Non-Point Source Ammonia Emissions in Texas: Estimation Methods, Pitfalls, Corrections, and Comparisons

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ABSTRACT

A Phase II study was recently completed to measure ammonia emission fluxes from pine and oak forest soils (including forest biogenic "litter") in East Texas during summertime conditions. The resulting field data indicate that actual summertime ammonia emissions from pine and oak forests are three to four orders of magnitude lower than those based on published emission factors and used for the Phase I inventory. The Phase I study was completed to estimate annual-average emissions of ammonia from 64 non-point source emission sub-categories in each of 254 counties in Texas. The 64 non-point source emission sub-categories fell into seven major source categories: animal husbandry, fertilizer applications, on-road vehicles, non-road sources, municipal wastewater disposal, domestic sources, and natural soil and vegetation. Statewide ammonia emissions for 1996 were estimated to be 921,000 metric tons, with greater than 50% originating from natural soil and vegetation, and 80% emitted from pine and oak forests, and cattle. However, the estimates for pine and oak forests were characterized as having a great deal of uncertainty. Thus, the revised statewide ammonia emissions estimates for summertime conditions are an approximate factor of two lower than previously predicted. Animal husbandry activities are predicted to nearly always contribute greater than 85% of non-point source ammonia emissions in rural counties in Texas. In urbanized counties, domestic sources and animal husbandry are estimated to be the two most important non-point sources of ammonia emissions, with dogs and cats being the greatest contributors within the domestic source category. Ammonia emission factors from pine and oak forest floors are presented.

INTRODUCTION

Ammonia (NH_3) emissions to the atmosphere are significant for several reasons. NH_3 transport and deposition can lead to nutrient over-saturation (eutrophication) of downwind terrestrial and aquatic environments.[1] Ammonia also interacts with regional and global atmospheric sulfur cycles, thus having a potential impact on regional visibility and global warming. Finally, the secondary fine particulate matter ($PM_{2.5}$) that is formed by reactions involving NH_3 are a growing concern in terms of their potential impacts on human health.

NH_3's role in atmospheric chemistry is a unique one, since it is the only identified gaseous basic constituent in an atmosphere that is relatively plentiful in the acidic products of oxidation of gases emitted from the ground. As such, resulting neutralization products such as ammonium bisulfate, ammonium sulfate, and ammonium nitrate are known to be important components of atmospheric aerosols, including cloud condensation nuclei.[2]

Southeastern Texas, which includes the densely populated ozone non-attainment areas of Houston/ Galveston and Beaumont/Port Arthur, experiences annual average concentrations of $PM_{2.5}$ in the range of 10-14 $\mu g/m^3$ and concentrations close to 15.0 $\mu g/m^3$ are experienced in Northeast Texas based on data collected from 2000 - 2001.[3] Given the recent courts ruling on the proposed EPA $PM_{2.5}$ standards (see http://pacer.cadc.uscourts.gov/common/opinions/200203/97-1440c.txt), Southeastern and Northeast Texas are close to exceeding the new national clean air standards of 15 $\mu g/m^3$ (over a 3-year averaging period).

Superimposed on these background concentrations there may exist areas in which industrial and urban emissions drive annual average concentrations of fine PM to higher levels. Although Southeastern Texas is designated as attainment under the current PM-10 standard, urban areas in this region may not be in attainment with the proposed $PM_{2.5}$ standard. The total economic benefit for reducing exposure associated with compliance of the $PM_{2.5}$ NAAQS in 2007 is estimated to be 3 billion dollars in Houston/Galveston.[4]

There is significant evidence that suggests that natural soil is an important contributor to global NH_3 emissions.[2] For example, ammonium is found at relatively high concentrations in rainwater and concentrations are greater over soils with high pH, a condition that shifts the acid-base equilibrium in soil from ammonium ion to NH_3, *i.e.*, the volatile species. Atmospheric NH_3 concentrations are greater over land than over oceans and increase with increasing soil temperature. However, measurements of NH_3 emissions from natural soils are sparse and corresponding emission factors are characterized by significant uncertainties. These facts are particularly true for NH_3 emissions from forested areas, *e.g.*, pine and oak forests that cover large areas of East Texas.

A Phase I study was completed for the Texas Natural Resource Conservation Commission (TNRCC) and provided a first estimate of non-point source NH_3 emissions in Texas.[5] A total of 64 non-point sources of NH_3 were considered. Each source required significant reviews of existing literature and relevant databases prior to the selection of appropriate emission factors and source activity data. The intent of the study was to develop county-by-county estimates of non-point source NH_3 emissions in Texas during the year 1996. This was accomplished for the 254 counties in Texas through the use of published emission factors and county-specific activity data for those sources. A total of 64 non-point source emission sub-categories were addressed, each falling into one of seven major source categories: animal husbandry, fertilizer applications, on-road vehicles, non-road sources, municipal wastewater disposal, domestic sources, and natural soil and vegetation. Statewide NH_3 emissions for 1996 were estimated to be 921,000 metric tons, with greater than 50% originating from natural soil and vegetation, a source that was predicted to be dominated by pine and oak forests in East Texas. However, estimates for pine and oak forests were characterized as having a great deal of uncertainty and a major recommendation stemming from the Phase I study was the need for improved emissions estimates for those sources. Omission of these two sources (pine and oak forests) lead to an approximate factor of two decrease in predicted NH_3 emissions from non-point sources in Texas. Natural soil and vegetation were predicted to be the dominant source of NH_3 emissions in rural East Texas and were significant even if predicted emissions from pine and oak forests are reduced by an order of magnitude.

Reported NH_3 emission factors (kg/km^2-year) for forests span nearly three orders of magnitude. One published emission factor is specific to oak forests. Several attempts to develop NH_3 emission inventories, *e.g.*, Radian,[6] have relied on an emission factor of 365 kg/km^2-year for forested areas as reported by Gharib and Cass.[7] However, this value was assumed based on an extrapolation from bare soil. Three sets of researchers measured NH_3 fluxes from coniferous forests that had been amended with fertilizer application to forest floors.[8, 9, 10] Reported emission factors ranged from 105 to 7,000 kg/km^2-year. Langford and Fehsenfeld [11] reported an emission factor of 35 kg/km^2-year for an unfertilized coniferous forest in the United States. Kim [12] reported mean emission factors of 17,700 kg/km^2-year and 13,600 kg/km^2-year for pine and oak forests, respectively, in South Korea.

Several authors have attempted to estimate global, continental, or regional-scale NH_3 emissions and have included natural soil and vegetation in their estimates. However, the role of forested lands in predicted emissions is often omitted or not clearly described.

Dawson [2] presented a simplified model in which global NH_3 emissions from soil were estimated based on the generation of soil ammonium from the microbial decomposition of organic matter and microbial nitrification rates. Chemical equilibrium was assumed between ammonium and NH_3 in the soil, and partitioning between soil moisture and air was calculated in accordance with Henry's law. Transport to the soil-atmosphere interface was estimated by Fick's first law (molecular diffusion). Dawson [2] estimated global NH_3 emissions from undisturbed soil and vegetation as 47 million tons/year but did not account for re-absorption by vegetation canopies. Given a global land area of 1.175×10^{10} km^2, this translates to a global-average emission factor of only 3.6 kg/km^2-year for undisturbed soil and vegetation, far less than the emission factors reported in the phase 1 study for forested areas. Predicted NH_3 emissions were greatest for the latitude band of 30-40^o N, within which global emissions estimates from undisturbed soil and vegetation were predicted to be 21% of global emissions. Interestingly, much of East Texas (north of Houston to the Oklahoma border) falls within this latitude band. Dawson [2] predicted that during summer periods, there should be little diurnal variation in NH_3 emissions but that nighttime reductions in NH_3 emissions should be significant during winter periods in the 30-40^o N latitude band. Predicted NH_3 emissions were only 13% lower in winter, relative to summer, during daytime conditions in the 30-40^o N band. However, in the same band, NH_3 emissions at night were predicted to be 74% lower in winter relative to summer conditions.

Schlesinger and Hartley [13] predicted global ammonia emissions (as NH_3-N) of 6.1 to 45.3 million metric tons per year contributed by "un-managed" soil. Thus, their upper-bound estimate of ammonia emissions from soil was similar to the value presented by Dawson,[2] but the lower bound was a factor of 7.7 lower than that predicted by Dawson. Schlesinger and Hartley [13] also provided a range of predicted global ammonia emissions estimates from temperate forests as 1.2 to 12 million metric tons per year.

Bouwman *et al.*[1] estimated global ammonia emissions in 1990 as 54 million metric tons per year (NH_3-N), with soils under natural vegetation predicted to contribute only 4.4% to the total. However, unlike others, Bouwman *et al.*[1] assumed a canopy re-absorption coefficient ranging from 0.8 for tropical forests to 0.5 for temperate forests and woodlands and 0.2 for other vegetation types. Their estimates of ammonia emissions from all sources in East Texas appear to range from approximately 100 to 500 kg/km^2-year (NH_3-N).

On a continental scale, Denmead [14] concluded that ammonia emissions from natural fields contribute 47% of total ammonia emissions in Australia. He used emission factors of 550 and 1,095 kg/km^2-year for each of two seasons. Lee and Langhurst [15] predicted that vegetated land contributes only 2.4% of total ammonia emissions in a densely-populated region of Northeast England, the dominant source being cows (2/3 of predicted total ammonia emissions in the region).

Finally, in a recent Phase I study completed for the TNRCC, Corsi *et al.* [5] estimated that natural soil and vegetation account for 52% of statewide non-point source NH_3 emissions in Texas. The majority of those emissions (94%) were predicted to be from pine and oak forests in East Texas. However, relatively large emission factors reported by Kim [12] were used for the Phase I study. Based on results of the Phase I study for TNRCC, obvious variations in reported emission factors, and contributions of forested lands to emission inventories, there was a significant need to improve the existing knowledge base related to NH_3 emissions from forested lands.

The large uncertainties and potential significance of NH_3 emissions from pine and oak forests in Texas as predicted during the Phase I study described above was the motivation for completion of this project described herein.

Project Scope and Limitations

Scope

1) Measurement of NH_3 fluxes from forest floors (soil + litter) and surrounding leaf litter and soil properties during 16 flux sampling event,
2) Two locations in each of two pine and two oak forests (eight combinations),
3) Sampling during summer months only,
4) NH_3 emissions from pine and oak forest floors in East Texas,
5) Presentation of emissions factors,
6) First cut model run results for emission rates, and
7) Implications of findings and conclusions.

Limitations

1) Neither dry nor wet deposition are addressed in this paper, however, the NH_3 deposition component of the project's final report [16] should address existing literature, methodologies, models, and present computational sensitivity analyses,
2) No part of the tree wood and bark surfaces, the stomata and leaf surfaces which serve as pathways for bi-directional exchange of NH_3 during the day, physical adsorption to leaf-surface waxes or dissolution in water films are addressed in this paper,
3) There was sampling during summer months only, and
4) Only first cut preliminary model run results have been used to address annual emissions implications.

The NASA CASA (version B) model [17] developed at NASA-Ames provided preliminary modeling results that are used in this paper. The model run used climate data for 1988, and default model soil pH data (vs. the pH values of the soil from the tested sites). [18] The run results were provided [18] to the authors as a courtesy and only as a first cut approximation. Even given the precipitation and pH variances (over time and space) between 1998 and 2001, the results were used to establish that the emission factors and estimates developed during this project were within less than an one order of magnitude of modeling results.

A considerable effort was made at the outset of this project to review available methods for analysis of airborne NH_3, and to determine the approach that was ultimately selected for field sampling. A summary of current NH_3 monitoring methods covering collection devices as well as analysis equipment and techniques is presented in this chapter. Both collection (time-averaged) and continuous measurement approaches are discussed covering detection limits, sampling time, and additional details related to instrumentation.

MEASUREMENT OF AMMONIA EMISSIONS

The Three Main Components

There are three main components of the NH_3 emission measurement system. These are an Advanced Pollution Instrumentation Model 701 zero air generator, an emission isolation flux chamber, and a Thermo Environmental Instruments Model 17C ammonia analyzer (a continuous flow chemiluminescent NH_3 analyzer). PFA Teflon tubing (¼-inch diameter) was used to provide the zero air feed to the chamber and connect the sample chamber port to the analyzer. See Figure 1 for system configuration schematic.

For this project, pressure release was provided by a 3 cm. diameter hole at the top of the chamber to allow excess supply air to escape and to allow access for measurement of ground and air properties inside the chamber. Not shown are the power conditioner which provided voltage regulation, keeping the supply voltage for the analyzer system stable at 117V±5% , sidewalls of a shade canopy which was moved as necessary as the position of the sun changed during the day, and a laptop computer which was used to control the analyzer and to provide real-time graphing of emission measurements. The computer was also used to log all analyzer output to the hard drive for later analysis. The analyzer has a data logger capable of storing 50,000 measurements for data backup in case of temporary computer communication problems.

Measurement Locations

A set of criteria for selecting appropriate locations for field measurements was developed, taking into account the mix of tree species at a given location and requirements for monitoring equipment and activities.

The first requirement for monitoring locations was that the forests be representative of typical Texas pine and oak forests. This helps ensure that the measurements taken at a relatively small sample of locations accurately reflect the overall behavior of pine and oak forests statewide. Selecting sites in pine forests for NH_3 emissions monitoring is fairly straightforward. Virtually all the pine forests in Texas consist of Loblolly Pine and are relatively homogeneous. The situation is not as simple with oak forests. There are 28 species of oak found in Texas, and they occur in a wide range of terrains and vegetation type groupings.

The analysis was based on recently-developed, detailed land use/land cover (LULC) and biomass density databases developed for other projects sponsored by the TNRCC.[20, 21, 22, 23] These databases were based on the national, county-level Biogenic Emission Landuse Database (BELD), the United States Geological Survey (USGS) Land Cover Characteristics database, and the Texas Parks and Wildlife Department’s vegetation database. The new databases enhanced the resolution of the LULC information, refining it to a 4-kilometer grid. In addition, extensive field surveys were used to determine the actual species vegetation mix and area fractions, along with improved leaf biomass density figures.

Oak Site Locations

Purtis Creek State Park is located about 3.5 miles north of the city of Eustace, Texas and about 15 miles northwest of Athens, Texas. The physical address of the park is 14225 FM 316, Eustace, TX 75124. The monitoring site was located at 32º 21' N, 96º 0' W.

Cooper Lake State Park has two units: Doctors Creek and South Sulphur Units. South Sulphur Unit was visited and is about 14 miles west of Sulphur Springs, Texas. The physical address of the park is Route 3, Box

741, Sulphur Springs, TX 75482. The monitoring site was located at 33º 22' N, 95º 40' W. See Figure 2 for locations of the most representative post oak forests in Texas.

Pine Site Locations

Loblolly Pine is the dominant pine species found in East Texas and is the cornerstone of East Texas wood harvesting and processing industries.[24] As such, sampling sites located in forests dominated by Loblolly Pine were selected. Both forests are owned and operated by the U.S. Department of Agriculture.

Davy Crockett National Forest is located near the city of Crockett, Texas, and the physical address of the Forest is Route 1, Box 55 FS, Kennard, Texas 75847. The monitoring site was located at 31º 24' N, 95º 10' W.

Sam Houston National Forest is New Waverly, Texas, and the physical address is 394 FM 1375 West, New Waverly, Texas 77358. The monitoring site was located at 30º 33' N, 95º 39' W. These forests are owned and operated by U.S. Department of Agriculture.

Sampling Sites and Events

Four sampling sites were selected at each location (4 sites/location x 4 locations = 16 sampling sites/events). A single sampling "event" was completed at each sampling site. A sampling event involved set-up of experimental instrumentation, at least one and possibly two sets of multi-hour flux chamber measurements, collection of soil samples, and ambient air sampling (at most sampling sites).

Soil Samples

The soil and leaf litter samples collected in the field were analyzed for ammonia nitrogen using EPA Methods 350.1 and 350.2, which were modified for the analysis of soil samples.[25] In EPA Method 350.1, the concentration of ammonia is determined colorimetrically whereas in the modified EPA Method 350.2 utilized in this project, the samples were first distilled in a boric acid solution and the concentration of ammonia in the distillate was then determined titrimetrically. Approximately half of the samples were analyzed in a laboratory at the University of Texas (UT) at Austin using modified Method 350.2. A commercial laboratory located in Austin, Texas analyzed the remaining soil and leaf litter samples using EPA Method 350.1.

The pH and moisture content of the soil and leaf samples were determined at the UT laboratories. The procedures for pH and moisture content were based on EPA Methods 150.1 and 160.3, respectively.

In all cases, representative sub-samples of the soils or leaf litter stored in the sampling jars were selected for ammonia, pH and moisture content analyses. No attempt was made to sieve or screen the samples prior to analysis. See Table 1 for mean soil properties at forest monitoring sites.

Time Frame

Sampling events occurred between July 19, 2001 and August 4, 2001. The initial plan was to evaluate and select sampling locations and to evaluate, purchase, and prepare field instrumentation in the fall of 2000. Field sampling events were then to be completed in the winter and spring of 2001 (8 sampling events per season).

However, significant delays were incurred with respect to acquisition and receipt of the NH_3 analyzer used for this project. Following acquisition, an additional delay of approximately five months occurred as a result of instrumentation problems and necessary trouble-shooting.

Experimental Measurements of Ammonia (Summertime Conditions)

Characteristic plots of NH_3 concentration measurements from the flux chamber system are shown in Figures 3 and 4. Figure 3 shows a plot of a typical primary flux (dynamic) measurement with an initial peak concentration due to entrained surface layer NH_3 and a slow decay of the concentration to below the analyzer's detection limit (. 1 ppb).

Figure 4 shows a typical secondary flux (static) NH_3 measurement plot. There is an initial peak due to the accumulation of NH_3 emissions while the flux chamber is sealed. The concentration decays rapidly as the sweep zero air mixes with the air in the chamber and dilutes the NH_3. This dilution continues until the NH_3 concentration drops below the detection limit.

Results associated with both dynamic (flow-through sweep air) and static (no sweep air) chamber experiments are presented in Table 2. Dynamic experiments were attempted at each site. However, 15 of 16 dynamic experiments lead to terminal NH_3 concentrations of less than 1 ppb, *i.e.*, the NH_3 concentration inside the chamber head space dropped to less than the manufacturer-specified method detection limit. As such, these emission factors are listed as less than a maximum value (1.2 kg-NH_3/km^2-month). During one dynamic chamber experiment in Sam Houston National Forest, the terminal NH_3 concentration in the chamber head space leveled at 1 ppb and, as such, the emission factor for this experiment is listed as 1.2 kg-NH_3/km^2-month. The reader is cautioned that this value is at the method detection limit.

Static chamber monitoring was completed during 10 of 16 experiments. Although this technique was not employed at every site, it lead to remarkably consistent results between those sites where it was employed. Arithmetic mean emission factors based on the use of the static chamber method at Sam Houston and Davy Crockett National Forests were 0.09 kg-NH_3/km^2-month and 0.08 kg-NH_3/km^2-month, respectively. The arithmetic mean emission factor over four static chamber experiments in oak forests (Purtis Creek and Cooper Lake State Parks) was 0.13 kg-NH_3/km^2-month. Due to the limitations associated with dynamic chamber experiments, we opted to use static chamber results as being representative of summertime emission factors for pine and oak forests in East Texas.

COMPARISONS

Comparison with Published Findings

Before comparing the emission factors derived from this project with previous measurements or estimates, it is instructive to review the state of knowledge related to NH_3 emissions from undisturbed soil, particularly as related to forest litter and soil. Of particular significance are the conflicting arguments made about NH_3 emissions from undisturbed soils and forests and the sparseness of measured emissions.

In a classic and often-referenced paper, Dawson[2] argued that undisturbed land is likely the primary source of global NH_3 emissions. This assertion was made based on relative NH_3 concentrations over land and sea, higher NH_3 concentrations over soil favorable to NH_3 emissions (low pH, high temperature), and application of a simple NH_3 emissions model for undisturbed non-fertilized soil. However, Dawson[2] acknowledged that, as of 1977, “emission from uncultivated, unfertilized vegetated land has never been measured.” Fifteen years later, Langford *et al.*[11] noted that gaseous NH_3 fluxes in unmodified forests are virtually non-existent.

Schlesinger and Hartley[13] indicated that little is known about the volatile loss of NH_3 from non-agricultural soils in which ammonium (NH_4^+) is derived from mineralization of organic nitrogen. Asman *et al.*[26] observed that emissions from *B-Napus* canopies following the deposition of leaf litter appear to be “significant”. They recommended that decomposition of leaf litter as a ground source of NH_3 emissions needs further investigation. However, in a recent paper by Pryor *et al.*,[27] the authors suggest that soil conditions, particularly surface soil $pH < 6.5$, precludes a large efflux of NH_3 emissions from forest floors.

While there are conflicting views on the relative importance of NH_3 emissions from forest floors, resolution of this issue has been difficult due to the sparseness of field data. In large part, this is due to the difficulty of measuring NH_3 fluxes in the space between a forest floor and overlying canopy. Aerodynamic gradient techniques that have been used to measure NH_3 fluxes in open fields and, in a few cases, above forest canopies are severely restricted by localized flow perturbations, *i.e.*, due to tree trunks and limbs above the forest floor. Schlesinger and Hartley[13] also described difficulties associated with gradient techniques affected by external agricultural and industrial sources, the former being of potential significance in many parts of East Texas. Langford *et al.*[11] and Schlesinger and Hartley[13] also described numerous difficulties associated with the use of surface flux chambers due to potential influences of the chamber on environmental forces (wind above surface, surface temperature) that affect NH_3 fluxes. Concerns regarding NH_3 sorption to chamber walls were also expressed.

Comparison with Previously Measured Emission Factors

For this project, we determined mean summertime NH_3 emission factors for pine and oak forest floors of 0.09 and 0.13 kg/km^2-month, respectively. These emission factors are significantly lower than any measured previously. Again, it is important to note that the forests used in this project were not artificially fertilized, while several of those that formed the basis for previous studies had been amended with urea-nitrogen.[8, 9, 10] The remaining two emission factors[11, 12] for pine/coniferous forests differ by a factor of 500 (2-3 orders of magnitude), suggesting the difficulties and potential errors associated with selecting a single emission factor for estimating NH_3 emissions from forests.

After dividing by 12 to convert the emission factor to a monthly basis, the emission factor reported by Kim[12] for pine forests in South Korea is over four orders of magnitude greater than the emission factor determined in this project. Similarly, Kim’s emission factor for oak forests is slightly less than four orders of magnitude greater than the emission factor for oak forest floors determined in this project. Although significantly lower than the emission factor reported by Kim[12] for pine forests, the emission factor reported by Langford and Fehsenfeld[11] for coniferous forests is 32 times greater than the summertime pine forest emission factor determined for this project.

The implications of the large differences in Kim’s emission factors with those reported herein are discussed below.

Comparison with Previously Predicted Emission Factors

A small number of researchers have predicted NH_3 fluxes from forest soils based on mathematical models that differ significantly in complexity. Bouwman *et al.*[1] developed a simple model to estimate global emissions of ammonia and included temperate forests in their predictions. They estimated 0.03 g/m^2-year (2.5 kg/km^2-

month) ammonia emissions from temperate forests, a value approximately 20-30 times greater than those measured in this study for East Texas. However, the Bouwman *et al.*[1] model did not account for soil pH effects and may therefore underestimate emissions from alkaline soils, while potentially over-estimating emissions from acidic soils, *e.g.*, soils in East Texas.

Dawson[2] developed a more sophisticated model than Bouwman *et al.*[1] to estimate global emissions of ammonia from undisturbed land. His model accounted for pH effects on ammonia/ammonium equilibrium partitioning in soil. It considered the degree of exchangeable ammonium resulting from a balance of litter decomposition and nitrification. Emissions were derived based on molecular diffusion of NH_3 through the top 10 cm. of top soil. Resulting emissions from undisturbed soil within 30-40° N latitude were predicted to be 9.2 billion kg/year over an area of 15.57 million km^2. Normalizing emissions by area and dividing by 12 (to obtain a monthly average) yields an emission factor of 49 kg/km^2-month, approximately 500 times greater than forest floor emission factors derived in this study for East Texas. Dawson[2] did not separate forest emissions from other land types.

Langford *et al.*[11] used the Dawson[2] model to estimate ammonia emissions from forest floors using soil-specific properties (surface pH and ammonium concentration) from three forests in the United States. For a mountain coniferous forest in Colorado (pH = 5.22; NH_4^+ = 17.3 g/kg), they estimated an emission factor (normalized here to a monthly average) of 0.25 kg/km^2-month. For a temperate coniferous forest in Alabama (pH = 5.3; NH_4^+ = 5.6 g/kg), they estimated an emission factor of 0.10 kg/km^2-month. For a temperate deciduous forest in Tennessee (pH = 4.7; NH_4^+ = 17.9 g/kg), they estimated an emission factor of 0.05 kg/km^2-month. These emission factors in U.S. forests bound the values that were derived based on our measurements in East Texas. While the assumed soil surface temperature of 20° C was less than those observed in this project, the soil pH and ammonium concentration levels were reasonably consistent with those measured in East Texas.

Potter *et al.*[28] recently completed a rigorous modeling evaluation of ammonia emissions from native soils in California. They employed the NASA-CASA model within a GIS framework with 8-km resolution. The model accounts for area water balances, soil pH and moisture content, litterfall, nutrient allocation, soil nitrogen mineralization, seasonal carbon fixation, surface temperature, and soil ammonia emissions. Evergreen needleleaf forests were assumed to have a litter C/N ratio of 100, with a nitrogen dry weight of 0.5%. Deciduous broadleaf forests were assumed to have a C/N ratio of 65, with a nitrogen dry weight of 0.77%.

Based on a Version A (moderate pH effects) model application, Potter *et al.*[28] estimated annual ammonia emissions from evergreen needleleaf forests in California to be 810 metric tons/year over a total area of 12.4 million hectares. This translates to an average emissions flux of 0.54 kg/km^2-month, six times greater than the summertime pine forest emission factor determined in this project for East Texas. Similarly, the average emission flux for deciduous broadleaf forests was estimated to be 2.6 kg/km^2-month, 20 times greater than the summertime oak forest emission factor determined in this project for East Texas.

While the recent ammonia flux estimates for California are greater than those measured in East Texas, Potter *et al.*[28] predicted significant seasonal variations in ammonia emissions, with 20-fold or greater differences in predicted emissions between different months. Soil moisture was predicted to have a significant effect on ammonia emissions, with much lower emissions from moist soils owing to lower gas diffusivities. Soil pH was also predicted to have a significant effect on ammonia emissions, with the highest emissions predicted to occur for conditions of high pH (alkaline soil) and low moisture content. In several California counties that are dominated by evergreen forests the soil pH ranged from 5.5 to 6.19. For comparison, 6 of the 8 pine forest locations that we studied in East Texas had soil surface (5 cm. depth) pH of less than or equal to 5.5, and 7 of 8 oak forest locations had soil surface pH less than 5.3. Using the same algorithm that was employed in the

NASA-CASA model, we estimated a 20-fold reduction in ammonia flux for a pH drop from 6 to 5 at a surface temperature of 30^{o} C, everything else being equal. Thus, the difference in predicted ammonia fluxes by Potter *et al.*[27] and those measured in East Texas may not be that great when corrected for pH effects.

IMPLICATIONS: NON-POINT SOURCE AMMONIA EMISSIONS IN TEXAS

Corsi *et al.*[5] previously completed a screening assessment of non-point source emissions in Texas for the TNRCC. Annual average non-point source emissions were estimated based on a rigorous review of published emission factors for 64 non-point sources and analysis of activity for each source in each of 254 counties. Statewide emissions for 1996 were estimated to be 921,000 metric tons. Natural soil and vegetation were predicted to account for 52% of statewide non-point source emissions. The dominant source was predicted to be pine and oak forests, the sum of which was estimated to contribute 94% of total emissions from soil and vegetation. However, emissions from pine and oak forests were based on emission factors published by Kim.[12] As noted above, Kim's emission factors were approximately four orders of magnitude greater than those observed in this project

The impact of replacing Kim's emission factors with those measured during this project is enormous. Predicted statewide non-point source emissions are reduced by almost a factor of two, from 921,000 metric tons per year (mtpy) to 467,000 mtpy.

Predicted statewide emissions from pine forests, located primarily in East Texas, are reduced from 257,000 mtpy to only 16 mtpy. Similarly, predicted statewide emissions from oak forests are reduced from 197,000 mtpy to 22 mtpy.

Reductions in predicted emissions from pine and oak forests have a significant effect on the overall contribution of natural soil and vegetation to statewide non-point source emissions. This source category drops from 52% to just 3.4% of statewide non-point source emissions.

The reduction in predicted emissions from pine and oak forests also has a significant effect on the relative importance of animal husbandry activities as a non-point source of emissions in Texas. The overall contribution of animal husbandry to non-point source emissions increases by a factor of two, from 39% to 77%. Beef cattle and milk cows are now predicted to contribute 61% of total non-point source emissions in Texas. Developing targeted strategies for effectively reducing emissions and therefore $PM_{2.5}$ in the atmosphere is the goal.

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Table 1. Mean soil properties at forest monitoring sites

Site	**Sam Houston**	**Davy Crockett**	**Purtis Creek**	**Cooper Lake**	**Range Observed**	
					min	**max**
Temperature (°C)						
Soil: Surface	26.2	25.3	27.7	28.9	23.7	30.9
Soil: 5 cm. down	25.1	23.8	25.5	26.2	22.7	27.1
Soil: 10 cm. down	24.8	24.4	25.1	25.9	23.3	26.6
Soil: 15 cm. down	24.6	24.1	24.4	25.7	23.1	26.1
pH [1]						
Leaf litter	5.0	5.3	5.3	5.9	4.2	6.3
Soil: 5 cm. down	5.3	5.2	5.1	4.8	4.3	6.1
Soil: 10 cm. down	5.5	5.4	5.6	*	*	*
Soil: 15 cm. down	5.4	5.4	5.6	*	*	*
Moisture Content [2] (%) [2]						
Leaf litter	24.6	27.9	22.8	14.2	11.6	36.3
Soil: 5 cm. down	4.3	12.5	2.8	7.5	1.8	20.0
Soil: 10 cm. down	3.3	10.9	2.8	*	1.4	17.3
Soil: 15 cm. down	3.8	11.4	3.1	*	2.2	14.8
NH3-N (mg/kg) [1]						
Leaf litter	20.7	11.5	27.7	10.5	0.7	47.3
Soil: 5 cm. down	10.3	3.8	1.8	5.3	0.4	23.1
Soil: 10 cm. down	5.5	5.4	*	*	5.4	5.5
Soil: 15 cm. down	2.8	*	*	*	2.8	2.8

[1] Soils inside flux chamber

[2] Soils immediately adjacent to flux chamber

Table 2. Summary of Measured Ammonia Emission Factors (Summer Months)

Pine Forests	**Emission Factor (kg/km^2-month)**		**Oak Forests**	**Emission Factor (kg/km^2-month)**	
Forest Name	**Dynamic**	**Static**	**Forest Name**	**Dynamic**	**Static**
Sam Houston	< 1.2	-	Purtis Creek	< 1.2	0.12
	1.2	-		< 1.2	0.12
	< 1.2	0.07		< 1.2	0.17
	< 1.2	0.11		< 1.2	-
Average	0.03 - 1.2	0.09	Average	< 1.2	0.14
Davy Crockett	< 1.2	0.05	Cooper Lake	< 1.2	-
	< 1.2	0.10		< 1.2	-
	< 1.2	0.12		< 1.2	0.08
	< 1.2	0.07		< 1.2	-
Average	< 1.2	0.08	Average	< 1.2	0.08

Figure 1. Schematic diagram of NH_3 emission collection and analysis system. Adapted from Ecklund [19] (1992).

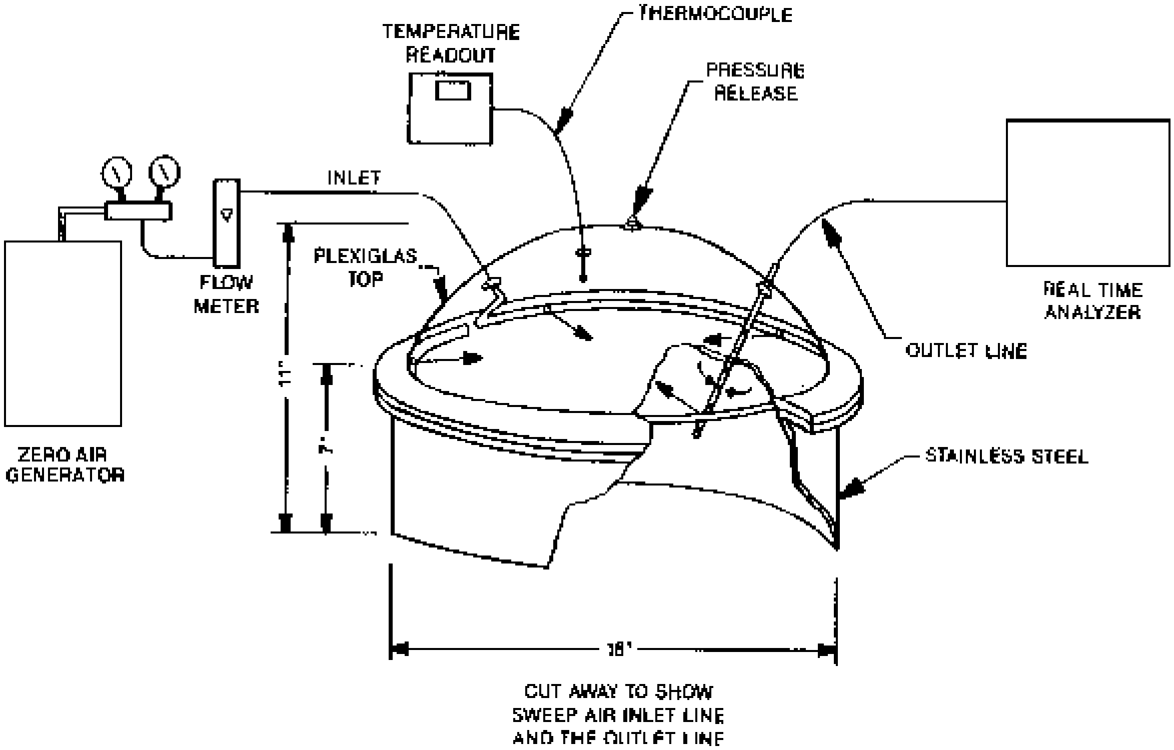

Figure 2. Location of Land Use Codes most representative of Post Oak forests, corresponding to ?Post Oak Woods, Forests & Grasslands" vegetation types for Central (37082), East (37083), and North-Central Texas (37085). Also shown are the locations of the four monitoring sites used for this project.

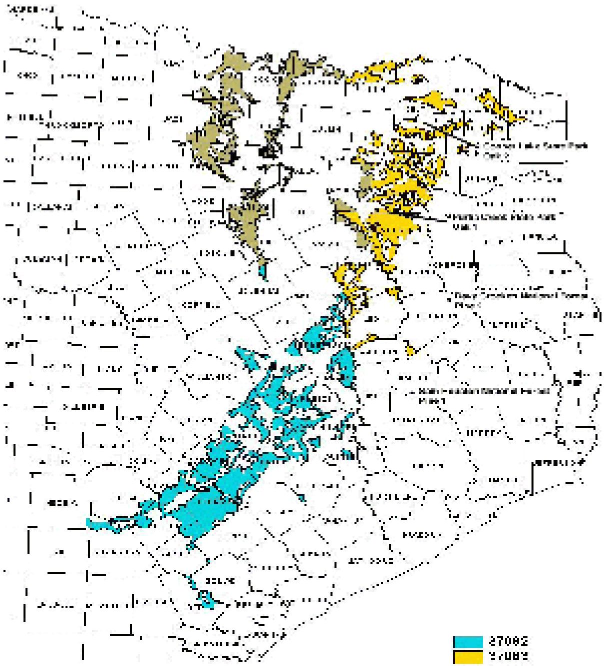

Figure 3. Typical primary flux (dynamic) NH_3 concentration measurement profile, showing decay to a level below the detection limit (1 ppb) of the NH_3 analyzer.

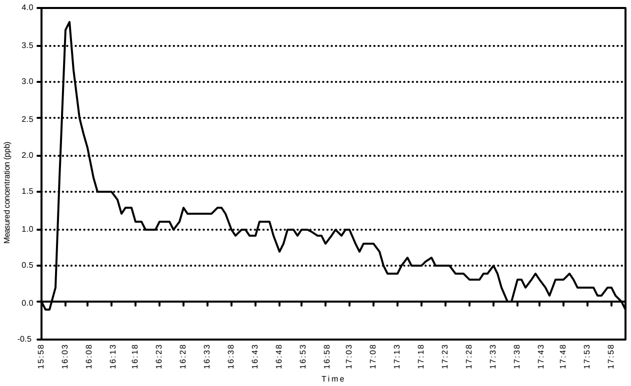

Figure 4. Typical secondary flux (static) NH_3 concentration measurement profile.

KEYWORDS

Emissions Inventory
Ammonia
Forest Floors
Area Sources