun-02	WHS	31.9	70.0	22.5	46.4	- 50.9
		house	38.1		23.9		
	Dec-02	WHS	9.5	43.1	3.7	26.5	-62.6
		house	33.6		22.8		
Vestal	Mar, 04	WHS	7.8	9.2	10.0	20.0	54.0
		house	1.4		10.0		
	August,04	WHS	19.6	33.3	38.3	48.3	31.1
		house	13.7		10.0		

WHS = Water-holding structures

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