Review of Ammonia Emission Modeling Techniques for Natural Landscapes and Fertilized Soils

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Disclaimer

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Abstract

The U.S. EPA and the Emissions Inventory Improvement Program (EIIP) have funded an effort to identify procedures for estimating short-term emissions from fertilized soils and natural landscapes. This effort is building upon the Carnegie-Mellon University methodology and enables improvements to hourly ammonia emissions estimates for regional air quality modeling assessments. Simulating fine-particulate ($PM_{2.5}$) concentrations in regional air quality models requires a representation of the emissions of ammonia. Air quality simulation modeling efforts are being hampered by uncertainties in the temporal and spatial patterns of ammonia emissions. These uncertainties are particularly large for natural landscapes and fertilized soils. A model is proposed to reflect the bi-directional movement of NH_3 into and out of natural landscapes. This model provides an improved characterization of diurnal variations in NH_3 flux, including the tendency of landscapes to emit NH_3 during warm conditions and absorb the gas at night. Improved emission factors and diurnal allocation factors are given for direct NH_3 emissions following the application of fertilizer. Monthly fertilizer application estimates developed by Carnegie-Mellon University should be used in determining monthly variations in fertilizer emissions. Emission flux estimates are also provided for crops after the initial decline in emissions from fertilizer, and from fallow soil.

Executive Summary

Ammonia (NH_3) is emitted to the atmosphere from a variety of natural processes and human activities. NH_3 reacts with other pollutants in the atmosphere to produce secondary particulate species, including ammonium sulfates (NH_4HSO_4 and $[NH_4]_2SO_4$) and ammonium nitrate (NH_4NO_3). These compounds are important constituents of ambient particulate matter ($PM_{2.5}$), and contribute to exceedences of the $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS) as well as to visibility impairment at many locations in the U.S.

The U.S. Environmental Protection Agency (EPA) has developed atmospheric simulation models to analyze the formation and transport of $PM_{2.5}$, and to assist in the evaluation of potential air pollution control strategies. However, efforts to assess the formation of sulfate and nitrate particulate matter have been hampered by variations and uncertainties in the temporal and spatial patterns of NH_3 emissions. These variations and uncertainties are particularly large for NH_3 emissions from fertilized soils and natural landscapes.

The EPA and the Emissions Inventory Improvement Program (EIIP) have funded an effort to identify procedures for estimating short-term NH_3 emissions from fertilized soils and natural landscapes, the results of which are reported in this document. This research is aimed at improving hourly NH_3 emissions estimates for regional air quality modeling assessments. This report is organized in two main sections, the first addressing NH_3 emissions from natural landscapes, and the second addressing NH_3 emissions from fertilized soils.

Natural Landscapes

Background

Plants will either absorb or give off NH_3, depending on the concentration of NH_4^+ ion in the plant, and the concentration of NH_3 gas in the surrounding air. The equilibrium air concentration has been termed the "compensation point." When the atmospheric concentration of NH_3 is above the compensation point, the plant will absorb NH_3. Below the compensation point, the plant will give off NH_3. The compensation point depends on the temperature, plant species, and the level of nitrogen nutrient in the plant.

Short term NH_3 fluxes from natural landscapes range from large deposition values to large emission values. The magnitude and direction of NH_3 flux depends on the NH_3 concentration in the air, levels of ammonium in leaves and in the soil, other conditions of vegetation, and meteorological and climactic conditions. Measured NH_3 fluxes over short time spans (typically less than one day) range from -1300 to 700 nanograms per square meter per second (ng m^{-2} s^{-1}), where negative values denote deposition. Longer term average NH_3 fluxes are much lower than short term peaks, but still vary over a wide range. Estimates of annual average emissions from forested landscapes range from -9.1 to 38 ng m^{-2} s^{-1}.

Emissions estimates from natural landscapes account for the largest differences among current NH_3 emissions inventories. EPA's National Emissions Inventory (NEI) does not include emissions estimates for natural landscapes, because of the variability of flux rates, and because they can act as either net sources or net sinks of NH_3.[1] A number of European inventories also exclude NH_3 emissions from natural landscapes. However, NH_3 emissions from landscapes are included in the the Central States Regional Air Planning Association (CENRAP) emissions inventory,[2] as well as in a number of state emissions NH_3 inventories. A recent national emissions inventory by Carnegie Mellon University (CMU) also includes NH_3 natural landscapes, although these emissions estimates are characterized as highly uncertain.[3]

Recommended Emission and Temporal Allocation Factors for Natural Landscapes

Table S1 lists recommended annual NH_3 emission factors for natural landscapes. These recommendations are based on a compilation of measured long-term average flux rates, as well as theoretical values estimated by Bouwman *et al*. (1997) based on nitrogen compound mineralization rates for natural soils.[4] Table S1 also estimates total annual NH_3 emission rates that would be obtained by applying these emission factors to natural landscapes in the continental U.S.

Table S2 gives recommended temporal allocation factors for natural landscapes. The diurnal factors are based on modeling of natural landscape emissions (discussed below), and some limited diurnal emission measurements. The seasonal allocation factors in Table S2 are based on limited seasonal emission measurements.

Table S1. Default Emission Factors for Natural Landscapes

Type of vegetation	Emission factor (ng m^{-2} s^{-1})	Estimated total emissions in the continental U.S. (Gg/yr)
Forests	1.2	58
Grasslands	0.9	32
Shrub Lands	1.3	46
Deserts	0.3	0.4
Total		137

Table S2. Proposed Temporal Allocation factors for Natural Landscapes

Time period	Fraction of emissions
Seasonal	
Spring	0.143
Summer	0.714
Autumn	0.143
Winter	0.000
Diurnal (hour)	
1	0.000
2	0.000
3	0.000
4	0.000
5	0.000
6	0.013
7	0.023
8	0.034
9	0.052
10	0.071
11	0.086
12	0.097
13	0.109
14	0.120
15	0.120
16	0.108
17	0.086
18	0.056
19	0.022
20	0.000
21	0.000
22	0.000
23	0.000
24	0.000

Recommended Model for Natural Landscapes

A approach for estimating NH_3 from natural landscapes is proposed based on a model developed by Sutton *et al*. (1995).[5] The overall flux from landscapes can be divided into two terms: (1) an emission flux that is dependent on the stomatal compensation point and independent of ambient NH_3 concentration, and (2) a deposition flux that is dependant on the ambient concentration and independent of stomatal compensation point:

$$F = F_{emis} - F_{depos} \tag{S1}$$

where F_{emis} is the gross potential emission flux if the ambient NH_3 concentration equals zero; and, F_{depos} is the the amount that the potential flux is reduced by in the presence of ambient NH_3. F_{emis} could be calculated to provide input to the atmospheric simulation model, while F_{depos} could be calculated within the atmospheric simulation model, and would replace the deposition rate for natural landscapes. When the Sutton model is rearranged, F_{emis} and F_{depos} can be computed as follows:

$$F_{emis} = \frac{C_s}{R_s + (R_a + R_b)(R_s / R_w + 1)} \tag{S2}$$

$$F_{depos} = \frac{C_a (R_s + R_w)}{R_w R_s + (R_a + R_b)(R_s + R_w)} \tag{S3}$$

where C_c is the canopy average compensation point (µg m^{-3}), C_s is the stomatal compensation point (µg m^{-3}), R_w is the cuticular resistance (s m^{-1}), and R_s is the stomatal resistance (s m^{-1}). The stomatal compensation point concentration C_s is determined by the apoplastic concentrations of NH_4^+ and H^+ in the leaf, the dissociation constant for NH_4^+, and the Henry's Law constant for NH_3. The cuticular resistance R_w is a function of relative humidity, and is also specific to the type of vegetation. This model reproduces bi-directional fluxes using a relatively simple parameterization of leaf uptake using resistance terms.

Figure 2 graphs the results of the recommended model for a midlatitude conifer forest on a summer day (high temperature = 30° C, relative humidity = 50%). The graph shows the diurnal pattern of the estimated net emission flux, and also breaks the net flux down into the components given by equations (S2) and (S3).

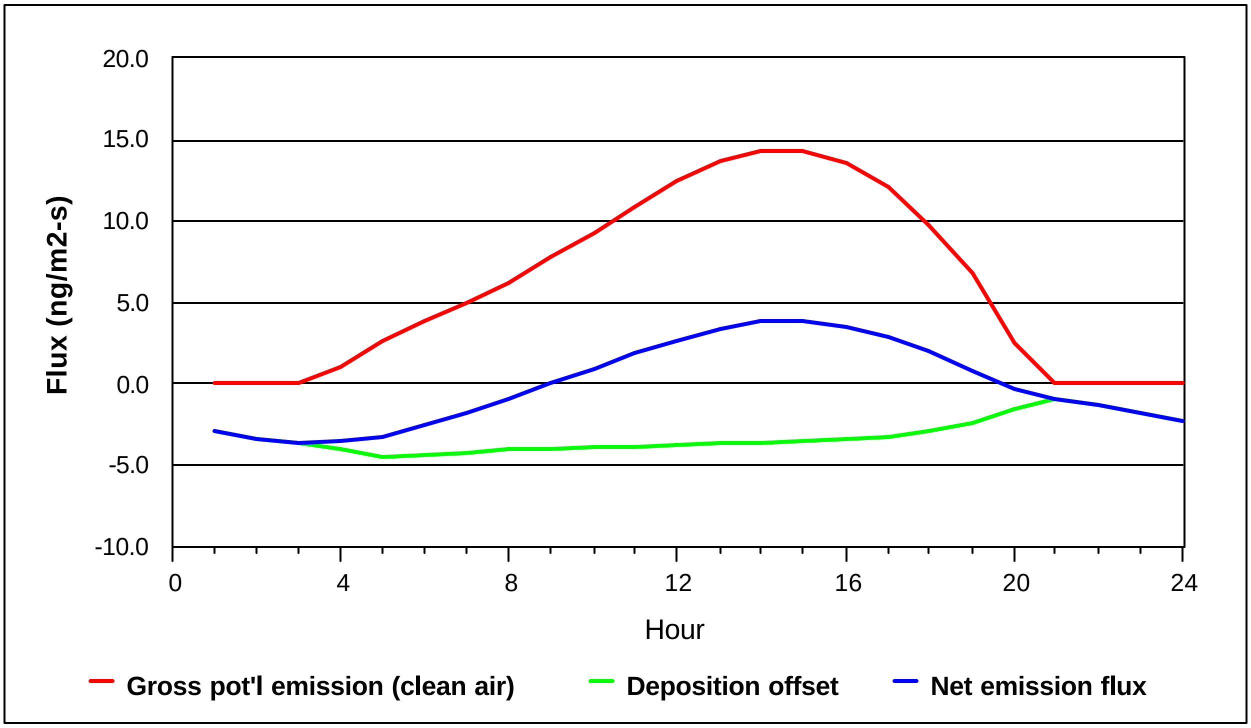

Figure S1. Model-predicted diurnal variations in emission flux components for a typical summer day.

Fertilized Soils

Background

This report addresses NH_3 emissions from synthetic nitrogen fertilizers. Animal wastes are also widely used to meet the nitrogen requirements of crops, and are also a source of NH_3 emissions. However, these emissions are included in the animal husbandry category of the NEI. The NEI estimates NH_3 emissions from synthetic fertilizers at about 630 Gg/year, or 21% of total emissions from all sources.[1]

The magnitude of NH_3 emissions from fertilizer application varies widely depending on the type of fertilizer used, the crop upon which the fertilizer is applied, the timing of application with respect to crop needs, the amount of fertilizer, application techniques, soil moisture content, other soil conditions, and meteorological conditions. The majority of NH_3 emissions occur within a few days of fertilizer application. However, NH_3 emissions have also been measured from maturing crops and from fallow fields after crop harvest.

NH_3 emissions inventories for synthetic fertilizer application are calculated by applying emission factors to activity data derived from fertilizer sales statistics. In the EPA NEI, fertilizer activity data are based on annual sales of different fertilizer compounds at the state level.[1] These annual sales are allocated to seasons using national seasonal allocation factors, and state level sales data are allocated to counties based on the acreage devoted to agriculture in each county. The CMU NH_3 emissions inventory provides extensive refinements in the spatial and seasonal allocation of fertilizer application.[3] The CMU inventory uses semiannual sales data for 1995 from the Association of American Plant Food Control Officials (AAPFCO), which are available at the county-level. Additionally, the CMU model includes data from the US Geological Survey (USGS) for fertilizer sales to farmers by county for 1987 through 1991. This information was combined with information from National Agricultural Statistics Service (NASS) crop calendars to estimate monthly fertilizer application rates for each county. The CENRAP inventory used an approach similar to CMU but combined the semiannual sales data before carrying out the monthly allocation based on crop calendars.[2] The CENRAP inventory also used updated 2002 AAPFCO sales data.

A number of emission models have been developed to evaluate the impacts of different fertilizer application conditions on evaporative losses of NH_3. These models offer some insight into the factors affecting NH_3, but present versions are not adaptable to the calculation of emission rates or temporal emission variations. In general, the NH_3 models require inputs for a wide array of parameters, including fertilizer application rate, time since application, soil type, pH, soil temperature, soil moisture content, air temperature, and wind speed. These parameters, especially the time since application, are not available on geographical scales above an individual farm. In addition, most of the NH_3 models were developed for fertilizers derived from animal wastes, and may not be transferable to chemical fertilizers.

Recommended Emission and Temporal Allocation Factors for Fertilized Soils

Table S3 gives recommended NH_3 emission factors for fertilizer application. These factors are based on estimates made by the European Environment Agency 2001 (EEA), which vary with soil type (pH) and climate.[6] These EEA emission factors have also been used in the CENRAP and CMU NH_3 inventories.

As noted earlier, Carnegie Mellon University has developed monthly estimates of fertilizer usage at the county level, based on crop calendars and fertilizer sales. Since most of the direct emissions from fertilizer occur within a few days of application, emissions in a given month can be estimated based on the fertilizer application for that month. This method gives greater accuracy than applying temporal allocation factors to an annual estimate. Therefore, we recommend using the CMU monthly fertilizer application data, and implementing equation (12) separately for each county and each month. The current NEI Input Format (NIF) gives the flexibility to store activity data (in this case fertilizer usage) in other time frames, including by month. This current report also outlines an approach for taking into account daily variations in NH_3 emissions when the date of fertilizer application is known.

Table S3. Recommended Emission Factors for Direct NH_3 Emissions from Fertilizer

	Emission factors based on fertilizer application (kg-NH_3 / Mg-N)			Emission factors based on fertilizer application (lb-NH_3 / ton-N)		
Fertilizer	Group I soils	Group II soils	Group III soils	Group I soils	Group II soils	Group III soils
Anhydrous ammonia	48	48	48	97	97	97
Nitrogen solutions (urea & AN)	97	97	97	194	194	194
Urea	242	182	182	484	363	363
Diammonium phosphate	61	61	61	121	121	121
Ammonium nitrate (AN)	36	24	12	73	48	24
Liquid ammonium polyphosphate	61	61	61	121	121	121
Aqueous ammonia	97	97	97	194	194	194
Ammonium thiosulfate	30	30	30	61	61	61
Calcium ammonium nitrate	36	24	12	73	48	24
Potassium nitrate	12	12	12	24	24	24
Monoammonium phosphate	61	61	61	121	121	121
Ammonium sulfate	182	121	61	363	242	121
Miscellaneous	97	73	48	194	145	97
Mix	36	24	12	73	48	24

Group I: Warm, temperate areas with a large proportion of calcareous soils

Group II: Temperate and warm-temperate areas with some calcareous soils (or managed with soil pH>7), but with large areas of acidic soils

Group III: Temperate and cool-temperate areas with largely acidic soils

The factors in Table S3 cover NH_3 emissions following fertilizer application. Crops have been shown to continue emitting NH_3 during the growing season. Emissions have also been measured from fallow soil following the harvest a crop. Combined, these emissions could represent an increase of about 10-20% above the emissions directly following fertilizer application. Because these emission rates were measured well after fertilizer application, they do not appear to be already included in the direct fertilizer emission factors. In many cases, however, emissions from maturing crops and fallow soils emissions may result from nitrogen-rich soil conditions produced by periodic applications of animal wastes to fields. As a result, it is believed that these emissions are generally already counted in emissions estimates for the animal husbandry category of the NEI.

Table S4 gives recommended diurnal allocation factors for direct emissions from fertilizer, emissions from crops, and emissions from fallow soil. Figure S2 compares the fertilizer factors those recently used in the CENRAP inventory (which were based on nitrogen oxide emissions from soil).

Table S4. Recommended Hourly Temporal Allocation Factors for Fertilized Soils

	Hourly allocation factor (fraction of daily emissions)	
Hour	Fertilizer and fallow soil	Crops
1	0.014	0.000
2	0.013	0.000
3	0.013	0.000
4	0.015	0.000
5	0.019	0.002
6	0.022	0.015
7	0.028	0.026
8	0.038	0.039
9	0.046	0.052
10	0.051	0.066
11	0.061	0.081
12	0.069	0.094
13	0.071	0.104
14	0.074	0.110
15	0.077	0.110
16	0.072	0.103
17	0.065	0.089
18	0.059	0.069
19	0.052	0.039
20	0.039	0.000
21	0.028	0.000
22	0.027	0.000
23	0.024	0.000
24	0.022	0.000

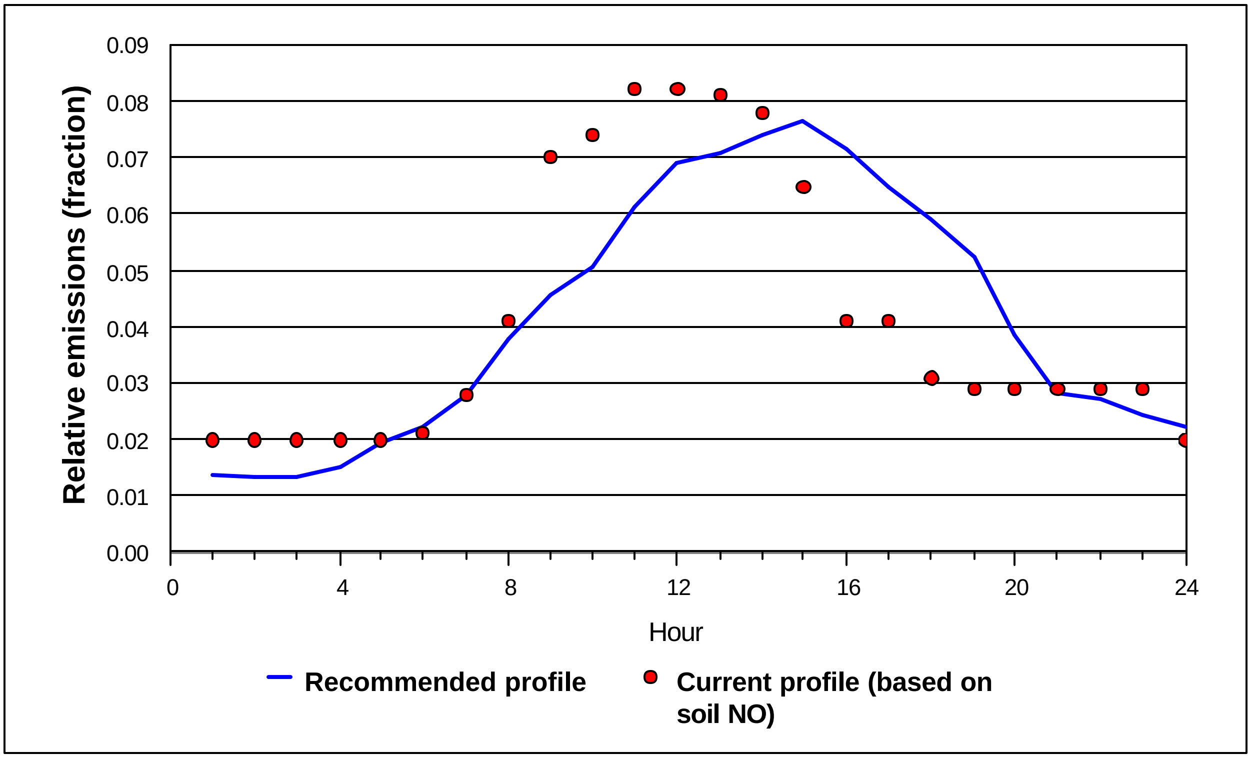

Figure S2. Diurnal allocation factors for fertilizer application.

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Introduction

Ambient concentrations of fine particulate matter ($PM_{2.5}$) have moved to the forefront of environmental and health issues in the United States over the last 10 years. $PM_{2.5}$ is one of the six criteria pollutants defined in the Clean Air Act (CAA), and can lead to regional haze and reduced visibility. The U.S. Environmental Protection Agency (EPA) is evaluating emission reduction strategies for implementing the 1997 National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$. EPA has also established Regional Haze Regulations to reduce emissions from air pollutants that cause visibility impairment. Ambient $PM_{2.5}$ is comprised both of particles that are directly emitted to the air, and of secondary particulates, formed from reactions of gaseous pollutants in the atmosphere.

Ammonia (NH_3) reacts with other pollutants in the atmosphere to produce secondary particulate species, including ammonium sulfates (NH_4HSO_4 and $[NH_4]_2SO_4$) and ammonium nitrate (NH_4NO_3). These pollutants account for up to 50% of the total mass of $PM_{2.5}$ in many areas of the U.S. The development of cost-effective control strategies for $PM_{2.5}$ will hinge on a thorough understanding of the relative abundance and distribution not only of primary $PM_{2.5}$ emissions, but also of secondary $PM_{2.5}$ precursor emissions.

The U.S. EPA has developed atmospheric simulation models to analyze the formation of secondary $PM_{2.5}$, and the atmospheric transport of $PM_{2.5}$ and its precursors. These models rely on detailed emissions inventories for primary $PM_{2.5}$ and secondary $PM_{2.5}$ precursors. Efforts to simulate the formation of secondary $PM_{2.5}$ have been hampered by variations and uncertainties in the temporal and spatial patterns of NH_3 emissions. These variations and uncertainties are particularly large for fertilized soils and natural landscapes.

Natural landscapes have not been included to date in EPA National Emissions Inventories (NEI) for NH_3 because of large uncertainties in their emission rates.[1] In fact, forests and other natural systems can alternate between emitting and absorbing NH_3. A recent national emissions inventory by Carnegie Mellon University (CMU) estimates that annual NH_3 from natural landscapes may be as high as 1.3 Tg yr^{-1} (1.4 million tons/yr), or about 16% of the total emissions in the continental U.S. (Davidson *et al.*, 2003).[2] Short term emission fluxes from natural landscapes can be orders of magnitude higher than long term fluxes. In addition, studies have shown an equilibrium between ammonia in the air and ammonium compounds in plant leaves. As a result, trees, crops and other plants might release more ammonia if emissions from other sources are reduced.

The 1999 NEI estimates that about 630 Gg/year (690,000 tons/year) of NH_3 emissions emanate from the application of synthetic nitrogen fertilizers to soil and crops. This is about 21% of total NH_3 from all anthropogenic sources. A more recent estimate of NH_3 emissions from fertilizers is available in the CMU inventory. The CMU inventory estimates direct NH_3 emissions following the application of fertilizer at 890 Gg yr^{-1} (970,000 tons/yr) or about 16% of total annual NH_3 emissions.[2]

Emissions from fertilizer usage are concentrated in a short period of time (1 to 2 weeks) after the application of fertilizer.

The EPA and the Emissions Inventory Improvement Program (EIIP) have funded an effort to identify procedures for estimating short-term NH_3 emissions from fertilized soils and natural landscapes, the results of which are reported in this document. This research is aimed at improving hourly ammonia emissions estimates for regional air quality modeling assessments. This report is organized in two main sections, the first addressing NH_3 emissions from natural landscapes, and the second addressing NH_3 emissions from fertilized soils.

Natural Landscapes

Natural landscapes can alternate between emitting ammonia (NH_3) and absorbing the gas from the atmosphere, depending on the NH_3 concentrations in the air, in the soil, and in plant tissues. Microbial reactions in soils convert organic nitrogen compounds to ammonium (NH_4^+) compounds in a process termed mineralization. These NH_4^+ compounds can, in turn, produce NH_3 emissions if the soil is alkaline. However, soils can absorb NH_3 from the air if the concentration in the air is high, and NH_3 is also deposited to soils in rainfall.

Plants also will either absorb or give off NH_3, depending on the concentration of NH_4^+ ion in the plant, and the concentration of NH_3 gas in the surrounding air. The equilibrium air concentration has been termed the "compensation point" (Farquhar *et al*, 1980).[3] When the atmospheric concentration of NH_3 is above the compensation point, the plant will absorb NH_3. Conversely, when the atmospheric concentration of NH_3 is below the compensation point, the plant will give off NH_3. The compensation point depends on the temperature, plant species, and the level of nitrogen nutrient in the plant.

Emissions Data

Table 1 summarizes available information on NH_3 emission and deposition fluxes in natural landscapes. Short term NH_3 fluxes can range from large deposition values to large emission values. As Table 1 shows, measured fluxes over short time spans (typically less than one day) range from −1300 to 700 nanograms per square meter per second (ng m^{-2} s^{-1}), where negative values denote deposition. For instance, Wyers and Erisman (1998) detected fluxes from −1000 to 700 ng m^{-2} s^{-1} in measurements over a 2-year period in a Douglas fir forest in the Netherlands.[4] As Table 1 shows, other researchers have also detected NH_3 fluxes over this broad range. Wyers and Erisman (1998) found that NH_3 emissions occurred mainly during the day and in warmer weather. They found that nighttime NH_3 fluxes were dominated by deposition, and deposition was also dominant during wet conditions. Pryor *et al.* (2001) found that the average flux in the spring tended toward deposition for a Southern Indiana deciduous forest. However, emission fluxes as high as 55 ng m^{-2} s^{-1} were also detected.[5] Figure 1 shows the diurnal pattern of emissions on a day when there was an apparant net emission flux from this study.

Longer term average NH_3 fluxes are much lower than short term peaks, but still vary over a wide range. For instance, in a pine forest on the eastern slope of the Rocky Mountains, Langford and Fehsenfeld (1992) measured a deposition flux averaging about 10 ng m^{-2} s^{-1} when the forest was exposed to NH_3-rich air, contrasted with an emission flux averaging about 1.2 ng m^{-2} s^{-1} when the forest was exposed to clean air from the mountains.[6] Wyers and Erisman (1998) also found that long-term average fluxes varied from year to year in the same forest.[4]

Table 1. Summary of Emissions Measurements for Natural Landscapes

	Range of NH_3 flux ($\text{ng}-NH_3\ m^{-2}\ s^{-1}$)[a]	
Landscape	Long term[b]	Short term[c]
Temperate forests		
Anderson, S. *et al.* (2003)[7]	0.03 to 0.05 [d]	
Pryor *et al.* (2001)[5]	−0.23	up to +55
Wyers and Erisman (1998)[4]	0.16 to 0.44	−1000 to +700
Andersen, H.V. *et al.* (1999)[8]	−9.1	
Langford and Fehsenfeld (1992)[6]	−10 to +1.2 [e]	
Bouwman *et al.* (1997)[9] - review of previous tests	0.06 [f] – 3 [g]	
- calculated from mineralization rates	0.3	
Schlesinger and Hartley (1992) - based on a review of 6 earlier studies[10]	3.8 – 38	
Andersen, H.V. *et al.* (1993)[11, h]		−300 to +50
Duyzer *et al.* (1994)[12, h]		−1300 to +300
Sutton *et al.* (1995)[13, h]		−950 to +630
Kim *et al.* (1973)[14]		570
Unfertilized grassland		
Sutton *et al.* (1993)[15, h]		−31 to −0.19
Schlesinger and Hartley (1992) - based on a review of 10 earlier studies[10]	0.38 – 38	
Bouwman *et al.* (1997)[9] - review of previous tests	<0.3 – 6	
- calculated from mineralization rates	0.9	
Shrub land		
Bouwman *et al.* (1997)[9] - review of previous tests	<0.16	
- calculated from mineralization rates	1.3	
Deserts		
Bouwman *et al.* (1997)[9] - review of previous tests	0.16 – 1.6	
- calculated from mineralization rates	0.3	

[a] Positive values denote emissions, negative values denote deposition.

[b] Annual unless otherwise noted.

[c] Typically less than one day.

[d] Isolation chamber measurements for forest soil.

[e] Deposition occurred when the forest was exposed to NH_3-rich air from emission source regions, and emissions occurred when the forest was exposed to clean air.

[f] Autumn and winter.

[g] Summer.

[h] As cited by Asman, *et al.* (1998).[16]

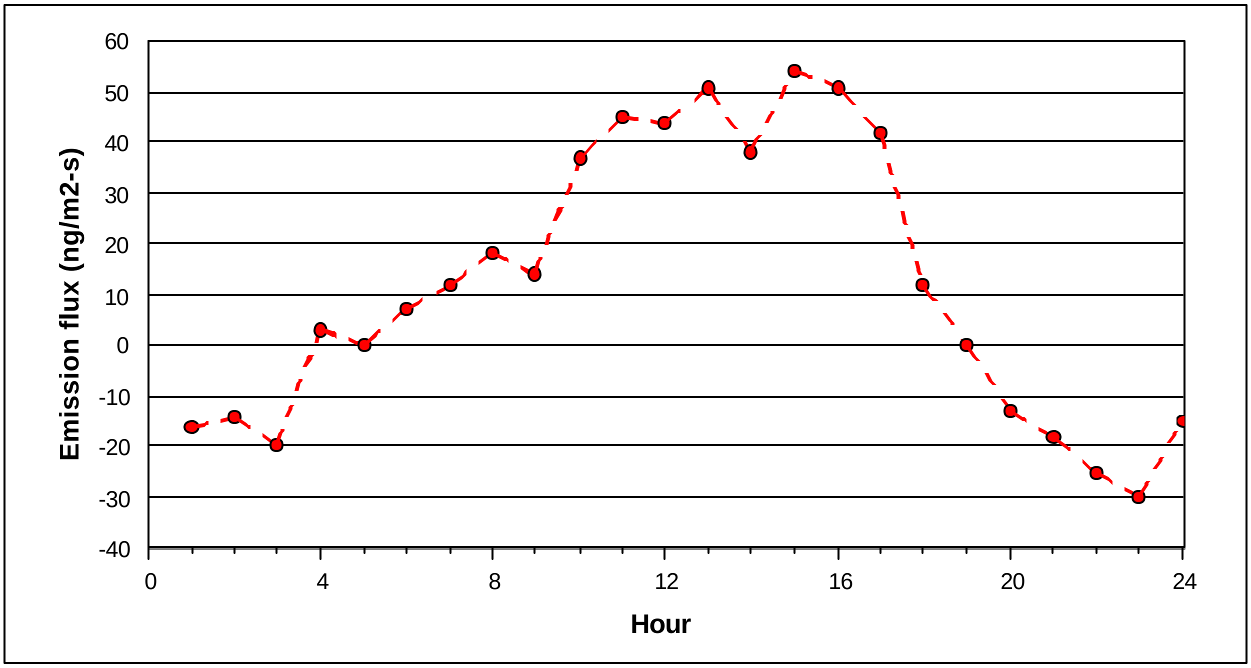

Figure 1. Diurnal pattern in spring forest emissions for a day with an apparent net emission flux (Pryor et al, 2001)

Schlesinger and Hartley (1992) estimated annual average average emissions based on a review of previous test data.[10] NH_3 emissions were estimated at 4 to 38 ng m^{-2} s^{-1} for forests (based on 6 studies); and 0.04–0.38 ng m^{-2} s^{-1} from grasslands (based on 10 studies).
Bouwman *et al.* (1997) have also estimated annual average emission rates for natural landscapes, based on a review of measurement data and on order-of-magnitude estimates of nitrogen mineralization rates in different ecosystems.[9] Long-term average NH_3 emissions were estimated at 0.3 ng m^{-2} s^{-1} from forests, 0.95 ng m^{-2} s^{-1} from unfertilized grassland, 1.3 ng m^{-2} s^{-1} from shrubland, and 0.3 ng m^{-2} s^{-1} from deserts. However, some researchers have also found net deposition fluxes on a long-term basis. H.V. Andersen *et al.* (1999) also measured an average deposition flux of 9.1 ng m^{-2} s^{-1} over all four seasons in a spruce forest in Denmark.[8] Also, As noted earlier, Pryor *et al.* (2001) found that the flux in the spring was primarily directed toward deposition for a southern Indiana deciduous forest.[5]

Treatment of Natural Landscapes in Existing Emissions Inventories

Emissions estimates from natural landscapes account for the largest differences among current NH_3 emissions inventories. Some inventories include emissions estimates for natural landscapes. Others exclude natural landscapes because of the variability of flux rates, and because they can act as either net sources or net sinks of NH_3.

The EPA emission factor report for NH_3 gives a range of potential emission rates for natural landscapes but does not recommend emission rates for developing an emissions inventory.[17] EPA's National Emissions Inventory (NEI) does not include emissions estimates for natural landscapes.[1] A number of European inventories also exclude NH_3 emissions from natural ecosystems, including estimates by Hov and Hjollo (1994) for Europe as a whole,[18] Hutchings *et al.* (2001) for Denmark,[19] and Sutton *et al.* (1995, 2000) for England.[20,21] Sutton (2000) indicates that any emissions from natural ecosystems are minor and temporary, and are outweighed by dry deposition.

In an initial estimate for the state of Texas, Corsi *et al.* (2000) estimated NH_3 emissions from natural landscapes at about 52% of the statewide annual emissions inventory.[22] However, this initial estimate used a relatively high emission factor based on short-term measurements by Kim *et al.* (see Table 1). Recent soil tests carried out in Texas have reduced the estimated contribution of natural landscapes to about 3% of statewide emissions (Anderson *et al*. 2003).[7]

NH_3 emissions from natural landscapes are included as part of a soils and vegetation category in an inventory for the San Joaquin Valley (SJV) region of California (Coe *et al.*, 1998).[23] The SJV inventory used NH_3 emission factors of $12 \text{ ng m}^{-2} \text{ s}^{-1}$ for forests and $17 \text{ ng m}^{-2} \text{ s}^{-1}$ for grasslands. With the above emission factors, forests and unfertilized grasslands accounted for roughly 20% of the overall SJV ammonia inventory. The same emission factors were used in a separate inventory for the South Coast Air Quality Management District (SCAQMD).[24]

In a later case study inventory for the SJV region, Battye *et al.* (2003) used lower emission factors for natural landscapes, and estimated their contribution to overall regional NH_3 emissions at 5%. This estimate was derived using NH_3 emission factors of $3.8 \text{ ng m}^{-2} \text{ s}^{-1}$ for forests, $0.95 \text{ ng m}^{-2} \text{ s}^{-1}$ for grasslands, and $1.3 \text{ ng m}^{-2} \text{ s}^{-1}$ for scrub brush,[25] based on the recommendations of Bouwman *et al.*[9] and Schlesinger and Hartley.[10] This set of factors was also used in an invenotry for the Central U.S. which estimated the contribution of natural emissions at about 7% of overall regional NH_3 emissions (Coe and Reid, 2003).[26]

The current Carnegie Mellon University (CMU) NH_3 emissions inventory estimates emissions from natural landscapes at about 1.3 Tg yr^{-1} (1.4 million tons/yr), or about 16% of the total emissions in the continental U.S. (Davidson *et al.*, 2003).[2] This estimate is based on emission factors of $4.4 \text{ ng m}^{-2} \text{ s}^{-1}$ for forests, $12 \text{ ng m}^{-2} \text{ s}^{-1}$ for grassland and shrubland, and $1.9 \text{ ng m}^{-2} \text{ s}^{-1}$ for barren land.

The emission inventories for the SJV and the Central U.S. are spatially and temporally resolved to meet the needs of air quality simulation models. Emissions in each grid were calculated based on the land use characteristics within that grid. However, emissions were not calculated for specific time periods. Rather, the inventories began with estimates of annual average NH_3 emissions based on estimated long-term average NH_3 emission factors. Temporal allocation factors were applied to the annual estimates to produce appropriate seasonal and diurnal patterns in NH_3 emissions.

Available Emission and Deposition Models

Dry deposition of atmospheric pollutants is frequently characterized using a resistance model. Both the EPA Regional Acid Deposition Model (RADM)[27, 28] and the Community Multiscale Air

Quality (CMAQ) chemical transport model[29] use this approach, with NH_3 deposition flux calculated from the modeled ambient NH_3 concentration and a series of resistances to bulk diffusion:

$$F = \frac{-C_a}{(R_a + R_b + R_c)} \tag{1}$$

where F is the mass flux of NH_3 ($\mu g\ m^{-3}$) (negative values represent deposition), C_a is the ambient concentration ($\mu g\ m^{-2}\ s^{-1}$), R_a is the atmospheric resistance ($s\ m^{-1}$), R_b is the quasi-laminar boundary layer resistance ($s\ m^{-1}$), and R_c is the canopy resistance ($s\ m^{-1}$). Hicks (1987) related the canopy resistance to the resistance of leaf stomata to NH_3 transport, which is a function of temperature and light intensity.[30]

Researchers have also used resistance models to characterize the bi-directional (emission and deposition) flux of NH_3 from landscapes. Sutton *et al.* (1995) found in croplands that bi-directional transport can occur not only through leaf stomata, but also in parallel onto and off of the leaf cuticle.[31] Wyers and Erisman (1998) and Milford *et al.* (2001) extended this observation to forests and moorlands, respectively.[4, 32] Sutton *et al*. (1995 and 1998[33]) and Milford *et al*. (2001) propose a multistage resistance model to characterize overall transport to or from the canopy, and define a canopy average compensation point which is determined by the interplay of various flux rates:

$$F = (C_c - C_a / (R_a + R_b) \tag{2}$$

$$C_c = \frac{C_a / (R_a + R_b) + C_s / R_s}{1/(R_a + R_b) + 1/R_w + 1/R_s} \tag{3}$$

where C_c is the canopy average compensation point ($\mu g\ m^{-3}$), C_s is the stomatal compensation point ($\mu g\ m^{-3}$), R_w is the cuticular resistance ($s\ m^{-1}$), and R_s is the stomatal resistance ($s\ m^{-1}$). The stomatal compensation point C_s concentration is determined by the apoplastic concentrations of NH_4^+ and H^+ in the leaf, the dissociation constant for NH_4^+, and the Henry's Law constant for NH_3. The cuticular resistance R_w is a function of relative humidity, and is also specific to the type of vegetation. This model reproduces bi-directional fluxes using a relatively simple parameterization of leaf uptake using resistance terms. Sutton *et al.* (1998) also developed an approach for treating cuticular uptake as a capacitance, which can account for the impacts of previous fluxes.

The resistance model matched the magnitude and structure of the fluxes measured above the moorland for the majority of the time. However, the model underestimated the magnitude of deposition during some daytime periods.

Recommended Model for Estimating Emissions

We are recommending an algorithm for calculating bi-directional NH_3 flux in natural landscapes based largely on the model developed by Sutton *et al.* (1995).[31] Measurement studies have shown a great deal of variability in NH_3 emission rates and deposition rates in natural landscapes (see Table 1). Short term flux rates can be 2 to 3 orders of magnitude larger than long term average flux rates, both in the emission direction and in the deposition direction. The direction of flux is believed to be determined by the local ambient NH_3 concentration and NH_4^+ concentrations in foliage and soil. Short term emission and deposition rates have been shown to depend on temperature, sunlight intensity, relative humidity, and other meteorological parameters that affect the rate of atmospheric transport (atmospheric resistance and quasi-boundary layer resistance).

Given the influences of meteorological parameters on emissions from natural landscapes, it is impossible to characterize the variations in these emissions using a simple emission factor methodology. Models developed by Sutton *et al.*(1995),[13] Milford *et al.*(2001),[32] and Hicks *et al.*(1987)[30] make it possible to calculate NH_3 emissions for specific ecosystem types and for the meteorological conditions observed in specific episodes. These models require a number of inputs, many of which need to be estimated. However, sufficient information is available to reproduce the emission patterns that have been observed in measurements.

As noted above, the model we are proposing is based on that developed by Sutton *et al.* (1995),[31] and shown in equations (2) and (3). This model estimates net NH_3 flux as a function of the NH_3 compensation point, the NH_3 in ambient air, and various resistance terms. However, as a practical matter, the air concentration, C_a, is not known when emissions are computed. To simplify the emission calculation, we can define two flux terms: (1) an emission flux dependent on the stomatal compensation point and independent of ambient NH_3 concentration, and (2) a deposition flux dependent on the ambient concentration and independent of stomatal compensation point. First, equations (2) and (3) can be combined, substituting for the canopy average compensation point C_c:

$$F = \frac{C_a\ /\ (R_a + R_b) + C_s\ /\ R_s}{[\ 1/(R_a + R_b) + 1/R_w + 1/R_s\ ](R_a + R_b)} - \frac{C_a}{(R_a + R_b)} \qquad \textbf{(4)}$$

This equation can then be simplified and rearranged, as follows:

$$F = \frac{[C_a\ /\ (R_a + R_b) + C_s\ /\ R_s\ ] - C_a[1\ /\ (R_a + R_b) + 1\ /\ R_w + 1\ /\ R_s\ ]}{[1/(R_a + R_b) + 1\ /\ R_w + 1/R_s\ ](R_a + R_b)} \qquad \textbf{(5)}$$

$$F = \frac{(C_s\ /\ R_s) - C_a\,(1\ /\ R_w + 1\ /\ R_s)}{1 + (R_a + R_b)(\ 1\ /R_w + 1/R_s)} \qquad \textbf{(6)}$$

$$F = \frac{(C_s\ /\ R_s)}{1 + (R_a + R_b)(\ 1\ /R_w + 1/R_s)} - \frac{C_a\,(1\ /\ R_w + 1\ /\ R_s)}{1 + (R_a + R_b)(1/\ R_w + 1\ /\ R_s)} \qquad \textbf{(7)}$$

$$F = \frac{C_s}{R_s + (R_a + R_b)(R_s / R_w + 1)} - \frac{C_a (R_s + R_w)}{R_w R_s + (R_a + R_b)(R_s + R_w)} \qquad \textbf{(8)}$$

Finally, the two terms of equation (8) can be separated into two equations, as follows:

$$F = F_{emis} - F_{depos} \qquad \textbf{(9)}$$

$$F_{emis} = \frac{C_s}{R_s + (R_a + R_b)(R_s / R_w + 1)} \qquad \textbf{(10)}$$

$$F_{depos} = \frac{C_a (R_s + R_w)}{R_w R_s + (R_a + R_b)(R_s + R_w)} \qquad \textbf{(11)}$$

Where F_{emis} is the gross potential emission flux if the ambient NH_3 concentration were equal to 0; and F_{depos} is the the amount that the potential flux is reduced by the presence of NH_3 in the atmosphere. F_{emis} would be calculated to provide input to the atmospheric simulation model, while F_{depos} would be calculated within the atmospheric simulation model, and would replace the deposition rate for natural landscapes.

The atmospheric resistance, R_a, and the quasi-laminar boundary layer resistance, R_b, are already calculated for the deposition calculations performed in RADM, CMAQ, and other atmospheric simulation models.[28,29] Milford *et al.* (2001) give the following algorithm for stomatal compensation point, C_s:[32]

$$C_s = \Gamma \left[\frac{161{,}500}{T} \right] \times \exp\left(\frac{10{,}380}{T} \right) \qquad \textbf{(12)}$$

$$\Gamma = \frac{\left[NH_4^+ \right]}{\left[H^+ \right]} \qquad \textbf{(13)}$$

where T is temperature (K), and Γ is the ratio of NH_4^+ to H^+ concentration in the apoplastic leaf tissue. Little data are available on the apoplastic ratio; however values have been calculated for some ecosystems based on micrometeorological measurements. These data are summarized in Table 2.[32]

Table 2. Example Values for the Apoplastic Ratio of NH_4^+ to H^+ (Γ)

Type of vegetation	Apoplastic Ratio of NH_4^+ to H^+
Upland moorland, Scotland	50
Lowland moorland, Scotland	132
Mixed pine, spruce, and aspen, Colorado	155
Wheat, England (in anthesis)	630
Grazing land, England	>3000

Source: Milford *et al*. (2001)[32]

The stomatal resistance can be calculated as follows, based on Hicks *et al*:[30]

$$R_s = R_{s,\min} \times (1 - b/I) \times f_T \tag{14}$$

$$f_T = \frac{(T - T_C)}{(T_0 - T_C)} \times \left[\frac{T_H - T}{T_H - T_0}\right]^{\left[\frac{T_H - T_0}{T_0 - T_C}\right]} \tag{15}$$

where $R_{s,min}$ is the minimum stomatal resistance, β is the light response coefficient (W m^{-2}), I is sunlight intensity (W m^{-2}), f_T is a temperature correction factor that accounts for the closing of stomata outside of a given temperature range, T is the ambient temperature (K), T_C is the minimum temperature for stomatal opening (K), T_H is the maximum temperature (K), and T_0 is the optimum temperature (K). EPA has estimated stomatal resistance parameters for a variety of vegetation types as part of the deposition calculations for the Clean Air Status and Trends Network (CASTNET).[34] These are summarized in Table 3.

Milford *et al.* (2001) give the following relationship for the cuticular resistance, R_w:[32]

$$R_w = R_{w,\min} \exp\left(\frac{100 - RH}{a}\right) \tag{16}$$

where $R_{w,min}$ is the minimum cuticular resistance (s m^{-1}), *RH* is the relative humidity (%), and *a* is the humidity response factor (%). $R_{w,min}$ was measured at 0.5 s m^{-1} and *a* was measured at 12% for moorland.[32] R_s and R_w could also be obtained from the Meteorology-Chemistry Interface Processor (MCIP) subsystem of the EPA Community Multiscale Air Quality (CMAQ) model.[35]

Table 3. Stomatal Resistance Parameters for Natural Vegetation

Species	Minimum stomatal resistance (s m^{-1})	Light response coefficient (W m^{-2})	Optimal tempera-ture (°C)	Maximum tempera-ture (°C)	Minimum tempera-ture (°C)
Spruce	225	40	9	35	-5
Ponderosa, lodgepole pine	500	40	25	40	5
Loblolly pine	200	55	25	40	5
White oak	100	50	25	45	5
Chestnut, red oak	100	40	25	45	5
Maple	100	50	25	45	5
White birch	300	40	25	40	5
Grass	50	20	25	45	5
Blue grass	150	50	30	40	5
Sugar maple	100	50	25	45	5
Beech	100	50	25	40	5
Yellow birch	300	40	25	40	5
White ash	100	40	25	40	5
Hemlock	225	10	25	35	-5
Yellow poplar	150	40	25	40	5
Gum	150	40	25	40	5
Apple, peach, pear	150	40	25	40	5
Black locust	150	40	25	40	5
Virginia pine	200	55	25	40	5
Red pine	200	55	25	40	5
Southern red oak	100	40	25	40	5
Southern yellow pine	200	55	25	40	5
White pine	225	40	25	35	-5
Subalpine fir	225	25	9	35	-5
Sagebrush	100	20	25	45	5
Juniper	225	25	9	35	-5
Velvet ash	100	40	25	40	5
Emory oak	100	25	25	45	5
Arizona cypress	225	25	25	45	5
Pinon pine	225	25	9	35	-5
Aspen	200	30	25	35	5
Desert shrub	200	55	25	45	5

The above-described model is a relatively simple parameterization of bi-directional NH_3 flux between a natural landscape and the atmosphere. The model focuses on the leaf canopy and expresses leaf uptake using only resistance terms. As noted earlier, Sutton *et al.* (1998) have developed an approach for treating cuticular uptake as a capacitance, which can account for the impacts of previous fluxes. Loubet *et al.* (2001) have also assessed an approach for estimating the impact of advection effects from nearby sources.[36] However, both of these refinements would require information on atmospheric NH_3 concentrations, which is not available when emissions are calculated.

Sensitivity Analysis

Figure 2 graphs the results of the recommended model for a midlatitude conifer forest on a summer day (high temperature = 30° C, relative humidity = 50%). The graph shows the diurnal pattern of the estimated net emission flux, and also breaks the net flux down into the components given by equations (5) and (6). The ambient NH_3 concentration was assumed to be 1 $\mu g\ m^{-3}$ for these calculations. Figure 3 shows predicted seasonal variations for net emission flux for a pine forest. Figure 4 shows predicted emission fluxes for different tree species based on stomatal resistance values from Table 3.

The most uncertain inputs to the model are the apoplastic ratio of NH_4^+ to H^+ and the cuticular resistance parameters from equation (11). Figures 5 through 7 show the impact of changes in these parameters. Of these parameters, the estimated emission flux appears to be most sensitive to the apoplastic ratio. However, uncertainties in cuticular resistance parameters also have significant impacts, especially on the estimates of offsetting deposition at night.

Default Emission and Temporal Allocation Factors

Modeling emissions from natural landscapes will require detailed information on meteorology and land cover, as well as inputs for numerous parameter values. This data-intensive effort will not be practical for all emissions inventory developers. Therefore, we have also evaluated emissions data to identify a set of default emission factors for different landscapes. The data in Table 1 suggest a best estimate emission factor of about 1.2 $ng\ m^{-2}\ s^{-1}$ for forests on an annual basis. This value is equal to the average emission flux measured by Langford and Fehsenfeld (1992) for a Rocky Mountain pine forest during periods of downslope winds.[6] It is higher than the flux estimated by Bouwman *et al.* (1997) based on nitrogen compound mineralization rates for forest soils;[9] and it is also higher than the results of some recent measurements. But it is within the possible range identified by Bouwman *et al.* (1997). The mineralization rate calculations by Bouwman are recommended for grasslands, shrub lands, and deserts, because of the limited availability of measurements for these landscapes.

Table 4 summarizes the recommended default emission factors for natural landscapes. The table also estimates total annual NH_3 emission rates that would be obtained by applying these emission factors to natural landscapes in the continental U.S. These estimates are based on land cover information from EPA's Biogenic Emissions Land Cover Database (BELD).[37]

Table 5 gives recommended default temporal allocation factors for natural landscapes. The diurnal factors are based on the proposed model discussed above, as well as diurnal values reported by Pryor *et al* (2001) for a spring day on which there was an apparent net emission flux. Figure 8 compares the recommended diurnal profile with hourly emissions predicted by the model and hourly emissions measured by Pryor *et al*.[5]

The seasonal allocation factors for spring, summer, and fall in Table 5 are based on the estimated average fluxes given by Bouwman *et al* (1997), based on their summary of available measurements.[9] The winter allocation factor is based on results given by the model described above, which predicts net deposition at low temperatures.

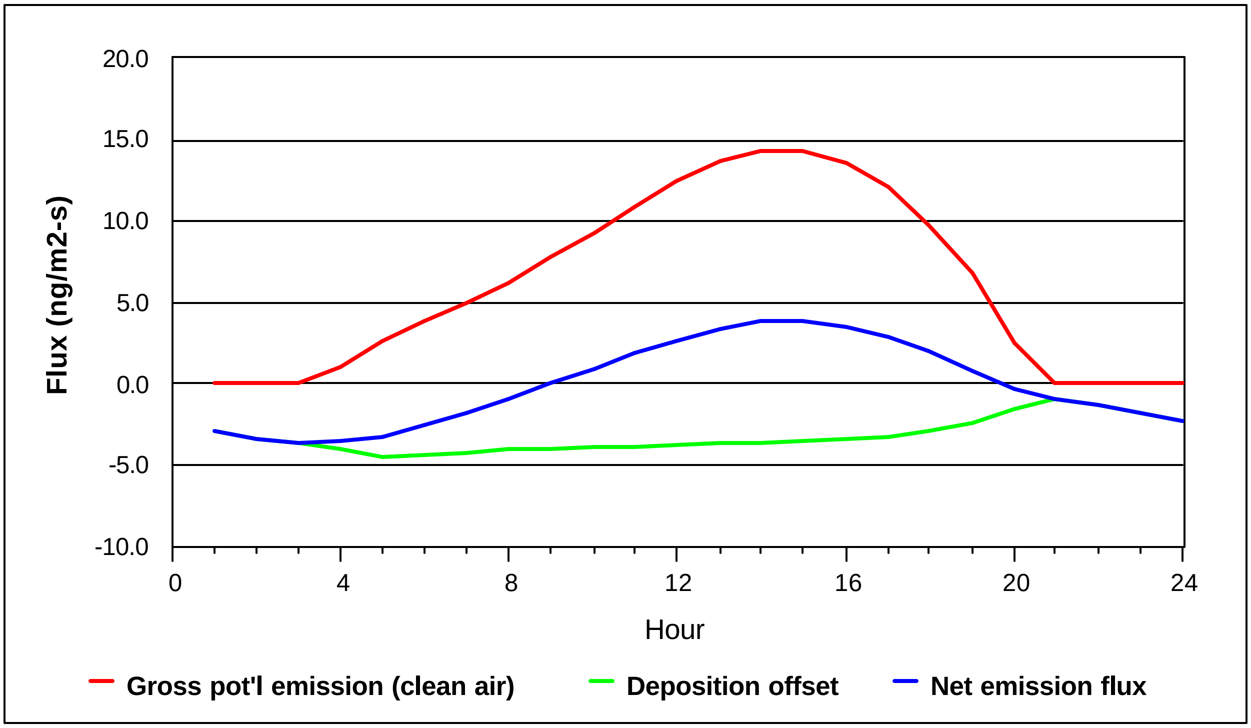

Figure 2. Model-predicted diurnal variations in emission flux components for a typical summer day.

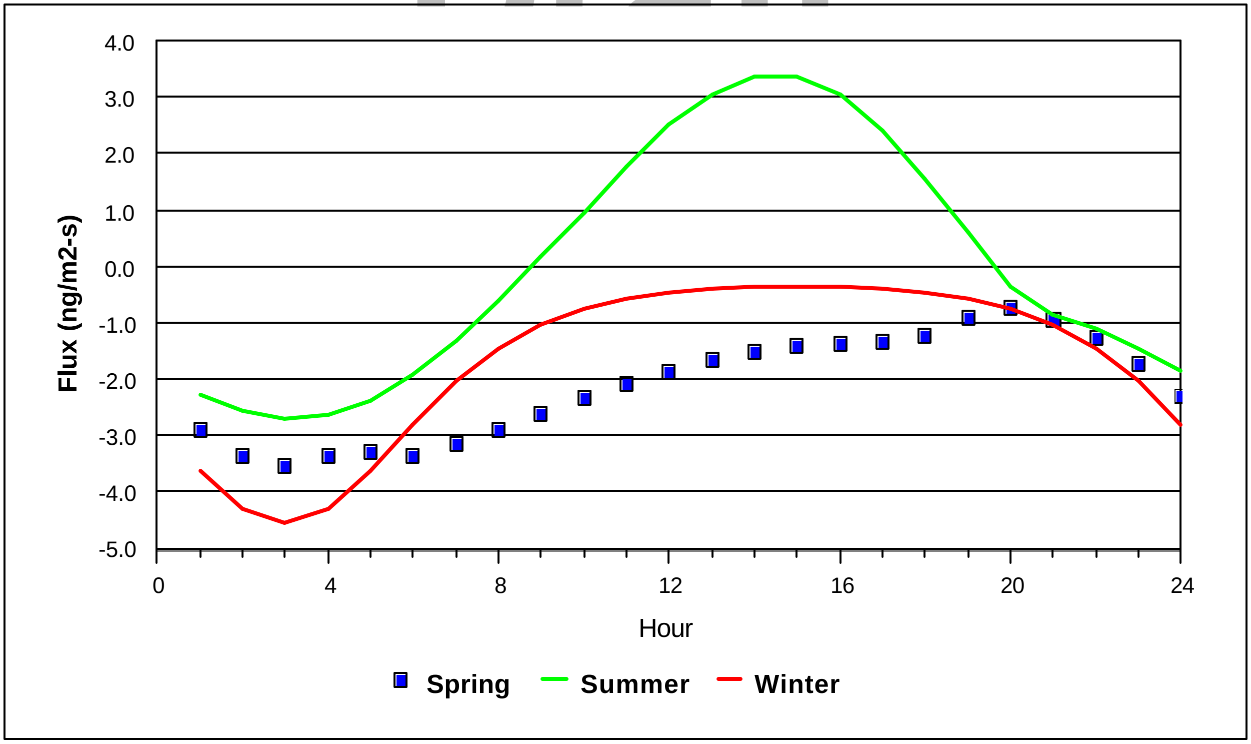

Figure 3. Estimated seasonal variability for a pine forest.

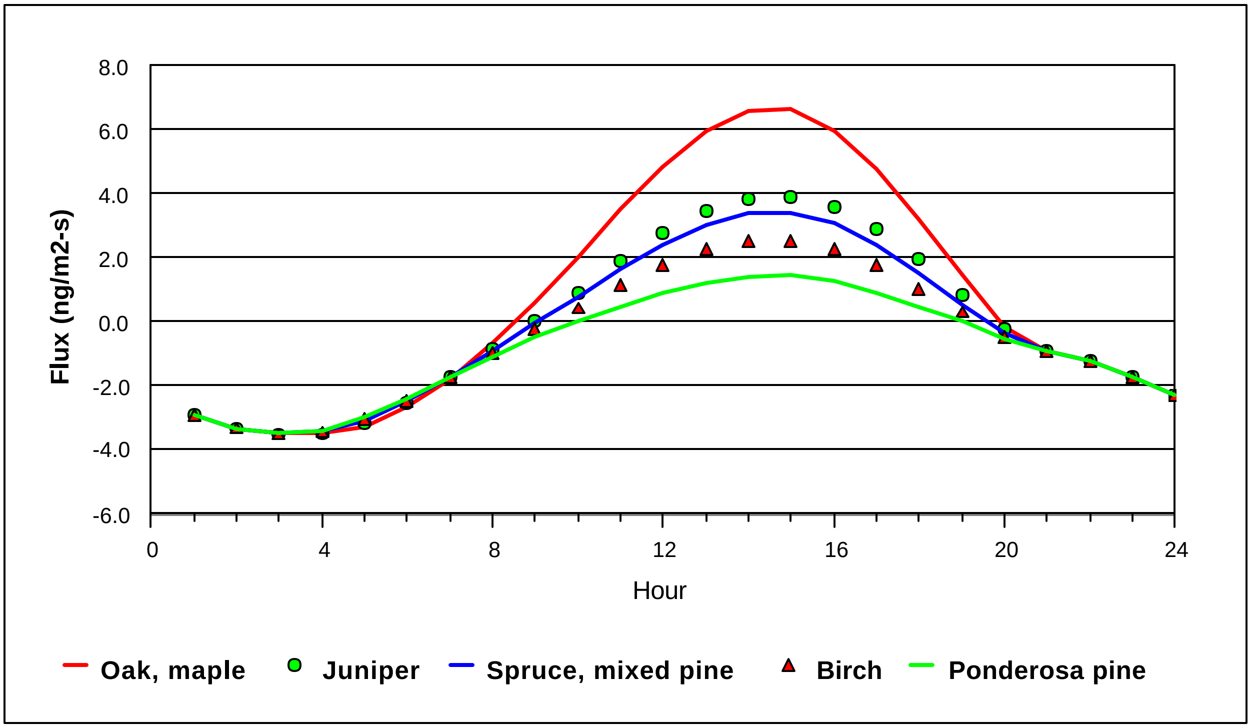

Figure 4. Sensitivity of net emissions to tree-specific inputs for stomatal resistance.
(Resistance parameters are taken from Table 3. Apoplastic ratio is assumed to be 155.)

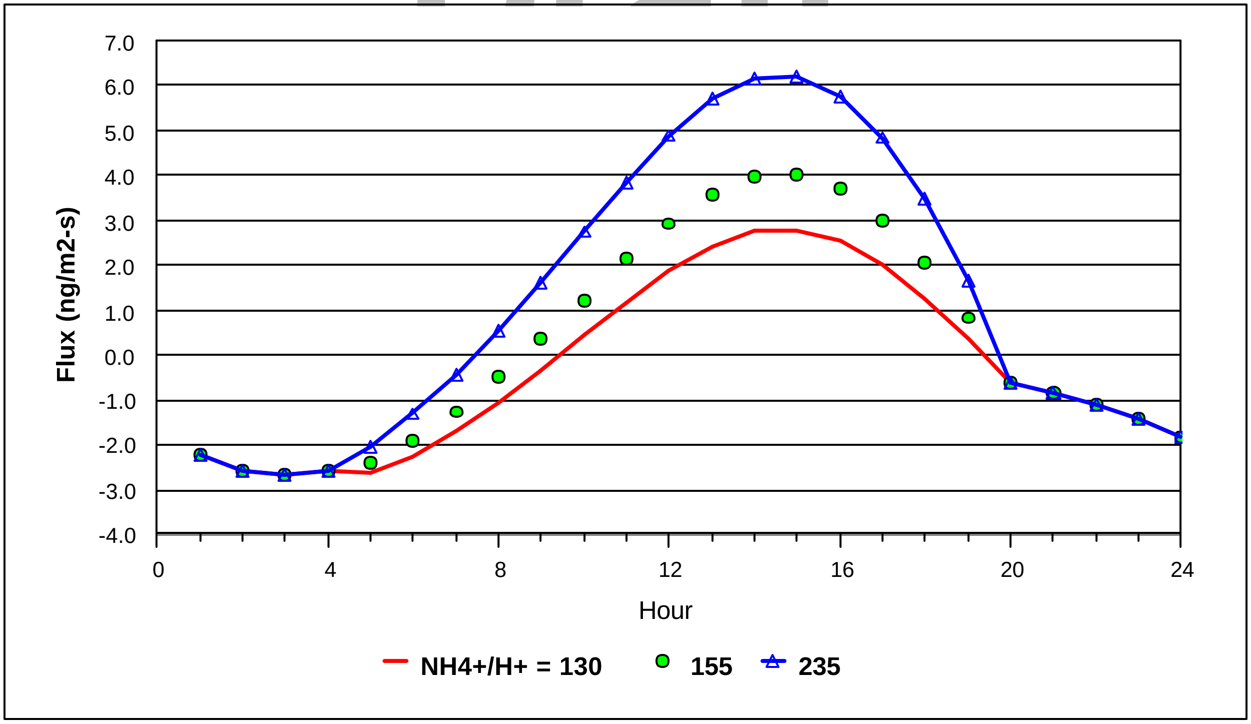

Figure 5. Sensitivity of estimate net emissions to apoplastic NH_4^+ to H^+ ratio.

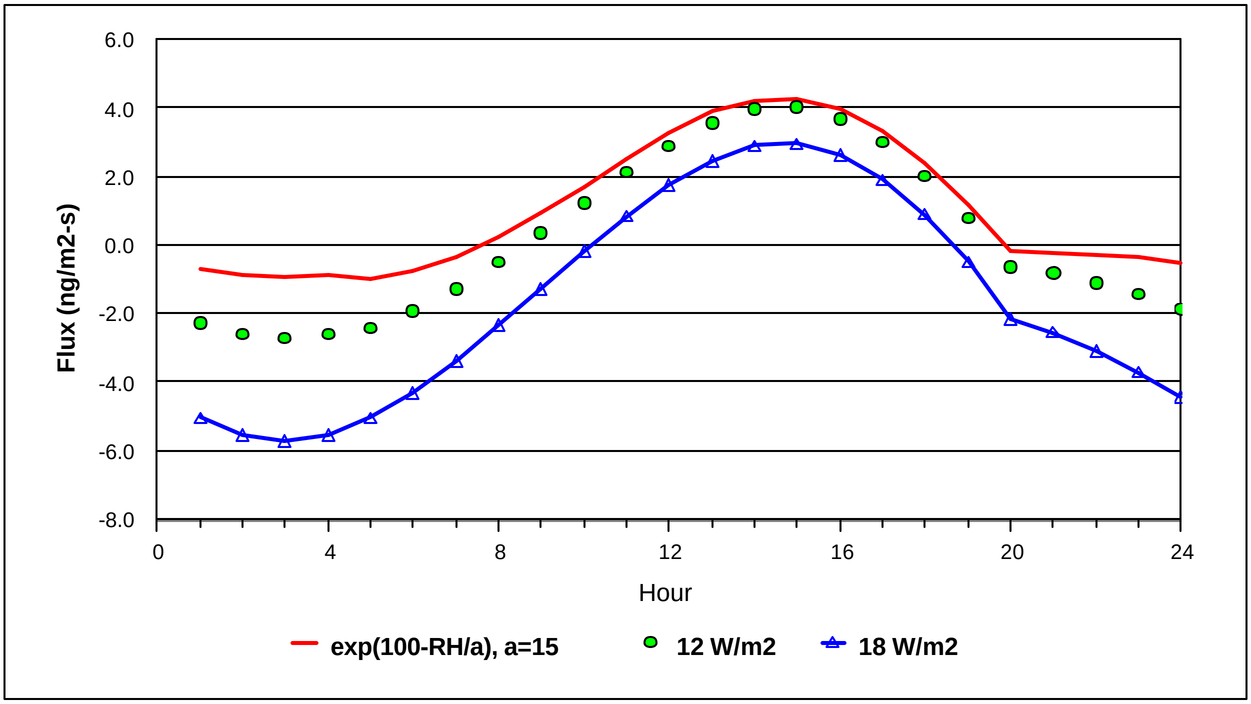

Figure 6. Sensitivity of estimated net emissions to humidity response coefficient.

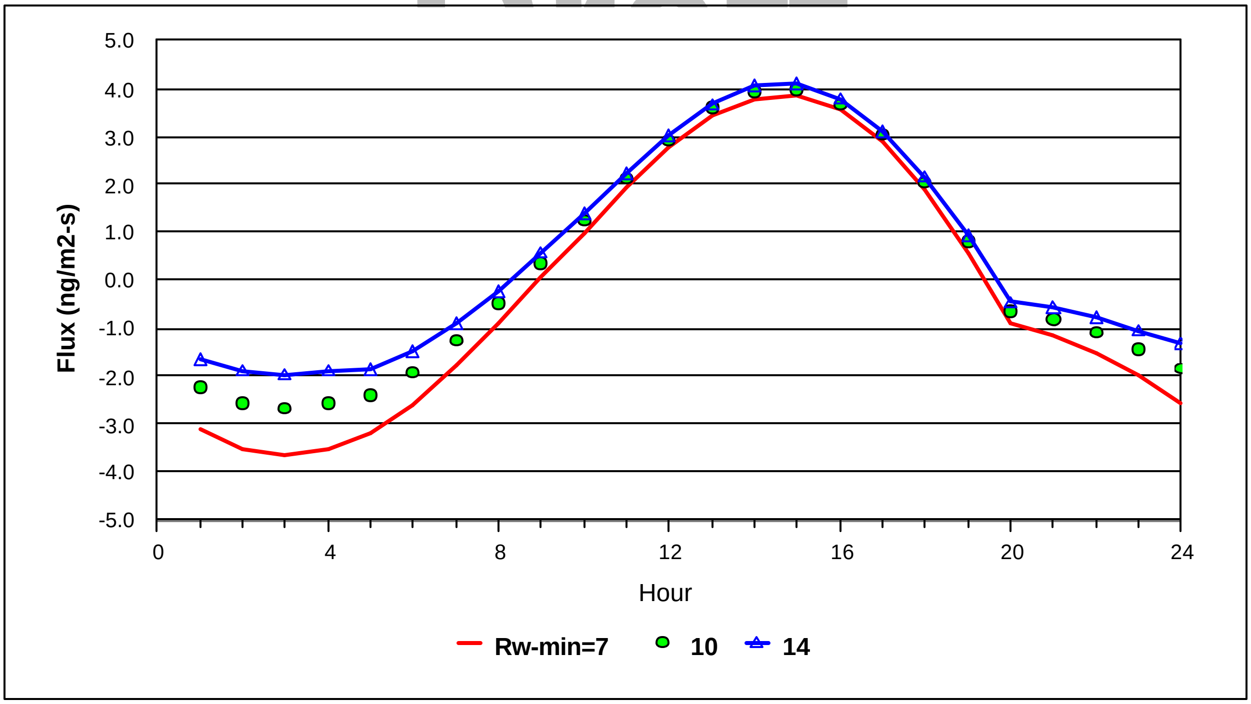

Figure 7. Sensitivity of estimated net emissions to minimum cuticular resistance.

Table 4. Default Emission Factors for Natural Landscapes

Type of vegetation	Emission factor ($ng\ m^{-2}\ s^{-1}$)	Estimated total emissions in the continental U.S. (Gg/yr)
Forests	1.2	58
Grasslands	0.9	32
Shrub Lands	1.3	46
Deserts	0.3	0.4
Total		137

Table 5. Proposed Temporal Allocation factors for Natural Landscapes

Time period	Fraction of emissions
Seasonal	
Spring	0.143
Summer	0.714
Autumn	0.143
Winter	0.000
Diurnal (hour)	
1	0.000
2	0.000
3	0.000
4	0.000
5	0.000
6	0.013
7	0.023
8	0.034
9	0.052
10	0.071
11	0.086
12	0.097
13	0.109
14	0.120
15	0.120
16	0.108
17	0.086
18	0.056
19	0.022
20	0.000
21	0.000
22	0.000
23	0.000
24	0.000

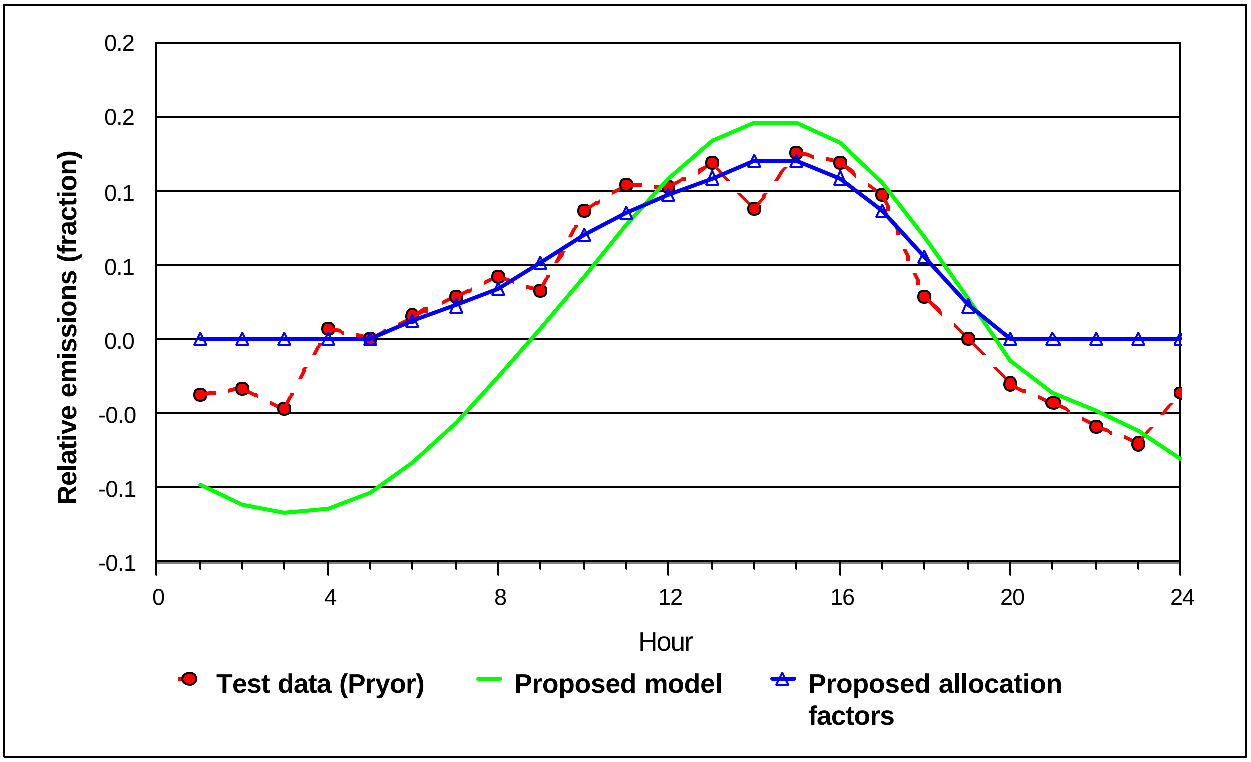

Figure 8. Comparison of proposed diurnal allocation factors with measured and modeled diurnal values.

Fertilized Soils

In the U.S., fertilized soils are estimated the second largest source of ammonia (NH_3) emissions, with animal husbandry being the first. The 1999 NEI estimates NH_3 emissions from fertilizer application at 630 Gg/year (690,000 tons/year), of approximately 21% of total NH_3 emissions from all sources. Other estimates range from 7% (Roe and Strait, 1998)[38] to 16% (Davidson *et al*, 2003, Goebes *et al*, 2003).[2,39] This report addresses NH_3 emissions from synthetic nitrogen fertilizers. Animal wastes are also widely used to meet the nitrogen requirements of crops, and are also a source of NH_3 emissions. However, these emissions are included in the animal husbandry category of the NEI.

The most widely used synthetic nitrogen fertilizer is anhydrous NH_3, which is injected into the soil in gaseous form. Ammonia can also be applied in the form of an aqueous solution (aqua ammonia). Other nitrogen fertilizers include synthetic urea, ammonium (NH_4^+) compounds, and nitrate (NO_3^-) compounds, all of which can be used in solid form or in solutions. Emissions from anhydrous NH_3 or aqua ammonia result from the evaporation of NH_3 following application and from the subsequent release of NH_3 that is initially adsorbed in the soil. Ammonium fertilizers can also break down and release NH_3 after they are applied to soils or crops. In the case of urea fertilizer, microbial reactions in soil convert the compound to ammonium carbonate, generally within a few days of application. NH_3 can be released to the air following these reactions. Nitrate fertilizers also can result in NH_3 emissions, but at a much lower rate than ammonia fertilizers, ammonium fertilizers, or urea fertilizers. In this case, nitrate must first be converted to ammonium by the fertilized plant.

Nitrogen fertilizers can be applied at a number of times during the growing season. Fertilizer can be added to the soil prior to crop planting, at the time of crop planting, or after crop emergence as a side dressing. Fertilizer can also be applied to fallow fields after crop harvest.

Emissions Data

This section divides NH_3 emissions from fertilized soil into three phases. The first phase covers emissions occurring within the first few weeks after fertilizer application, up to about one month. The second phase reflects emissions during crop growth and well after the application of any side-dressing fertilizers. The third phase covers emissions from bare soil after crop harvest, and long after the application of any fertilizers to the bare soil.

Direct Emissions from Fertilizer Application

Direct ammonia emissions from fertilizer have been evaluated for a number of previous emissions inventories. Table 6 provides a summary of emission factors that have been used for different fertilizers in more recent ammonia emissions inventories. These will be discussed in more detail in a subsequent section on the treatment of fertilizer emissions in current emissions inventories.

Table 6. Summary of Emission Factors for Ammonia from Fertilizers

	Emission factors (kg NH_3/Mg Nitrogen and lb/ton Nitrogen, in parentheses)				Estimated Total Emissions in U.S. 1999 [c]	
Source Category	**EPA emission factor report (1994)[17]**	**CENRAP Inventory, 2003[a]**	**Dämmgen and Grünhage, 2002[40]**	**CMU Inventory 1998 [b]**	**Mg**	**Tons**
Anhydrous ammonia	12 (24)	49 (98)	--	12 (24)	39,483	43,522
Nitrogen solutions	30 (60)	97 (194)	97 (194)	97 (194)	77,888	85,855
Urea	182 (364)	194 (388)	182 (364)	182 (364)	346,648	382,108
Diammonium phosphate	49 (98)	61 (122)	61 (122)	49 (98)	--	--
Ammonium nitrate	26 (52)	24 (48)	--	24 (48)	14,027	15,462
Liquid ammonium polyphosphate	49 (98)	61 (122)	--	49 (98)	--	--
Aqueous ammonia	12 (24)	97 (194)	--	12 (24)	821	905
Ammonium thiosulfate	30 (60)	30 (60)	--	30 (60)	1,238	1,365
Calcium ammonium nitrate	--	24 (48)	24 (48)	24 (48)	--	--
Potassium nitrate	--	12 (24)	--	24 (48)	--	--
Monoammonium phosphate [d]	49 (98)	61 (122)	61 (122)	49 (98)	39,526	43,569
Ammonium sulfate	97 (194)	121 (242)	--	97 (194)	19,215	21,181
Mix	--	--	--	49 (98)	58,151	64,099
Miscellaneous	--	85 (170)	24 (48)	182 (364)	60,024	66,164

[a] From the Central Central States Regional Air Planning Association (CENRAP) emissions inventory, compiled by Sonoma Technology, Inc. (STI).[26]

[b] Carnegie Mellon University (CMU) NH_3 emissions inventory.[39]

[c] From the 1999 EPA National Emissions Inventory (NEI).[41] (The 1999 estimates for fertilizer were also retained in the 2002 NEI.[42])

[d] NEI estimate includes all ammonium phosphates.

Despite the similarities among emissions inventory estimates for fertilizer usage, the ammonia emission rates from nitrogen fertilizers are still subject to considerable uncertainty. The range of ammonia emission factors for different fertilizer types (more than two orders of magnitude between anhydrous ammonia and urea) gives an indication of the variability of processes governing ammonia losses. Emissions for a particular type of fertilizer depend on a number of factors, including:

- type of crop on which the fertilizer is applied
- timing of application with respect to the nitrogen demand of the crop
- amount of fertilizer and other sources of nitrogen (for instance animal waste) applied per unit area
- application technique
- irrigation or soil moisture
- soil characteristics (pH, soil type)
- temperature and wind speed

The majority of ammonia emissions occur after fertilizer application but prior to plant emergence. Figure 9 shows day-to-day variations in NH_3 emissions from urea and urea solution fertilizers following application, and Figure 10 shows cumulative emissions over time. Each figure shows eight different scenarios representing urea and urea solutions used in combination with different crops and/or application techniques. Clay *et al* (1990)[43] measured emissions from urea spread on one field at a rate of 160 kg N/ha on bare soil and soil covered with crop residue in Minnesota. The figures indicate considerable variation in emissions. However, most of the trend lines show a peak in ammonia emissions emitted soon after application followed by a gradual decline. Their results show that ammonia emissions peak at day three with rapid decline thereafter. Watson *et al* (1992)[44] show day-specific ammonia emission measurements from urea and urea solutions applied to one field. These emissions peak between one and three days, and decline to about 10 days. Although they had three sampling times, the most significant results are shown for July only. Additionally, there does not appear to be a difference between the emissions from urea and urea solution fertilizers, the only difference is that the ammonia emissions from urea solution appears to peak sooner, on day 1, and declines less rapidly than the urea fertilizer. When urea and ammonium nitrate solution (UAN) fertilizer is used, on two separate fields of corn, similar emission patterns are observed, with the highest emissions resulting when UAN is not tilled into the soil (Al-Kanani and MacKenzie, 1991).[45] These results indicate that the application technique is very important regarding reduced emissions. To reduce emissions from UAN, it should be tilled into the soil, and to reduce emissions from urea, it should be applied when the field is not bare. Application rate does not appear to affect ammonia emissions from urea fertilizers. When urea is applied at a rate of 120 kg N/ha on bare soil, the emissions also follow a similar pattern, as found by McInnes *et al.* (1986).[46] In one case however, emissions do not seem to abate after 16 days. This anomaly occurred due to insufficient rainfall during the sampling period.

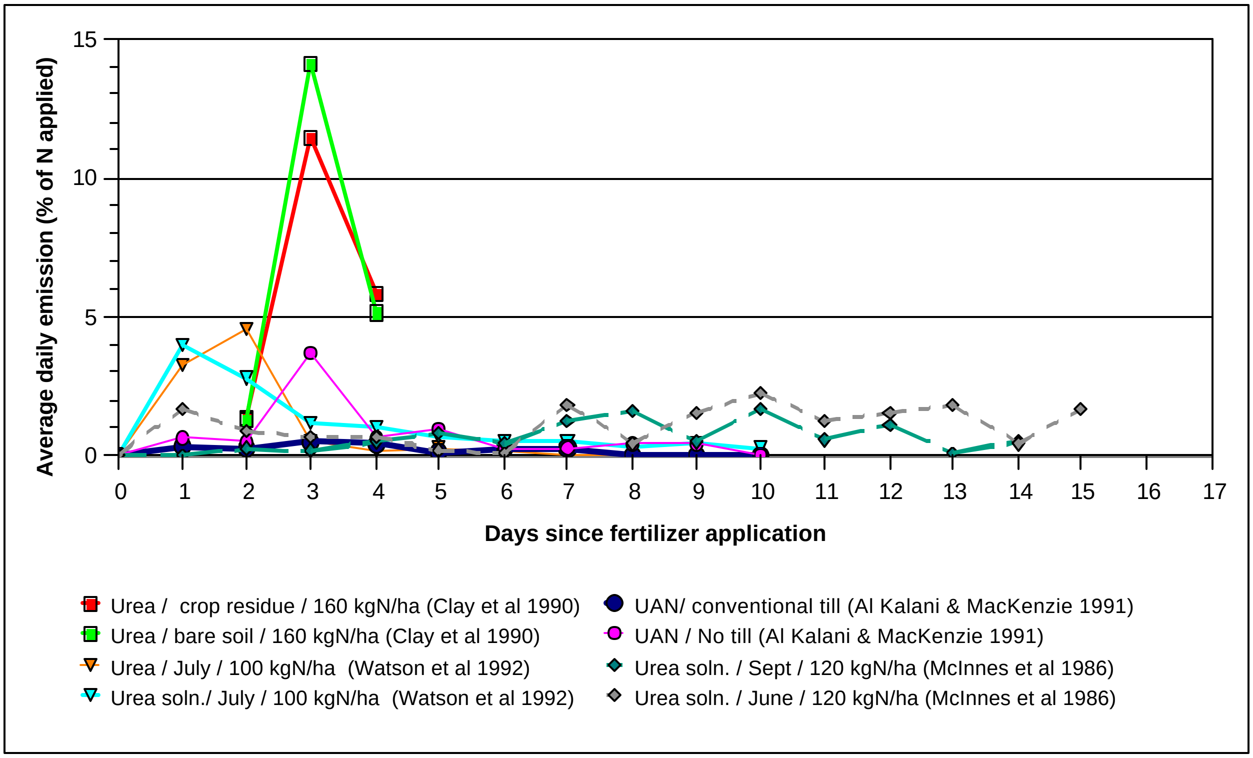

Figure 9. Day-to-day variation in NH_3 emissions after fertilizer application.

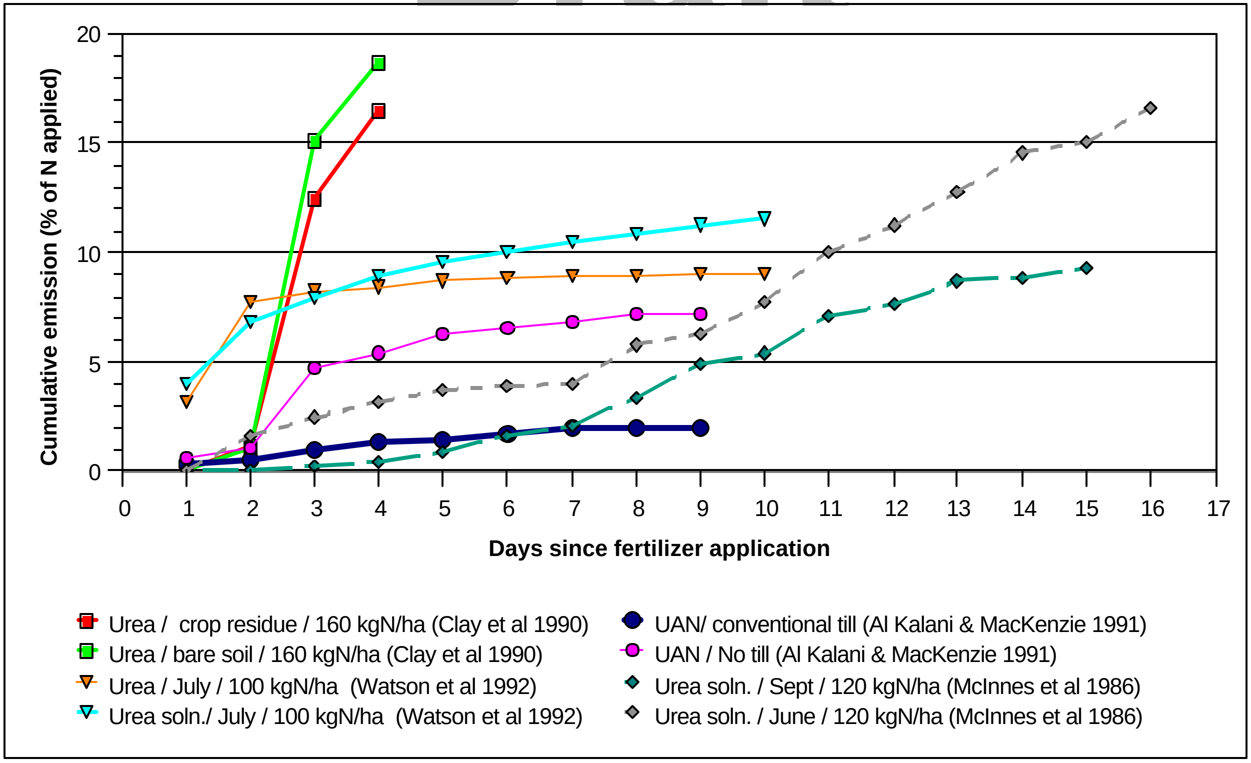

Figure 10. Cumulative NH_3 emissions after fertilizer application.

Rainfall is important for governing NH_3 emission release from fertilizers. If no rain occurs after application, emissions will remain high because of elevated urease activity, provided the soil is suitably moist. If too much rain occurs, emissions decline substantially because of a reduction in urease activity and leaching of the fertilizer. Fenn and Hossner (1985)[47] noted that when there was less than 10 mm of rainfall 3 days after urea application the emissions were less than 10%, however if only 6 mm of rain fell between five and nine days then the emissions could be as high as 30%. Most interestingly, if there was no rain after six days, then the emissions would be 30% or greater. In most instances, fertilizer requires a small amount of rain after application to help it remain in the soil, for plant uptake. Urea, specifically, is governed by enzymatic reactions, which makes rainfall very important for proper uptake. When there is little or no rainfall then the urease activity is high, when there is significant rainfall, there is no urease activity. Of course, the more rain that falls, the more ammonia will be leached out of the soil, which makes it unavailable to enzymatic activity and volatilization. A daily pattern is clear for NH_3 emissions from urea, where the majority of the emissions occur within the first week after application given there is some soil moisture. While most farmers would only apply fertilizers when the soil conditions are at an optimum, planting schedules, timing, and farm size often dictate the fertilizer application schedule.

Figure 11 shows that hourly NH_3 emission rates vary with temperature usually showing a peak in the middle of the day when temperature peaks. Previous and current research promotes the use of diurnal nitric oxide flux (Coe *et al* 2003, Geobes *et al* 2003),[26,39] however, there is research regarding urea fertilizers which supports NH_3 diurnal flux (Clay *et al* 1990,[43] Hatch *et al* 1990,[48] Yamulki *et al*

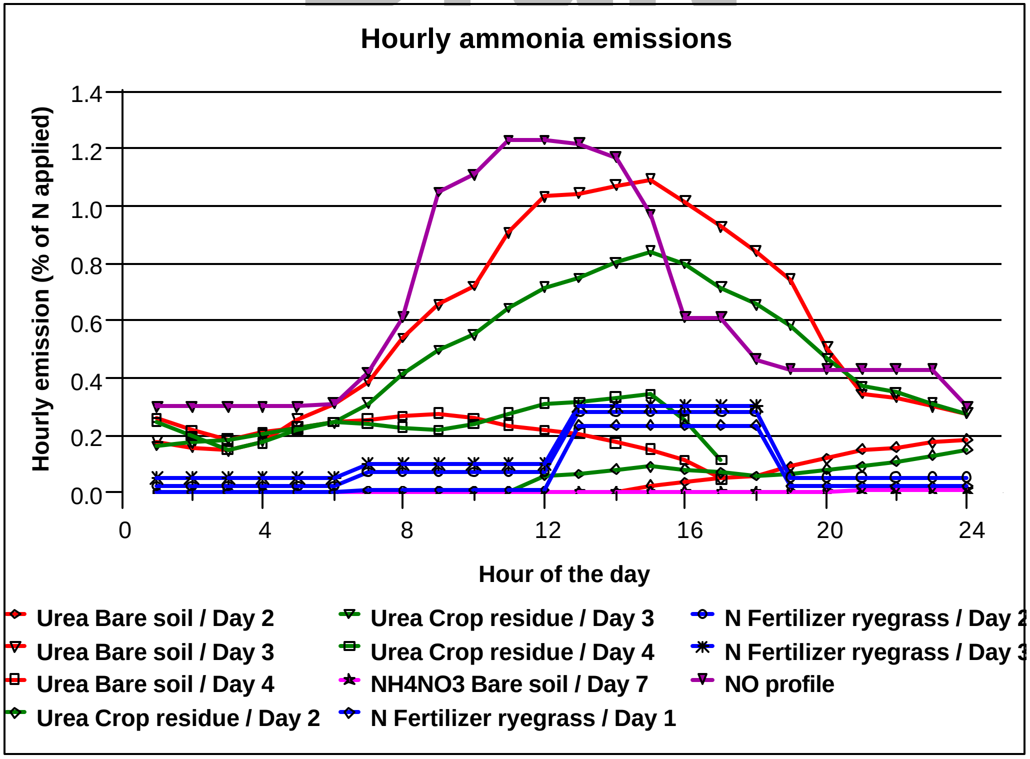

Figure 11. Hourly NH_3 Emissions from Urea Fertilizers

1996[49]). Figure 11 shows NH_3 emissions occurring over the course of one day as determined by these studies.

Emissions from Maturing Crops

Yamulki *et al* (1996) found that a wheat field generally emitted NH_3 during warm and dry conditions, regardless of time since fertilization.[49] The average NH_3 emission flux was about 35 ng m^{-2} s^{-1}. Dabney and Bouldin (1990) also found net NH_3 emissions from an alfalfa field in New York state.[50] The emisison flux was not calculated, but the NH_3 compensation point for the alfalfa crop was estimated at about 1.3 µg m^{-3}. Sutton *et al* (2000) made extensive measurements of NH_3 flux over an oilseed rape crop. The flux was found to be bidirectional, with the largest emissions occurring during the day, and both emissions and deposition occurring at night. During the period leading up to harvest, NH_3 fluxes ranged from −150 to +180 ng m^{-2} s^{-1}, with an average of 25 ng m^{-2} s^{-1} during the day, 3.4 ng m^{-2} s^{-1} at night, and 17 ng m^{-2} s^{-1} overall.[51]

Emissions from Fallow Soil

Emissions from fallow soils are sometimes included in emission inventories under a biogenic soils category. Emissions from this category are highly uncertain. There are some scientists who believe that soil serves as a sink for NH_3 and therefore there will be no emissions. Others believe that there are some emissions from soil, based upon studies and research. Of interest was a study conducted by Roelle and Aneja (2002), in which a corn crop was sprayed with hog slurry.[52] NH_3 emissions were measured after the corn was harvested, and the soil was covered with shredded corn stalks. The measured NH_3 flux over a six day period in December ranged from 4.1 to 32 ng N m^{-2} s^{-1}, with a mean value of 14 ng m^{-2} s^{-1} and a standard deviation of 17 ng m^{-2} s^{-1}. In comparison to Clay *et al* (1990),[43] where a urea fertilizer was applied directly to bare soil and measured (9800 ng m^{-2} s^{-1}), these measurements are several orders of magnitude smaller. The flux observed by Roelle and Aneja should not be discounted however, as these measurements were made in December when soil microbe activity level and temperature are low. Low temperatures inhibit NH_3 volatilization, therefore it is possible that with warmer temperatures in the spring more NH_3 could be volatilized prior to fertilization or planting. Lastly, the NH_3 emissions measured in this study more closely resemble an actual fertilized crop, where the crop is fertilized before planting and during growth, is harvested and then the soil is not fertilized again until the following spring when planting begins anew.

Treatment of Fertilized Soils in Existing Emissions Inventories

Direct Emissions from Fertilizer Application

Emission factors

NH_3 emissions inventories for synthetic fertilizer application are calculated by applying emission factors to activity data derived from fertilizer sales statistics. The emission factors are specific to different nitrogen fertilizer compounds and are expressed in terms of emissions per mass of nitrogen nutrient in the applied fertilizer (see Table 6). The current EPA National Emissions Inventory (NEI) estimate for fertilizer is based on emission factors compiled in 1994. Carnegie Mellon University (CMU) has recently developed NH_3 inventory for fertilizer which uses updated emission factors from the European Environment Agency 2001 (EEA).[39, 53] The EEA factors depend on on fertilizer type, soil type (per pH) and climate, as shown in Table 7. In the CMU fertilizer inventory, climate and soil differences are reflected at the state level. Another recent inventory for the Central States Regional Air Planning Association (CENRAP) uses data from the NRSC State Soil Geographic database (STATSGO) to provide a county-level resolution of predominant soil type (Coe *et al* 2003).[26] The CENRAP inventory also uses emission factors from the EEA.

Table 8. Classification System for Emission Factors

Group I	Warm, temperate areas with a large proportion of calcareous soils
Group II	Temperate and warm-temperate areas with some calcareous soils (or managed with soil pH>7), but with large areas of acidic soils
Group III	Temperate and cool-temperate areas with largely acidic soils

Activity data on fertilizer application

In the EPA NEI, fertilizer activity data are based on annual sales of different fertilizer compounds at the state level.[41] These annual sales are allocated to seasons using national seasonal allocation factors, and state level sales data are allocated to counties based on the acreage devoted to agriculture in each county.

The CMU NH_3 emissions inventory provides extensive refinements in the spatial and seasonal allocation of fertilizer application.[39] The CMU inventory uses semiannual sales data from the 1995 Association of American Plant Food Control Officials (AAPFCO), which are available at the county-level. Additionally, the CMU model includes data from the US Geological Survey (USGS) for fertilizer sales to farmers by county for 1987--1991. This information was combined with information from National Agricultural Statistics Service (NASS) crop calendars to estimate monthly fertilizer application rates for each county.

In preparing the CENRAP inventory, Coe *et al* (2003) used an approach similar to CMU but combined the semiannual sales data before carrying out the monthly allocation based on crop calendars. This adjustment was made because farmers often return the unused portions of fertilizer in the autumn, which can result in an underestimation of fertilizer use in that season.[26] In addition the CENRAP inventory used updated 2002 AAPFCO sales data.

Emissions from Maturing Crops and Fallow Soils

The EPA NEI does not provide separate emissions estimates for maturing crops or fallow soils.[41] EPA's 1994 NH_3 emission factor report compiled data on emissions from soils and vegetation, however these emissions were believed to be already included in the emissions factors for fertilizer application.[17]

The CMU and CENRAP emissions inventories both include emissions estimates for fertilized soils, which are separate from direct emissions from fertilizer application. These soil emission estimates include both emissions from fallow soil and emissions from maturing crops. The CMU NH_3 inventory estimates gives an estimate of 3.0 Tg yr^{-1} (3.3 million tons/yr) for agricultural soils, based on emission factors of 38 ng m^{-2} s^{-1} for croplands and 41 ng m^{-2} s^{-1} for pasture land. However, these estimates are characterized as very uncertain (Davidson *et al.*, 2003).[2] The CENRAP inventory uses an emission factor of 0.95 ng m^{-2} s^{-1} for croplands and pasture land.[26]

Two previous California NH_3 emissions inventories also included estimates for a soils and vegetation category, which was separate from fertilizer application. These inventories – for the the San Joaquin Valley (SJV) region and the South Coast Air Quality Management District (SCAQMD) – used emission factors of 41 ng m^{-2} s^{-1} for agricultural land, and 17 ng m^{-2} s^{-1} for grazing lands.[23, 24]

Available Emission Models

A number of emission models have been developed to evaluate the impacts of different fertilizer application conditions on evaporative losses of NH_3. In general, the goal of these models is to help optimize the management of nitrogen nutrients by improving the understanding of the uptake of nitrogen by plants, the assimilation of nitrogen into soils, losses through NH_3 evaporation, and losses through leaching. Some of these are empirical regression models, and others are mechanistic resistance models which attempt to simulate the physical processes involved in NH_3 evaporation from fields. Table 8 gives a list of available models, showing the fertilizer that is covered by each model, the parameters that are included, and the type of model.

As Table 8 illustrates, the models for fertilizer emissions require inputs for a wide array of parameters, including fertilizer application rate, time since application, soil type, pH, soil temperature, soil moisture content, air temperature, and wind speed. Some of these parameters are not easily determined on a national scale, specifically time since application. Many of the models were developed from laboratory studies, which are valuable for model development, however often hold environmental conditions constant, which decreases their ability to predict emissions accurately in field conditions. Additionally, a majority of the models were developed for use with animal wastes, and may not be transferable to chemical fertilizers.

Table 8. Overview of Available Models for Fertilizer Emissions

Reference	Fertilizer	Parameters	Model Type
Fenn and Hossner, 1985[47]	Urea, nitrogen solutions	Time, temperature, application rate	Regression
Al-Kanani and MacKenzie, 1991[45]	Urea, UAN	Temperature, thermodynamic force, wind velocity, soil surface roughness, adsorption and desorption rate constants	Mechanistic
Ismail *et al.*, 1991[54]	Urea solution	Soil temperature, application rate, initial soil moisture content, soil pH, application depth	Regression
Kirk and Nye, 1991[55]	Urea	Time, soil moisture content, diffusion factor in soil, verticle distance, water flux, diffusion of solute in soil	Mechanistic
Misselbrook and Hansen, 2001[56]	Urea, Slurry, Manure	Equilibrium concentration of NH_3 at and above the emitting surface, mass transfer coefficient	Mechanistic
Plochl, 2001[57]	Manure	Time, maxium emission value, application rate, climate	Mechanistic
Riedo *et al.*, 2002[58]	NH_4NO_3	Atmospheric deposition, NH_4^+ contributions from fertilizer, manure, urine excreted by grazing animals, soil surface exchange of NH_3, convection, diffusion	Mechanistic
Roelle and Aneja, 2002[52]	Hog slurry	Soil temperature	Regression
Sogaard *et al.*, 2002[59]	Cattle and pig slurry	Soil water content, air temp, wind speed, slurry type, dry matter content of slurry, TAN content of slurry, application method, application rate	Mechanistic
Huijsmans, *et al.*, 2003[60]	Slurry	Air temperature, application rate, application method, content of N in slurry, wind speed	Mechanistic

Recommended Approach for Estimating Ammonia Emissions from Fertilizer

The current National Emissions Inventory (NEI), as well as other existing inventories, relate fertilizer NH3 emissions to the total nitrogen content of fertilizer used in a given geographical area:[61]

$$E = \sum_i A_i \times EF_i \qquad \textbf{(17)}$$

where E is total NH_3 emissions from fertilizer application in a given time period (kg), A_i is the amount of nitrogen that has been applied in the form of fertilizer i (Mg-N), and EF_i is the emission factor for fertilizer i (kg-NH3/Mg-N).

Historically, this calculation has been performed with annual fertilizer application data. However, the current NEI Input Format (NIF) gives the flexibility to store activity data (in this case fertilizer usage) in other timeframes, including by month. As noted earlier, Carnegie Mellon University has developed monthly estimates of fertilizer usage at the county level, based on crop calendars and fertilizer sales. Since most of the direct emissions from fertilizer occur within a few weeks of application, emissions in a given month can be estimated based on the fertilizer application for that month. This method gives greater accuracy than applying temporal allocation factors to an annual estimate. Therefore, we recommend using the CMU monthly fertilizer application data, and implementing equation (12) separately for each county and each month.

This approach does not take into account day-to-day variations over the course of a month. As shown in Figure 9, the emission rate from a given field declines gradually after application as the fertilizer is taken up by plants or incorporated into the soil. Therefore, day-specific emissions from a particular farm or field can be a factor of 2 to 3 higher than the monthly average. These variations could be taken into account by relating emissions to the nitrogen fertilizer level in the field, rather than the application rate. The nitrogen level can in turn be estimated from the application rate and the time that has elapsed since application:

$$E_k = \sum_{i,j} N_{i,j,k} \times EFN_i \qquad \text{(day-specific approach)} \ \textbf{(18)}$$

$$N_{i,i,k} = A_{i,j} \times \left(1 - t_k / t\right) \qquad \text{(alternative day-specific approach)} \ \textbf{(19)}$$

where E_k is total NH_3 emissions on day k for all fields j in a given region (kg/day), $N_{i,j}$ is the level of unassimilated nitrogen from fertilizer i in field j, and on day k (Mg), EFN_i is the emission factor for fertilizer i based on the field nitrogen fertilizer level (kg-NH3/Mg-day), $A_{i,j}$ is the amount of fertilizer i that was applied to field j (Mg), t_k is the time since application of fertilizer i on field j for day k (days), and τ is a time constant for fertilizer assimilation (estimated at 7 days). The NIF structure provides the needed flexibility to use a different activity parameter (N) for some emission records.

Tables 9 provides recommended emission factors for computing total emissions following fertilizer application. Table 10 gives factors for computing daily emissions when the date of fertilizer application is known. Both sets of factors are based on the estimates made by the EEA (see Table 8), which have also been recently adopted in the CENRAP emissions inventory and in the CMU inventory.

Crops have been shown to continue emitting NH_3 during the growing season, regardless of the time since fertilization.[49,50,51] The emission factor for maturing crops is estimated at 17 ng m^{-2} s^{-1} based on measurements by Sutton *et al* (2000).[51] Roelle and Aneja (2002) estimated emissions of 14.5 ng m^{-2} s^{-1} for fallow soil following the harvest of a corn crop.[52] However, it must be noted that this measurement is very uncertain, with a standard deviation of 17 ng m^{-2} s^{-1}. These estimated emission factors are lower than the factors used for agricultural soils in the CMU inventory or the California SJV or SCAQMD inventories, but higher than the factor used for agricultural soils in the CENRAP inventory. As noted earlier, the EPA NEI does not separate agricultural soil and crop emissions from direct fertilizer emissions.

Combined, the emissions estimates of 17 ng m^{-2} s^{-1} for maturing crops and 14.5 ng m^{-2} s^{-1} for fallow soil would add about 10–20% to the emission estimate for direct emissions from fertilizer application. Because these emission rates were measured well after fertilizer application, they do not appear to be already included in the direct fertilizer emission factors. In many cases, however, these emissions may result from previous application of animal wastes to fields. Thus, it is believed that emissions are generally already counted in emissions estimates for the animal husbandry in the NEI.

Table 11 gives recommended diurnal allocation factors for direct emissions from fertilizer, emissions from crops, and emissions from fallow soil. The allocation factors for fertilizer and soil are based on measurements by Clay *et al* (1990).[62] Allocation factors for crop emissions are based on measurements by Sutton *et al* (2000).[51] These factors are recommended for diurnal emissions as the algorithms reviewed did not adequately address the main components of diurnal emissions, treating temperature as a minor component and disregarding the time since application component. Although these studies include diurnal estimations, those emissions were not the main focus of the study, and did not fully explain the physical processes involved. Figure 12 compares these factors to those recently used in the CENRAP inventory (which were based on nitrogen oxide emissions from soil).

Table 9. Recommended Emission Factors for Direct NH_3 Emissions from Fertilizer

Fertilizer	Emission factors based on fertilizer application (kg-NH_3 / Mg-N)			Emission factors based on fertilizer application (kg-NH_3 / Mg-N)		
	Group I soils	Group II soils	Group III soils	Group I soils	Group II soils	Group III soils
Anhydrous ammonia	48	48	48	97	97	97
Nitrogen solutions (urea & AN)	97	97	97	194	194	194
Urea	242	182	182	484	363	363
Diammonium phosphate	61	61	61	121	121	121
Ammonium nitrate (AN)	36	24	12	73	48	24
Liquid ammonium polyphosphate	61	61	61	121	121	121
Aqueous ammonia	97	97	97	194	194	194
Ammonium thiosulfate	30	30	30	61	61	61
Calcium ammonium nitrate	36	24	12	73	48	24
Potassium nitrate	12	12	12	24	24	24
Monoammonium phosphate	61	61	61	121	121	121
Ammonium sulfate	182	121	61	363	242	121
Miscellaneous	97	73	48	194	145	97
Mix	36	24	12	73	48	24

Group I: Warm, temperate areas with a large proportion of calcareous soils

Group II: Temperate and warm-temperate areas with some calcareous soils (or managed with soil pH>7), but with large areas of acidic soils

Group III: Temperate and cool-temperate areas with largely acidic soils

Table 10. Factors for Calculating Daily NH_3 Emissions when the Date of Fertilizer Application is Known

Fertilizer	Emission factors based on unassimilated fertilizer in soil (kg-NH_3 / Mg-N / day) (see equations 18 and 19)			Emission factors based on unassimilated fertilizer in soil (lb-NH_3 / ton-N / day) (see equations 18 and 19)		
	Group I soils	Group II soils	Group III soils	Group I soils	Group II soils	Group III soils
Anhydrous ammonia	12.1	12.1	12.1	24	24	24
Nitrogen solutions (urea & AN)	24.2	24.2	24.2	48	48	48
Urea	60.5	45.4	45.4	121	91	91
Diammonium phosphate	15.1	15.1	15.1	30	30	30
Ammonium nitrate (AN)	9.1	6.1	3.0	18	12	6
Liquid ammonium polyphosphate	15.1	15.1	15.1	30	30	30
Aqueous ammonia	24.2	24.2	24.2	48	48	48
Ammonium thiosulfate	7.6	7.6	7.6	15	15	15
Calcium ammonium nitrate	9.1	6.1	3.0	18	12	6
Potassium nitrate	3.0	3.0	3.0	6	6	6
Monoammonium phosphate	15.1	15.1	15.1	30	30	30
Ammonium sulfate	45.4	30.3	15.1	91	61	30
Miscellaneous	24.2	18.2	12.1	48	36	24
Mix	9.1	6.1	3.0	18	12	6

Group I: Warm, temperate areas with a large proportion of calcareous soils

Group II: Temperate and warm-temperate areas with some calcareous soils (or managed with soil pH>7), but with large areas of acidic soils

Group III: Temperate and cool-temperate areas with largely acidic soils

Table 11. Recommended Hourly Temporal Allocation Factors for Fertilized Soils

	Hourly allocation factor (fraction of daily emissions)	
Hour	Fertilizer and fallow soil	Crops
1	0.014	0.000
2	0.013	0.000
3	0.013	0.000
4	0.015	0.000
5	0.019	0.002
6	0.022	0.015
7	0.028	0.026
8	0.038	0.039
9	0.046	0.052
10	0.051	0.066
11	0.061	0.081
12	0.069	0.094
13	0.071	0.104
14	0.074	0.110
15	0.077	0.110
16	0.072	0.103
17	0.065	0.089
18	0.059	0.069
19	0.052	0.039
20	0.039	0.000
21	0.028	0.000
22	0.027	0.000
23	0.024	0.000
24	0.022	0.000

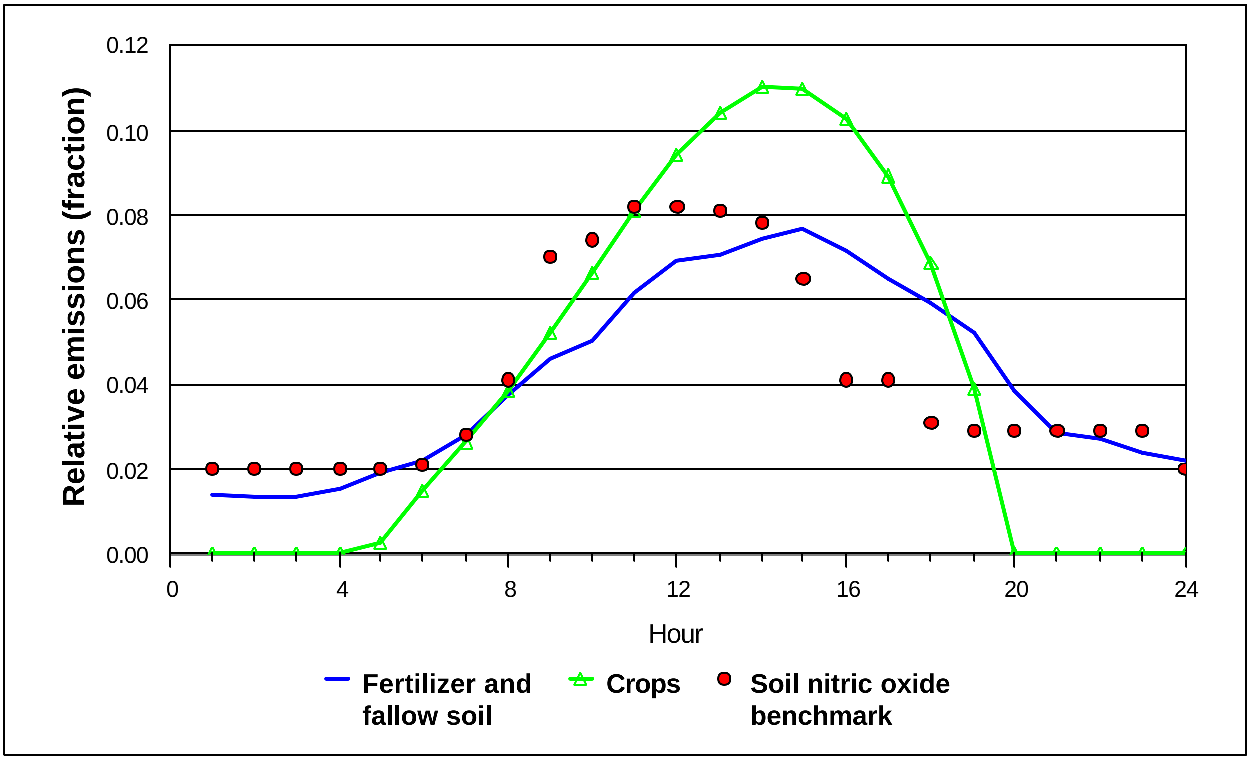

Figure 12. Diurnal allocation factors for NH_3 from fertilizer, crops, and fallow soil, compared with the profile for nitric oxide from soil.

Conclusions and Recommendations

A model is proposed to reflect the bi-directional movement of NH_3 into and out of natural landscapes. This model provides an improved characterization of diurnal variations in NH_3 flux, including the tendency of landscapes to emit NH_3 during warm conditions and absorb the gas at night. A sensitivity analysis of this model is presented for forest emissions, focusing on the most uncertain input parameters. In addition, default emission factors, and seasonal and diurnal allocation factors are given for calculating net NH_3 emission fluxes from forests, unfertilized grasslands, shrub lands, and deserts.

Considerable uncertainties remain in the calculation of NH_3 emissions from natural landscapes. Natural landscapes alternate between being sources of and sinks for NH_3, and short term emission and deposition fluxes can be orders of magnitude higher than long term net fluxes. As a result, any model of NH_3 emissions and deposition in natural landscapes will be very sensitive to input data. Limited data are available on the apoplastic ratio NH_4^+ to H^+. This ratio is used to compute the NH_3 compensation point, which determines whether NH_3 is emitted or absorbed by plant canopies. Additional data are needed to better characterize NH_3 compensation points for different crops and under different ambient conditions. Data are also needed on cuticular resistance. These are the key issues for future research projects.

Improved emission factors and diurnal allocation factors are given for direct NH_3 emissions following the application of fertilizer. Monthly fertilizer application estimates developed by CMU should be used in determining monthly variations in fertilizer emissions. However, the emission rate from a given field declines gradually after application as the fertilizer is taken up by plants or incorporated into the soil. Therefore, day-specific fertilized emissions from a particular farm or field can be a factor of 2 to 3 higher than the monthly average. The current study provides a method of incorporating this variability when fertilizer application dates are available.

Emission flux estimates are also provided for crops after the initial decline in emissions from fertilizer, and from fallow soil. However, in using these factors, care must be taken to avoid double counting emissions from the application of additional fertilizer or animal wastes to crops and fallow soil.

Monthly fertilizer application estimates developed by CMU provide a good indication of monthly variations in fertilizer emissions. These monthly estimates were developed at the county level based on semiannual fertilizer sales data and state-specific crop calendars. However, the national scale of the CMU analysis results in uncertainties at the local level, particularly in determining the schedules for fertilizer application to specific crops. To suggest a process-based bi-directional NH_3 model, more highly resolved spatial (sub-county) data on soils, crops, and vegetation will be required to adequately resolve the variability and bi-directionality of NH_3 emissions, which is an area for future research. Where local variations in NH_3 from fertilizer are important, the crop schedules should be reviewed by local agricultural experts, if possible.

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Appendix A:

Bibliography of Sources Related to Ammonia Emissions from Natural Landscapes

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes

Source	Landscape	Results	Comment
Anderson H.V. et al, 1999[1]	Spruce forest in Western Denmark, surrounded by agriculture	Seven, one-week period evaluations in all seasons from 1991 to 1995. Average deposition velocity was 2.7 cm/s and average deposition flux was 9.1 ng-NH_3/m^{-2}-s. Relatively high net deposition velocities are observed during conditions with relative humidity above 80% or at ammonia levels moderately higher than the compensation point. The following relationships were plotted for deposition flux, F (ng/m^2-s), versus air concentration, C (µg/m^3) and compensation point, CP (µg/m^3): $F = -10 + 128 \times (C - CP)$ where $C - CP < 0.4$ $F = -95.5 + 75.1 \times (C - CP)$ where $C - CP > 0.4$	Dry conditions produced outlier data points, where emissions occurred even at high air concentrations. This may have resulted from an emission from saturated surfaces or from mineralization of soil nitrogen.
Anderson, N. et al, 2003[2]	Soil, general	Carnegie Mellon Ammonia Model. For landscapes refers to Cass et al 1982.	Review article.
Anderson, S. et al, 2002[3]	Pine and oak forests, East Texas, summer	NH_3 emissions were 0.09 kg/km^2-mo from detritus on a pine forest floor, and 0.13 kg/km^2-mo from detritus on an oak forest floor.	Soils were acidic, and measurements did not take into account reabsorption by the forest canopy.

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Asman, 2001[4]	Mature forest, deposition from urine patches	A model is applied to examine the fraction of the NH_3 emission (Fr) from a point source that is deposited within different distances from the source in relation to factors affecting dispersion and deposition. The results show that Fr at 2000m distance from the source may be as large as 60% for a 3m high source when ammonia deposits to mature forest at rates limited only by atmospheric transfer.	The DEPOI-model is a steady-state K-model.
Bouwman et al, 1997[5]		Review available measurement data, and also give order-of-magnitude estimates of long-term emissions based on the rates of nitrogen mineralization in different ecosystems. Estimated NH_3 emissions at 0.1 kg/ha-yr from forests, 0.3 from unfertilized grassland, 0.4 from shrubland, and 0.1 from deserts.	
Burns, 2003[6]	Rocky Mountains	Rockies ecosystems therefore sequester much less N than those in the east because they are snow-covered for 7–9 months a year. For example, only 1–2% of N storage in alpine tundra at Niwot Ridge is in the form of living biomass, and the majority of this biomass is stored in roots (Fisk et al., 1998[7]), whereas in a hardwood forest at Hubbard Brook, New Hampshire about 30% of N is stored in living biomass that is at least 5 times greater than in the alpine tundra at Niwot Ridge, and the majority of this living biomass is stored above ground (Likens and Bormann, 1995[8]).	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Bytnerowicz et al, 2002[9]	Sequoia National Park	NH_3 declines with distance from polluted areas. Seasonal average (May-November) at most-polluted site is 4.5 µg/m^3 (sd = 2.4, range: 1.0–8.0 [daily concentrations]). Least polluted site concentration is 1.6 µg/m^3 (sd = 0.9, range: 0.4–3.2)	NH_3 is being absorbed on almost all days, but the concentration pattern is reversed (showing possible release of NH_3) when the mid-altitude NH_3 concentration falls below ~0.3 µg/m^3.
Bytnerowicz and Fenn, 1996[10]	California	Compiles ambient measurements for NH_3 and other pollutants in various forests in California and similar ecosystems. NH_3 concentrations rang from 0.04–5.47 µg/m^3. Concentrations were higher in the daytime than at night, and higher in summer than in spring or fall.	
Dabney and Bouldin, 1990[11]	Alfalfa, New York	Measured flux of NH_3, NH_4^+, and ammonium nitrate in alfalfa in NY. Compensation point = 2 ppb	
Denmead et al 1974, as cited in Schlesinger	Grazed Pasture in Australia	Ammonia losses per day of 0.26 kg ha^{-1} day^{-1}.	
Denmead *et al*, 1976[12]	Grazed Pasture	Grazed grass-clover pasture. When the canopy of clover was reduced from grazing the NH_3 emissions increased. Grazed = 13 g N ha^{-1} hr^{-1} vs. Ungrazed = 2 g N ha^{-1} hr^{-1}.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Denmead *et al*, 1978[13]		Emissions over a corn field. Observed a net loss of NH_3 between 1400 & 2100 hrs = 70 g N ha^{-1}. $F = -(\tau/\rho)\ dc/du$ F = new vertical transfer NH_3 τ= momentum flux ρ = density of air c = gradients or difference in atmospheric NH_3 concentration *u* = horizontal wind speed	
Denmead 1990	Grazed Pasture in Australia	Ammonia losses per day of 0.25 kg ha^{-1} day^{-1}. About 30 g N ha^{-1} day^{-1} for six months over 164 million hectares of forest and uncultivated country in the humid, sub-humid and monsoonal zones delineated in the Atlas of Australian Resources (1980) and at negligible rates in drier zones. This corresponds to Dawson's (1977) average soil emission of 3 kg N ha^{-1} per year plus a net emission from the vegetation of 2.4 kg N ha^{-1} per year.	
Dentener and Crutzen, 1994[14]	Global	Develops a global model of the nitrogen cycle. The natural ecosystem algorithms use a mean canopy resistance of 1 cm/s, which is scaled by the amount of vegetation (3 cm/s in the tropics and 0 in desert areas). Compensation points are 1 ppb for trees (2.5 at 25 C and 0.2 at 5 C), 3–5 ppb for herbaceous plants, and >10 ppb for wheat.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Dragosits et al, 2002	3000 ha region of Britain	A fine resolution model for ammonia emission, transport, and deposition. NH_3 deposition is based on a series resistance model which includes aerodynamic resistance, laminar boundary layer resistance, and canopy resistance. Specific canopy resistances are used for different land use categories: 1000 s/m for arable land, 20 s/m for forest, 600 s/m for grassland, 20 s/m for moorland, and 240 s/m for unban areas.	See also Fournier et al, 2002
Elliot *et al*, 1971[15]	Grazed pasture	Measured losses from grazed pasture land. Distillable nitrogen averaged 15 kg ha^{-1} yr^{-1}	
Eugster et al, 1998[16]	Switzerland	Model of emissions, transport, and deposition of NH_3. Canopy resistance is assumed to be 20% of that for SO_2.	
Fournier et al, 2002[17]	Great Britain	The Fine Resolution Ammonia Exchange (FRAME) model was applied to Great Britain. NH_3 deposition is based on a series resistance model which includes aerodynamic resistance, laminar boundary layer resistance, and canopy resistance. Specific canopy resistances are used for different land use categories: 1000 s/m for arable land, 20 s/m for forest, 600 s/m for grassland, 20 s/m for moorland, and 240 s/m for unban areas.	See also Dragosits et al, 2002

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Fowler et al, 1998a[18]	Europe	There is not enough information on apoplastic NH_4^+ and H^+ to estimate compensation points for NH_3 in semi-natural vegetation. Further, emissions are believed to be offset by deposition most of the time. Therefore, emissions were neglected in estimating regional mass budgets for NH_3. Deposition was es were estimated using a resistance model.	
Fowler et al, 1998b[19]	Great Britain	Canopy resistance *increases* with NH_3 concentration, as a result of a decreased uptake efficiency of foliar surfaces.	
Gilliland et al, 2003[20]	Eastern U.S.	Scaling factors for the NH_3 emissions inventory were computed by inverse modeling using CMAQ and wet deposition and atmospheric concentrations of NH_4^+. Calculated scaling factors, based on the 1990 NEI, with uniform seasonal allocation, were: –68 to –73% for January, –58to –46% for March, –38 to –33% for April, –23 to –24% for May, +6% for June, –10% for July, –24% for August, and –75% for October.	
Hesterberg et al., 1996[21]	Extensively managed grassland surrounded by agricultural land, Switzerland	The total dry deposition was between 15 and 25 kg N ha^{-1} y^{-1}. Deposition velocity of NH_3 was between 0.13 and 1.4 cm s^{-1}, and a compensation point between 3 and 6 ppbV NH_3 was found. The arithmetic average NH_3 flux varied only between 8.2 and 8.9 kg N ha^{-1} y^{-1}.	Between 60 and 70% of dry deposition originated from NH_3 emitted by farms in the neighborhood. N deposition is highly correlated to local NH_3 emissions.

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Hicks, 1987[22]	General	Outlines calculation methods for aerodynamic, boundary layer, and canopy resistances. Stomatal resistance is expressed as: $r_s = r_{s,min} \times (1 + b/I) \times f_e f_w f_T f_s$ where: I is light intensity (W/m^2); b is an illumination factor estimated at 22 W/m^2 for oak and 25 W/m^2 for spruce; $r_{s,min}$ is the minimum stomatal resistance, estimated at 145 s/m for oak and 232 s/m for spruce; and f's are correction factors for humidity, water stress, temperature, and diffusivity. Temperature effects can be reflected as follows: $f_T = [(T-T_e)/(T_0-T_e)]\times[(T_h-T)/(T_h-T_0)]^{[(Th-T0)/(T0-Te)]}$ where: T_e is the lower temperature extreme at which stomata close, estimated at –5 C for spruce and 10 C for oak; T_h is the upper temperature extreme, 35 C for spruce and 45 C for oak; and T_0 is the temperature at which stomatal transport is maximized, 9 C for spruce and 25 C for oak. A method is also suggested for extending this surface resistance to the entire canopy, and taking into account the impact of shading on the lower canopy: $L_s = [1 - \exp(K\times LAI)]/K$ $1/R_s = L_s/r_s\ (KI_{sun}) + (LAI - L_s)/r_s\ (0.5\ I_{shade})$ where: LAI is the leaf area index, L_s is the sunlit portion of the LAI, K is the extinction coefficient (0.5/cos[zenith angle])	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Hov et al, 1994[23]	Northern Europe	Documents Lagrangian modeling of Europe. For NH_3, local dry deposition of emissions is taken as 19% (within the same grid cell). Compensation point is assumed to be 0. The 1 m deposition velocity over land is calculated as follows: $V_D = V_D^0 (\delta \sin^2 D + r/(R \cos^2 D))$ where V_D^0 for NH_3 is 1.0 cm/s, δ is 1.0 in the daytime and 0.25 at night, D is a day-of-the-year term with a maximum sin function on August 1 and a minimum on February 1, r is the distance from the North Pole and R is the distance from the equator.	
Husted et al., 2000[24]	Oilseed Rape Plant	Compensation points for gaseous exchange of ammonia (NH_3) between stomata and the atmosphere were determined in an oilseed rape (*Brassica napus*) canopy by analysing the concentrations of NH_4^+ and H^+ in leaf apoplastic solution. This bioassay approach allowed an intercomparison with compensation points derived from micrometeorological measurements.	
Hutchings et al, 2001[25]	Denmark	Produces a detailed emissions inventory for Denmark. Emissions from natural ecosystems are not explicitly included.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Kiefer and Fenn, 1997[26]	Southern California	Fertilizer was applied (500 kg N ha^{-1}) in spring. Areas with high N deposition showed that N is not growth limiting, and that N is in excess of biotic demand. Chronic deposition > 25 kg $ha^{-1}yr^{-1}$ indicates N saturation, and N deposition of 6–11 kg N $ha^{-1}yr^{-1}$ indicates that the system is not saturated. When the system is saturated more NO_3^- exists in the soil.	San Gabriel Mountains and San Bernardino Mountain sites, with Ponderosa pine and Jeffery pine.
de Kluizenaar, 2000[27]	Ireland	Integrated assessment of NH_3 concentrations and deposition in Ireland. Dry deposition velocities from various sources were reviewed, and the following values were selected: 3.0 cm/s for coniferous forests (see Wyers and Erisman, 1998), 2.5 cm/s for mixed forests, 2.0 cm/s for broadleaf forests (Zapletal, 1998), 1.5 cm/s for moors and heathland (Fowler et al, 1998), 0.5 cm/s for urban areas (Zapletal, 1998), and 1.0 for agricultural land (Zapletal).	
Langford and Fehsenfeld, 1992[28]	Pine forest, Colorado	Measured ammonia emissions and deposition in a pine forest (Lodgepole, Ponderosa Pine, spruce, and aspen) on the eastern slope of the Rocky Mountains. A bidirectional flux was observed with a canopy average compensation point of 0.8 ppb. Emissions of about 1.2 ng-NH_3/m^2-s were measured during downslope wind conditions, when the forest was exposed to NH_3-poor air. Deposition of about 10 ng-NH_3/m^2-s were observed during upslope winds, when the forest was exposed to NH_3-rich air.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Lawrence et al, 2000[29]	Mississippi River Basin, (1998-1999)	Atmospheric transport eastward across the basin boundary is greater for NO_3^- than NH_4^+, but a significant amount of NH_4^+ is likely to be transported out of the basin through the formation of $(NH_4)_2SO_4$ and NH_4NO_3 particles – a process that greatly increases the atmospheric residence time of NH_4^+. This process is also a likely factor in the atmospheric transport of nitrogen from the Midwest to upland forest regions in the NE, where NH_4^+ constitutes 38% of the total wet deposition of N.	
Losleben et al, 2000[30]	Rocky Mountains, Colorado	In the Rocky Mountain Front Range study, high pH precipitation (>6 pH) was associated with wind from the Northwest.	
Mansell and Koisumi, 2002	Southern California	Developed an updated 1997 emissions inventory for Southern California. However, emission factors from non-agricultural soils were not altered from the earlier Radian inventory.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Mathur and Dennis, 2003[31]	Eastern U.S.	Documents RADM modeling of NH_3 transport, deposition and ambient concentrations. The authors cite a range of NH_3 deposition rates measured or estimated in previous studies: 0.5–5 cm/s for a variety of natural ecosystems by Sutton et al, 1994; 1.9 cm/s over heathland in the daytime by Duyzer, 1994; 1.2 cm/s for low vegetation landscapes and 2.5 cm/s for forests by Asman, 2001; and 3.2–3.6 cm/s for forests by Wyers et al, 1992, and Duyzer et al, 1992. Dry deposition in RADM is estimated using a resistance analog with three resistance terms: aerodynamic resistance, laminar sub-layer resistance, and canopy resistance (R_C). R_C was estimated based on measurements for SO_2, reduced by 1/3. This produced deposition rates of 1–1.25 cm/s (still somewhat lower than European measurements and estimates).	
Mendoza-Dominguez and Russell, 2001[32]	Eastern U.S.	Scaling factors for the NH_3 emissions inventory were computed by inverse modeling using four-dimensional data assimilation with the CIT airshed model. Calculated factors, based on the seasonally allocated 1995 NEI, were 0.59 for May and 0.52 for July.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Milford et al, 2001[33]	Moorland, England	Parameterizes NH_3 exchange based on long term micrometeorological measurements: $F_x = [X_c - X_a]/[R_a + R_b]$ $X_c = \{X_s/R_s + X_a/[R_a + R_b]\} / \{1/[R_a + R_b] + 1/R_w + 1/R_s\}$ where: F_x = emissions (or deposition); X_c = canopy level compensation point; X_s = stomatal compensation point; X_a = air concentration; R_b = atmospheric resistance; R_a = quasi-laminar sublayer resistance; R_w = resistance to cuticular deposition; R_s = stomatal resistance $R_s = (D_{H2O} /D_{NH3})\, R_{s,min}\, (1 + \beta/S)$ where: D = diffusivity, $R_{s,min}$ = 150 s/m (for moorland); β = 25 W/m^2 (for moorland); S = solar radiation $R_w = R_{w,min} \exp[(100 - RH)/a]$ where: $R_{w,min}$ = 0.5 s/m; a = 12 (for moorland); RH = relative humidity $X_s = (1.615\times10^5 /T) \exp(1.038\times10^4 /T) \times [NH_4^+]/[H^+]$ where: T = temperature (K), $[NH_4^+]/[H^+]$ is the ratio of intercellular concentrations (estimated at 50 for moorland)	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Mugasha and Pluth, 1995[34]	Alberta, Canada	Measured NH_3 losses following application of urea fertilizer to drained and undrained forested peatlands. Mean losses from the undrained site were 3% for urea applied at a rate of 200 kg-N//ha and 4% for 400 kg-N/ha. Mean losses from the drained site were 0.7% and 7%. Most volatilization occurred within 9 days. Losses abated after precipitation on day 9.	
Neftel *et al*, 1998[35]	Pore space in soil	Determined NH_3 concentrations in the soil from the open pore space. Proposed a soil compensation point method. Concentrations = $<0.1\ \mu g^{-3}$. $\chi_{soil} = C_{NH4+} \times 10^9 / K_H (1 + 10^{-pH} / K_a)$ χ_{soil} = ammonia concentration in pore space (ppb) C_{NH4+} = ammonia concentration in soil liquid (mol/L) K_H = Henry coefficient (mol/L atm) K_a = equilibrium constant between NH_4^+ and NH_3 in aqueous solution	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Nemitz et al., 2000a[36]	Oilseed rape, Scotland	Two and three layer models were used for the bi-directional ammonia surface/atmosphere exchange, taking both canopy concentrations and litter emissions. The measurements show the diurnal cycle typical for agricultural canopies with emission of up to 150 ng m^{-2} s^{-1} during the day. The application of an inverse Lagrangian technique estimated an average leaf litter emission of 32 ng m^{-2} s^{-1}, with peaks of 150 ng m^{-2} s^{-1}. Using the foliage-litter model, a stomatal compensation point of 0.58 µg m^{-3}.	This is the beginning of the series of the studies with oilseed rape. The equation above was used to calculate the compensation point.. See also Nemitz et al, 2000b and Sutton et al, 2000.
Nemitz et al., 2000b[37]	Oilseed rape, Scotland	The largest concentrations at the ground caused by NH3 release from decomposing litter leaves on the ground surface with values of up to 150 ng m^{-2} s^{-1} (typical emission were 10-50). Despite the large estimated ground emission (26 g NH_3-N ha^{-1} per day), all NH3 is recaptured by the lowest 0.7m of the 1.38m tall canopy (and the bi-directional net exchange with the atmosphere is governed by the top 0.5m), leading to a net emission from the canopy of 12 g NH_3-N ha^{-1} per day.	See also Nemitz et al, 2000a and Sutton et al, 2000.
Peterjohn and Schlesinger, 1990[38]	Desert soil, southwest	Determined nitrogen loss from desert soils in the U.S. using mass balance. Loss = 2.32 kg N m^{-2} or 77%.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Pryor et al., 2001[39]	Deciduous forest in southern Indiana	Above canopy NH3 concentrations measured continuously indicate mean concentrations of 0.6–1.2 $\mu g\ m^{-3}$ during the spring and 0.3 $\mu g\ m^{-3}$ during the winter (geometric means of 0.4-0.8 and 0.3 $\mu g\ m^{-3}$, respectively). Measurements suggest that on average the forest act as a sink of NH_3 with a representative daily deposition flux of 1.8 mg-NH_3 m^{-2} during the spring. Observed concentrations seldom dropped below 0.1 $\mu g\ m^{-3}$ indicating that this may be a regionally representative background concentration. An hourly profile is given for one day when emissions occurred.	The region has a ridge/ravine topography with a canopy approximately 25 meters above the forest floor. The soil consists of sandstone, siltstone, and shale. The forest is a secondary successional broadleaf forest: tulip poplar, white oak, red oak, and sugar maple.
Rattray et al., 2001[40]	Alpine tundra site on Niwot Ridge, Colorado	The concentrations of NH_3, HNO_3, NH_4^+, and NO_3^- were extremely low and ranged between 5 and 70 ng N m^{-3}. The NH_3 compensation point at this alpine tundra site appears to have been at or below about 20 ng N m^{-3}. Large deposition velocities (>2 cm s^{-1}) were determined for nitrate and ammonium and may result from reactions with surface derived aerosols. Based on our calculated dry deposition fluxes ammonia contributed 20-25% of the N dry deposition total to the alpine tundra.	The site is an E-W trending ridge on the eastern slope of the Front Range of Colorado, at an elevation of 3517 meters. The site, bounded by low rounded hills, is contained within an alpine tundra ecosystem consisting of low perennial sedges and grasses broken by rock debris. Samples occurred between August-September 1998.

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Reido et al, 2002[41]	Grassland, Britain	Presents a two stage resistance model for soil-to-canopy and canopy-to-atmosphere exchange. $F_{TOT} = (X_{Z0} - X_A)/R_A$ $F_{TOT} = F_{SOIL} + F_{CAN}$ $F_{SOIL} = (X_{SOIL} - X_{Z0})/R_{AC}$ $F_{CAN} = (X_C - X_{Z0})/R_B$ $F_{CAN} = (X_S - X_C)/R_S – X_S/R_W$ where $R_W = f(RH)$	Based on measurements in an intensively managed grassland.
Robarge et al, 2002[42]	Agricultural site, North Carolina	Analyzes NH_3 concentrations in the air over agricultural land. The logarithm of NH_3 concentration is correlated with temperature. There is also a correlation with relative humidity up to about 50% relative humidity.	
Sakurai and Fujita, 2002[43]	Japan	Model of the ammonia budget for the Kanto region of Japan. Uses a deposition velocity of 1.7 cm/s.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Schjoerring *et al*, 1998[44]	N.W. Europe	Measured NH_3 flux from 2 different indigenous species of plants in N.W. Europe. Interested in the measurements taken after harvest. Initial measurements indicate that NH_3 is absorbed into the soil, however after 26 days NH_3 is volatilized from soil until the air concentration of NH_3 is ~ 10 nmol/mol air or greater. Highest flux measured = ~5 nmol $^{-2}$ s^{-1}. Interestingly commented that the rates of absorption/loss for NH_3 from bare soil were similar to those seen with plant growth.	
Schlesinger and Hartley, 1992[45]	Global	Review of available data on emissions from natural ecosystems. Estimates NH_3 emissions at 1.2 - 12 kg/ha-yr from forests (based on 6 studies); and 0.12 - 12 from grasslands, based on 10 studies.	
Shahin et al, 1999[46]	Chicago	Measured deposition to simulated water body and building surfaces. NH_3 deposition velocity was 2.46 cm/sec. Deposition rates averaged 2.64 mg/m^2-day overall, 3.21 when the wind was from land, 1.37 for wind from Lake Michigan. These rates imply average NH_3 concentrations of 1.5 µg/m^3 during the daytime, and 0.64 µg/m^3 at night. Deposition rates were lower during the day (2.26 mg/m^2-day) than at night (3.02 mg/m^2-day), but the difference was not statistically significant.	
Sievering et al, 2000[47]	Spruce forest, Maine	Average monthly dry deposition rates were measured for NH_3 from April thru November: 0.026, 0.060, 0.057, 0.059, 0.058, 0.057, 0.039, and 0.028 kg-N/ha.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Smith et al, 2000[48]	General, United Kingdom	Develops a mechanistic model for ammonia deposition. The model also includes stomatal emissions when air concentrations are below the compensation point.	
Sorteberg and Hov, 1996[49]	General, Europe	Mechanistic model for deposition and emissions. Gives dry deposition velocities for different land uses.	See also Smith et al, 2000
Sutton et al., 2000[50]	Oilseed rape, Scotland	Fluxes of NH_3 were bi-directional (-200 to 620 ng m^{-2} s^{-1}), with deposition generally occurring when the canopy was wet and emission when it was dry, particularly during the day. The NH_3 mean concentrations were 1.03 (pre-cutting of oilseed) to 2.48 µg m^{-3} (post-cutting). The net emissions of NH_3 for the examined period was 0.7 kg N (0.1 total deposition and 0.8 total emission). Extrapolation to May-Augusts suggests a net emission of around 2.5 N ha^{-1}.	This was called the EXAMINE experiment. See also Nemitz et al, 2000a and 2000b.
Sutton et al, 1998[51]	Moorland, Devon, England	A compensation point of over 50 µg/m^3 was measured for cut grass located within 1 km of land treated with animal slurry.	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Sutton et al, 1997[52]	Grass moorland and bog, Great Dun Fell	Ammonia was generally deposited to the Fell, but some periods of emissions were also observed at air concentrations less than 0.3 µg/m^3. During periods of deposition, canopy resistance (R_C) was measured at 5 and 27 s/m on two example days. A more complex model was developed to cover the bidirectional flux, with parallel deposition to leaf cuticles and emissions from stomata. Terms were estimated as follows: resistance to deposition onto leaf cuticles (R_W) = 10s/m; stomatal compensation point (X_S) = 5µg/m^3;	Emissions can only escape the leaf surface when the leaf is dry.
Sutton et al, 1995,[53] 2000[54]	Great Britain	Develops a detailed emission inventory for Great Britain. Emissions from natural soils are taken as 0, stating: "any minor temporary emissions treated in definition of net dry deposition."	
Sutton et al, 1994[55]	General	Measurement data on ammonia deposition and emission are compiled for a wide array of land uses. A net deposition flux is found for forested and semi-natural ecosystems, and a net emission flux is found in agricultural lands. Emissions are typically 0–10 kg-N/ha-yr for croplands, and 1–40 kg-N/ha-yr for intensively grazed pastures.	
Swank and Vose, 1997[56]	North Carolina	Indicated when the forested system is disturbed it becomes a source of N instead of a sink. Mature healthy forests are generally sinks for N, whereas a forest that was transformed into a grassland became a source. Mentions a forest nutrient cycling model (Johnson *et al.*, 1995).	

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Tarnay et al., 2001[57]	Lake Tahoe Basin,	Total flux from dry deposition ranges from 1.2 to 8.6 kg N ha^{-1} for the summer and fall dry season and is significantly higher than wet deposition, which ranges from 1.7 to 2.9 kg N ha^{-1} $year^{-1}$. The results of the study suggest that dry N deposition is more important than wet deposition for forest canopies.	Summer and fall, July through September 1997 and 1998.
Van Drecht et al, 2003[58]	Global model	A global model was developed for nitrogen in the hydrosphere, including emissions and wet and dry deposition. The model assumes 50% of emissions are deposited within the same (5°) grid cell.	
Van Hove et al., 2002[59]	Rye grass (*Lolium perenne L.*) in an intensively managed grassland.	The calculated values for compensation point varied between 0.5 and 4 μg m^{-3}. The gaseous NH_3 concentrations inside the grass leaves were, with a few exceptions, always smaller than the measured ambient NH_3 concentrations. Temperature appeard to have a predominant effect on compensation point, partly by affecting the equilibrium between gaseous NH_3 inside the leaf and NH_3 dissolved in the apoplast and partly by affecting physiological processes influencing the NH_4^+ concentration in the apoplast. The low NH_4^+ concentrations during spring and summer coincided with a low total leaf N content (<3% dw).	Grassland located west of Wageningen, the Netherlands is a temperate humid perennial ryegrass pasture on a heavy clay soil with previous dairy slurry and artificial fertilizer N in previous years. Slurry was applied three times (60 kg N ha^{-1}) and calcium nitrate fertilizer was added at four other times (27 kg N ha^{-1}). The pH varied between 5.9 and 6.5 throughout the experimental period.

Summary of Recent Studies of Ammonia Emissions from Natural Landscapes (continued)

Source	Landscape	Results	Comment
Wyers and Erisman, 1998[60]	Douglas Fir forest, Netherlands	Continuous record of NH_3 fluxes for a period of more than two years. Net emissions were 0.14 kg/ha-yr for 1993, and 0.05 kg/ha-yr for 1994. Ambient NH_3 concentration during these measurements was about 5 $\mu g/m^3$.	Ambient NH_3 may have exceeded the compensation point for a significant portion of the year.

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Appendix B:

Bibliography of Sources Related to Ammonia Emissions from Fertilizer

Summary of Recent Studies of Ammonia Emissions from Fertilizer

Source	Type of fertilizer	Results	Comment
Al-Kanani et al, 1991[1]	Urea, UAN	Cumulative emissions are: 47–55% and 17–19% for urea and UAN in moist soils; 2.8–18 and 0.3–6.6 for urea and UAN in dry soils. Moist soil emissions are highest for the first 4 days. Dry soil emissions are steady over about 10 days (with no sign of abating).	Laboratory simulations
Al-Kanani and MacKenzie, 1991[2]	Urea and UAN	Emissions abate after about 10 days	
Bless *et al.*, 1991[3]	Slurry	Field experiments measuring NH_3 flux from wheat stubble and rape using differing application techniques. Used a mass balance method. Results from wheat stubble and surface spreading or incorporation into soil showed that the latter reduced the flux overall. Drag horses were used with rape, which was in it's growing season and taller, and this proved to be the best method for application. Climatic conditions indicated that warmer/windier conditions led to higher volatilization than cool/rainy conditions.	
Bouwman et al, 1997[4]	synthetic N fertilizers, manure	Compiled global emission inventory of N emissions from various sources, to include synthetic N fertilizers. Primarily based emission factors on previous research from laboratory studies. Results include experiments using urea with rice which indicate that NH_3 losses are greater after the first application of urea than the second. The increased canopy over the water reduces turbulence, thereby restricting the exchange process. When anhydrous ammonia is not injected deep enough, or the soil is too wet or dry, then emissions may occur. Also, injection spacing may play an important role in emissions, however this entire theory is old (1956). Fertilizer use was distributed on a 1° x 1° country database.	Corn is generally "side dressed" when it is "knee high", yet the canopy is greater, which in theory could reduce the turbulence and decrease the exchange.

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Bouwman et al, 2003[5]	All, manure	Literature review of existing studies regarding NH_3 volatilization from synthetic fertilizers and animal manure. Calculation of global NH_3 volatilization losses using relationships between regulating factors and NH_3 volatilization rates in an empirical summary model.	
Branch et al. 1985	Ammonium sulfate	Losses were unexpectedly high for the 14 day trials in the field: The recovery was 84.7% for wet soil and 82.9% for dry soil in May and 86.3% from wet soil in July. (Losses-subtract from 100%)	
Burch and Fox, 1989[6]	Urea, $(NH_4)_2SO_4$F allow soil	Urea and ammonium sulfate($(NH_3)_2SO_4$) applied to bare soil at 200 g N ha^{-1}. Measured losses in May and July. Losses ranged from 63.5 to 95.5 % dependant on soil moisture content more than temperature.Emissions are higher for wet conditions. Peak occurs within 4–8 days.	Emissions not measured directly, but by material balance
Clay et al, 1990[7]	Urea	Day-specific and 3-hour measurements of emissions. Peak emissions occur between 2 and 3 days from application.	
Cookson et al. 2001[8]	Granular Urea	This article focuses on the fates of autumn, late winter, and spring-applied nitrogen fertilizer to perennial ryegrass. Losses are lower for more dispersed fertilizer application (temporally).	
Dabney and Bouldin, 1990[9]	New York	Measured flux of NH_3, NH_4^+, and AN in alfalfa in NY. Compensation point = 2 ppb	
De Datta et al, 1991[10]	Urea on rice	Reports hourly emissions for 2 days.	
De Kluizenaar and Farrell, 2000[11]	Ireland	Report of deposition monitored at 40 stations around Ireland. Measured NH_3 emissions, Table 5.1. Prior research estimated emissions at 117 kt NH_3 for Ireland.	

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Dragosits *et al.*, 2002[12]	NH_3	NH_3 inventory for central England, using 5 x 5 km grid. Inputs: livestock grazing, livestock housing and manuer storage, landspreading of manuer, and N-fertilizer application. Emissions from fertilizer proportional to amount of N-fertilizer applied. Volatilization factor = 2.94% of N. Estimated N content and application rates. Manuer: cattle = 0.39 kg N/t; poultry = 4.06 kg N/t. See Table 3.	
Erismann and Monteny, 1998[13]	Manure and slurry	Charts hourly emissions over about 14 hours from surface spreading and sod injection. Emissions decline roughly linearly for about 7 hours after application, then stabilize at a rate about half the initial instantaneous rate.	
Fenn and Hossner, 1985[14]	All	The following model is given for emissions, E (%-N) from NH_4NO_3 based on time, t (hr), temperature T (C), and application rate, U (kg-NH_4-N/ha): $E = -18.44 + 1.24\,t + 0.42\,T + 0.091\,U - 0.021\,t^2 + 1.68 \times 10^{-4}\,t^3 - 4.71 \times 10^{-7}\,t^4 - 8.97 \times 10^{-5}\,U^2$ $(R^2 = 0.98)$ In the laboratory there were reported losses of 55 to 65 % losses from $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, and NH_4F at 22 degrees Celcius. In the greenhouse there was 61% NH_3-N loss from $(NH_4)_2SO_4$ and there was a 55% NH_3-N loss from $(NH_4)_2SO_4$ when measured in the field.. Temperate region losses of NH_3 from urea surface-applied to pasture have been found to range from 15 to 20% on a long-term average.	Not a primary reference

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Galle et al, 2000	Pig slurry	Emission decays with time from application (4.4% of N on day 2, 2.4% on day 3), function of windspeed and temperature (emission becomes negligible when wind speed drops below ~2 m/s [at 1.5 m above ground] – temperature also declines from ~14 C to ~8 C)	60 kg-N/ha; soil is 40% clay, 3-6% organic
Genermont and Cellier, 1997[15]	Slurry	Developed a mechanistic model that simulates NH_3 volatilization as it is influenced by various factors and accounts for transfers between the soil and atmosphere. Model consists of 6 submodels; 3 deal with AN transfers and equilibria between AN species; the other 3 simulate heat and water transfers in the soil. Includes short term and long term capability.	This may be a better option than PaSim as all the equations are in the paper.
Genermont *et al.*, 1998[16]	Slurry	Mass balance method used to calculate emission for large areas within first few hours of spreading. Aerodynamic gradient method used for longer term flux. Results indicate it can operate under real field conditions. See Tale 1 for emissions over time.	
Goebes et al, 2003[17]	All types	Documents the Fertilizer subsystem of the Carnegie Mellon University ammonia emission model. Presents an ammonia emission inventory for fertilizer application that for the first time incorporates county-level data at monthly resolution, and includes more accurate activity levels and emission factors.	
Harper and Sharpe, 1998[18]	Urea, Georgia	Measured NH_3 loss from soil and plants using ^{15}N and micrometeorological techniques. Also determined adsorption of NH_3 using both methods and measured transport. When there was drought conditions both measurements were the same. When there was plant activity however NH_3 losses as determined by the ^{15}N method were 2 to 6 times greater than the net NH_3 losses measured by the micrometeorological technique. See Table 1	

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	**Type of fertilizer**	**Results**	**Comment**
Harper et al, 2000	Dairy slurry	Emissions were 1.5 kg-N/ha-da on days of application and 0.9 kg-N/ha-da on other days. Losses appeared to be roughly constant during daylight hours. About 113 kg-NH_4/ha was applied over the course of the season.	Assumes overnight emissions are small, and 12% of N is emitted on spraying
Hertel *et al.*, 1995[19]		Developed a trajectory model ; ACDEP (Atmospheric Chemistry and Deposition), to calculate nitrogen deposition to Danish seawaters. Uses land-use data and detailed emissions for Denmark. Transport, chemical transformations, and depositions are computed by following an air parcel along a trajectory to a given receptor point. The results show that computations of concentrations and depositions can e made for a limited area with high geographical resolution. Deposition of nitrogen compounds were calculated in Danish seawater. Uses Lagrangian framework.	
Huijsmans, et al., 2003[20]	Manure	The experiments included various application techniques (surface spreading, surface incorporation, deep placement), incorporation techniques, soil types (sand, sandy loam, and clay), soil water contents, stubble heights, manure characteristics and weather conditions. The mean total volatilization, expressed as % of the total ammoniacal nitrogen (TAN) applied, was 68% for surface spreading, 17% for surface incorporation and 2% for deep placement: $E(\ln z_k(t)) = \alpha_0 + F_k + \alpha_t \ln(t) + \alpha_1 ATAN + \alpha_2 rate + \alpha_3 wind + \alpha_4 temp + F_{kw} wind$	Observed in the Netherlands between March and September from 1990 to 1998.

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Ismail et al. 1991[21]	Urea solution applied to loamy sand	Gives the following model for total ammonia emissions, E (kg-N/ha), temperature, T (C), soil pH, soil moisture, MC (g-water/g-dry soil), urea application rate, R (kg-N/ha), application depth, D (cm): $E = -11 + \exp[-0.935 - 0.04017\,T + 0.570\,pH + 0.00367\,R + 0.178\,MC - 0.445\,D + 0.00154\,T^2 - 0.00739\,MC^2 + 0.00285\,D^2 - 0.000378\,R\times D]$	Based on laboratory measurements.
Jambert et al, 1994[22]	All	Experiments over 1 year period testing the emissions from a maize field and pine forest located in France. Measurements taken before, during, and after fertilization, and again after harvest. Identification of type of gases, understanding of emission mechanism in relation to soil characteristics, fertilizer type, and application method are the goals of this research. Relationship of maize field and pine tree forest determined to reduce N_2O emissions to atmosphere, as pine forest acts as a sink for the emissions. See Table 2 for NH_3 flux.	Total denitrification had not been measured, yet, look for other reports.
Kirk and Nye, 1991[23]	Urea	Expands on a mechanistic model by Rachhpal-Singh and Nye to add drainage and moisture evaporation.	

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Lewis et al, 2003[24]	N fertilizer, and slurry	Simulated long-term effects of nitrogen fertilizer and slurry use in agricultural systems using SOIL and SOILN (Swedish based models), over a 12-year period. SOIL is a multilayer model which can indicate the sol water content and horizontal movement of water to field drain backfill at different depths, as well as deep percolation, with a range of drainage system options. The model has a sophisticated treatment of soil heat processes including freezing, and representation of falling and lying snow. SOILN was designed to work with SOIL, and includes major processes that describe the N cycle. SOILN was designed primarily when solid manure and ploughing following application are used, so adaptation is required for slurry and grassland applications apply. NH_3 volatilization from slurry is estimated using Hutchings' model, which combines the partition of ammonia molecules in air and liquid through Henry's Law, with aerodynamic resistance and surface boundary layer resistance terms. Knowledge of atmospheric windspeed and pressure, and slurry temperature and pH are required to calculate volatilization rates. Study conducted in Scotland & Ireland where high winter rainfall and low soil moisture shortages are typical. This is part of a larger project sponsored by the EC initiative on Slurry Waste and Agriculture Management (SWAMP). Results show (Table 2) that the most important decision regarding slurry spreading is the selection of the spreading date, and field (soil) selection. For instance a spring slurry application produces a marked decrease in overall leaching compared to autumn spreading.	Includes some volatilization data, with the main focus on leaching. Figures indicate that volatilization is constant for each spreading option.

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Marshall and Debell, 1980[25]	Urea	Forest soils fertilized with 220 kg N ha^{-1}. Measured data indicate an emission of 22-26% of the applied fertilizer as NH_3, with the closed-dynamic method, which most closely resembled observations from field measurements.	From CMU
McInnes et al 1986[26]	Urea solution	Day-specific emissions estimates from field measurements. Roughly steady for 10–16 days.	In one case, emissions do not seem to abate after 16 days.
Menzi et al, 1998[27]	Animal slurry	Gives the following model for total emissions, E (%-N), as a function of temperature, T ©): $E \approx 28 + (2 \times T)$	$R^2 = 0.68$
Milford *et al.*, 2001[28]	Scotland	Developed a canopy compensation point model for measured events. NH_3 flux resulted in primarily deposition with emission occurring only 12% of the time. Uptake of NH_3 from the atmosphere was 30 $\mu mol/m^2d$. The greatest emissions occur in the morning between 9 and 12. When measuring NH_3 flux near other agricultural sources there is an underestimation of flux when using the gradient method. Using the compensation point model revealed that NH_3 flux in this landscape is dominated by deposition rather than stomatal response. Contrasts to agricultural crop (general term) emissions where stoma plays a much larger role.	
Misselbrook et al, 2000[29]	Urea, NH_4NO_3, other	Presents emission factors used in an inventory for the UK: 23%, 1.6%, and 1.6% for urea, AN and other N fertilizers applied to grasslands; 11.5%, 0.8%, and 0.8% for the same fertilizers applied to arable land.	Not a primary reference

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Misselbrook et al. 2001[30]	Urea, cattle slurry and solid pig manure	Field evaluation of the equilibrium concentration technique (JTI method).	No numbers.
Mugasha and Pluth, 1995[31]	Urea	Tested N limited flora in peatland soil; compared drained vs. undrained soil. Applied 200 or 400 kg N/ha. For undrained soils N emissions were 3% and 4% for 200 and 400 applications. For drained soils N emissions were 0.7% and 7% for 200 and 400 applications.	Did not discuss why emissions seemed to show an order of magnitude difference for the drained soils whereas the undrained only showed a change of one percentage point, with an increase in fertilization.
O'Deen and Follett, 1992[32]	Soybean tissue	Measured NH_3 volatilization from calcareous soil amended with soy bean tissue. Experimental/laboratory/Measured values only. Confirms others research indicating that NH_3 volatilizes more readily at higher temperatures and lower pH. *OF NOTE:* if more soybean residue is present **MORE** NH_3 will volatilize.	
Pain *et al.*, 1998[33]	Slurry, manuer	Compiled an extensive NH_3 inventory in the United Kingdom from most animal practices, to include: cattle, poultry, sheep, pigs, and others. Included land spreading of manuer/slurry. Tables 1-7 provide specific information regarding losses.	
Plochl 2001[34]	Manure	It can be illustrated that the time course of accumulated ammonia emission follows a non-linear Michaelis-Menten-like function.	Model cannot determine what occurs in the first 2 hours

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Reido et al, 2002[33]	NH_4NO_3	Presents a two stage resistance model of an intensively managed grassland, receiving about 270 kg-N/ha-yr.	
Rodhe and Rammer, 2002[34]	Slurry	Evaluated methods of application for slurry applied to ley in Sweden. Used a mass balance method to determine the NH_3 emissions from field study measurements. Slurry applied at 25 T/ha. Evaluated differing application methods to include: band spreading, pressurized injection, shallow injection with 1 open slot V-disc tine, and shallow injection with 2 open slots 2 angled disc coulters. Shallow injection methods led to ½ entire amount of NH_4-N applied being volatilized, also mitigated by hot, dry conditions. The lowest ΦNH_3 = shallow injection with twin discs (33%), and then band spreading (44%).	
Roelle and Aneja, 2002[35]	Hog slurry, corn crop	Corn crop sprayed with hog slurry. Measurements made after the harvest, when the soil is bare. Flux ranged from 3.4 to 26.1 ng N m^{-2} s. Soil temperature, soil pH, soil moisture, total Kjeldahl nitrogen were monitored. Soil temperature was found to explain the largest variability in soil NH_3 emissions: $(\mathrm{Log}_{10}NH_3\text{-N Flux}=0.054T_{soil}+0.66;\ R^2 = 0.71)$ and soil nitrogen was also significant in predicting NH_3 flux: $[NH_3\ \text{Flux}=55.5(NH_3\text{-N})-160,\ R^2=0.86$ $NH_3\ \text{Flux}=0.6(\text{TKN})-410,\ R_2=0.27]$.	An analysis of the source strengths confirmed that lagoon emissions are a larger flux source than soil flux

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Ross et al, 2001[36]	Cattle urine	The wind-tunnels were used to examine the effects of herbage length, cutting and N status on rates of NH_3 fluxes from a grass sward with cattle urine. Between 20 and 60% of the NH_3 emitted was deposited within 2m. Compensation points of between 1.0 and 2.3 μgm^{-3} were calculated for the grass sward. One significant relationship was found for NH_3 and environmental conditions (in multiple linear regression model): $\log NH_4\text{-Nlos s} = -94.75 - 4.99(\underline{+}2.5)\times\log(\text{air temp.}) + 65.8(\underline{+}13.9)\times\log(\text{soil temp}) - 15.4(\underline{+}6.8)\times\log(\%RH)$ (Adjusted $r^2=0.59$, $p=0.002$, $df=16$)	Heavy impermeable clay soil
Schoop, 1998[37]	All, Germany	Developed a multiple regression model to estimate adequate N fertilization with no net residue using measured data and compiling it with N-PROG. See Table 2.	Does not discuss volatilization. Residue = $N_{fert} - N_{plant\ uptake}$ therefore merely N that is not used.
Sogaard et al, 2002[38]	Cattle and pig slurry	The ALFAM model estimates of NH_3 volatilization from typical cattle and pig slurries show the variables that significantly affect this include: soil water content, air temperature, wind speed slurry type, dry matter content of slurry, total ammoniacal nitrogen content of slurry (TAN = $NH_3 + NH_4^+$), application method and rate, slurry incorporation and measuring technique. The application times modeled were 1 week before spring sowing, mid-season grass cut, and 1 week after harvesting of spring crop. The model predictions of the cumulative NH_3 loss 7 days after slurry application.	Michaelis-Menten-type neural network model was used to fit measured NH_3 loss rates.

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Sommer et al, 2000[39]	Slurry	Developed a regression model that related emissions to wind speed, soil slurry surface water content, global radiation, soil slurry surface pH and precipitation. A statistical analysis of data showed that NH_3 volatilization rate during the first 4-5 hours after slurry application increased significantly ($P<5\%$) with wind speed and soil slurry surface water content. NH_3 volatilization in the six measuring periods during the experiments increased significantly ($P<5\%$) with relative water content of the soil slurry surface, global radiation, and pH. Six experiments were conducted in 1997 from March 17 to June 30. The soil was loamy sand and the pig or cattle slurry was applied at rates from 2.87 to 3.13 kg/m^{-2}.	Cereal Crops at the Research Center Foulum in Demark
Sommer *et al.*, 2001[40]	Sow urine	Measured NH_3 volatilization from urine patches from sows on grasslands. Used a mass balance method. See equation 1. Flux highly variable due to distribution of urine. At feeding areas = 2.8 g NH_3-N/m^{2}day; 40 m from feeding areas = no losses; pastureland = 0.07 to 2.1 kg NH_3/ha/day.	
Tian et al, 2001[41]	Urea	Day specific emissions are given for a rice-wheat rotational system, with application rates of 0,100, 200 or 300 kg-/ha/growing season, and 200 kg N/ha without rice straw amendment. The results show that N losses through NH_3 volatilization accounted for 4-19% of N applied during the wheat growing season and for 5-11% during the rice growing season. Ammonia volatilization was affected significantly by soil moisture and temperature before and after fertilizer application during the wheat growing season. The soil type was paddy soil.	
Tiquia and Tam, 2000[42]	Chicken litter	Used mass balance approach to measure NH_3 emissions from composted chicken litter. Results follow previous manuer studies. No equations for flux.	

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
van der Weerden and Jarvis, 1997[43]	Urea, AN	Estimated NH_3 emissions from urea and AN for two soil types in UK on grasslands (Table 2). Determined new emission factors (Table 4).	
Watson et al, 1992[44]	Urea prills and solution	Day-specific emission measurements show a peak between 1 and 3 days, and declining emissions to about 10 days.	Northern Ireland
Webb *et al.*, 2000[45]	N-fertilizer	Measured N-outputs via leaching, NH_3 volatilization, N_2O and N_2 emissions, and crop takeoff, together with N-fertilization and wet deposition over 2 arable rotations on contrasting soil types. Mass balance. N-fertilizer not specified. Fluxes measured for 5 years, these results indicate the first 3 years of measurements. Flux ranged from 3 g N/ha/day to 131 g N/ha/day for alluvial silt site.	
Yamulki et al, 1996[46]	Nitram (NH_4NO_3 $Ca(NO_3)_2$ mix)	Seasonal variations in emissions. Ammonia emission was favored regardless of fertilization in dry and warm conditions in summer with an average NH_3 flux of about 0.03 $\mu g\ N\ m^{-2}s^{-1}$, while an average flux of -0.068 $\mu g\ N\ m^{-2}s^{-1}$ was observed during wet conditions in winter. The average apparent deposition velocity was about 1.6 cm s^{-1}. Ammonia exchange patterns throughout the whole experimental study showed a dependence on the ambient NH_3 concentration with a compensation point of 3-4 μg^{-3}. Loss to the atmosphere accounted for approximately 1% of the fertilizer applied to the soil. From March 1991 and April 1992. Fertilizer was applied twice at a rate of 200 and 150 kg N/ha. The soil pH of this field was 6.8 ± 0.4.	

Summary of Recent Studies of Ammonia Emissions from Fertilizer (continued)

Source	Type of fertilizer	Results	Comment
Yang et al, 2003[47]	Manure	Reports the measurement of ammonia emission from cattle slurry manure applied to upland in Miyazaki, Japan. The emission flux of the first day was 110 µg N ha^{-1} s^{-1}. The loss of NH_4^+–N in the applied slurry was 60% five days after application. A diurnal cycle of volatilization is apparent and it indicates that the volatilization of NH_3 is positively related to the air temperature. The soil properties are sandy loam, a CEC 18.9 cmol kg^{-1}, a water content of 33%, 2.0 mg kg^{-1} NH_4^+–N, 125 mg kg-1 NO_3^---N, 6.12 pH (H_2O), and 5.55 pH (KCl).	The results did not show a statistically significant relationship between the wind speed and NH_3 flux.

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