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DEVELOPMENT AND SELECTION OF AMMONIA EMISSION FACTORS

Final Report

by

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EXECUTIVE SUMMARY

This report compiles and reviews recent (published after 1985) literature on sources of ammonia (NH_3) emissions and NH_3 emission factors. This compilation contains the most recent research in the field of NH_3 emission factors. The primary focus of this report is on NH_3 emission factors, as opposed to estimates of total NH_3 emissions. Emission estimates are, however, made for some categories, in Order to determine the relative importance of the source category to NH_3emissions, and to assist in developing priorities for future NH_3 emission factor research.

Ammonia emissions can not be speciated from VOC or PM emissions, because as an inorganic gaseous chemical, NH_3 is not included in YOC emissions estimates and, as a gas, it is not included in PM emissions estimates. Therefore, it is necessary to utilize emission factors for estimating NH_3 emissions.

Ammonia emissions are important in atmospheric models, because ammonia is the most important almine constituent in the atmospheric boundary layer. The fate of NH_3 released from the ground into the atmosphere is complex and varied, but this NH_3 can have a significant effect on oxidation rates, particularly in clouds, and hence on deposition rates of acidic -species. This effect is predicted not only by models for the heterogeneous chemistry of cloud droplets, but has also been confirmed by observation and experimentation. The long range transport of atmospheric sulfur dioxide and nitrogen oxide, and the products of their reactions, have long been studied in relation to acidic deposition. However, much less research has been done on the effects of atmospheric NH_3, although it is well known that over large areas of Europe, acid precipitation is failing in which up to 70 percent of the original acid is neutralized by NH_3.

This report presents a narrative on the recent research for the known substantial sources of ammonia emissions. Emission factors resulting from this investigation are compared with the factors published by National Acid Precipitation Assessment Program (NAPAP), as compiled by Misenheimer *et al* (1 987), and later by Warn *et al.* (I 990). Recommendations on the most reliable NH_3emission factors for use in the United States are made. For each recommended emission factor, a point source classification code (SCC) or area and mobile source (AMS) code is presented, along with an emission factor rating.

Recent research on NH_3 emissions as it relates to acid deposition, is concentrated in the ' European community (specifically, in the Netherlands, Great Britain, and Scandinavia). In addition, there has been some research conducted in Australia. The majority of the NH_3 emissions studied in current inventories originates from agricultural sources. These agricultural sources are mainly livestock wastes, with fertilizer applications also providing a significant proportion. NH_3 emission estimate numbers vary widely between different studies, but the authors of recent European inventories all consider animal wastes and fertilizers to be responsible for 90% or more of the anthropogenic NH_3 emissions. Some of the more recent inventories in Europe even exclude contributions from industrial facilities entirely, noting that they are insignificant relative to the agricultural sources.

Although the European inventories currently focus on agricultural sources, there is evidence that additional, significant sources of ammonia may exist. In a modelling study of acid deposition, Metcalfe *et al.* (1989) suggested that the current estimates of NH_3 emissions in the U.K. were too low to explain the concentrations of ammonium in precipitation, and that there may be other sources of NH_3 which have not yet been considered in budget studies (Lee *et al.*, 1992). Other research, principally in support of global climate change research, suggests that there may be significant NH_3 emissions from undisturbed soils and biomass burn-ing.

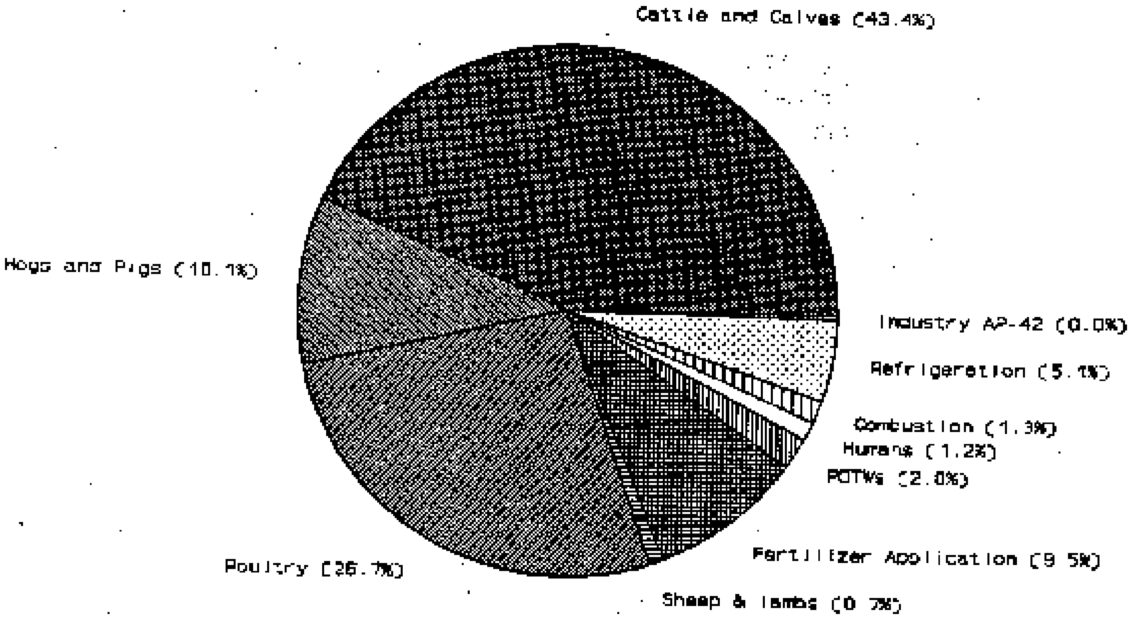
Much of the research obtained and reviewed',in this report concerns the measurement of NH_3, in which results were generally reported as. experimental, rather than as emission factors- The majority of NH_3 emission factors available in the literature are discussed relative to the development of an emission inventory. In the development of an emission inventory, emission factors are often either developed from the experimental measurement literature, or are borrowed directly from other bodies of work. The primary source for the emission factors reviewed in this report is the body of recent emission inventory literature. The experimental measurement literature is also reviewed, to provide detail on how the measurements were made. This review contributes to understanding the uncertainty of the emission factors, addresses the extent to which the factors presented incorporate the most recent research, and identifies data gaps for future emission factor development.

The most recent NH_3 inventory prepared in the U.S. is the *Emissions Inventory for the National Particulate Matter Study* which used Bureau of Economic Activity data to grow the 1985 NAPAP inventory to the 1990 study year. Other recent studies include the following: ApSimon *et al.* (1987) published an inventory for the U.K. for the 1981 study year; Buijisman (1987) published a 1982 inventory of NH, for Europe the same year; Erisman (I 989) published a 1987 and 1988 inventory for the -Netherlands; M61ler and Schieferdecker (1989) published NH_3 estimates through 1985 for the G.D.R.; Kruse *et al* (1989) published an updated inventory for Great Britain; Denmead (1990) published an inventory for Australia; and, finally, the most recent inventory of Europe was published by Asman (1992). Lee and Longhurst (1993) published the most recent inventory for Great Britain. Additional inventories have been published for European countries; however, these publications were not translated into English and were not reviewed in this report.

The NH_3 emission factors recommended for use in future U.S. inventories include the European factors for agricultural sources (animal husbandry and fertilizer application), the *Compilation of Air Pollutant Emission Factors - Volume I (AP-42)* for the majority of the stationary industrial sources, and the NAPAP factors for the majority of the combustion sources (including coal, oil, natural gas, and mobile sources), human breath and perspiration, and publicly owned treatment works (POTW's). New emission factors are developed for beet sugar production, froth flotation in mineral processing, mineral wool (fiberglass) production, refrigeration, and selective catalytic and noncatalytic reduction (SCR and SNCR) for control of nitrogen oxide (NOx) emissions. Discreet industrial sources of NH_3 with no corresponding emission factors, are identified through the Toxic Release Inventory.

Estimates of NH_3 emissions in the U.S. are graphically illustrated in Figure 7-1. These emission estimates are not comprehensive, and are presented only to illustrate the relative magnitude of these emissions, in order to frame the recommendations for future research. These rough estimates of U.S. NH_3emissions indicate that agricultural practices, specifically animal husbandry and fertilizer application, dominate emissions here just as they do in Europe. Industrial emissions of ammonia and ammonia emissions from combustion (excluding, open or biomass burning) are relatively insignificant. Emissions from POTWs and refrigeration may be significant, based upon the current information gathered. Emission factors for refrigeration and POTWs have a rating of E, and further research into these sources is recommended.

Figure 1. Relative contribution of ammonia mwons from different source categories.



Estimates of NH_3 from biomass burning and undisturbed soils were not made, due to the unavailability of an emission factor for biomass burning and of activity data for undisturbed soils. Recent research indicates that these two categories may contribute significantly (up to half) to the global budget of NH_3 emissions.

Five research areas are recommended to enhance the quality of ammonia emission factors presented in this report. The five research areas are:

- Investigate the recent global climate literature on ammonia from undisturbed soils. Merge the literature on emission fluxes with ammonia new land use land cover data categories, to develop emission factors for the biogenic plants area and mobile source, classification category.

- Investigate recent literature on ammonia emissions from biomass burning. Integrate the data results with information in the U.S. on naturally occurring fires to develop emission factors for the U.S. Also, investigate any information on NH_3 emissions from the chemical agents used to fight these naturally occurring fires.

- Research the primary references for the animal husbandry emission factors, in order to provide more accurate linkages with the U.S. Department of Agricultare statistics. In addition, investigate the discrepancy in the emission factors for sheep presented by Asman (1992) and Denmead (1990).

- Develop temporal profiles for the larger NH_3 emissions categories. Specifically,
- investigate the seasonal nature of the animal husbandry and fertilizer application emissions.

- Confidence in the emission factors reported for refrigeration, POTWS, and selective catalytic and non-catalytic reduction (for control of NO. emissions), may be improved with additional research. Refrigeration contributes a significant portion of the ammonia inventory (about 5 %); however, this factor was developed based on a material balance. P0TWs also contribute a significant amount of ammonia (about 2 %); however, additional research is ongoing in the United Kingdom and California that may improve the accuracy of this emission factor.

SECTION 1

INTRODUCTION

Sources of ammonia (NH_3) emissions and NH_3 emission factors that have been reviewed in publications written since 1985 are assembled and reviewed in this report, in an effort to create a compilation of the most recent research in this field. The primary focus of this report is, however, on NH_3 emission factors, as opposed to estimates of NH_3 emissions Emission estimates are made for some categories to assist in the determination of the relative importance of various emission source categories to total NH_3 emissions. The compilation of emission factors presented in this report updates and adds to the body of emission factors that can be used to produce future emissions inventories for NH_3.

Ammonia emissions can not be speciated from VOC or PM emissions, because as an inorganic gaseous chemical, NH_3 is not included in VOC emissions estimates, and, as a gas, it is not included in PM emissions estimates. Therefore, it is necessary to utilize emission factors for estimating NH_3 emissions.

Ammonia emissions are important in atmospheric models, because NH_3 is the most important e constituent in the atmospheric boundary layer. The fate of NH_3 released from the ground into the atmosphere is complex and varied, but this NH_3 can have a significant effect on oxidation rates, particularly in clouds, and hence on deposition rates of acidic species. This effect is predicted not only by models for the heterogeneous chemistry of cloud droplets, but has also been confirmed by observation and experiment.[1] The long range transport of atmospheric sulfur dioxide and nitrogen oxide and the products of their reactions have long been studied in relation to acidic deposition. However, much less research has been done on the effects of atmospheric NH_3, although it is well known that over large areas of Europe acid precipitation is falling, in which up to 70 percent of the original acid is neutralized by NH_3.

This report presents a narrative on the recent research for the known substantial sources of NH_3 emissions. Emission factors resulting from this investigation are then compared with the factors published by National Acid Precipitation Assessment Program (NAPAP), as compiled by Misenheimer *et al.* (198V and later by Warn *et al.* (1990).[3] Recommendations on the most reliable NH emission factors for use in the United States are NH^3 emission factors for use in the United States are made. For each recommended emission factor, a point source classification cod e (SCC) or area and mobile source (AMS) code is presented, along with an emission factor rating.

Recent research on NH_3 emissions as it relates to acid deposition is concentrated in the European community (specifically, in the Netherlands, Great Britain, and Scandinavia). In addition, there has been some research conducted in Australia. The majority of the NH_3 emissions studied in current inventories originates from agricultural sources. These agricultural sources are mainly livestock wastes, with fertilizer applications also providing a significant proportion. NH_3

emission estimate numbers vary widely between different studies, but the authors of recent European inventories all consider animal wastes and fertilizers to be responsible for 90% or more of the anthropogenic NH_3 emissions. Some of the more recent inventories in Europe even exclude contributions from industrial facilities entirely, noting that they are insignificant relative to the agricultural sources.

Although the European inventories currently focus on agricultural sources, there is evidence that additional significant sources of NH_3 may exist. in a modelling study of acid deposition, Metcalfe *et al* (1989)4 suggested that the current estimates of NH_3 emissions in the U.K. were too low to explain the concentrations of ammonium in precipitation and that there may be other sources of NH_3 which have not yet been considered in budget studies (Lee *et al*, 1992).[5] Other research, principally in support of global climate change research, suggests that there may be significant NH_3 emissions from undisturbed soils and biomass burning.[7]

Much of the research obtained and reviewed in this report concerns measurements of NH_3, in which results were generally reported as experimental results rather than as emission factors. The majority of NH_3 emission factors available in the literature are discussed relative to the development of an emission inventory. In the development of an emission inventory, emission factors are often either developed from the experimental measurement literature, or are borrowed directly from other bodies of work. The primary source for the emission factors reviewed in this report is the body of recent emission inventory literature. The experimental measurements literature is also reviewed, to provide detail on how the measurements were made. This review contributes to understanding the uncertainty of the emission factors, addresses the extent to which the factors presented incorporate the most recent research, and identifies data gaps for future emission factor development.

The most recent NH_3 inventory prepared in the U.S. is the *Emissions Inventory for the National Pailiculate Matter Study*[8] which used Bureau of Economic Activity data to grow the 1985 NAPAP inventory to the 1990 study year. Other recent studies include the following: ApSimon *et al.* (1987) published an inventory for the U.K. for the 1981 study year; Buijisman (1987)[9] published a 1982 inventory of NH_3 for Europe the same year; Erisman (1989)[10] published a 1987 and 1988 inventory for the Netherlands; Mö1ler and Schieferdecker (1989)[11] published NH_3 estimates through 1985 for the G.D.R.; Kruse *et al* (1989)[12] published an updated inventory for Great Britain; Denmead (1990)[13] published an inventory for Australia; and, finally, the most recent inventory of Europe was published by Asman (1992),[14] and Lee and Longhurst (1993)[15] published the most recent inventory for Great Britain. Additional inventories have been published for European countries; however, these -publications were not translated into English and were not reviewed in this report.

This report is organized into seven sections. After this introduction, the next five sections discuss NH_3 emission factors, and present recommendations for their use. These five sections address NH_3 emissions from animal husbandry, fertilizer application, industrial sources combustion, and miscellaneous categories. The final section presents the conclusions of this report and includes recommendations on further research,that will enhance the understanding of NH_3 emissions in the United States.

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SECTION 2

AMMONIA EMISSIONS FROM ANIMAL HUSBANDRY

Ammonia emissions from animal husbandry are a significant portion of total NH_3 emissions in recent inventories. In the 1985 NAPAP inventory, twelve categories of animal husbandry accounted for over 70 percent of the total NH_3 emissions. In recent studies of NH_3 emissions in Europe, animal husbandry accounted for over 80 percent of NH_3 emissions.

2.1 SUMMARY OF RECENT RESEARCH IN EUROPE

Recent NH_3 emission factor research in Europe, and specifically in the Netherlands, has focused primarily on increasing the accuracy and resolution of NH_3 emission factors for various classes or subcategories of animal husbandry. Two predominant European NH_3 emission inventories have been located in the literature. The first is a 1982 inventory developed by Buijsman (1987).[1] The work of Buijsman (1987) was followed by a 1987 and 1988 inventory of NH_3 emissions in the Netherlands by Erisman (1989).[2] Both of these inventory efforts identified uncertainties in emission factors for various classes of animal husbandry and resulted in additional field measurement programs designed to increase the understanding of NH_3 emissions and the effectiveness of various control programs.

In 1992, a report on the NH_3 emissions in Europe was published by Asman (1992).[3] This report incorporates research conducted in the Netherlands through about 1990. The estimates presented by Asman (1992) (for all categories) are approximately 21% higher than the estimates presented by Buijsman (1987), due to the application of different emission factors and due, in minor part, to differences in the number of animals. In our review of the recent literature, the emission factors presented by Asman (1992) are the most recent and accurate emission factors for animal husbandry. An emission factor manual for Europe was developed by van der Most and Veldt in 1992[4] that utilizes the same emission factors that are published by Asman (1992) for NH_3 emissions from animal husbandry. Table 2-1 lists the animal subcategories and the emission factors developed in the Netherlands.

Additional work on NH_3 emissions from animal husbandry has been conducted by many researchers in Europe. Specifically, there have been numerous inventories developed for countries and regions within Europe and Australia.

ApSimon *et al.* (1987)[5] and later Kruse *et al.* (1989)[6] developed NH_3 emission inventories from agriculture in Great Britain, using 1981 census of agriculture data. Both utilized the research conducted by Kruse (1986)[7] on NH_3 volatilization from agricultural sources. Kruse compared the emission factors that he had generated with the emission factors used by Buijsman (1987) and noted that they are in agreement. Lee (1993)[8] also developed an NH_3 emission inventory for the United Kingdom for the 1987 study year. The NH_3 emissions from animal husbandry in this research effort were based on the factors used by ApSimon (1987) and Kruse (1989). These factors were slightly different than the factors that

TABLE 2-1. ANIMALS OF HUSBANDRY EMISSION FACTORS (kg NH_3/Animal/Yr) [Asman (1992)]

Animal	Stable + storage	Spreading	Grazing	Total
Young cattle	3.87	6.34	2.83	13.04
Dairy & calf cows	12.87	21.09	5.76	39.72
Breeding bulls > 2 yr	10.58	17.33	0	27.91
Fattening calves	1.6	3.63	0	5.23
Young cattle for fattening	5.76	9.43	0	15.19
Fattening/grazing cattle > 2 yr	0	0	8.22	8.22
Fattening pigs	3.18	3.8	0	6.98
Breeding sows 20-50 kg	2.42	2.8	0	5.22
Breeding sows > 50 kg	8.09	8.04	0	16.13
Other sows	8.09	8.04	0	16.13
Boars > 50 kg	3.18	3.8	0	6.98
Mature boars	5.52	5.48	0	11
Broilers	0.065	0.102	0	0.167
Mother animals < 6 mo.	0.141	0.128	0	0.269
Mother animals > 6 mo.	0.315	0.283	0	0.598
Laying hens < 18 wks.	0.05	0.12	0	0.17
Laying hens > 18 wks.	0.1	0.205	0	0.305
Ducks	0.117	0	0	0.117
Turkeys for slaughter	0.429	0.429	0	0.858
Turkeys < 7 mo.	0.445	0.445	0	0.89
Turkeys > 7 mo.	0.639	0.639	0	1.278
Horses & ponies	3.9	3.6	4.7	12.2
Ewes	0.7	1.28	1.39	3.37
Milch goats	2.3	4.1	0	6.4

Buijsman (1987) used to develop a European NH_3 inventory.

Möller (1989)[9] developed an NH_3 emission inventory in the German Democratic Republic (G.D.R.). He based his work on emission factors developed by Auermann and Meyer (1978)[10] and stated that the emission factors are of the same order as the total emission factors used by Buijsman (1987).

Denmead (1990)[11] developed an NH_3 inventory for Australia. He compared a daily emission factor developed in Australia for sheep (5.8 and 5.2 g N/sheep) with the value used by Buijsman *et al.* (1987) for European sheep (8.5 g N/day). The work of Denmead is not referenced in the work of Asman (1992). This discrepancy in the NH_3 emission factor for sheep is a fairly large one. Inventories in areas that have a large sheep population may want to examine this discrepancy to determine the most applicable factor.

The inventory developed by Asman (1992) and the NH_3 emission factors published by van der Most (1992) reference the research results of De Winkel (1988)[12] and Van der Hoek (1991).[13] Unfortunately, the work of De Winkel (1988) is published only in Dutch and appears to be a primary reference in terms of describing the research methods and the actual derivation of the emission factors.

More recently, additional studies have been published which are not incorporated into the Asman (1992) NH_3 emission factors. In 1987, four experiments were carried out, during a period of 3 weeks in May/June, on a cattle and pig farm in The Netherlands.[14] Small wind-tunnels were used to make direct measurements of NH_3 volatilization from the different types of slurry and manure applied to the surface of grassland. NH_3 was collected at the inlet and outlet of the wind tunnels in absorption flasks containing orthophosphoric acid and emissions were determined by using a modified Berthelot method, as conducted by Krom (1980).[15]

Kirchmann and Witter (1989) analyzed NH_3 volatilization during aerobic and anaerobic poultry manure decomposition.[16] Their analytical method involved the absorption of NH_3 in boric acid and back-titration with carbon dioxide. Total nitrogen was analyzed with the regular Kjeldahl method.

2.2 FACTORS INFLUENCING AMMONIA EMISSIONS FROM ANIMAL HUSBANDRY

There are several factors that have been shown to influence NH_3 emissions from livestock. These factors include:

- Nitrogen content of the feed and its relative share of different amino acids.
- Conversion factor between N in animal food and N in the meat and in the milk (which determines the amount of N waste available).
- Kind of animal and age/weight.

- Housing system.
- The manner in which the manure is stored (pile, open/closed tanks).

There are additional NH_3 emissions after the spreading of manure. Factors influencing these emissions include:

- Meteorological/climatological conditions: temperature, turbulence, air humidity and precipitation. Emissions generally increase with temperature and turbulence, but decrease with air humidity (which slows down the evaporation of water from manure, and leads to a lower concentration of NH_3 in the air, if the components are dissolved in manure) and during and after precipitation periods.
- Irrigation. If a field is irrigated, the manure is diluted and enters the soil at a larger rate, both of which lead to a lower emission.
- Properties of the soil (pH, calcium content, water content, buffer capacity and porosity etc.). The emissions generally increase with increasing pH, calcium content, and porosity, but decrease with increasing buffer capacity and water content.
- Properties of the manure (pH, viscosity, content of dry matter). The emissions generally increase with increasing pH, viscosity and content of dry matter. A high viscosity prevents the manure or fertilizer from entering the soil.
- Amount applied per hectare. The fraction of N in manure which evaporates increases with the amount applied.
- The way of applying the manure or fertilizer. If the manure is injected, a much lower emission results.
- Time between spreading and plowing (for arable land). The emission is generally largest during the first hours after spreading. Ploughing shortly after spreading can reduce the emissions considerably.

If the animals are grazing in the meadows, the manure is not stored, but deposited directly and it is therefore exposed immediately to loss processes other than volatilization of NH_3 to the atmosphere. These processes are uptake by the grass, wetting by precipitation, leading to dilution and penetration of the soil with diluted manure, and nitrification. The NH_3 emission rate during the grazing period is, for this reason, less than if the animals were in the stable, including the contribution during storage and subsequent spreading. The total emission from animals, therefore, depends on the fraction of the time that they are in the meadows.[17]

2.3 NAPAP EMISSION FACTORS FOR ANIMAL HUSBANDRY

The NAPAP NH_3 emission factor report presented emission factors for twelve categories of animal husbandry.[18] None of the recent research conducted in Europe (in either the Netherlands or Great Britain) was included in the development of the NAPAP NH_3 emission factors. In addition, the NAPAP factors were given a quality rating of E (lowest possible).

The 1980 NAPAP emission inventory utilized an NH_3 emission factor for beef cattle feedlots developed in the U.S. in 1977.[19] This emission factor is cited in the current *Compilation of Air Pollutant Emission Factors - Volume I (AP-42)*.[20] The measurement of NH_3 in this study was conducted using 10 ml of dilute sulfuric acid. The NH_3 concentration was measured using nesslerization. A second study of NH_3 emissions from cattle feedlots again used sulfuric acid in the collection of NH_3, and then used the indophenol method and GC analysis of a pentafluorobenzamide derivative of NH_3 to calculate NH_3 emissions. An average of these measurements resulted in the point source emission factor from beef cattle feedlots of 5.9 kg/year/animal (13 lbs/year/animal).

The 1980 NAPAP emission inventory utilized a second set of research results on manure production and characterization data to develop emission factors for land-spreading of livestock and poultry manure. Ammonia content of four types of animal manure (dairy cows, beef cattle, swine, and poultry) was measured in different waste management systems (fresh, scraped, slurry, or lagoon). These data were averaged over the various livestock groups and assumptions were made on the relative percentage of solid versus liquid manure that are surface-applied. A second assumption that 75% is surface applied and 25% is injected was made. No information was provided in the NAPAP NH_3 emission factor reports on the laboratory methods utilized in this series of research. This analysis resulted in NH_3 emission factors for cropland spreading of livestock manure.

The 1985 NAPAP emission inventory utilized the beef cattle feedlot emission factor, revised the emission factors for cropland spreading of livestock manure, and developed NH_3 emission factors for range animals. The initial NAPAP NH_3 emission factor for cropland spreading of animal manures was revised to reflect individual NH_4-N contents of manure by livestock category. Previously, an average NH_4-N content was used over all animal types. The factors were also revised to present the emission factors in terms of NH_3 emitted per animal rather that NH_4-N. No information on the analytical methods was provided.

The 1985 NAPAP emission inventory utilized new emission factors for range animals. The range animal emission factors were developed based on 1978 data on typical stocking rates and animal weights for four livestock categories (beef cattle, dairy cattle, sheep, and swine). Emissions were calculated using the cropland spreading factor for confined animals and the range emission factor for the unconfined animals. With the exception of beef cattle feedlots, the NH_3 emissions during the housing of the animals does not appear to be addressed. For beef cattle and swine, the same volatilization rates as were used for cropland spreading were used for range animals. The value used for dairy cattle was based on three data points and was judged to be low. No value was provided for sheep so an average of beef and dairy cattle was used for sheep.

The twelve NAPAP emission factors and the activity data that were utilized in the development of 1985 emission estimates are presented in Table 2-2. Using the 1985 populations for these animal classes allowed for the development of averages for the four major categories (cattle, pigs, poultry, and sheep), for comparison with the European research.

TABLE 2-2. 1985 NAPAP ANIMAL HUSBANDRY EMISSION FACTORS AND ANIMAL POPULATIONS

Animal Category	1982 Population[a]	Emission Factor (lbs/animal/yr)	Emission Factor (kg/animal/yr)
Cattle			
Beef cattle feedlots	2.3×10^7	13.0	5.90
Confined Beef - spreading	6.5×10^6	1.7	0.77
Ranging Beef	2.6×10^7	44.4	20.14
Confined Dairy-spreading	4.5×10^6	27.0	12.25
Ranging Dairy	4.9×10^6	45	20.41
Poultry			
Laying hens	2.9×10^8	0.34	0.15
Broilers	5.0×10^8	0.043	0.02
Turkeys	3.9×10^7	0.29	0.13
Ranging Swine	4.8×10^6	39	17.69
Confined Swine	4.9×10^7	4.3	1.95
Ranging Sheep	1.0×10^7	4.5	2.04
Confined Sheep	1.9×10^6	1.9	0.86

[a] The 1985 estimates are based on 1982 population statistics. The split of confined versus unconfined animals is based on 1978 data.

2.4 COMPARISON OF AMMONIA EMISSION FACTORS FOR ANIMAL HUSBANDRY

Asman (1992) developed average emission factors by dividing the emission of a category by the number of animals in that category. These values were then used for the calculation of NH_3 emissions from animal husbandry for all of Europe. The relative contribution of each subcategory to each category for all European countries is the same as for the Netherlands. Average factors for the 1985 NAPAP inventory can be derived using the published 1985 activity or animal population data and emission factors. Table 2-3 presents averages developed from the Dutch data, from the values utilized by Buijsman (1987) and from the factors published in the NAPAP report.

TABLE 2-3. COMPARISON OF ANIMALS OF HUSBANDRY EMISSION FACTORS (kg NH_3/Animal/Yr)

Animal	Asman (1992)				Buijsman *et al.* (1987)	NAPAP (1990)
	Stable + storage	Spreading	Grazing	Total		
Cattle	7.396	12.244	3.403	23.043	18.	12.6
Swine	2.521[a]	2.836[a]	0	5.357[a]	2.8	3.35
Poultry	0.095	0.154	0	0.249	0.26	0.071
Horses	3.9	3.6	4.7	12.2	9.4	--
Sheep	0.381	0.693	0.623	1.697	3.1	1.85

[a] These composites appear to have been calculated using the incorrect number of swine in the Netherlands and are therefore too low. The correct values are 4.006, 4.506, and 8.512 respectively.

As shown in Table 2-3, the NAPAP emission factors, with the exception of sheep, are significantly lower than the values used by both Asman (1992) and Buijsman (1987). The emission factor for sheep in the NAPAP inventory was derived from an average NH_3 volatilization rate for dairy and beef cattle.

A manuscript by Lee (1994)[21] explores the uncertainties in current NH_3 estimates for the United Kingdom. This manuscript presents a comparison of the NH_3 animal husbandry emission factors recently utilized throughout Europe and the U.S. Table 2-4 presents the comparison made by Lee (1994).

2.5 ANIMAL HUSBANDRY ACTIVITY DATA FOR THE UNITED STATES

The usefulness of the emission factors presented by Asman (1992) in the development of an NH_3 emission inventory are dependent upon the availability of supporting activity data. The U.S. Department of Agriculture (USDA), National Agricultural Statistics Service, maintains annual records at both the national and state levels. These statistics are published in a variety of reports and numerous spreadsheets containing raw data are available through bulletin boards.[†] The following statistics on animal populations were obtained from an

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[†] The USDA National Agricultural Statistics Service (Washington, DC) has a joint project with the Albert Mann Library of Cornell University (Ithica, NY) to maintain the Economics and Statistics system which can be accessed on the internet through the U.S. EPA IBM gopher.

TABLE 2-4. EMISSION FACTORS USED IN DIFFERENT EMISSION INVENTORIES FOR ANIMAL SOURCES OF AMMONIA[a] (kg NH_3 as N/Animal/Year)[b]

Animal	NAPAP[c]	Cass *et al.* (1982)	Kruse *et al.* (1989)	Jarvis & Pain (1990)	Asman (1990)	Buijsman *et al.* (1987)	Möller & Schieferdecker (1989)
Beef cattle	0.63	--	--	--	--	--	--
Dairy cattle	27.0	27.0	19.31	7.8	20.7	14.8	22.1
Pigs	1.6	4.5	2.86	4.35	3.96	2.3	5.2
Sheep	0.7	2.7	2.68	0.36	1.57	2.5	3.0
Laying hens	0.12	0.24	0.233	0.13	0.26	0.21	0.22
Broilers	0.016	0.24	0.233	0.13	0.26	0.21	0.22
Turkeys	0.10	0.66	0.233	--	0.26	0.21	--
Horses	--	33	31.6	--	10.3	7.7	15.0
Cats	--	0.66	--	--	--	--	--
Dogs	--	1.98	--	--	--	--	--

[a] Lee & Dollard, 1994

[b] To convert the units to kg NH_3/Animal/Year, multiply the emission factor by the stoichiometric ratio of N to NH_3, 14/17.

[c] The calculation of the NAPAP average emission factors is not documented by Lee (1994).

annual report on agricultural statistics.[22]

2.5.1 Cattle and Calves

There are eight readily available classifications for cattle and calves for the U.S. In 1992 there were 100 million cattle and calves. The eight classifications, 1992 populations, and the animal classifications currently listed in Asman (1992) are provided in Table 2-5. Additional statistics on the number of cattle and calves on feed[††] in the U.S. indicate that in 1992, approximately 12 percent of the total cattle and calves were on feed. Not all of the calf and cow classifications would have an equal percentage on feed. Additional information is needed prior to utilizing the statistics of cattle and calves on feed to determine the relative distributions of animals in stable + storage versus those animals that are grazing.

As shown in Table 2-5, most of the links between the U.S. agricultural categories for cattle and calves have a corresponding category presented by Asman (1992). The only exceptions is the category of Heifers, 226.8 kg and over. It is unclear if the appropriate category is young cattle, or young cattle for fattening. The assumption is that young cattle for fattening applies to beef cow replacements but not to milk cow replacements or other.

A composite emission factor for cattle and calves is developed using the 1992 cattle and calves populations. The composite factor is 22.9 kg NH_3/animal. This factor is very similar to the composite factor of 23.043 kg NH_3/animal/year developed by Asman (1992) for use in the European inventories.

2.5.2 Hogs and Pigs

Preliminary statistics for 1991 indicate there were 57.7 million hogs and pigs in the United States. The USDA classifies hogs and pigs into six general categories based primarily on animal weight. Table 2-6 lists the six classifications, 1991 populations, and the animal classifications currently listed in Asman (1992). Hogs and pigs are generally not grazing animals.

As shown in Table 2-6, the links between the U.S. agricultural categories and the emission factor categories presented by Asman (1992) are not clear cut. Asman (1992)

[††] Cattle and calves on feed are animals for slaughter market being fed a full ration of grain or other concentrates and are expected to produce a carcass that will grade Select or better.

TABLE 2-5. U.S. AGRICULTURE ACTIVITY CLASSIFICATION AND EMISSION FACTORS FOR CATTLE AND CALVES

U.S. Agricultural Statistics Classifications	1992 Populations (10^6 animals)	Emission Factor Classifications Asman (1992)	Emission Factor (kg NH_3/animal)
Cows and heifers that have calved (Beef cows)	33.8	Dairy & calf cows	39.72
Cows and heifers that have calved (Milk cows)	9.90	Dairy & calf cows	39.72
500 pounds and over: Heifers - Beef cow replacements	5.75	Young cattle for fattening	15.19
500 pounds and over: Heifers - Milk cow replacements	4.20	Young cattle	13.04
500 pounds and over: Heifers - Other	8.68	Young cattle	13.04
500 pounds and over: Steers	16.7	Fattening/grazing cattle > 2 yr	8.22
500 pounds and over: Bulls	2.28	Breeding bulls > 2 yr	27.91
Calves under 500 pounds	18.7	Fattening Calves	5.23
Total	100.		

presents two emission factors for sows based on weight. In the U.S., statistics are presented for hogs and pigs kept for breeding and sows farrowing. In 1991, 7.25 million hogs and pigs were kept for breeding with approximately 6 million sows farrowing. The difference is either immature sows (i.e. < 50 kg) or male pigs kept for breeding. A composite emission factor for hogs and pigs kept for breeding is presented based on the 1991 statistics and the assumption that the 6 million sows farrowing are breeding sows > 50 kg and the remaining 1.25 million hogs and pigs kept for breeding are breeding sows 20-50 kg.

The U.S. also keeps statistics on market hogs by weight groups. Asman (1992) presents three categories but only two emission factors (fattening pigs and boars> 50 kg have the same emission factor). The link between the emission factors and the U.S. agricultural statistics assumes that pigs and hogs under 54 kg are fattening pigs and pigs and hogs over 54 kg are mature boars.

TABLE 2-6. U.S. AGRICULTURE ACTIVITY CLASSIFICATIONS AND EMISSION FACTORS FOR HOGS AND PIGS

U.S. Agricultural Statistics Classifications	1991 Populations (10^6 animals)	Emission Factor Classifications Asman (1992)	Emission Factor (kg NH_3/animal)
Kept for breeding			
Sows farrowing[a]	6.02	Breeding sows > 50 kg	16.13
Other - kept for breeding[b]	1.25	Breeding sows 20-50 kg	5.22
Market hogs by weight groups			
Under 27.2 kilograms	18.7	Fattening pigs	6.98
27.3 to 54.0 kilograms	13.0	Fattening pigs	6.98
54.1 to 81.2 kilograms	10.4	Mature boars	11
81.3 to 99.3 kilograms and 99.4 kilograms and over	8.4	Mature boars	11
Total	57.7		

[a] An average of the sows farrowing in December through May and the sows farrowing in June through November.
[b] Kept for breeding minus sows farrowing.

A composite emission factor for hogs and pigs is developed using the 1991 populations. The composite factor is 9.21 kg NH_3/animal. This factor is higher than the composite factor of 8.512[†††] kg NH_3/animal/year developed by Asman (1992) based on the swine populations in the Netherlands.

2.5.3 Poultry

Poultry includes chickens, ducks, and turkeys although chickens represent the largest source of NH_3 emissions. Chickens in the U.S. are classified into hens, pullets, other chickens and broilers with three subcategories of pullets. It is unclear what the difference is between hens and pullets. Asman (1992) presents emission factors for mother animals, laying hens, and broilers. It is also unclear what the difference is between mother animals and laying hens. Asman (1992) also presents an emission factor for ducks and two factors for turkeys based on age. The U.S. has statistics on turkeys (with no distinction in age) but does not keep statistics on ducks.

[†††] There was a mathematical error in the composites presented by Asman (1992). The value of 8.512 kg NH_3/animal/year was calculated directly from animal populations and emission factors presented by Asman (1992).

Table 2-7 illustrates the readily available agricultural classifications, latest population estimates, and the link to the emission factors of Asman (1992). As mentioned above there is some ambiguity in the distinctions between hens, pullets, mother animals, and laying hens as used by Asman (1992) and the U.S. Department of Agriculture, however the populations (and consequently the emissions) of hens and pullets is dwarfed by the population of broilers. A composite emission factor for chickens was developed based on the links provided in Table 2-7 and the 1991 population statistics. The composite emission factor of 0.179 kg NH_3/animal/year is also recommended for use in the other chickens category.

2.5.4 Sheep and Lambs

There were 10.85 million sheep and lambs in the U.S. in 1991. The five classifications for sheep and lambs in the Agriculture statistics are:

- sheep and lambs on feed
- stock sheep - lambs - ewes
- stock sheep - lambs - wethers and rams
- stock sheep - 1 year and over - ewes
- stock sheep - 1 year and over - wethers and rams

Asman (1992) presents one set of emission factors for ewes and these are recommended for use for all categories of sheep and lambs in the U.S.

2.6 AMMONIA EMISSION FACTORS FOR MISCELLANEOUS ANIMAL CATEGORIES

In addition to the more common animals presented above, emission factors have been developed for three animal types that are bred for fur (foxes and mink) or for meat and fur (rabbits). These emission factors were estimated by van der Hoek but apparently have not been published in any sources other than Erisman (1989). In addition, Erisman (1989) uses data developed by Cass (1982)[23] to estimate NH_3 emissions from domestic cats and dogs. The emission factors for these miscellaneous types of animals are listed in Table 2-8.

In the USDA agricultural statistics there were 3.27 million mink pelts produced in 1991. Statistics were not readily available for fox, rabbit, cats or dogs.

2.7 RECOMMENDED ANIMAL HUSBANDRY EMISSION FACTORS AND SOURCE CLASSIFICATION CODES

National inventories developed in the United States utilize source classification codes (SCCs) to describe point source emissions and area and mobile source (AMS) codes to describe area source emission categories. Although there are point source SCCs for beef cattle feedlots, the emission factors recommended for use in this section are for area source categories.

TABLE 2-7. U.S. AGRICULTURE ACTIVITY CLASSIFICATION AND EMISSION FACTORS FOR POULTRY

U.S. Agricultural Statistics Classifications	1991 Populations (10^6 animals)	Emission Factor Classifications Asman (1992)	Emission Factor (kg NH_3/animal)
Hens	116	Mother animals > 6 mo.	0.598
Pullets - Of laying age	162	Laying hens > 18 wk.	0.305
Pullets - 3 months old and older not of laying age	33.5	Mother animals < 6 mo.	0.269
Pullets - Under 3 months old	40.8	Laying hens < 18 wk.	0.17
Other chickens	6.85	Composite factor for chickens	0.179
Broilers	6,138	Broilers	0.167
Ducks	20.0[a]	Ducks	0.117
Turkeys	285[b]	Turkeys for slaughter	0.858
		Turkeys < 7 mo.	0.89
		Turkeys > 7 mo.	1.278

[a] The number of ducks reported are the number of ducks inspected in 1991. The number of ducks inspected is a conservative estimate and is smaller than the actual population of ducks.
[b] There is no breakdown on the population of turkeys based on age.

Table 2-9 shows recommended emission factors for animal husbandry. We have recommended use of the latest European emission factors (Asman, 1992) for the animal husbandry categories. The emission factor ratings for Cattle and Calves, Hogs and Pigs, and Poultry range between B and C. The emission factors presented by Asman (1992) represent a large body of literature, however, there are many factors influencing NH_3 emissions from animals and because many of the primary references are in foreign languages, it is not clear that the database represents a good cross section of the U.S. agricultural practices. The emission factors presented by Asman (1992) are therefore assigned a B rating.

The emission factors presented by Asman (1992) are linked to animal husbandry categories reported by the United States Department of Agriculture. Although the best information available was used to link the emission factors to the activity data, additional uncertainty is introduced in this process and therefore, some of the animal husbandry emission factors are given a rating of C to reflect the uncertainty of the link. This uncertainty could be reduced with additional research into the primary references from which the data are

TABLE 2-8. AMMONIA EMISSION FACTORS FOR MISCELLANEOUS ANIMALS ($\mathbf{kg\ NH_3/Animal/Year}$).

Animal	Stable + storage	Spreading	Total
Mink	0.58	0	0.58
Fox[a]	2.25	0	2.25
Rabbit	1	1.8	2.8
Cats			0.83
Dogs			2.5

[a] Weighted average for blue-foxes (2/3) and silver foxes (1/3).

extracted. In addition, there is a large discrepancy in the factor for sheep and lambs that was presented by Asman (1992) for Europe and the value that was presented by Denmead (1990) for Australia. Therefore, the emission factor rating for sheep is currently D.

The emission factors for the miscellaneous animal categories including mink, fox, rabbit, dogs and cats are all given an E rating due to the small size of the data sets used to derive these factors.

TABLE 2-9. RECOMMENDED AMMONIA EMISSION FACTORS FOR ANIMAL HUSBANDRY

Source (U.S. Agricultural Statistics Classifications)	AMS Classification Codes	1991 Populations (10^6 animals)	Emission Factor Classifications (Asman, 1992)	Emission Factor (kg NH_3/animal)	Factor Rating	Emission Factor (lb NH_3/animal)	Estimated emissions (Gg/year)
Cattle and Calves - Composite	28-05-020-000	100		22.9	B	50.5	2,290
Cows and heifers that have calved (Beef cows)	28-05-020-001	33.8	Dairy & calf cows	39.72	B	87.57	1,342
Cows and heifers that have calved (Milk cows)	28-05-020-002	9.90	Dairy & calf cows	39.72	B	87.57	393
226.8 kg (500 pounds) and over: Heifers - Beef cow replacements	28-05-020-003	5.75	Young cattle for fattening	15.19	B	33.49	87
226.8 kg (500 pounds) and over: Heifers - Milk cow replacements	28-05-020-004	4.20	Young cattle	13.04	C	28.75	55
226.8 kg (500 pounds) and over: Heifers - Other	28-05-020-005	8.68	Young cattle	13.04	B	28.75	113
226.8 kg (500 pounds) and over: Steers	28-05-020-006	16.7	Fattening/grazing cattle > 2 yr	8.22	C	18.12	137
226.8 kg (500 pounds) and over: Bulls	28-05-020-007	2.28	Breeding bulls > 2 yr	27.91	C	61.53	64
Calves under 226.8 kg (500 pounds)	28-05-020-008	18.7	Fattening Calves	5.23	B	11.53	98
Hogs and Pigs - Composite	28-05-025-000	57.75		9.21	B	20.30	531
Kept for breeding	28-05-025-010	7.25					
Sows farrowing	28-05-025-011	6.02	Breeding sows > 50 kg.	16.13	B	35.56	97.1
Other - kept for breeding	28-05-025-012	1.23	Breeding sows 20-50 kg	5.22	C	11.5	6.52
Market hogs by weight groups	28-05-025-020						
Under 27.2 kg (60 pounds)	28-05-025-021	18.7	Fattening pigs	6.98	B	15.4	131
27.2 to 54.0 kg (60 to 119 pounds)	28-05-025-022	13.0	Fattening pigs	6.98	C	15.4	90.7

(Continued)

TABLE 2-9 (Continued)

Source (U.S. Agricultural Statistics Classifications)	AMS Classification Codes	1991 Populations (10^6 animals)	Emission Factor Classifications (Asman, 1992)	Emission Factor (kg NH_3/animal)	Factor Rating	Emission Factor (lb NH_3/animal)	Estimated emissions (Gg/year)
54.1 to 81.2 kg (120 to 179 pounds)	28-05-025-023	10.4	Mature boars	11	B	24.3	114
81.3 to 99.3 kg and 99.4 kg (180 pounds) and over	28-05-025-024	8.4	Mature boars	11	B	24.3	92
Poultry - Chickens - Composite	28-05-030-000	6,497		.1787	B		1,161
Hens	28-05-030-001	116	Mother animals > 6 mo.	0.598	B	1.32	69.4
Pullets - Of laying age	28-05-030-002	162	Laying hens > 18 wk.	0.305	B	.672	49.4
Pullets - 3 months old and older not of laying age	28-05-030-003	33.5	Mother animals < 6 mo.	0.269	C	.593	9.01
Pullets - Under 3 months old	28-05-030-004	40.8	Laying hens < 18 wk.	0.17	B	.375	6.94
Other chickens	28-05-030-005	6.85		0.179	C	.395	1.23
Broilers	28-05-030-006	6,138	Broilers	0.167	B	.368	1,025
Poultry - Other	28-05-035-000						247.3
Ducks	28-05-035-001	20.0	Ducks	0.117	B	.258	2.34
Turkeys	28-05-035-002	285	Turkeys for slaughter	0.858	B	1.89	245
Young turkeys	28-05-035-003		Turkeys < 7 mo.	0.89	B	1.96	
Old turkey	28-05-035-004		Turkeys > 7 mo.	1.278	B	2.82	
Fryer-roasted turkey	28-05-035-005		Turkeys for slaughter	0.858	C	1.89	
Sheep and Lambs - Composite	28-05-040-000	10.85	Ewes	3.37	D	7.43	36.56
Sheep and lambs on feed	28-05-040-001		Ewes	3.37	D		
Stock sheep-lambs-ewes	28-05-040-002		Ewes	3.37	D		
Stock sheep-lambs-wethers and rams	28-05-040-003		Ewes	3.37	D		
Stock sheep- 1 yr. and over-ewes	28-05-040-004		Ewes	3.37	D		

(Continued)

TABLE 2-9 (Continued)

Source (U.S. Agricultural Statistics Classifications)	AMS Classification Codes	1991 Populations (10^6 animals)	Emission Factor Classifications (Asman, 1992)	Emission Factor (kg NH_3/animal)	Factor Rating	Emission Factor (lb NH_3/animal)	Estimated emissions (Gg/year)
Stock sheep- 1 yr. and over-wethers and rams	28-05-040-005		Ewes	3.37	D		
Miscellaneous Farm Animals	28-05-045-000						
Goats	28-05-045-001		Milch goats	6.4	E	14.1	
Mink	28-05-045-002	3.27	Mink	0.58	E	1.28	1.90
Fox	28-05-045-003		Fox	2.25	E	4.96	
Rabbit	28-05-045-004		Rabbit	2.8	E	6.2	
Miscellaneous Domestic Animals	27-10-020-000						
Cats	27-10-020-010		Cats	0.83	E	1.83	
Dogs	27-10-020-020		Dogs	2.5	E	5.5	
Horses	27-10-020-030		Horses & ponies	12.2	E	26.9	

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SECTION 3

AMMONIA EMISSIONS FROM FERTILIZER APPLICATION

Nitrogen fertilizers are extremely important to agriculture in the United States. Of the 49 million tons of commercial fertilizer consumed in the U.S. in 1993, 39 million tons contained nitrogen, either as a single nutrient, or mixed with other nutrients such as phosphorus and potassium. The total nitrogen content of U.S. fertilizers in 1993 was about 8 Teragrams.[1] Many different chemical compounds are used to provide nitrogen in fertilizer, including ammonia, urea ($(NH_2)_2CO$), ammonium nitrate (NH_4NO_3), mono- and di-ammonium phosphates ($(NH_4)H_2PO_4$ and $(NH_4)_2HPO_4$), ammonium sulfate ($(NH_4)SO_4$), ammonium thiosulfate ($(NH_4)HSO_4$), potassium nitrate (KNO_3), calcium nitrate ($Ca(NO_3)_2$), and sodium nitrate ($NaNO_3$). Table 3-1 summarizes the national application rates and nitrogen contents for different nitrogen fertilizers.

Most of the compounds listed in Table 3-1 (with the exception of potassium nitrate, calcium nitrate, and sodium nitrate) can decompose to release NH_3 after they are applied to croplands. This is commonly termed "ammonia volatilization," and is quantified based on the percentage of nitrogen in the applied fertilizer that is lost to the air in the form of NH_3. In the case of urea, NH_3 volatilization can be a significant economic concern.[2] Nitrogen losses of 50 percent and more can occur with improper application conditions.

The 1985 NAPAP emissions inventory addressed NH_3 volatilization from only one type of nitrogen fertilizer, anhydrous NH_3.[3] Thus NH_3 emissions from fertilizer application accounted for only 46,382 Mg, or about 3 percent of 1985 NAPAP NH_3 emissions. In contrast, volatilization from fertilizer application accounts for about 17 percent of NH_3 emissions in recent European NH_3 emission inventories.[4] The following sections discuss the emission factors used in Europe, as well as recent research on NH_3 volatilization in the U.S. and Europe.

3.1 EUROPEAN EMISSION FACTORS

Buijsman *et al* of the Netherlands, prepared a detailed NH_3 emission inventory for Europe in 1986 (published in 1987), which included emissions from the application of most major nitrogen fertilizers.[5] Ammonia volatilization factors for these fertilizers were deduced from several sources, published in the 1970’s and early 1980’s. Sources used by Buijsman *et al* (1987) included Terman (1979),[6] Fenn and Kissel (1974),[7] Fenn *et al* (1981),[8] Fenn and Miyamoto (1981),[9] the U.S. National Research Council (1978),[10] Forster and Lippold (1975),[11] Cass *et al* (1982),[12] Bottger *et al* (1978),[13] Slemr and Seiler (1984),[14] and Sanders (1980).[15]

Another detailed NH_3 emission inventory for Europe was prepared by Asman (1992) at the Netherlands’ National Institute for Public Health and Environmental Protection. Asman

TABLE 3-1. SUMMARY OF U.S. NITROGEN FERTILIZER USAGE

	Fertilizer consumed, year ending 6/30/93 (Mg)	Nitrogen content (weight percent)	Total N content (Mg)
Anhydrous ammonia	3,593,380	82.0	2,946,572
Aqua ammonia	271,288	20.4	55,343
Nitrogen solutions	7,162,419	33.9	2,428,060
Urea	3,247,631	45.9	1,490,663
Ammonium nitrate	1,582,039	33.9	536,310
Ammonium sulfate	718,400	21.0	150,864
Ammonium thiosulfate	156,047	12.0	18,726
Potassium nitrate	702,378	15.1	106,059
Calcium nitrate	70,659	13.7	9,680
Sodium nitrate	43,993	16.0	7,039
Other straight nitrogen	944,803	20.0	188,960
Ammonium phosphates	5,813,042	15.5	901,022
N-P-K[a]	8,191,414	11.2	917,439
Total	32,497,492	30.0	9,756,736

[a] Nitrogen(N)-phosphorus(P)-potassium(K) mixtures.

updated Buijsman's emission factors for fertilizer application using more recent laboratory measurements by Whitehead and Raistrick (1990).[16] These updated factors were also included in the Netherlands' 1992 Emission Factors Manual.[17] Asman's factors are generally somewhat lower than the factors used by Buijsman.

Table 3-2 summarizes the NH_3 emission factors adopted by Buijsman (1987), and later adopted by Asman (1992) for fertilizer application. For comparison, the NAPAP emission factor for anhydrous NH_3 is also presented.[3]

TABLE 3-2. SUMMARY OF EUROPEAN EMISSION FACTORS FOR FERTILIZER APPLICATION

	Emission factors (kg NH_3/Mg nitrogen)		
	Buijsman (1987)[a]	Asman (1992)[a]	NAPAP (1990)
Anhydrous ammonia	121	12	12
Aqua ammonia	121	12	b
Nitrogen solutions	b	30	b
Urea	121	187	b
Ammonium nitrate	121	25	b
Ammonium sulfate	182	97	b
Ammonium thiosulfate	b	30	b
Other straight nitrogen	b	30	b
N-P-K	12	48	b
Ammonium phosphates	60	48	b

[a] Buijsman and Asman expressed ammonia volatilization in terms of percent, or grams of nitrogen emitted as ammonia per 100 grams of nitrogen in the fertilizer.
[b] No emission factor was used for the noted category.

3.2 RECENT VOLATILIZATION RESEARCH

A good deal of research on NH_3 volatilization has been carried out since the development of the European emission factors discussed above. This research is motivated mainly by the economic impact of the NH_3 losses, with a focus on application parameters that might aggravate or reduce potential volatilization losses. Table 3-3 summarizes the results of recent volatilization studies. For each study, the table gives the lowest measured NH_3 volatilization rate (expressed in terms of mole-percent of nitrogen), the highest measured rate, and the average for the study. The average value is also converted to an emission factor, in kilograms of NH_3 per Megagram of nitrogen in the fertilizer.

Table 3-3 also gives the applicable European emission factors for comparison. In compiling the volatilization studies, we have focused on tests carried out since 1985. The European emission factor work (carried out in 1986 and 1992) included a fairly thorough survey of prior work.

TABLE 3-3. SUMMARY OF RECENT MEASUREMENTS OF AMMONIA VOLATILIZATION FROM FERTILIZER

Study	Conditions	Percent of nitrogen lost as NH_3			Average emission factor (kg/Mg N)
		Minimum	Maximum	Average	
UREA					
European Emission Factors[a]					
Buijsman (1987)		na	na	10.0	122
Asman (1992)		na	na	15.0	182
Test results - urea on soil					
Shahandeh et al (1992)	Solution, lab	13	19	16.1	196
Watson et al (1992)	Solution, field	4.7	12	8.5	103
Watson et al (1992)	Solid, field	3.4	9.1	5.6	68
Al-Kanani, et al (1991)	Solution, lab	2.8	55	30.8	374
Ali and Stroehlein (1991)	Solution, lab	1.5	23	6.7	82
Ali and Stroehlein (1991)	Solid, lab	2.3	17	6.7	82
Ismail, et al (1991)	Solution, lab	0	59	9.4	114
Burch and Fox (1989)	Solid, field	4.5	40	19.5	237
Burch and Fox (1989)	Solid, lab	18	31	24.5	298
McInnes, et al (1986)	Solution, field	4	17	11.0	134
Average				13.9	169
Test results - urea mixtures on soil					
Ali and Stroehlein (1991)	UP[b] solution, lab	0.83	3.3	1.0	12
Al-Kanani, et al (1991)	UAN[b] solution, lab	0.3	19	10.7	130
Al-Kanani and MacKenzie (1991)	UAN[b] solution, field	2	8.5	5.0	61
Average for UAN[b]				7.9	95
Test results - urea on flooded paddies					
DeDatta, et al (1991)	Field	46	54	50.0	607
Bouldin et al (1991)	Lab	4	40	20.0	243
Average				35.0	425
AMMONIUM SULFATE					
European Emission Factors					
Buijsman (1987)		na	na	15.0	182
Asman (1992)		na	na	8.0	
Test Results					
Shahandeh et al (1992)	Solution on soil, lab	0.2	1	0.6	8
Jayaweera and Mikkelson (1990)	Flooded paddy, lab	9	50	15.5	188
Burch and Fox (1989)[c]	Solid on soil, field	14	17	15.0	182

[a] The emission factors presented by Buijsman and Asman are based on data gathered through about 1985, and therefore do not incorporate the test results presented in the balance of this table.

[b] UP = Urea phosphoric acid, UAN = urea-ammonium nitrate.

[b] Higher than expected, may be due to dust erosion.

3.2.1 Urea Applied to Soils

As Table 3-3 shows, urea has been a particular focus of research, because it is more susceptible to NH_3 volatilization than are other fertilizers. It is also the largest volume and fastest growing nitrogen fertilizer worldwide, with consumption increasing at 5 to 6 percent per year (Bock & Kissel, 1988). We identified seven recent studies of NH_3 losses from urea applied to soils. Some of these used urea in solution form, some used solid urea, and some assessed both solutions and solids.

These studies showed a substantial variability in NH_3 volatilization, with NH_3 nitrogen losses ranging from 0 to 60 percent. On average, the studies show a nitrogen volatilization rate of about 14 percent. (That is, 14 percent of the nitrogen in the urea is lost to the air as NH_3.) This agrees well with the 1992 European emission factor of 15 percent.

The urea studies in Table 3-3 quantified impacts of several parameters on the NH_3 volatilization rate. These parameters include soil moisture content, pH, soil carbonate content, temperature, and depth of tilling, with the specific parameters varying from study to study. The most consistent findings were related to soil moisture content. Al-Kanani *et al* (1991),[18] Ismail *et al* (1991),[19] Burch and Fox (1989),[20] and McInnes *et al*[21] all showed increases in NH_3 volatilization with increased soil moisture content. High soil moisture enhances the hydrolysis of urea ($(NH_2)_2CO$) to ammonium carbonate ($(NH_4)_2CO_3$), which can evaporate as NH_3 and carbon dioxide.

Ismail *et al* (1991) developed a multiple regression model relating NH_3 volatilization from urea to soil temperature, pH, urea application rate, and depth of tilling. The model is as follows:

$$\begin{aligned}ER = \exp[&-0.935 - 0.0417\,T + 0.57\,pH + 0.00367\,R + 0.178\,MC - 0.445\,D \\ &+ 0.00154\,T^2 - 0.00739\,(MC)^2 + 0.0285\,D^2 - 0.000378\,(R)(D)] - 11\end{aligned}$$

where:

ER = NH_3 emissions (kilograms NH_3 per hectare per fertilizer application)

T = soil temperature (°C)

MC = initial soil moisture content (percent by weight)

pH = soil pH

R = rate of fertilizer application (kg nitrogen per hectare per application)

D = application depth (centimeters)

The Tennessee Valley Authority (Bock & Kissel, 1988), and Rachhpal and Nye[22,23] have also both developed computer models of NH_3 volatilization from urea applied to soils.

The studies of pure urea show no significant difference between urea applied in solid form (with 14.1 percent nitrogen loss) and urea applied as solution (13.7 percent). In addition, two studies of urea-ammonium nitrate (UAN) solutions applied to soils (Al-Kanani *et al* [1991], and Al-Kanani and MacKenzie [1991][24]) gave an average NH_3 loss close to that of pure urea. However, Ali and Stroehlein (1991) found that mixing urea with phosphoric acid substantially reduced NH_3 emissions by reducing pH and slowing urea hydrolysis.[25]

The sampling and analytical methods used to quantify NH_3 losses varied somewhat. Most of the investigators studied NH_3 emissions from soil placed in a container under controlled laboratory conditions. The containers were generally swept with clean, moist air at a controlled rate. Other investigators studied emissions in the field under various conditions.

Watson (1992)[26] made field tests using an emission isolation flux chamber. Ammonia vapors in the flux chamber outlet were captured in a phosphoric acid (H_3PO_4) impinger, and NH_3 concentrations were quantified using flow injection. McInnes *et al* (1986) made field tests without using an isolation chamber. In this case, the atmospheric NH_3 concentration and wind speed were measured at several heights above the soil. The NH_3 flux was determined by mass transfer calculations using a vertical concentration gradient. Ammonia in the ambient air was captured in a sulfuric acid (H_2SO_4) impinger and was quantified using colorimetry.

Ali and Strohlein (1991) made laboratory tests, capturing NH_3 vapors in a sulfuric acid impinger, and analyzing the NH_3 concentration by using a micro-Kjeldahl distillation procedure. The flowrate through the soil container was 15 volume changes per hour. Al-Kanani *et al* (1991), Ismail *et al* (1991), and Burch and Fox (1989) all used similar analytical procedures for laboratory soil containers. Ammonia vapors were captured in boric acid (H_3BO_3) impingers, and NH_3 concentrations were quantified by back-titration with sulfuric acid (H_2SO_4). The container purge rates varied, with Al-Kanani operating at 30 air changes per minute, Ismail at 15 changes per minute, and Burch and Fox at 20 changes per minute. However, all of these purge rates are high enough so that NH_3 build-up in the sample container would not have been a rate limiting factor.

Shahandeh (1992)[27] captured NH_3 vapor in a polyurethane sponge soaked in a phosphoric acid, glycerine solution; and quantified the NH_3 concentration using colorimetry. In these experiments, the sponge was placed in the lid of a container of soil, with no forced air flow through the container.

In general, the sponge capture technique with no forced air flow (Shahandeh) would probably result in lower measured NH_3 emissions than the forced flow techniques. In addition, O'Halloran (1993)[28] compared boric acid impingers with sulfuric acid impingers, and concluded that the boric acid appeared to trap less NH_3. However, these differences between capture techniques appear to be small in comparison with the variations caused by other parameters, such as soil moisture and soil pH.

3.2.2 Urea Applied to Flooded Paddies

DeDatta *et al* (1991)[29] measured NH_3 emissions from urea applied to flooded rice paddies. He measured NH_3 concentrations and wind speeds at different heights above the paddy, and calculated NH_3 flux from the vertical concentration gradient. Bouldin *et al* (1991)[30] compiled NH_3 emissions data from previous studies of urea used on rice paddies. DeDatta and Bouldin found average volatilization rates of 20 to 50 percent, which are substantially higher than rates for urea applied to unflooded soils.

3.2.3 Ammonium Sulfate

Three recent studies addressed NH_3 volatilization from ammonium sulfate. Shahandeh *et al* (1992) studied ammonium sulfate solution applied to soil in the laboratory and obtained a very low NH_3 volatilization rate. Only about 1 percent of the nitrogen was volatilized when the ammonium sulfate solution was applied. Shahandeh technique (discussed further under "Urea Applied to Soil") involved capturing NH_3 in a saturated sponge, with no forced air flow through the soil container. The low measured emission rate may in some part be due to the absence of air flow in the container.

Burch and Fox (1989)[21] found a substantially higher rate, about 15 percent, in a field study. However, they indicated that this loss was higher than expected and may be at least partially attributable to wind erosion.

Jayaweera and Mikkelson (1990)[31] developed a mathematical model of NH_3 emissions from a flooded paddy treated with ammonium sulfate. The model took into account pH, temperature, application rate, and wind speed. The predicted loss rate under typical conditions was about 15.5 percent of the applied nitrogen.

The average of the rates determined in the studies by Shahandeh, Burch and Fox, and Jayaweera and Mikkelson agrees reasonably well with the emission factor used by Asman (1992). However, the variability among the three studies is so large that any conclusion is uncertain.

3.3 SUMMARY OF PARAMETERS AFFECTING AMMONIA EMISSIONS

In both the European inventory efforts described above, the investigators noted a high level of variability in NH_3 emissions from fertilizer application. Emission measurements made since the compilation of these inventories continue to exhibit this variability (Table 3-3). Emissions depend on several parameters in a complex manner; however, some general correlations can be drawn:[5,6]

- Under comparable circumstances, NH_3 emissions from ammonium (NH_4^+) fertilizers can be ranked as follows: ammonium sulfate > ammonium nitrate > ammonium phosphate[6]

- Ammonia losses increase with increasing pH, but decrease with increasing soil cation exchange capacity[6]

- Ammonia losses are reduced if the fertilizers are incorporated into the soil, with the exception of urea. This is because urea must be hydrolyzed before NH_3 is released. The hydrolysis reaction generally depends on the enzyme urease, which is found in organic matter in the soil.[5,6]

- For acid soils, irrigation or rain following fertilizer application generally reduces NH_3 losses. Again, the situation is somewhat more complex for urea, because increased soil moisture promotes hydrolysis, which increases NH_3 emissions from urea based fertilizers.

- Ammonia losses are higher when soil with a high moisture content is subjected to "drying conditions," such as wind or high temperatures.

3.4 AVAILABILITY OF ACTIVITY DATA

Information on the application of nitrogen fertilizers is routinely compiled by a number of groups, because of the importance of these fertilizers to agriculture in the U.S. and in the world as a whole. Table 3-4 summarizes available activity data. The Tennessee Valley Authority compiles detailed annual, State-level data on the application of nitrogen fertilizers.[1] The U.S. Department of Agriculture compiles similar data.

The Census of Agriculture compiles county-level data on total agricultural chemical usage, and on the acreage devoted to various crops.[32] Many agricultural States compile county data on the application of specific fertilizers, including nitrogen fertilizers. Some States also compile data on fertilizer application by month.[33]

3.5 RECOMMENDED NH_3 EMISSION FACTORS

Table 3-5 shows recommended NH_3 emission factors for fertilizer application. For comparison, the NAPAP emission factor for anhydrous NH_3 is also presented. In addition, the latest available national activities are given and annual NH_3 emissions are estimated. Total annual NH_3 emissions from fertilizer application are estimated at over 550,000 Mg.

We have recommended use of the latest European emission factors (Asman, 1992) for all nitrogen fertilizers. As noted above, extensive recent measurements of NH_3 emissions from urea application yield essentially no change from the latest European factor. For ammonium sulfate, the results of recent measurements were too widely varied to draw any

TABLE 3-4. ACTIVITY DATA AVAILABLE FOR FERTILIZER APPLICATION

Source	**Information available**	**Spatial resolution**	**Temporal resolution**
TVA, and U.S. Department of Agriculture	Application rates for individual nitrogen fertilizers	State	Annual
Census of Agriculture	Overall agricultural chemical usage	County	na
	Acreage devoted to individual crops	County	na
State Agriculture Departments	Application rates for individual nitrogen fertilizers	County	Annual
	Overall fertilizer application (temporal information)	State	Month

firm conclusions. For the remaining nitrogen fertilizers, no recent studies were identified to update or improve on the European factors.

The emission factor for urea application is assigned a quality rating of "B." The data base for urea is large, but because of the high degree of variability it is not clear that it represents a good cross section of the source category. The emission factors for other nitrogen fertilizers are ranked "C," in that the database consists of a few good sources [the two European compilations by (Asman, 1992) and (Buijsman, 1987)].

In addition to the emission factors given in Table 3-5, a number of models have been developed for NH_3 losses from urea fertilizer. These relate NH_3 losses to parameters such as soil temperature, pH, application rate, and depth of tilling. One of these models, a multiple regression model by Ismail *et al* (1991), has been reproduced in Section 3.2.1. In addition, the Tennessee Valley Authority (Bock & Kissel, 1988), and Rachhpal and Nye (1986 & 1991) have both developed computer models of NH_3 volatilization from urea applied to soils.

TABLE 3-5. RECOMMENDED AMMONIA EMISSION FACTORS FROM FERTILIZER APPLICATION

Description	AMS code	Emission factor (kg NH_3/Mg N)	Factor rating	Emission factor (lb NH_3/ton N)	Estimated annual emissions (Mg)
Anhydrous ammonia	28-01-700-001	12	C	24	35,353
Aqua ammonia	28-01-700-002	12	C	24	664
Nitrogen solutions	28-01-700-003	30	C	61	74,042
Urea	28-01-700-004	182	B	364	271,250
Ammonium nitrate	28-01-700-005	25	C	49	13,137
Ammonium sulfate	28-01-700-006	97	C	194	14,631
Ammonium thiosulfate	28-01-700-007	30	C	61	571
Other straight nitrogen	28-01-700-008	30	C	61	5,763
Ammonium phosphates	28-01-700-009	48	C	97	44,487
N-P-K[b]	28-01-700-010	48	C	97	43,692
Total					503,590

[a] No factor was developed for the noted category.
[b] Nitrogen(N)-phosphorus(P)-potassium(K) mixtures.

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SECTION 4

AMMONIA EMISSIONS IN INDUSTRY

4.1 CATEGORIES INCLUDED IN THE 1985 NAPAP INVENTORY

The 1985 NAPAP inventory included the following six industrial categories for which NH_3 emission factors were developed:

- Ammonium Nitrate Production
- Ammonia Synthesis
- Urea Manufacture
- Ammonium Phosphate Manufacture
- Petroleum Refineries
- Coke Manufacture

A research and development study report, prepared for NAPAP in 1990, identified and compared emissions factors developed by NAPAP with emissions factors developed by others.[1] The report recommended emission factors for inclusion in the 1985 NAPAP Emissions Inventory. In general, the NAPAP NH_3 emission factors for industrial sources were the same factors as those presented in the U.S. EPA emission factor manual AP-42.[2]

The U.S. EPA has recently updated the emission factor manual AP-42. The fifth edition of AP-42 has revised sections for ammonium nitrate production, NH_3 synthesis, urea manufacture, and ammonium phosphate manufacture. The revised sections present changes to the emission factors and the quality rating associated with the factors from both the earlier AP-42 sections and the NAPAP NH_3 emission factors. For all six of the industrial categories listed above, the AP-42 factors are recommended for use in future NH_3 inventory development efforts. Table 4-1 presents the NH_3 emission factors from the latest version of AP-42.

4.2 ADDITIONAL SOURCES OF AMMONIA EMISSIONS

Several industrial sources of NH_3 emissions were identified in the current study, which had not been included in the 1985 NAPAP inventory or in other previous NH_3 emissions inventories. The sources and methods used to identify these additional sources included:

- EPA's Toxics Release Inventory System (TRIS) data base
- The California "hot spot" air toxics emissions inventory
- Contacts with State agencies
- Literature on industrial users of ammonia

TABLE 4-1. SUMMARY OF INDUSTRIAL AMMONIA EMISSION FACTORS

Source	Point Source SCC[a]	Emission Factor (kg/unit)	Units	Emission Factor Rating[b]	Emission Factor (lb emitted/ SCC unit)[c]	1985 Emissions (kg/yr)[d]
Ammonium Nitrate Manufacture[e]						
Neutralizer	3-01-027-04 3-01-027-11 3-01-027-21	0.43-18.0	Mg of product	B	0.86-36.0	8,082 9,898 3,665
Evaporation/concentration	3-01-027-17 3-01-027-27	0.27-16.7	Mg of product	A	0.54-33.4	2,225 1,237
Solids Formation Operations						
high density prill towers	3-01-027-12	28.6	Mg of product	A	57.2	30,955
low density prill towers	3-01-027-22	0.13	Mg of product	A	0.26	38
rotary drum granulators	3-01-027-07	29.7	Mg of product	A	59.4	1,819
pan granulators	3-01-027-08	0.07	Mg of product	A	0.14	f
Coolers and dryers[g]						
high density prill coolers	3-01-027-14	0.02	Mg of product	A	0.04	7.3
low density prill coolers	3-02-027-23	0.15	Mg of product	A	0.30	0
low density prill dryers	3-01-027-25	0-1.59	Mg of product	A	0-3.18	52.6
Petroleum Refineries						
FCC units	3-06-002-01	0.155	10^3 liters fresh feed	B	54	19,411
TCC units (moving bed catalytic cracking units)	3-06-003-01	0.017	10^3 liters fresh feed	B	6	24
Reciprocating engine compressors	h	3.2	10^3 m^3 gas burned	B	0.2	h

(Continued)

TABLE 4-1 (Continued)

Source	Point Source SCC[a]	Emission Factor (kg/unit)	Units	Emission Factor Rating[b]	Emission Factor (lb emitted/ SCC unit)[c]	1985 Emissions (kg/yr)[d]
NH_3 Synthesis						
Carbon dioxide regeneration	3-01-003-08	1.0	Mg of product	E	2.0	2,221
Condensate steam stripping	3-01-003-09	1.1	Mg of product	E	2.2	1,571
Urea Manufacture						
Solution formation/concentration	3-01-040-02	9.23[i]	Mg of product	A	18.46[i]	20,014
Solids formation						
nonfluidized bed prilling						
agricultural grade[j]	3-01-040-08	0.43	Mg of product	A	0.87	0
fluidized bed prilling[k]				A		
agricultural grade	3-01-040-10	1.46	Mg of product		2.91	340
feed grade	3-01-040-11	2.07[l]	Mg of product	A	4.14[l]	9.5
drum granulation	3-01-040-04	1.07[m]	Mg of product	A	2.15[m]	1,314
rotary drum cooler	3-01-040-12	0.0256	Mg of product	A	0.051	.045
Coke Manufacture[n]						
Wet coal oven charging - Larry car	3-03-003-02	0.01	Mg coal charged	D	0.02	162
Door leaks	3-03-003-08	0.03	Mg coal charged	D	0.06	293
Coke pushing	3-03-003-03	0.05	Mg coal charged	D	0.1	618.7
Ammonium Phosphate Manufacture	3-01-030[o]	0.07	Mg P_2O_5 produced	E	0.14	259

[a] Refers to SCCs that were in the 1985 NAPAP Emission Inventory.

[b] See Appendix A of this report for a definition of the ratings.

[c] All factors chosen are from *AP-42*.

(Continued)

TABLE 4-1 (Continued)

[d] Emissions are from the 1985 NAPAP emission inventory and totals do not include 20,057 Mg from minor point source process emissions; area source category 99.

[e] Given as ranges because of variation in data and plant operations. All factors are uncontrolled, factors for controlled emissions are not presented due to conflicting results on control efficiency.

[f] NH_3 emissions from pan granulators were not presented by Warn *et al.* (1990) and were not included in the 1985 NAPAP emission inventory.

[g] Factors for coolers represent combined precooler and cooler emissions, and factors for dryers represent combined predryer and dryer emissions.

[h] Not available.

[i] EPA test data indicated a range of 4.01 to 14.45 kg/Mg (8.02 to 28.90 lb/ton).

[j] Feed grade factors were determined at an ambient temperature of 14° to 21° C (57° to 69°F).

[k] Feed grade factors were determined at an ambient temperature of 29°C (85°F) and agricultural grade factors at an ambient temperature of 27°C (80°F).

[l] For fluidized bed prilling, feed grade, there is a controlled emission factor with an A rating of 1.04 kg/Mg (2.08 lb/ton of product) based on use of an entrainment scrubber.

[m] EPA test data indicated a range of 0.955 to 1.20 kg/Mg (1.90 to 2.45 lb/ton).

[n] All factors are for uncontrolled emissions.

[o] The emission factor is for the whole plant, all processes.

(Continued)

The following additional industrial sources of NH_3 were identified:

- Beet Sugar Production
- Froth Flotation
- Mineral Wool Production
- Pulp and Paper
- Metals Processing
- Other Miscellaneous Sources

Each of these industries was investigated to determine the potential for the development of an NH_3 emission factor. Wherever possible, emission factors were developed. The following sections present recommendations for emission factors and for the treatment of emission sources for which emission factors could not be developed.

4.2.1 Beet Sugar Production

A review of the 1992 TRIS database revealed that there are 11 major (>90.72 Mg per year NH_3 emissions) beet sugar processing plants, which have combined NH_3 air emissions of 2,323 Mg per year. Of these 11 plants, The Amalgamated Sugar Company (Amalgamated) operates 4 plants, accounting for 55 percent of the total NH_3 emissions reported by the 11 major plants. The Corporate Environmental Engineer for Amalgamated, as well as the Kirk-Othmer Encyclopedia of Technological Processes, were consulted to determine the sources of NH_3 in the industry.[3,4]

Ammonia is a by-product of beet-sugar production. All North American beet-sugar factories use lime and carbon dioxide juice purification. The effectiveness of this process is based on the direct action of the lime on impurities, and on the special adsorptive properties of the calcium carbonate precipitate formed after carbonation. Treatment with lime produces precipitates and soluble solids. The reactions leading to soluble solids are mostly caused by the hydroxyl ions produced by the lime. Of the soluble products of this process:

- ammonium salts give off NH_3;

- asparagine and glutamine are converted to their respective amides, which are hydrolyzed with the evolution of NH_3, and accumulate as calcium salts in the juices;

- allantoin decomposes slowly to NH_3, carbon dioxide, calcium glycolate, and a precipitate of calcium oxalate; and

- oxamic acid decomposes, also rather slowly, yielding free NH_3 and calcium oxalate.

Amalgamated provided the estimation method that they used for determining total NH_3 emissions for use in the TRIS. Amalgamated calculates NH_3 releases from air stacks and vents, from wastewater which is treated by land application, and from wastewater in surface impoundments. To determine total NH_3, they estimate the sum of the quantity of NH_3 contributed from the sugar beets and the quantity of NH_3 contributed from the addition of ammonium bisulfite, which is used as a biocide to control bacteria growth.

After calculating the total NH_3 contributions, a material balance is used to determine the fate of NH_3 in the process. Their total NH_3 release is equal to the sum of the quantity of NH_3 in wastewater applied to land, the quantity of NH_3 in storage ponds, and the quantity of NH_3 released from stacks and vents. The NH_3 present in the wastewater applied to land and the wastewater in surface impoundments is determined by analyzing water samples. The balance is assumed to be emitted to the air.[5]

Since all North American beet sugar production plants utilize the same technology, it is believed that the method which Amalgamated uses to calculate NH_3 emissions is an acceptable method to apply industry-wide. As previously stated, total annual NH_3 is derived by calculating NH_3 contributed from beets to NH_3 contributed from ammonium bisulfite. Ammonia from beets, in kilograms, is estimated by multiplying the annual amount of beets sliced by 0.9916×10^{-4}. NH_3 from ammonium bisulfite, in kilograms, is estimated by multiplying the number of liters of ammonium bisulfite used annually by 0.1603. Amalgamated estimates that NH_3 from ammonium bisulfite contributes about 20 percent of the total NH_3 emissions. It is assumed that total annual NH_3 is emitted, unless sampling results of other treatment or control (e.g., influent streams to wastewater treatment, water contained in impoundments) processes indicate that the NH_3 is recovered or destroyed. The NH_3 emission factor for the beet sugar production industry is listed in Table 4-2. The emission factor quality is rated B, in that the factor is based on a sound engineering estimate.

TABLE 4-2. AMMONIA EMISSION FACTORS FOR BEET SUGAR PRODUCTION

Source	Point Source SCC	Emission Factor (kg NH_3/Mg)	Factor rating	Emission Factor (lb NH_3/ton)	Estimated national emissions (Mg/yr)
Sugar Beets	3-02-016-01	0.00262	B	0.00524	2,323

4.2.2 Froth Flotation in Mineral Processing

Froth flotation is used at minerals processing plants as a minerals separation technique. While the basic concept of selectively floating minerals applies to all ores, floatation procedures vary tremendously. In 1991, the U.S. Department of the Interior, Bureau of Mines performed a flotation survey of all U.S. mineral processing and coal cleaning plants that were believed to use froth flotation.[6] The plants were surveyed for, among other things, their consumption of the reagents typically used in flotation, including NH_3. Data were received from 133 of the 260 active flotation plants. Of the plants not responding to the survey, 100 were coal preparation plants and the majority of the remaining 27 were industrial mineral producers. The operating status of the non-responding plants was not determined.

The results of the survey indicate that 7,691 Mg of NH_3 or ammonium hydroxide were consumed in 1991. Of this, 71 Mg were used in the froth flotation of 2,300,659 Mg of glass sand ore; 7,593 Mg were used in the froth flotation of 96,833,621 Mg of phosphate ore; and 27 Mg were used in the froth flotation of 17,115,235 Mg of bituminous coal. Ammonia is used as a reagent for pH adjustment, to lower acidity. Emission factors were estimated by mass balance, assuming that all of the NH_3 used is ultimately evaporated to the air. These emissions factors are presented in Table 4-3. Although these factors are viewed as reasonable estimates, it should be noted that the mass balance calculation involves the conservative assumption that the NH_3 does not leave the flotation process as a salt, in solid waste or wastewater. The factors are assigned quality ratings of D, because they are based on material balance with incomplete data.

TABLE 4-3. AMMONIA EMISSION FACTORS FOR MINERAL ORE PROCESSING BY FROTH FLOTATION

Source	Point Source SCC	Emission Factor (kg/Mg)	Factor rating	Emission Factor (lb/ton)	1991 Emissions (Mg/yr)
Glass Sand	3-05-014-20	1000[a]	D	2000	70
Phosphate	3-05-019-10	1000[b]	D	2000	7,690
Bituminous Coal	3-05-010-18	1000[c]	D	2000	27

[a] About 70 Mg of NH_3 is used per year, or an average of 0.0307 kg/Mg of glass produced.
[b] About 7,690 Mg of NH_3 is used per year, or an average of 0.784 kg/Mg of phosphate ore.
[c] About 27 Mg of NH_3 is used per year, or an average of 0.00159 kg/Mg of coal processed.

4.2.3 Mineral Wool (Fiberglass) Production

A thorough review of the U.S. Environmental Protection Agency's 1992 Toxic Release Inventory System (TRIS) database reveals that of the 23 fiberglass manufacturing plants that reported NH_3 emissions, 10 are major (>90.72 Mg/year) sources. Of these 10 plants, Owens-Corning Fiberglass, Incorporated operates 6 and Schuller International, Incorporated operates one, accounting for 80% of the total NH_3 emissions reported by the 10 major plants.[7]

All fiberglass manufacture in the U.S. is conducted using the same process; therefore, information obtained from Owens-Corning Fiberglass and Schuller International can be applied to all fiberglass manufacturing plants. Briefly, in the manufacture of fiberglass, a phenol formaldehyde resin is used as a component of the binder. The binder is then sprayed on the fiberglass to allow it to be bound into usable form as insulation. Aqueous NH_3, a component in the resin, is used for adjustment of pH. During the manufacturing process, virtually all the NH_3 is released and, typically, emitted to the atmosphere. Other sources of emissions of NH_3 at a fiberglass plant include emissions from storage tank facilities, although these emissions are very minor when compared to emissions from the production process. In addition, urea is also used in the process as a prill, and is a source of some NH_3 emissions. However, the NH_3 emitted from this source is very minor in comparison to emissions from the production process.[8,9,10]

The fiberglass production facilities approximate their NH_3 emissions from records of the amount of NH_3 utilized in the production process. In addition, they add a small amount (one facility stated that they included approximately 1/2 megagram, or approximately 0.1% of their total emissions) to their NH_3 use numbers, to account for NH_3 emissions from urea use in the production process. The NH_3 used in the manufacture of fiberglass can be related to fiberglass production numbers, thus it would be possible to estimate an NH_3 emission factor based on fiberglass production.

However, the fiberglass production industry is currently aggressively researching ways to reformulate the resins used in the production process to reduce or eliminate the use of certain organic compounds. As resin reformulation occurs, pH adjustment is likely not to be required, due to the constituents of the resins, and, as a result, NH_3 use will be drastically reduced. Therefore, the use of an NH_3 emission factor, based on the current NH_3 use during fiberglass production, will likely be inaccurate in the near future, and would require revision as advances are made in the research. As a result, NH_3 use during fiberglass production will likely provide the best method of estimating NH_3 emissions from these facilities. In general, the NH_3 usage figures appear to have been reported as emissions in TRIS.

4.2.4 Pulp and Paper

Chemical pulping of wood involves mixing the raw materials (pulp wood) with cooking chemicals under controlled temperature and pressure conditions to yield a variety of pulps with unique properties. Three types of chemical pulping are currently used in the U.S.; kraft, sulfite, and soda pulping. Of the three types, only sulfite pulping uses NH_3 as an added reagent. The sulfite process uses an acid solution of sulfurous acid and bisulfite ion. The bisulfite may be an ionic salt of calcium, magnesium, sodium, or ammonium. At sulfite mills that use ammonium salts, energy and sulfur are recovered; however, pulping liquor cannot be recovered, because ammonium combustion generates elemental nitrogen and water. The composition of the cooking liquor is 7 percent sulfur dioxide, by weight, of which 4.5 percent is present as sulfurous acid and 2.5 percent as calcium, sodium, NH_3, or magnesium bisulfite.[11] There are currently eight ammonium-based pulping mills in the U.S.

The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) published a *Handbook of Chemical Specific Information for SARA Section 313 Form R Reporting* in March 1990.[12] This publication contains information on NH_3 use and emissions in the pulp and paper industry, which is summarized and presented in the following text.

Ammonia is produced or used in various processes throughout the pulp and paper industry. It is coincidentally manufactured in the Kraft pulping process in the recausticizing area and the anaerobic treatment systems. No data on NH_3 production were available to NCASI, however they estimated that only trace amounts may be present in these processes. NH_3 may also be present in dyes, coatings, and inks which would be used to produce a final product. NCASI indicated that recent measurements at one mill showed that 50 percent of the NH_3 applied to the paper machine with coating chemicals was released to the atmosphere. Ammonia may also be used as an additive to the wastewater, for nutrient purposes, prior to secondary wastewater treatment. Typically, this NH_3 is added as aqueous NH_3, of which only a fraction is in the free form, and 90 to 95 percent is expected to be consumed during the treatment process. NCASI studies have found that NH_3 is present in very small quantities (0.5 ppm as total NH_3) in treated mill effluents. And, finally, NH_3 is used as a raw material in pulping liquor used in the sulfite pulping process. This pulping liquor is typically not recovered, however NH_3 emissions may be incidentally controlled via the control methods used for sulfur dioxide to reduce odor emissions.

The information on estimating NH_3 air emissions from fugitive or non-point sources indicates that most of the NH_3 would be released as fugitive emissions from a secondary, biological waste treatment facility, and would amount to less than 226.8 kg (or 500 lbs) per year. Additional potential emission sources include accidental or fugitive emissions from tank car loading, and emissions from vents on storage tanks; however, no estimates of emissions were available to NCASI.

The information on estimating NH_3 air emissions from stack or point sources indicates that there are four potential sources: dryer/printing press vents, paper machine vents, recausticizing area vents, and anaerobic treatment system vents. As previously stated, NCASI indicated that recent measurements at a mill showed that 50 percent of the NH_3 applied to the paper machine with coating chemicals was released to the atmosphere. No data were available to NCASI on the other three potential point sources.

The data collected and analyzed on NH_3 air emissions from the pulp and paper industry were not sufficient to develop an NH_3 emission factor for the industry. However, the guidance provided to the industry by the trade group NCASI seems to be comprehensive and would allow plants to adequately calculate NH_3 emissions, based on their specific plant operating factors. As a result, NH_3 emissions, as reported in TRIS, will likely provide the most accurate report of NH_3 emissions from pulp and paper facilities and is recommended for use. It is also recommended that further research be conducted in the pulp and paper industry to determine if development of an NH_3 emission factor is feasible and can be accomplished.

4.2.5 Emission Factors Provided by Other Sources

California maintains an Air Toxics Emission Data System (ATEDS) under its Air Toxics Hot Spots program. This data system contains plant- and point-specific information for specific toxic pollutants, including NH_3, at the same level of detail as the EPA AIRS point source inventory for criteria pollutants. The data include plant name, equipment type, SCC, SIC, emission factor (for each specific pollutant), and emissions. The emission factors in ATEDS are plant-specific, and generally vary from plant to plant within the same SCC.

Ammonia emissions data and emission factors were obtained from ATEDS, and reviewed to assess their applicability to a national inventory. Most of the NH_3 emissions reported in ATEDS derive from the use of NH_3 in selective catalytic reduction and selective non-catalytic reduction processes for controlling nitrogen oxide emissions from combustion sources. NH_3 emissions from these processes are discussed in Section 5. Another large fraction of the NH_3 emissions in ATEDS is reported in the form of plant totals, with no source specific information on emissions or emission factors. A relatively small portion of the inventory deals with source-specific industrial NH_3 emissions data.

Table 4-4 gives emission factors for industrial sources of NH_3 emissions, which were developed from the California ATEDS data base.[13] For each source type, the table presents the average ATEDS NH_3 emission factor, the range of NH_3 emission factors, the emission factor units, the applicable AIRS SCC, the number of plants included in ATEDS, and the recommended emission factor rating. A rating of D is used in all cases because of the limited number of sources in each category, and because emission factors for the California sources may not be representative of the nation as a whole. EPA does not recommend using fixed emission factors for emissions from storage tanks, but instead recommends a case by case use of the EPA "TANKS" program, which will work for ammonia, with use of the proper constants.

4.2.6 Other Sources (For Which Emission Factors Have Not Been Developed)

The TRIS data base stems from the toxic release report requirement in Section 313 of SARA Title III. In summary, annual toxic release reports must be submitted for any manufacturing plant (SICs 20-39) that produces or processes more than 11,340 kg (25,000 lb) per year of a listed chemical, or that otherwise uses more than 4,536 kg (10,000 lb) per

TABLE 4-4. AMMONIA EMISSION FACTORS DEVELOPED FROM THE CALIFORNIA ATEDS DATA BASE

Category Description	Emission factors (kg/unit) Average	Emission factors (kg/unit) Range	Units	SCC	No. of plants	Rating[a]
Ammonia storage	6.6×10^{-8}		10^3 liters capacity	30188501	1	D
Gold processing, electrowinning	0.029	7×10^{-7} to 0.17	Mg	30301301	6	D
Coal mining, unloading (cyanide ponds)	0.017		Mg	30504099	1	D
Crude oil production						
Complete well, fugitives	5.9×10^{-7}	2.3×10^{-7} to 1.1×10^{-6}	Wells	31000101	3	D
Crude oil sumps	2.1×10^{-5}	3×10^{-7} to 4.3×10^{-5}	Meters^2	31000104	2	D
Storage - breathing	2.6×10^{-6}	7×10^{-11} to 7×10^{-6}	10^3 liters capacity	40400301	2	D
Storage - working	1.7×10^{-8}	5×10^{-10} to 7×10^{-7}	10^3 liters thruput	40400302	4	D
Crude oil loading	3×10^{-9}	7×10^{-10} to 6×10^{-7}	10^3 liters thruput	40600132	1	D

[a] A rating of D is used in all cases because of the limited number of sources in each category, and because emission factors for the California sources may not be representative of the nation as a whole. EPA does not recommend using fixed emission factors for emissions from storage tanks, but instead recommends a case by case use of the EPA "TANKS" program, which will work for ammonia, with use of the proper constants.

year.[14] NH_3 is one of the listed chemicals for TRIS. SARA reports provide estimates of fugitive and stack emissions; releases to surface water or land (including deep well injection); transfers to publicly-owned wastewater treatment works (POTWs); and transfers to off-site waste treatment, storage and disposal facilities (TSDFs). Information is also provided on emission controls, on-site treatment, and pollution prevention measures. Unfortunately, no direct link is made in the data base between pollution controls and specific emission streams. Thus, no information is available on the fraction of total plant emissions routed to a given control device or, consequently, on the exact magnitude of emissions collected. In addition, TRIS provides no details on individual sources of emissions for any pollutant, beyond the gross plant level.

Table 4-5 gives a summary by industry category of NH_3 emissions reported in TRIS for 1992 and 1990, along with an indication of which categories are covered by emission factors. With the available emission factors for fertilizer manufacture, refrigeration, coke production, petroleum refining, and other categories, about 75 percent of the 1992 emissions in Table 4-5 are covered by emission factors.

In cases where there are no applicable emission factors, it is recommended that plants reporting NH_3 emissions in TRIS be incorporated into the emission inventory as "discrete point sources." TRIS gives information on latitude and longitude, as well as State and county codes, which can be used to give the location of these discrete sources. Tabe 4-6 gives a list of discrete sources, with no applicable emission factors, that are reported to emit more than 90.72 Mg of NH_3 annually in the 1992 TRIS data base.

NH_3 emissions from the discrete source groups were assessed with the goal of developing emission factors. One problem is that there are only a few cases where there is a well defined "category" with more than a few sources. For instance, the nonferrous metals group (SIC 3339) includes four major sources, but these produce a variety of different metals. Similarly, SICs 2819 and 2869 are both broad categories that include a variety of inorganic chemicals and organic chemicals, respectively.

TABLE 4-5. SUMMARY OF AMMONIA EMISSIONS REPORTED IN TRIS

SIC and Category Description		Reported emissions in 1992 (Mg)	Reported emissions in 1990 (Mg)	Emission factor available?[a]	Emission factor description
20	Food products	7,818	7,158	Yes	Sugar and refrigeration
21	Tobacco products	613	655		
22	Textiles	670	779		
23	Apparel	100	88		
24	Lumber and wood products	411	290		
25	Furniture and fixtures	8	9		
26	Paper	1,948	1,650		
27	Printing and publishing	55	50		
281	Industrial inorganic chemicals	4,466	4,941	Yes	Ammonia and some overlap with fertilizers
282	Plastics and resins	901	860		
283	Pharmaceuticals	356	293		
284	Soap and detergents	463	829		
285	Paints and varnishes	12	9		
286	Industrial organic chemicals	2,895	2,932		
287	Agricultural chemicals	37,584	56,554	Yes	Nitrogen fertilizers and phosphate ore processing
289	Miscellaneous chemicals	511	582		
29	Petroleum refining	3,566	3,978	Yes	Petroleum refining
30	Rubber and plastic products	1,021	1,072		
31	Leather	259	186		
32	Stone, clay, glass, and concrete	2,656	1,108		
33	Metal smelting and refining	5,476	7,759	Yes	Coke manufacture
34	Fabricated metal products	263	349		
35	Industrial machinery	147	446		
36	Electronic and electrical equipment	579	431		
37	Transportation equipment	261	237		
38	Measurement and control instruments	35	90		
39	Miscellaneous manufacturing	106	18		

[a] Emission factors are presented in earlier tables in this section.

TABLE 4-6. LIST OF DISCRETE MAJOR SOURCES (>90.72 Mg or >100 tons) OF AMMONIA WITH NO APPLICABLE EMISSION FACTORS (based on 1992 TRI reports)

				SICs			Reported emissions
Category[a]	Plant	City	State	1st	2nd	3rd	(Mg/yr)
Electrometallurgy	Elkem Metals Co.	Marietta	OH	3313			1,542
Misc. Nonferrous Metals	Climax Molybdenum Co.	Fort Madison	IA	3339	2819		814
	U.S. Vanadium Corp.	Hot Springs	AR	3339	1094		261
	GTE Prods. Corp.	Towanda	PA	3339	3341	2819	154
	Cabot Corp.	Boyertown	PA	3339	2819		152
	GE Co.	Euclid	OH	3399	3356	3357	305
Plastic Parts	Teepak Inc.	Swansea	SC	3089			753
Fertilizer Mixing	O. M. Scott & Sons Co.	Marysville	OH	2875			680
Misc. Inorganic Chemicals	W. R. Grace & Co.	Sulphur	LA	2819			640
	Du Pont Repauno Plant	Gibbstown	NJ	2819			474
	Calgon Carbon Corp.	Pittsburgh	PA	2819			273
	Engelhard Corp.	Attapulgus	GA	2819			210
	Westinghouse	Columbia	SC	2819			166
	Filtrol Corp.	Los Angeles	CA	2819			163
	Peninsula Copper Ind. Inc.	Hubbell	MI	2819			160
	Griffin Corp.	Casa Grande	AZ	2819			122
	Kerr-Mcgee Chemical Corp.	Hamilton	MS	2819	3313		108
	W. R. Grace & Co.	Baltimore	MD	2819			98
	PPG Ind. Inc.	New Martinsville	WV	2812	2819	2865	97
	United Catalysts Inc.	Louisville	KY	2819			91
Tobacco Products	Philip Morris USA	Richmond	VA	2141			530
Mineral Wool and Fiberglass	Owens-Corning Fiberglas	Newark	OH	3296			436
	Owens-Corning Fiberglas Corp.	Kansas City	KS	3296			276
	Owens Corning Fiberglas Corp.	Waxahachie	TX	3296			180
	Schuller Intl. Inc.	Defiance	OH	3296			161
	Owens-Corning	Fairburn	GA	3296			145
	Manville Sales Corp.	Winder	GA	3296			143
	Certainteed Corp.	Mountain Top	PA	3269			127
	Owens-Corning Fiberglas Corp.	Santa Clara	CA	3296			119
	Owens-Corning Fiberglas Corp.	Delmar	NY	3296			113
	Partek Insulation Inc.	Phenix City	AL	3296			93
Secondary Nonferrous Smelting	Gulf Chemical & Metallurgical	Freeport	TX	3341			318
	Alabama Reclamation Plant	Sheffield	AL	3341			281
Steel Wiredrawing	Indiana Steel & Wire Corp.	Muncie	IN	3315			313
Forging	National Forge Co.	Irvine	PA	3462			132
Pulp and Paper	Bowater Inc.	Catawba	SC	2611	2621		282
	Mead Coated Board Inc.	Cottonton	AL	2631			245
	Champion Intl. Corp.	Hamilton	OH	2621			114
Miscellaneous Organic Chemicals	Sherex Chemical Co. Inc.	Mapleton	IL	2843	2899	2869	318
	PCR Inc.	Gainesville	FL	2869			204
	Ethyl Petroleum Additives Inc.	Natchez	MS	2869			181
	Du Pont	Orange	TX	2869			165
	Rohm & Haas Texas Inc.	Deer Park	TX	2869			165
	Exxon Chemical Americas	Baytown	TX	2869	2821		149
	Ethyl Corp.	Orangeburg	SC	2869	2834		118
	BASF Corp.	Freeport	TX	2869			110
	Du Pont	Victoria	TX	2869			104
Cyclic Organics and Dyes	Sandoz Chemicals Corp.	Charlotte	NC	2865			126
	Buffalo Color Corp.	Buffalo	NY	2865			104
Synthetic Rubber	Ameripol Synpol Corp.	Port Neches	TX	2822			118
Wood Preserving	J. H. Baxter & Co.	Weed	CA	2491			117
Miscellaneous	M-Pact	Eudora	KS	3998			100

[a] Plants are grouped by SIC code and sorted in descending order of ammonia emissions. The following SICs are excluded because of overlap with emission factor categories: 20xx - food processing (ammonia refrigeration, see Section 6), 2873 - Nitrogen fertilizers, 2874 - phosphates, 29xx - petroleum refining, and 3312 - steel works (coke ovens).

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SECTION 5

AMMONIA EMISSIONS FROM COMBUSTION

Ammonia is emitted from several types of combustion processes, including boilers, cars, and open burning. In the United States, emissions from electric and industrial combustion may be the largest source of NH_3 emissions from combustion; however, in recent global climate studies, NH_3 from biomass burning is estimated to be a significant source of NH_3. There is a great deal of uncertainty associated with all of the NH_3 emission factors from combustion. In addition to the release of NH_3 as a byproduct of incomplete combustion, NH_3 is used as an agent in NO_x control technology; specifically, it is used in selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). Ammonia is also believed to be emitted from the chemical agents used to fight forest fires, although this source has not been found in the literature.[1] This section presents a discussion of the NH_3 combustion emission factors used in different inventory efforts and a discussion of the plausible emissions of NH_3 from NO_x control technology.

Asman (1992)[2] created an emission inventory for all of Europe, but he stated that although car exhaust, sewage sludge, combustion/coking of coal, and landfill are sources of NH_3, they are very uncertain and not very important sources.

5.1 AMMONIA EMISSION FACTORS FOR COAL COMBUSTION

Among recent NH_3 inventory efforts, there is large variability in the emission factors used to estimate NH_3 emissions from coal combustion. A review of recent literature uncovered one test program, conducted by Bauer and Andren (1985)[3] in 1980, where NH_3 emissions from a coal-fired power plant in Portage, Wisconsin were measured. The results of this study were used by Warn (1990)[4] to develop the NAPAP coal combustion emission factor of 0.28 kg $NH_3/10^3$ Mg coal (0.56 lbs $NH_3/10^3$ tons coal).[5] Use of this factor in the 1985 NAPAP inventory resulted in 0.02% of the NH_3 inventory. The data of Bauer and Andren (1985) appear to be the most recent measurements of NH_3 from coal combustion.

Lee and Longhurst (1993)[6] developed an NH_3 emission factor for the United Kingdom for the 1987 study year. They cite several emission factors for coal combustion, including 1 kg NH_3/Mg coal combusted, as reported by the Subcommittee on Ammonia (1979).[7] This value was also used by Buijsman (1986).[8] Möller & Schieferdecker (1989)[9] use the factor of 6-9 g $NH_3(N)$/Mg of coal in their development of an NH_3 emission inventory for the G.D.R. They cite as their source Bottger *et al.* (1978), and note that the value used by Buijsman (1986) of 1 kg NH_3/Mg is improbably high. Kruse *et al.* (1989),[10] in his work on the validity and uncertainty of NH_3 emissions from agriculture, also notes that the value of 1 kg NH_3/Mg coal combusted appears to be too high, because most coal is used in highly oxidizing combustion processes, leaving little scope for the formation of NH_3.

Lee (1994)[11] has recently submitted a manuscript on the uncertainties of NH_3 emission factors. He cites the work of Warn (1990) for NAPAP as an emission factor of 0.21 g NH_3-N for coal combustion based on measurements from one plant. Geadah (1985)[12] gives a residential coal burning emission factor of 1 kg NH_3/Mg of coal combusted. He does not explain how this emission factor was derived, but he justifies the magnitude of the estimate on the basis that most domestic coal burning occurs in less than ideal combustion conditions.

Denmead (1990)[13] developed an NH_3 budget for Australia and included an estimate from coal burning using an emission factor by Robinson and Robins (1972)[14] of 1 kg NH_3-N/Mg coal.

Table 5-1 summarizes the various emission factors presented in the literature for coal combustion. Although the NAPAP factor of 0.28 kg $NH_3/10^3$ Mg (0.56 lb $NH_3/10^3$ tons) burned is based on only 1 test, it remains the most tenable factor and is recommended for continued use as the NH_3 emission factor for coal combustion. The rating for the coal combustion emission factor is E, consistent with the rating provided by Warn *et al.* (1990).

TABLE 5-1. COAL COMBUSTION AMMONIA EMISSION FACTORS

Source	Emission Factor (kg/Mg coal)	Emission Factor (lb/ton coal)
NAPAP	0.00028	0.000565
Subcommittee on Ammonia (1979)	1.0	2.0
Buijsman (1986)	1.0	2.0
Lee and Longhurst (1993)	.009	0.0018
Möller & Schieferdecker (1989)	0.006-0.009	0.0012-0.0018
Bottger *et al.* (1978)	0.006-0.009	0.0012-0.0018
Denmead (1990)	1	2.0

5.2 AMMONIA EMISSIONS FROM FUEL OIL AND NATURAL GAS COMBUSTION

Only the NAPAP NH_3 emission factor documentation includes factors for fuel oil and natural gas combustion. The NAPAP factor for fuel oil is the average of two factors, 0.023 and 0.18 kg $NH_3/10^3$ liters (0.19 and 1.5 lbs $NH_3/10^3$ gallons) that were reported by EPRI in a 1976 document.[15] The factor lies within the range 0.0072 to 0.96 kg $NH_3/10^3$ liters (0.06 to 8 lbs $NH_3/10^3$ gallons) that was established in two studies conducted in the 1950's.[16] Ammonia emissions from natural gas combustion were estimated in the 1950's and 1960's to range from 5 to 300 kg $NH_3/10^6$ m^3 (0.3 to 20 lbs $NH_3/10^6$ ft^3). The 1976 EPRI study also measured NH_3 from natural gas combustion at excess oxygen levels of 2, 4, and 6 percent. These data were combined with excess oxygen statistics that were presented by Cass (1982)[17] to calculate average emission factors for utility, industrial, and commercial boilers. The emission factors used for fuel oil and natural gas combustion in the NAPAP inventory are presented in Table 5-2.

TABLE 5-2. NAPAP FUEL OIL AND NATURAL GAS EMISSION FACTORS

Source	Emission Factor	Factor Rating	Emission Factor
Fuel Oil	0.096 kg/10^3 liter	E	0.8 lb/10^3 gal
Natural gas - utility and industrial boilers	51. kg/10^6 m^3	C	3.2 lb/10^6 ft^3
Natural gas - commercial boilers	7.8 kg/10^6 m^3	C	0.49 lb/10^6 ft^3

Although emission factors were developed for fuel oil and natural gas combustion, NH_3 emission estimates for these categories were not included in the 1980 NAPAP emission inventory. Using these factors in the 1985 NAPAP inventory resulted in NH_3 emissions of 1.2% for fuel oil and 2.2% for natural gas combustion. (Both of these emission estimates are substantially higher than for coal combustion.) The quality rating for these factors is consistent with the rating given by Warn *et al.* (1990).

None of the European or Australian work included emission estimates for fuel oil or natural gas combustion.

5.3 MOBILE SOURCES

The NAPAP program developed NH_3 emission factors for mobile sources from a limited series of test data collected from 1973 to 1980. Use of these factors resulted in 2.8% of the NH_3 emissions in the 1985 NAPAP inventory. In the NAPAP documentation, 8 sets of data are reported. There is one data set for diesel, two data sets for leaded gasoline (for a 1956 Oldsmobile and a 1972 Pontiac, both V-8 engines), and five data sets for unleaded gasoline. The five unleaded gasoline data sets include cars with and without catalytic converters. The emission factors used in NAPAP are consistent with an analysis of a range of concern for mobile source emissions of NH_3 conducted by the EPA Office of Mobile Sources.[18]

Möller & Schieferdecker (1989) use the factor of 25 mg $NH_3(N)$/km in their development of an NH_3 emission inventory for the German Democratic Republic (G.D.R.) As their source, they cite Bottger *et al.* (1978).[19] It is unclear how these factors were developed, but because they were developed so long ago, they could not have included the test data of Cadle and Mulawa (1980)[20] for unleaded gasoline engines with catalytic converters.

In a recent analysis of uncertainties in NH_3 emissions in the United Kingdom, Lee and Dollard (1994) use the NAPAP factors for mobile sources.

The mobile source emission factors are presented in Table 5-3 and the NAPAP factors are determined to be the best available; however, these factors are all very uncertain and their use in an inventory would be of questionable validity. The ratings presented in Table 5-3 are consistent with Warn *et al.* (1990).

5.4 USE OF AMMONIA AND UREA TO REDUCE, CATALYTICALLY OR NONCATALYTICALLY, NITROGEN OXIDES IN COMBUSTION GASES

The formation of NO_x is a major problem associated with fuel combustion. NO_x is formed when nitrogen and oxygen combine at the high temperatures of combustion, and is a major contributor, with other pollutants, to urban ozone (smog) problems, and to acid precipitation. NO_x also causes detrimental health and ecological effects. NO_x has not been as amenable to traditional pollution controls as other pollutants, because it is present in low concentrations in combustion gases. However, its high impact, with regard to urban ozone problems and acid rain deposition, has prompted a number of innovative developments in the control of NO_x.

Two important developments for NO_x control in combustion gases are "selective catalytic reduction" (SCR), and "selective non-catalytic reduction" (SNCR). Both of these processes involve the chemical reduction of NO_x to elemental nitrogen (N_2). For stationary

TABLE 5-3. MOBILE SOURCE EMISSION FACTORS

Source	Emission Factor ($kg/10^3$ liter)	Quality Rating	Emission Factor ($lb/10^3$ gallons)
Mobile sources - unleaded gasoline	0.075	D	0.63
Mobile sources - leaded gasoline	0.050	D	0.42
Mobile sources - diesel	0.11	E	0.95
Möller & Schieferdecker (1989)	0.218[a]	E	1.82

[a] Converted from 25 mg NH_3(N)/km to $kg/10^3$ liter based on 4.5 km/liter (16.9 miles/gallon).

source combustion, SCR and SNCR systems use NH_3 or urea (an NH_3 derivative) as chemical reducing agents. With either reducing agent, some NH_3 remains after the NO_x reduction reaction, and is emitted in the flue gas. This NH_3 emission is termed "NH_3 slip." The following sections give more detail on the SCR and SNCR processes, and on NH_3 slip emissions from these processes.[21]

5.4.1 Selective Catalytic Reduction

In SCR systems, NH_3 is injected into the combustion flue gas, which is then passed through a catalyst bed. The NH_3 reacts with NO_x to produce nitrogen and water in the following reactions:

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

$$8\ NH_3 + 6\ NO_2 \rightarrow 7\ N_2 + 12\ H_2O$$

The catalyst lowers the activation energy of these reactions, allowing them to proceed at typical flue gas temperatures. The catalyst may consist of precious metals (platinum or palladium), base metal oxides (vanadium, titanium, or others), or zeolites (crystalline aluminosilicates).

The effectiveness of SCR systems in reducing NO_x is strongly influenced by the NH_3-to-NO_x ratio. Typically, a 1:1 stoichiometry can only achieve an 80 percent reduction of NO_x. Excess NH_3 can produce greater NO_x reductions, but this also results in more NH_3 slip. A number of other factors also affect both the NO_x reduction efficiency and the NH_3 slip.

Most important, the NO_x efficiency is reduced and the NH_3 slip is increased when the catalyst condition and the catalyst bed temperature are not optimum.

5.4.2 Selective Non-Catalytic Reduction

The SNCR process involves the injection of NH_3 or urea into the flue gas without any catalyst. Because no catalyst is used, NH_3 or urea used in SNCR must be injected into the flue gas at higher temperatures. The reactions of NH_3 with NO_x have been presented above. Urea ($(NH_2)_2C{=}O$) reacts with NO_x and oxygen to produce elemental nitrogen, water, and carbon dioxide (CO_2). (The reaction of urea with NO_x is not well understood because of the complexity of urea pyrolysis and subsequent free radical reactions.) However, urea also decomposes to NH_3 and to other products at elevated temperatures, producing NH_3 slip.

As in SCR, the NH_3-to-NO_x ratio has a strong influence on NO_x reduction efficiency. A 1:1 ratio results in NO_x reductions of less than 40 percent, while a 2:1 ratio can produce up to 60 percent reduction in NO_x. Again, there is a trade-off between NO_x reduction efficiency and NH_3 slip.

5.4.3 Ammonia Emissions and Emission Factors

In analyzing alternative control technologies for NO_x, EPA's Emission Standards Division compiled performance data on a number of SCR and SNCR systems. In addition, NH_3 slip emission factors are available in the California "Hot Spots" Air Toxics Emissions Data System (ATEDS) for several natural gas combustion facilities equipped with SCR. Table 5-4 summarizes NH_3 slip data from EPA control alternative analyses and the ATEDS system.[22,23,24] As the table shows, NH_3 slip is extremely variable, ranging from less than 1 ppm in the flue gas up to 100 ppm. Manufacturers typically cite NH_3 slip values of 5 to 10 ppm for SCR, and 20 to 30 ppm for SNCR.[25] For the purposes of emission factor development, an average NH_3 slip of 15 ppm was used for SCR systems, and 30 ppm for SNCR systems. These values represent a synthesis of manufacturers' information and the data in Table 5-4.

Table 5-5 gives NH_3 emission factors for SCR and SNCR, as applied to various fuel types. The emission factors are linked to the appropriate SCCs and AIRS control device codes. AIRS control code 65 applies to SCR, and AIRS control code 32, "Ammonia Injection," applies to SNCR with NH_3. There is presently no control code for urea injection. All of the NH_3 slip emission factors for SCR and SNCR are rated as C. For coal, oil, and other fuels, there are a few good sources of data, which show considerable variability. For natural gas SNCR systems, more data exists, but the variability of that data is extremely high. Variability is much lower for the natural gas SCR installations listed in the California ATEDS data base, but no information is available from the data base on the conditions existing during the NH_3 testing.

TABLE 5-4. SUMMARY OF AMMONIA SLIP DATA FOR SCR AND SNCR INSTALLATIONS

Control	Fuel/ system	Reagant	Generating Capacity (MW)	NO_x reduction (percent)	Ammonia slip (ppm)	Reference
SCR	Coal	NH_3	1	80	<1	22
		NH_3	1	70 - 80	1 - 20	22
	Oil	NH_3	1	60 - 80	<20 - <50	22
		NH_3	107	90	10 - 40	22
	Gas	na	na	na	20	24
		na	na	na	13	24
		na	na	na	28	24
		na	na	na	16	24
		na	na	na	22	24
		na	na	na	18	24
		na	na	na	20	24
		na	na	na	28	24
		na	na	na	12	24
		na	na	na	5	24
		na	na	na	8	24
SNCR	Coal (FBC)	NH_3	25	na	28	22
		NH_3	57	na	<20	22
		Urea	na	57	<18	23
		Urea	na	70	<10	23
	Oil	Urea	110	42	3 - 75	22
		Urea	185	38 - 48	5 - 10	22
	Gas	Urea	110	35 - 50	10 - 50	22
		Urea	156	26 - 40	13 - 18	22
		Urea	333	7 - 14	6 - 9	22
		Urea	342	23 - 36	7 - 17	22
		Urea	345	30	80 - 110	22
		NH_3	345	30	50 - 110	22
	Wood	Urea	na	25 - 50	<10 - <40	23
	MSW	Urea	na	41- 70	<5 - 22	23

Table 5-5 also gives activities for combustion sources controlled by SCR and SNCR, as taken from the 1990 Interim Emissions Inventory.[26] It should be pointed out that the control information for SCR and SNCR systems in the Interim Inventory actually dates back to the 1985 NAPAP inventory. As a result the activities are expected to be understated. In fact, reported SCR and SNCR NH_3 emissions in the California Hot Spots are about 68 Mg

(75 tons) per year, higher than the national NH_3 emissions given by the Interim Inventory activity data. Further, SCR and SNCR are expected to expand drastically over the next two decades as a result of the 1990 Clean Air Act Amendments.

5.5 BIOMASS BURNING

Nitrogen, as an essential ingredient of proteins, is present in all biomass. For instance, the average concentration of nitrogen in wood is about 0.1 percent.[27] This nitrogen is in a "reduced" chemical state, typically as amides ($R{-}(C{=}O){-}NH{-}R'$), and amines ($R{-}NH_2$). The equilibrium products of this fuel nitrogen under combustion conditions are elemental nitrogen (N_2) and nitrogen oxides (NO and NO_2, or NO_x). However, because it is initially in a chemically reduced state, and because biomass burning typically occurs under poor mixing conditions, the biomass nitrogen can be released as NH_3.

Lee and Atkins (1994)[28] conducted a field measurement program of NH_3 and ammonium aerosol during straw and stubble burning. They concluded that NH_3 emissions over the six to eight week period during which this burning typically occurs were calculated to be 27% of the total U.K. emissions over the equivalent period in 1981, and 7% in 1991. The decline is due to changes in agricultural practices in response to impending U.K. legislation.

Denmead (1990) developed an NH_3 budget for Australia and included a method for estimating NH_3 emissions from biomass burning that is dependent upon an emission ratio for NH_3 relative to the increase in CO_2. Denmead (1990) uses an emission ratio of 1.5×10^{-3} mole/mole. In order to calculate emissions, data on carbon released in vegetation fires in Australia was used with the ratio of 0.1 mole CO/mole CO_2. This led to the conclusion that biomass burning may contribute 1/16 to 1/6 of the NH_3 released in Australia.

Schlesinger and Hartley (1992) compiled a global budget for atmospheric NH_3 in which they estimated that biomass burning may contribute up to twelve percent of the total annual global flux.[29] The uncertainty of these estimates is very high, and additional research into the primary references is needed prior to the establishment of emission factors.

5.6 RECOMMENDED COMBUSTION AMMONIA EMISSION FACTORS AND CLASSIFICATION CODES

Table 5-6 summarizes the emission factors for combustion sources and presents the applicable point, area, and mobile source classification codes.

TABLE 5-5. SCR AND SNCR AMMONIA EMISSION FACTORS

Control technique/ fuel		NH_3 slip (ppm)	Emission factor	Emission Factor Units	Control device code	Applicable SCCs	Factor rating	Emission Factor (lb/SCC Unit)	Activity (SCC units)	Estimated emissions (Mg/yr)
SCR	Coal	15	0.155	kg/Mg	65	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103001xx, 103003xx, 10500102, 10500202	C	0.31 lb/ton		
	Oil	15	0.17	kg/10^3 liters	65	101004xx, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 201001xx, 201009xx, 202001xx, 202003xx, 20200401, 20200501, 202009xx, 203001xx, 20300301	C	1.4 lb/1000 gal		
	Gas	15	146.	kg/10^6 m^3	65	101006xx, 102006xx, 103006xx, 10500106, 10500206, 201002xx, 202002xx, 203002xx	C	9.1 lb/MMscf	2,249	0.91
	Wood	15	0.155	kg/Mg	65	101009xx, 102009xx, 103009xx	C	0.31 lb/ton		
SNCR	Coal	30	0.315	kg/Mg	32	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103001xx, 103003xx, 10500102, 10500202	C	0.63 lb/ton		
	Oil	30	0.35	kg/10^3 liters	32	101004xx, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 201001xx, 201009xx, 202001xx, 202003xx, 20200401, 20200501, 202009xx, 203001xx, 20300301	C	2.9 lb/1000 gal	33,461	44.
	Gas	30	288.	kg/10^6 m^3	32	101006xx, 102006xx, 103006xx, 10500106, 10500206, 201002xx, 202002xx, 203002xx	C	18 lb/MMscf		
	Wood	30	0.315	kg/Mg	32	101009xx, 102009xx, 103009xx	C	0.63 lb/MMscf		

[a] Activity levels are taken from the 1990 Interim Inventory. However, the Interim Inventory values are actually projections from the 1985 NAPAP inventory, and are believed to be underestimates.

TABLE 5-6. RECOMMENDED EMISSION FACTORS FOR COMBUSTION SOURCES

Source	Source Classification Codes	Emission Factor (metric units)	Factor Rating	Emission Factor (english units)
Coal Combustion	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103002xx, 103003xx, 10500102, 10500202 21-99-001-000, 21-99-002-000, 21-99-003-000	0.00028 kg/Mg	E	0.565 lb/10^3 ton
Fuel Oil Combustion	101004XX, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 21-99-004-000, 21-99-005-000	0.096 kg/10^3 liters	E	0.8 lb/10^3 gal
Natural Gas Combustion - Utility and Industrial Boilers	101006xx, 102006xx, 21-01-006-xxx, 21-02-006-xxx	51. kg/10^6 m^3	C	3.2 lb/10^6 ft^3
Natural Gas Combustion - Commercial Boilers	103006xx, 21-03-006-xxx	7.8 kg/10^6 m^3	C	0.49 lb/10^6 ft^3
Mobile Sources - Leaded Gasoline[a]	22-01-xxx-xxx	0.050 kg/10^3 liter	D	0.42 lb/10_3 gallons
Mobile Sources - Diesel	22-30-xxx-xxx	0.11 kg/10^3 liter	E	0.95 lb/10_3 gallons
SCR - Coal	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103002xx, 103003xx, 10500102, 10500202	0.155 kg/Mg	C	0.31 lb/ton
SCR - Oil	101004xx, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 201001xx, 201009xx, 202001xx, 202003xx, 20200401, 20200501, 202009xx, 203001xx, 20300301	0.17 kg/10^3 liters	C	1.4 lb/10_3 gallons

(Continued)

Table 5-6 (Continued)

Source	Source Classification Codes	Emission Factor (metric units)	Factor Rating	Emission Factor (english units)
SCR - Gas	101006xx, 102006xx, 103006xx, 10500106, 10500206, 201002xx, 202002xx, 203002xx	146. kg/10^6 m^3	C	9.1 lb/MMscf
SCR - Wood	101009xx, 102009xx, 103009xx	0.155 kg/Mg	C	0.31 lb/ton
SNCR - Coal	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103002xx, 103003xx, 10500102, 10500202	0.315 kg/Mg	C	0.63 lb/ton
SNCR - Oil	101004xx, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 201001xx, 201009xx, 202001xx, 202003xx, 20200401, 20200501, 202009xx, 203001xx, 20300301	0.35 kg/10^3 liters	C	2.9 lb/10^3 gallons
SNCR - Gas	101006xx, 102006xx, 103006xx, 10500106, 10500206, 201002xx, 202002xx, 203002xx	288 kg/10^6 m^3	C	18 lb/MMscf
SNCR - Wood	101009xx, 102009xx, 103009xx	0.315 kg/Mg	C	0.63 lb/MMscf

[a] Emission factors for leaded gasoline are not presented because leaded gasoline is almost completely phased out and the source category classifications for the U.S. do not distinguish between leaded and unleaded gasoline.

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SECTION 6

MISCELLANEOUS SOURCES

Additional sources of NH_3 emissions include, at a minimum, human breath and perspiration, publicly owned treatment works (POTW's), non agricultural soils, and refrigeration. Although these sources are known to contribute, the emission factors for them are very uncertain. Asman (1992)[1] discussed many of these sources and provided emissions estimates for some categories, but did not include these sources in his recent inventory of NH_3 emissions in Europe. This exclusion was either due to their contribution being too small, too uncertain, or due to the geographical location of the specific emission source being unknown, making it impossible to incorporate the source into his gridded inventory. Of these sources of NH_3, nonagricultural or undisturbed soils, according to some researchers, have the potential of emitting up to 40 to 50% of the NH_3 measured in the atmosphere.

6.1 HUMAN BREATH AND PERSPIRATION

The NH_3 emission factors for humans used in recent inventories vary widely, ranging from 0.25 to 1.3 kg NH_3/person/year. Asman (1992) notes that using either factor to calculate emissions from humans still produced an insignificant amount of NH_3 emissions, when compared to those estimated for agricultural sources.

At the low end of this estimated range, emission factors for human breath and perspiration were prepared by Warn *et al.* (1990)[2] for NAPAP, although NH_3 emissions were not included in the 1985 NAPAP emission inventory. The NAPAP report presented human breath emission factors of 4.1 kg/10^3 smokers and 5.4 kg/10^3 non-smokers (9.1 lb/10^3 smokers and 12.0 lb/10^3 non-smokers). An additional 0.82 kg/10^3 smokers (1.8 lb/10^3 smokers) is added for the NH_3 released from the cigarette. The NAPAP NH_3 emission factors for humans are predominantly from perspiration, which is estimated at 0.25 kg/person (0.55 lb/person). Emission factors for smokers and non-smokers are 0.25 kg NH_3/person (0.56 lb/person). Cass *et al.* (1982)[3] also used an emission factor of 0.25 kg NH_3-N/person/year.

At the high end of the estimates, Möller and Schieferdecker (1989)[4] used an emission factor of 1.3 kg NH_3-N/person/year in a recent inventory of NH_3 emissions in the G.D.R. This factor is based on an estimated nitrogen production of around 5 kg NH_3-N/person/year, and assumes an NH_3 release of 25 percent.

Healy *et al.* (1970)[5] is quoted in one source as using a value of 0.31 kg NH_3-N/person/year, and is quoted in another source as using a factor of 0.54 kg NH_3-N/person/year.

Atkins and Lee (1993)[6] recently re-examined data collected in 1978 by Harwell Laboratory. Indoor NH_3 concentrations were measured in a number of homes of Harwell Laboratory staff, using a passive diffusion tube sampler. The NH_3 was collected on an absorbing surface of sulfuric acid-impregnated glass-fibre filters, and the quantity was determined spectrophotometrically by the phenol/hypochlorite (indophenol blue) method. Using calculated sampling rates, the diffusion tubes were found to give atmospheric NH_3 levels in satisfactory agreement with those found using a simple filter-bubbler technique. This method is not subject to interference from particulate ammonium compounds.

Atkins and Lee (1993) report mean NH_3 concentrations of 38.7 $\mu g/m^3$ in a kitchen, 37.4 $\mu g/m^3$ in a living room, and 32.5 $\mu g/m^3$ in a bedroom. These values do not compare particularly well with other measurements of Sisovic *et al.* (1987),[7] and Bracer *et al.* (1989),[8] which ranged from 23 to 280 $\mu g/m^3$ and 3 to 23 $\mu g/m^3$, respectively. Atkins and Lee (1993) calculate that an expected household concentration, based on a mid-range of available emission factors of 1 kg NH_3/person/year, should be 431 $\mu g/m^3$, which is an order of magnitude higher than the values measured.

Lee and Dollard (1994)[9] summarized all of the available information on NH_3 from humans and noted that the research has documented a range of 0.25 to 1.3 kg NH_3/person/year. They also noted that additional research is ongoing and will soon be published.

Table 6-1 summarizes the available emission factors for human sources. Based on the information presented, it seems likely that the factor of 1.3 kg NH_3/person/year is too high, therefore, until new research is published, the NAPAP factor of 0.25 kg/person is recommended for use. An emission factor rating of E is assigned to the factor, based on the rating for human perspiration that was provided in the NAPAP report.

6.2 PUBLICLY OWNED TREATMENT WORKS

In the mid 1980's, Allen *et al.* (1988)[10] measured ground-level concentrations of NH_3 and ammonium (NH_4^+), using filter packs, at nineteen sites within a 35-km radius of Colchester, U.K. The sampling sites were selected to verify the influence of possible sources on NH_3 concentrations. The six sites included livestock farms (sheep at one site, pigs at one site, turkeys kept seasonally at both sites, and sheep kept seasonally at a third site), landfill sites, sewage treatment works, an arable farm, urban sites, and a marine site. Other samplers were sited at typical rural locations without obvious influences of specific NH_3 sources. Although the livestock farms showed pronounced elevations of NH_3, the sewage treatment plant showed concentrations that were not greatly different than the other non-agricultural sites, leading Allen *et al.* to conclude that sewage treatment is a minor or insignificant source of NH_3 emissions. The water treatment plant was of the percolating filter type, where the wastewater is trickled downwards as a part of the purification process, rather than the plant being of the more common, larger, activated sludge type of treatment plant. Because of the work of Allen *et al.* (1988), emissions of NH_3 during the normal operation of waste water treatment plants have not been considered as a significant source in the more recent emission inventories.

TABLE 6-1. AMMONIA EMISSION FACTORS FOR HUMAN SOURCES

Source	Emission Factor (kg/person/year)	Factor Rating	Emission Factor (lb/person)
NAPAP - Smokers	0.0041	D	0.0091
NAPAP - Nonsmokers	0.0054	D	0.012
NAPAP - Cigarette smoke	0.00082	C	0.0018
NAPAP - human perspiration	0.25	E	0.55
Buijsman (1984)	0.3		0.7
Atkins and Lee (1993)	1		2.2
Möller & Schieferdecker (1989)	1.3		2.9
Cass *et al.* (1982)	0.25		0.55
Healy *et al.* (1970)	0.31 to 0.54		0.7 to 1.2
Lee and Dollard (1994)	0.25 to 1.3		0.55 to 2.9

Buijsman *et al.* (1987)[11] included sewage sludge applied to land as a minor source of atmospheric NH_3, based on data reported by King (1973)[12] and Beauchamp (1978).[13] Kruse *et al.* (1989)[14] developed an NH_3 emission inventory for Great Britain, and stated that sewage may be another potentially important source of NH_3, although it was not included in the inventory. Asman (1992) states that sewage sludge is a source of NH_3 emissions, but that emissions are very uncertain and not very important.

Recently, Lee *et al.* (1992)[15] reported preliminary data on NH_3 concentrations in the vicinity of an activated sludge sewage treatment plant. Many of the larger sewage treatment plants use the activated sludge process. In the activated sludge process, large solids are removed by sedimentation. Bubbles of air are then blown up through the solution, and are seeded with the sludge at a pH of approximately 7 to 8. During this process, NH_3 is oxidized to NO_2^- and NO_3^-. It is likely that some of the ammoniacal nitrogen will be lost to the atmosphere as NH_3 gas. The fraction of NH_3 lost to the atmosphere is dependent upon the pH of the solution. Lee *et al.* (1992) have preliminary results of concentrations of 12 to 100 $\mu g/m_3$, which is substantially higher than the concentrations measured by Allen *et al.* (1988), of 3 $\mu g/m_3$ near a percolating filter waste water treatment plant.

The 1985 NAPAP emission inventory utilized a POTW emission factor of 2.2 kg/10^6 liters (19 lb $NH_3/10^6$ gallons) treated, resulting in an emission estimate of 6.6% of the 1985 NAPAP emission inventory. The NAPAP factor was developed based on the 1984 Needs Survey, which included influent and effluent NH_3 concentrations for over 850 wastewater treatment facilities nationwide, and was also developed based on research on NH_3 stripping from treatments plants (Warn *et al.*, 1990).

Recent analysis of the Hot Spot Toxic Inventory for the State of California provided NH_3 emission rates that were reported for several plants.[16] It should be noted that some of names of the emission points in the California data do not match well with the SCCs chosen, resulting in confusing emission factors. Specifically, an aerobic digester was coded as an entire plant, and a sludge thickener was coded as an aeration tank. The NAPAP factor and the factors reported in California are summarized in Table 6-2. Until the data from Lee *et al.* (1992) are published, the NAPAP values are recommended for continued use. The emission factor for POTWs is assigned a quality rating of E which is consistent with the rating provided by Warn *et al.* (1990).

TABLE 6-2. AMMONIA EMISSION FACTORS FOR POTW'S

Source (SCC)	Emission Factor (kg/10^6 liters treated)			Emission Factor (lbs/10^6 gallons treated)		
	Avg	Max	Min	Avg	Max	Min
NAPAP 5-01-007-01	2.2			19		
California - Entire plant[a] 5-01-007-01	1.93	5.39	0.012	16.1	45	0.099
California - Primary settling 5-01-007-02	0.00023			0.0019		
California - Aeration[a] 5-01-007-04	14	29	0.00066	120	240	0.00552

[a] The throughput for an entire plant is considerably higher than the throughput of an aeration tank resulting in a higher emission rate for the aeration tank.

6.3 NON-AGRICULTURAL SOILS

There is a great deal of uncertainty surrounding NH_3 emissions from undisturbed land or nonagricultural plants and soils, because of the ability of soils and plants to act as both sources and sinks of NH_3. Due to this uncertainty, Asman (1992) did not include this potential source of emissions in his recent inventory of NH_3 emissions in Europe. NAPAP did not include undisturbed land in the 1985 emission inventory. Erisman (1989)[17] noted a range of 0.009 g NH_3/m_2/year to 0.03 g NH_3/m_2/year (0.09 kg NH_3/ha/year to 0.3 kg N/ha/year) for natural soils, and did not include natural NH_3 emissions due to the large uncertainty in these values.

Buijsman *et al.* (1987) discussed natural NH_3 emissions from undisturbed land. Using a flux of 10 µg/m^2/h, which was within the range of various researchers cited, he estimated a natural annual NH_3 flux of 0.75 gigagrams (Gg) NH_3, which is far exceeded by the anthropogenic emissions (6.4 Gg NH_3) and, therefore, NH_3 emissions from undisturbed land are not included in the final inventory. Lee & Longhurst (1993)[18] used the factor from Buijsman (1986)[19] of 0.009 g NH_3/m^2/year for vegetated land in their NH_3 inventory for densely populated regions of the United Kingdom. Möller & Schieferdecker (1989) use an emission factor for arable land (agricultural and forests) of 0.03 g NH_3/m$_2$/year (3 kg NH_3(N)/ha/year) in their NH_3 inventory for the G.D.R. The value of 0.03 g/m^2/yr (3 kg N/ha/yr) may originate with Dawson (1977)[20] who apparently developed one of the first models for NH_3 emission estimates from undisturbed lands.

Denmead (1990)[21] concluded that NH_3 emissions from natural fields were the most important source of NH_3 in Australia, providing 47% of the NH_3. He discussed soils, plants, and plant communities, and used measurement in an ungrazed, unfertilized, grass-clover pasture to estimate emissions from uncultivated land. He estimated NH_3 emissions by assuming that 30 g N/ha/day are produced in a 6-month period (0.55 g N/m^2/year, assuming 183 days/year) over the 164 million hectares of forest and uncultivated country in the humid, sub-humid and monsoonal zones delineated in the Atlas of Australian Resources. He estimated that NH_3 emission rates were negligible in the drier zones.

In a recent study of the uncertainties in current estimates of NH_3 in the United Kingdom, Lee and Dollard (1993) note that Metcalfe *et al.* (1989)[22] suggested that the emissions of NH_3 may be as high as 5 g/m^2 (50 kg/ha).

Schlesinger & Hartley (1992)[23] compiled research on the soil flux of NH_3 from the world's undisturbed ecosystems, and derived a global estimate for the total flux of NH_3 to the atmosphere from all sources. Studies on NH_3 from undisturbed ecosystems included data obtained by chamber measurements, as well as regional estimates from atmospheric concentration gradients. Problems with both methods are acknowledged. Hourly rates of NH_3 volatilization range over four orders of magnitude, with the highest values found in some grassland ecosystems. Much of the variation is believed to be due to differences in soil temperature and moisture during the period of measurement. Many of the measurements were taken in midday and/or the summer season when the volatilization rates are highest; therefore, extrapolation of these values to provide annual estimates would produce high estimates. Schlesinger & Hartley (1992) limited the NH_3 volatilization losses in their estimations to 20% of annual net mineralization of soil nitrogen, because this is the average loss of NH_3 during fertilizer applications.

Table 6-3 summarizes NH_3 emission rates that have been cited in the literature. Due to the extensive review provided by Schlesinger and Hartley (1992), their emission factors are recommended for use. All four of the factors from Schlesinger and Hartley (1992) are assigned an emission factor rating of E.

TABLE 6-3. AMMONIA EMISSION FACTORS FOR NON-AGRICULTURAL SOILS

Source	Emission Factor ($g\ NH_3$-N/m^2)[a]	Factor Rating	Emission Factor (lb NH_3/acre)
Lee and Longhurst (1993)	0.009		0.97
Moller & Schieferdecker (1989)	0.03		0.32
Metcalfe *et al.* (1989)	0.5		5.4
Denmead (1990)	0.56		6.0
Schlesinger and Hartley *Temperate forest and Woodland & Shrubland*	0.1 to 1.0	E	1 to 10.
Schlesinger and Hartley *Tropical Savanna*	0.25 to 0.75	E	2.7 to 8.1
Schlesinger and Hartley *Temperate Grassland*	0.01 to 1.0	E	0.1 to 10.
Schlesinger and Hartley *Desert Scrub*	0.01 to 0.25	E	0.1 to 2.7

[a] A hectare is equal to 10,000 m^2 or 2.471 acres.

6.4 USE OF AMMONIA AS A REFRIGERANT

Ammonia is used extensively as a refrigerant in large industrial and commercial installations. It has the advantages of a high heat of vaporization and a favorable pressure-volume relationship. However, it also has the disadvantage of being toxic and corrosive to some materials, most notably copper.[24] The consumption of NH_3 for refrigeration applications in the U.S. is estimated at 270,000 Mg/year.[25]

It is assumed that all of the NH_3 used in refrigeration is ultimately emitted to the atmosphere. Because NH_3 refrigeration is a mature technology (its use in this application precedes that of Freons), it is further assumed that there is a steady state relationship between NH_3 refrigerant consumption and emissions. Therefore, the annual emission rate for NH_3 from refrigeration is also estimated at 270,000 Mg/year.

There were no emission factors for NH_3 from refrigeration in the literature. Because NH_3 is most commonly used in large commercial or industrial refrigeration systems, emissions of NH_3 refrigerant are probably best estimated using employee statistics which are readily available and allow for NH_3 refrigerant usage to be apportioned to the State and county level. Refrigeration is probably used in many industries, however, the knowledge is incomplete and fuurther research into the development of an NH_3 emission factor for refrigeration is recommended for future research. Intuitively it is assumed that the majority of the industrial and commercial refrigeration is in the Major SIC group 20, Food and Kindred Products. Using a national employment of 1,453,000 for SIC 20xx, the average emission factor for NH_3 used as a refrigerant is 187 kg/employee (413 lb/employee). This emission factor is given a rating of E, because the factor is derived from a national level material balance, and not on test data.

6.5 AMMONIA SPILLS

Under Section 302 of the Superfund Amendments and Reauthorization Act, accidental releases of NH_3 exceeding 45 kg (100 pounds) must be reported to the National Response Center, at the U.S. Coast Guard. The reports must contain the nature and amount of the release, the cause, the location, the responsible party, and other information. The National Response Center maintains these release reports in a computerized data base.

Release reports for NH_3 were obtained from the National Response Center for 1991 through early 1994.[26] During this period, a total of 1648 releases to the atmosphere were reported. The largest reported release was 295 Mg (325 tons) and the average release was 1.5 Mg (1.6 tons). Table 6-4 summarizes release data by year and by the type of vessel from which the spills originated.

The NH_3 emitted through these spills was primarily from fixed storage, and was the result of spills from refrigeration units. These data could be processed to provide county-level totals reported through the area source classification code 28-30-000-000 *Miscellaneous Area Sources - All Catastrophic/Accidental Releases - Composite*. Including the spills in an inventory effort would, however, double count the emissions from refrigeration sources; therefore, an emission factor is not being presented for this category of emissions.

6.6 RECOMMENDED AMMONIA EMISSION FACTORS FOR MISCELLANEOUS SOURCE CATEGORIES

Table 6-5 summarizes the NH_3 emission factors for the miscellaneous source categories discussed in this section. It should be emphasized that all of these emission factors have a quality rating of E and are very uncertain. Of the source categories discussed, the NH_3 emissions from nonagricultural lands have the potential for introducing the largest uncertainty into an emission inventory development effort.

TABLE 6-4. SUMMARY OF ACCIDENTAL RELEASES OF AMMONIA

Source	Ammonia releases reported to National Response Center (Mg)			
	1990	1991	1992	1993
Fixed storage	161.5	1,014.0	334.4	498.2
Pipeline	206.0	0.6	0.3	0.5
Highway vehicles	25.4	14.4	22.6	54.6
Marine vessels	0.0	0.1	0.2	0.0
Railroads	1.0	1.3	0.3	0.1
Unknown	1.5	3.1	0.2	4.7
Totals	395.4	1,033.5	358.0	558.1

TABLE 6-5. RECOMMENDED EMISSION FACTORS FOR MISCELLANEOUS SOURCES

Classification Code	Description	Emission Factor (kg NH_3/unit)	Unit	Factor Rating	Emission Factor (lb NH_3/SCC or AMS unit)	Estimated annual emissions (Mg)
28-10-010-000	Humans	0.25	person	E	0.55	62,500[a]
5-01-007-01 26-30-000-000	POTWs Wastewater treatment - Composite	2.2	10^6 liters	E	19	107,000[b]
27-01-001-000	Natural sources - Biogenic - plants - forests - Composite	0.1 to 1.0	g $NH_3(N)/m^2$	E	1 to 10	c
27-01-470-000	Natural sources - Biogenic - plants - Tropical savannah - Composite	0.25 to 0.75	g $NH_3(N)/m^2$	E	2.7 to 8.1	c
27-01-240-000	Natural sources - Biogenic - plants - Vegetation/grassland - Composite	0.01 to 1.00	g $NH_3(N)/m^2$	E	0.1 to 10.	c
27-01-450-000	Natural sources - Biogenic - plants - desert scrub - Composite	0.01 to 0.25	g $NH_3(N)/m^2$	E	0.1 to 2.7	c
23-02-080-002	Food & Kindred Products - Misc. - Refrigeration	187	kg/employee	E	413	270,000

[a] Based on a U.S. population of 250 million people.
[b] Based on annual estimate of 12.4 x 10^{12} gallons treated.
[c] Unknown.

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SECTION 7

CONCLUSIONS AND RECOMMENDATIONS

A review of the literature published since 1985 has revealed new data on sources and rates of NH_3 emissions. The majority of the literature has been published in Europe in support of acid deposition research. The literature and the NH_3 emission measurement programs in Europe have focused on agricultural sources: primarily, animal husbandry and fertilizer application. Recent inventories for Europe and European nations indicate that these agricultural sources contribute up to 80 percent of the NH_3 emissions. Additional studies, relating to global climate research, indicate that biomass burning and undisturbed soils may contribute up to half of the global NH_3 emissions; however, these sources are generally excluded from the European NH_3 inventory work.

Ammonia emission factors were developed for the National Acid Precipitation Assessment Program (NAPAP). The NAPAP factors were compared with the available information on NH_3 emissions and emission rates. Recommendations on NH_3 emission factors for future emission inventory development work in the United States are presented. These recommendations include the use of the European results for agricultural sources, and the use of the *Compilation of Air Pollutant Emission Factors - Volume I*[1] for the majority of the stationary industrial sources. Factors for three new industrial categories have been developed. These are beet sugar production, froth flotation in mineral processing, and mineral wool (fiberglass) production. Discreet industrial sources of NH_3, with no corresponding emission factors, are identified through the Toxic Release Inventory. Additional sources of NH_3 include combustion (and control methods for NO_x emissions from combustion), human breath and perspiration, publicly owned treatment works (POTW's), and NH_3 as a refrigerant.

The following discussion summarizes the emission factors recommended for use in future inventories and discusses additional research that could be conducted to enhance future NH_3 inventory efforts in the U.S.

7.1 RECOMMENDED EMISSION FACTORS

Tables 7-1 through 7-5 present the recommended emission factors, classification codes for U.S. inventory efforts, the emission factor ratings based on the criteria presented in Appendix A, and estimates of NH_3 emissions, where available.

7.2 RELATIVE SOURCE STRENGTH IN THE U.S.

Estimates of NH_3 emissions in the U.S. are graphically illustrated in Figure 7-1. These emission estimates are not comprehensive and are presented only to illustrate the relative magnitude of the emissions, in order to frame the recommendations for future

TABLE 7-1. RECOMMENDED AMMONIA EMISSION FACTORS FOR ANIMAL HUSBANDRY

Source (U.S. Agricultural Statistics Classifications)	AMS Classification Codes	1991 Populations (10^6 animals)	Emission Factor Classifications (Asman, 1992)	Emission Factor (kg NH_3/animal)	Factor Rating	Emission Factor (lb NH_3/animal)	Estimated emissions (Gg/year)
Cattle and Calves - Composite	28-05-020-000	100		22.9	B	50.5	2,290
Cows and heifers that have calved (Beef cows)	28-05-020-001	33.8	Dairy & calf cows	39.72	B	87.57	1,342
Cows and heifers that have calved (Milk cows)	28-05-020-002	9.90	Dairy & calf cows	39.72	B	87.57	393
226.8 kg (500 pounds) and over: Heifers - Beef cow replacements	28-05-020-003	5.75	Young cattle for fattening	15.19	B	33.49	87
226.8 kg (500 pounds) and over: Heifers - Milk cow replacements	28-05-020-004	4.20	Young cattle	13.04	C	28.75	55
226.8 kg (500 pounds) and over: Heifers - Other	28-05-020-005	8.68	Young cattle	13.04	B	28.75	113
226.8 kg (500 pounds) and over: Steers	28-05-020-006	16.7	Fattening/grazing cattle > 2 yr	8.22	C	18.12	137
226.8 kg (500 pounds) and over: Bulls	28-05-020-007	2.28	Breeding bulls > 2 yr	27.91	C	61.53	64
Calves under 226.8 kg (500 pounds)	28-05-020-008	18.7	Fattening Calves	5.23	B	11.53	98
Hogs and Pigs - Composite	28-05-025-000	57.75		9.21	B	20.30	531
Kept for breeding	28-05-025-010	7.25					
Sows farrowing	28-05-025-011	6.02	Breeding sows > 50 kg.	16.13	B	35.56	97.1
Other - kept for breeding	28-05-025-012	1.23	Breeding sows 20-50 kg	5.22	C	11.5	6.52
Market hogs by weight groups	28-05-025-020						
Under 27.2 kg (60 pounds)	28-05-025-021	18.7	Fattening pigs	6.98	B	15.4	131
27.2 to 54.0 kg (60 to 119 pounds)	28-05-025-022	13.0	Fattening pigs	6.98	C	15.4	90.7
54.1 to 81.2 kg (120 to 179 pounds)	28-05-025-023	10.4	Mature boars	11	B	24.3	114

(Continued)

TABLE 7-1. RECOMMENDED AMMONIA EMISSION FACTORS FOR ANIMAL HUSBANDRY (Continued)

Source (U.S. Agricultural Statistics Classifications)	AMS Classification Codes	1991 Populations (10^6 animals)	Emission Factor Classifications (Asman, 1992)	Emission Factor (kg NH_3/animal)	Factor Rating	Emission Factor (lb NH_3/animal)	Estimated emissions (Gg/year)
81.3 to 99.3 kg and 99.4 kg (180 pounds) and over	28-05-025-024	8.4	Mature boars	11	B	24.3	92
Poultry - Chickens - Composite	28-05-030-000	6,497		.1787	B		1,161
Hens	28-05-030-001	116	Mother animals > 6 mo.	0.598	B	1.32	69.4
Pullets - Of laying age	28-05-030-002	162	Laying hens > 18 wk.	0.305	B	.672	49.4
Pullets - 3 months old and older not of laying age	28-05-030-003	33.5	Mother animals < 6 mo.	0.269	C	.593	9.01
Pullets - Under 3 months old	28-05-030-004	40.8	Laying hens < 18 wk.	0.17	B	.375	6.94
Other chickens	28-05-030-005	6.85		0.179	C	.395	1.23
Broilers	28-05-030-006	6,138	Broilers	0.167	B	.368	1,025
Poultry - Other	28-05-035-000						247.3
Ducks	28-05-035-001	20.0	Ducks	0.117	B	.258	2.34
Turkeys	28-05-035-002	285	Turkeys for slaughter	0.858	B	1.89	245
Young turkeys	28-05-035-003		Turkeys < 7 mo.	0.89	B	1.96	
Old turkey	28-05-035-004		Turkeys > 7 mo.	1.278	B	2.82	
Fryer-roasted turkey	28-05-035-005		Turkeys for slaughter	0.858	C	1.89	
Sheep and Lambs - Composite	28-05-040-000	10.85	Ewes	3.37	D	7.43	36.56
Sheep and lambs on feed	28-05-040-001		Ewes	3.37	D		
Stock sheep-lambs-ewes	28-05-040-002		Ewes	3.37	D		
Stock sheep-lambs-wethers and rams	28-05-040-003		Ewes	3.37	D		
Stock sheep- 1 yr. and over- ewes	28-05-040-004		Ewes	3.37	D		
Stock sheep- 1 yr. and over- wethers and rams	28-05-040-005		Ewes	3.37	D		

(Continued)

TABLE 7-1. RECOMMENDED AMMONIA EMISSION FACTORS FOR ANIMAL HUSBANDRY (Continued)

Source (U.S. Agricultural Statistics Classifications)	AMS Classification Codes	1991 Populations (10^6 animals)	Emission Factor Classifications (Asman, 1992)	Emission Factor (kg NH_3/animal)	Factor Rating	Emission Factor (lb NH_3/animal)	Estimated emissions (Gg/year)
Miscellaneous Farm Animals	28-05-045-000						
Goats	28-05-045-001		Milch goats	6.4	E	14.1	
Mink	28-05-045-002	3.27	Mink	0.58	E	1.28	1.90
Fox	28-05-045-003		Fox	2.25	E	4.96	
Rabbit	28-05-045-004		Rabbit	2.8	E	6.2	
Miscellaneous Domestic Animals	27-10-020-000						
Cats	27-10-020-010		Cats	0.83	E	1.83	
Dogs	27-10-020-020		Dogs	2.5	E	5.5	
Horses	27-10-020-030		Horses & ponies	12.2	E	26.9	

TABLE 7-2. RECOMMENDED AMMONIA EMISSION FACTORS FROM FERTILIZER APPLICATION

Description	AMS code	Emission factor (kg NH_3/Mg N)	Factor rating	Emission factor (lb NH_3/ton N)	Estimated annual emissions (Mg)
Anhydrous ammonia	28-01-700-001	12	C	24	35,353
Aqua ammonia	28-01-700-002	12	C	24	664
Nitrogen solutions	28-01-700-003	30	C	61	74,042
Urea	28-01-700-004	182	B	364	271,250
Ammonium nitrate	28-01-700-005	25	C	49	13,137
Ammonium sulfate	28-01-700-006	97	C	194	14,631
Ammonium thiosulfate	28-01-700-007	30	C	61	571
Other straight nitrogen	28-01-700-008	30	C	61	5,763
Ammonium phosphates	28-01-700-009	48	C	97	44,487
N-P-K[b]	28-01-700-010	48	C	97	43,692
Total					503,590

[a] No factor was developed for the noted category.

[b] Nitrogen(N)-phosphorus(P)-potassium(K) mixtures.

TABLE 7-3. SUMMARY OF INDUSTRIAL AMMONIA EMISSION FACTORS

Source	Point Source SCC[a]	Emission Factor (kg/unit)	Units	Emission Factor Rating[b]	Emission Factor (lb emitted/ SCC unit)[c]	1985 Emissions (kg/yr)[d]
Ammonium Nitrate Manufacture[e]						
Neutralizer	3-01-027-04	0.43-18.0	Mg of product	B	0.86-36.0	8,082
	3-01-027-11					9,898
	3-01-027-21					3,665
Evaporation/concentration	3-01-027-17	0.27-16.7	Mg of product	A	0.54-33.4	2,225
	3-01-027-27					1,237
Solids Formation Operations						
high density prill towers	3-01-027-12	28.6	Mg of product	A	57.2	30,955
low density prill towers	3-01-027-22	0.13	Mg of product	A	0.26	38
rotary drum granulators	3-01-027-07	29.7	Mg of product	A	59.4	1,819
pan granulators	3-01-027-08	0.07	Mg of product	A	0.14	f
Coolers and dryers[g]						
high density prill coolers	3-01-027-14	0.02	Mg of product	A	0.04	7.3
low density prill coolers	3-02-027-23	0.15	Mg of product	A	0.30	0
low density prill dryers	3-01-027-25	0-1.59	Mg of product	A	0-3.18	52.6
Petroleum Refineries						
FCC units	3-06-002-01	0.155	10^3 liters fresh feed	B	54	19,411
TCC units (moving bed catalytic cracking units)	3-06-003-01	0.017	10^3 liters fresh feed	B	6	24
Reciprocating engine compressors	h	3.2	10^3 m^3 gas burned	B	0.2	h
NH_3 Synthesis						
Carbon dioxide regeneration	3-01-003-08	1.0	Mg of product	E	2.0	2,221

(Continued)

TABLE 7-3. SUMMARY OF INDUSTRIAL AMMONIA EMISSION FACTORS (Continued)

Source	Point Source SCC[a]	Emission Factor (kg/unit)	Units	Emission Factor Rating[b]	Emission Factor (lb emitted/ SCC unit)[c]	1985 Emissions (kg/yr)[d]
Condensate steam stripping	3-01-003-09	1.1	Mg of product	E	2.2	1,571
Urea Manufacture						
Solution formation/concentration	3-01-040-02	9.23[i]	Mg of product	A	18.46[i]	20,014
Solids formation						
nonfluidized bed prilling						
agricultural grade[j]	3-01-040-08	0.43	Mg of product	A	0.87	0
fluidized bed prilling[k]				A		
agricultural grade	3-01-040-10	1.46	Mg of product		2.91	340
feed grade	3-01-040-11	2.07[l]	Mg of product	A	4.14[l]	9.5
drum granulation	3-01-040-04	1.07[m]	Mg of product	A	2.15[m]	1,314
rotary drum cooler	3-01-040-12	0.0256	Mg of product	A	0.051	.045
Coke Manufacture[n]						
Wet coal oven charging - Larry car	3-03-003-02	0.01	Mg coal charged	D	0.02	162
Door leaks	3-03-003-08	0.03	Mg coal charged	D	0.06	293
Coke pushing	3-03-003-03	0.05	Mg coal charged	D	0.1	618.7
Ammonium Phosphate Manufacture	3-01-030[o]	0.07	Mg P_2O_5 produced	E	0.14	259

[a] Refers to SCCs that were in the 1985 NAPAP Emission Inventory.

[b] See Appendix A of this report for a definition of the ratings.

[c] All factors chosen are from *AP-42*.

[d] Emissions are from the 1985 NAPAP emission inventory and totals do not include 20,057 Mg from minor point source process emissions; area source category 99.

(Continued)

TABLE 7-3. SUMMARY OF INDUSTRIAL AMMONIA EMISSION FACTORS (Continued)

[e] Given as ranges because of variation in data and plant operations. All factors are uncontrolled, factors for controlled emissions are not presented due to conflicting results on control efficiency.

[f] NH_3 emissions from pan granulators were not presented by Warn *et al.* (1990) and were not included in the 1985 NAPAP emission inventory.

[g] Factors for coolers represent combined precooler and cooler emissions, and factors for dryers represent combined predryer and dryer emissions.

[h] Not available.

[i] EPA test data indicated a range of 4.01 to 14.45 kg/Mg (8.02 to 28.90 lb/ton).

[j] Feed grade factors were determined at an ambient temperature of 14° to 21° C (57° to 69°F).

[k] Feed grade factors were determined at an ambient temperature of 29°C (85°F) and agricultural grade factors at an ambient temperature of 27°C (80°F).

[l] For fluidized bed prilling, feed grade, there is a controlled emission factor with an A rating of 1.04 kg/Mg (2.08 lb/ton of product) based on use of an entrainment scrubber.

[m] EPA test data indicated a range of 0.955 to 1.20 kg/Mg (1.90 to 2.45 lb/ton).

[n] All factors are for uncontrolled emissions.

[o] The emission factor is for the whole plant, all processes.

TABLE 7-4. RECOMMENDED EMISSION FACTORS FOR COMBUSTION SOURCES

Source	Source Classification Codes	Emission Factor (metric units)	Factor Rating	Emission Factor (english units)
Coal Combustion	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103002xx, 103003xx, 10500102, 10500202 21-99-001-000, 21-99-002-000, 21-99-003-000	0.00028 kg/Mg	E	0.565 lb/10^3 ton
Fuel Oil Combustion	101004XX, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 21-99-004-000, 21-99-005-000	0.096 kg/10^3 liters	E	0.8 lb/10^3 gal
Natural Gas Combustion - Utility and Industrial Boilers	101006xx, 102006xx, 21-01-006-xxx, 21-02-006-xxx	51. kg/10^6 m^3	C	3.2 lb/10^6 ft^3
Natural Gas Combustion - Commercial Boilers	103006xx, 21-03-006-xxx	7.8 kg/10^6 m^3	C	0.49 lb/10^6 ft^3
Mobile Sources - Leaded Gasoline[a]	22-01-xxx-xxx	0.050 kg/10^3 liter	D	0.42 lb/10_3 gallons
Mobile Sources - Diesel	22-30-xxx-xxx	0.11 kg/10^3 liter	E	0.95 lb/10_3 gallons
SCR - Coal	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103002xx, 103003xx, 10500102, 10500202	0.155 kg/Mg	C	0.31 lb/ton
SCR - Oil	101004xx, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 201001xx, 201009xx, 202001xx, 202003xx, 20200401, 20200501, 202009xx, 203001xx, 20300301	0.17 kg/10^3 liters	C	1.4 lb/10_3 gallons
SCR - Gas	101006xx, 102006xx, 103006xx, 10500106, 10500206, 201002xx, 202002xx, 203002xx	146. kg/10^6 m^3	C	9.1 lb/MMscf

(Continued)

TABLE 7-4. RECOMMENDED EMISSION FACTORS FOR COMBUSTION SOURCES (Continued)

Source	Source Classification Codes	Emission Factor (metric units)	Factor Rating	Emission Factor (english units)
SCR - Wood	101009xx, 102009xx, 103009xx	0.155 kg/Mg	C	0.31 lb/ton
SNCR - Coal	101001xx, 101002xx, 101003xx, 102001xx, 102002xx, 102003xx, 103001xx, 103002xx, 103003xx, 10500102, 10500202	0.315 kg/Mg	C	0.63 lb/ton
SNCR - Oil	101004xx, 101005xx, 102004xx, 102005xx, 103004xx, 103005xx, 10500105, 10500205, 201001xx, 201009xx, 202001xx, 202003xx, 20200401, 20200501, 202009xx, 203001xx, 20300301	0.35 kg/10^3 liters	C	2.9 lb/10^3 gallons
SNCR - Gas	101006xx, 102006xx, 103006xx, 10500106, 10500206, 201002xx, 202002xx, 203002xx	288 kg/10^6 m^3	C	18 lb/MMscf
SNCR - Wood	101009xx, 102009xx, 103009xx	0.315 kg/Mg	C	0.63 lb/MMscf

[a] Emission factors for leaded gasoline are not presented because leaded gasoline is almost completely phased out and the source category classifications for the U.S. do not distinguish between leaded and unleaded gasoline.

TABLE 7-5. RECOMMENDED EMISSION FACTORS FOR MISCELLANEOUS SOURCES

Classification Code	Description	Emission Factor (kg NH_3/unit)	Unit	Factor Rating	Emission Factor (lb NH_3/SCC or AMS unit)	Estimated annual emissions (Mg)
28-10-010-000	Humans	0.25	person	E	0.55	62,500[a]
5-01-007-01 26-30-000-000	POTWs Wastewater treatment - Composite	2.2	10^6 liters	E	19	107,000[b]
27-01-001-000	Natural sources - Biogenic - plants - forests - Composite	0.1 to 1.0	g NH_3(N)/m^2	E	1 to 10	c
27-01-470-000	Natural sources - Biogenic - plants - Tropical savannah - Composite	0.25 to 0.75	g NH_3(N)/m^2	E	2.7 to 8.1	c
27-01-240-000	Natural sources - Biogenic - plants - Vegetation/grassland - Composite	0.01 to 1.00	g NH_3(N)/m^2	E	0.1 to 10.	c
27-01-450-000	Natural sources - Biogenic - plants - desert scrub - Composite	0.01 to 0.25	g NH_3(N)/m^2	E	0.1 to 2.7	c
23-02-080-002	Food & Kindred Products - Misc. - Refrigeration	187	kg/employee	E	413	270,000

[a] Based on a U.S. population of 250 million people.
[b] Based on annual estimate of 12.4 x 10^{12} gallons treated.
[c] Unknown.

research. These rough estimates of U.S. NH_3 emissions indicate that agricultural practices, specifically animal husbandry and fertilizer application, dominate emissions here, just as they do in Europe. Industrial emissions of NH_3 and NH_3 from combustion (excluding open or biomass burning) are relatively insignificant. Emissions from POTW's and refrigeration may be significant, based upon the current information gathered. Emission factors for both of these source categories have a rating of E, and further research into these sources is recommended. Estimates of NH_3 from biomass burning and undisturbed soils were not made, due to the unavailability of an emission factor for biomass burning and of activity data for undisturbed soils. Recent research indicates that these two categories may contribute significantly (up to half) of global NH_3 emissions. Additional research into these two categories of emissions is recommended.

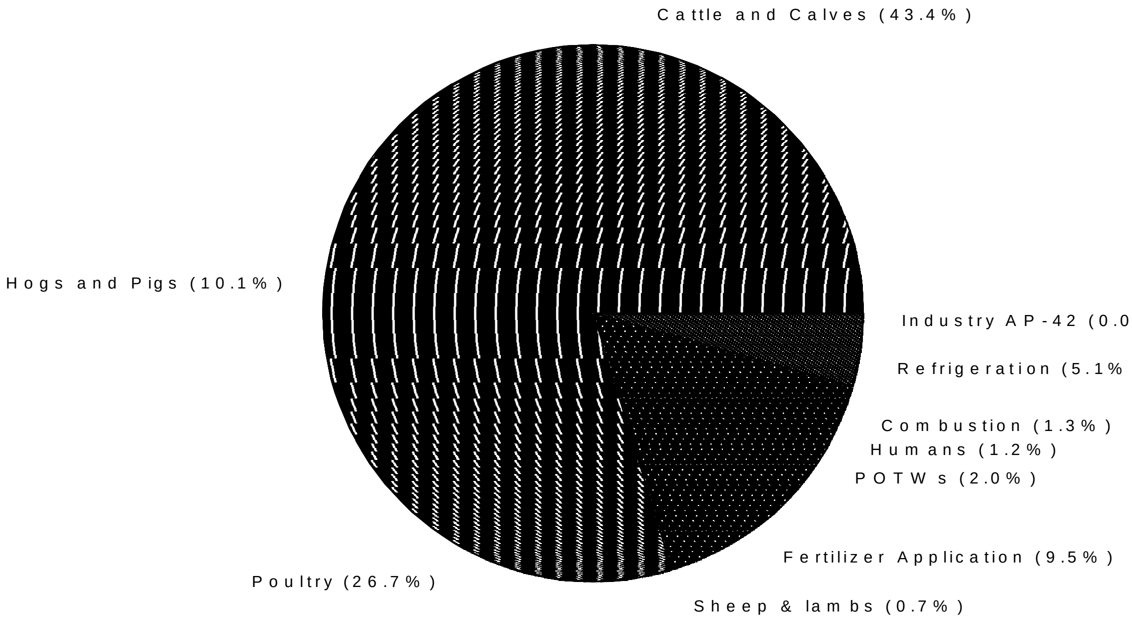

Figure 7-1. Relative contribution of ammonia emissions from different source categories.

In the mid 1980's, Allen *et al.* (1988)[2] measured ground-level concentrations of NH_3 and ammonium (NH_4^+) at nineteen sites within a 35-km radius of Colchester, U.K. The sampling sites were selected to reflect the influences of different possible sources upon concentration of NH_3. The six sites included livestock farms (sheep at one site, pigs at one site, turkeys kept seasonally at both sites, and sheep kept seasonally at a third site), landfill sites, sewage treatment works, an arable farm, urban sites, and a marine site. Other samplers were sited at typical rural locations, without obvious sources of specific NH_3 emissions. The livestock farms show very pronounced elevations, and the site used seasonally for sheep shows a possible slight elevation. Thus, livestock farming appears to be confirmed as a major local influence. Other sites show minor variations in NH_3 concentrations, but no major inter-site differences are seen. Arable farming apparently raises arithmetic mean concentrations, but the influences of landfill operations, sewage treatment by percolating filters, or urban activities are minor or insignificant. These data support the conclusions in this report.

The data collected by Allen *et al.* (1988) show a very pronounced seasonal variation, with the highest levels occurring in the summer and the lowest levels occurring during the winter months. This finding is consistent with those regarding the influence of temperature upon both biogenic and chemical releases of NH_3 from soils and fertilizers. The NH_3 concentrations failed to demonstrate any consistent diurnal patterns. Additional investigation into both the seasonal and diurnal pattern of emissions is recommended to support future atmospheric modeling efforts.

7.3 RECOMMENDED RESEARCH

European researchers have conducted the majority of the research in NH_3 emissions. In addition, several articles were uncovered in the European literature that represent new field measurement programs whose results have not yet been incorporated into the literature. Specifically, there is ongoing research in the United Kingdom to improve the emission factors from humans and from POTWs.

Table 7-6 summarizes potential research projects that could enhance the quality of the NH_3 emissions estimates.

TABLE 7-6. RECOMMENDED AMMONIA EMISSION FACTOR RESEARCH PROJECTS

Source Category	Description of Research
Activity data	In order to properly rank research programs, additional confidence on recent activity for known sources of NH_3 would result in increased knowledge of relative strength and, consequently, the impact of various uncertainties in the emission factors. For example, biomass burning, acreage and type of undisturbed land, and pet (including horses) populations, should be investigated to provide increased resolution on the emission estimates presented above.
Animal Husbandry	Asman (1992)[3] presents very detailed emission factors for most categories of animal husbandry. Investigation into the primary sources of data used by Asman (1992) would result in more confidence in the link between the European factors and the U.S. statistics and agricultural practices and, therefore, increased accuracy in the use of the factors for U.S. inventories.
	Examination of the differences between the values used for sheep by Denmead (1990)[4] for Australia and by Asman (1992) for Europe will increase the confidence in the value recommended for use in the U.S.
	Only one research program has quantified NH_3 from cats and dogs (Cass *et al*, 1982).[5] Due to the datedness of this effort, it was not obtained and reviewed for the present report. It is, therefore, not known how much domestic pet populations contribute to NH_3 emissions. Additional field level research on emissions from domestic animals may be warranted.

(Continued)

TABLE 7-6. RECOMMENDED AMMONIA EMISSION FACTOR RESEARCH PROJECTS (Continued)

Source Category	Description of Research
Fertilizer Application	Ammonia emissions from urea fertilizer application range from 5 to 50 percent of the applied nitrogen content. Although we are comfortable with the average emission factor of 15 percent, the wide range in potential emissions can have a strong impact on the overall NH_3 emission inventory in a given area. There are some very comprehensive models that relate NH_3 emissions to various parameters, including temperature, soil conditions, and application practices. These models could be used to develop State-specific or crop-specific emission factors, if more information were gathered on fertilizer application practices. In addition, various investigators have been studying methods for reducing NH_3 losses from urea. This may warrant future downward adjustments to the urea emission factor. The present study focused on data published since 1985. Review of European inventories revealed extensive emissions from various ammonium fertilizers. In general, the European emission factors for ammonium fertilizer are adopted in this report without revision, because there have not been subsequent measurements. A review of the pre-1985 measurements used in the European studies may give factors that are somewhat different.
Nonagricultural Soils	There is huge variability (four orders of magnitude) in the emission factors used to develop the composite factors presented. Additional effort could be expended on analyzing the primary data sources to gain confidence in the composite factors developed. In addition, the emission factors should be linked to the land use land cover categories recently developed to support biogenic emission estimation models.
Refrigeration	The emission factor presented is a per employee factor based on the amount of NH_3 used in this application. The data on the quantity of NH_3 used should be verified, due to its large contribution. The method used to allocate these emissions (employment statistics) may be inconsistent with the way in which these emissions occur. As freon is phased out, the emissions from refrigeration may change.
POTW's	The article on *Atmospheric Ammonia in the Vicinity of a Sewage Treatment Plant - results from a preliminary investigation.* (Lee *et al*, 1992)[6] indicates that further work is currently being undertaken to clarify the precise sources of NH_3 and their contribution to atmospheric budgets. This research is believed to be on-going in the United Kingdom by D.S. Lee, P.D. Nason, and S.L. Bennett. Research is also ongoing in California to improve emission estimates from POTWs.
Industrial Sources	Analysis of ambient air quality data collected in Louisiana and Alaska may provide increased accuracy in emission factors for those sources (fertilizer manufacturing sources).

(Continued)

TABLE 7-6. RECOMMENDED AMMONIA EMISSION FACTOR RESEARCH PROJECTS (Continued)

Source Category	Description of Research
	Further analysis of the TRIS data as indicators of potential industrial NH_3 sources, and the extrapolation of that data, with the NAPAP inventory and information collected through MACT surveys, may provide additional information on the types, locations, and numbers of industrial processes that may warrant emission factor development.
Combustion	An examination of the factors and research used to estimate NH_3 from biomass burning, and the search for the most appropriate source of activity data is recommended. Biomass burning includes naturally occurring fires and may also include prescribed agricultural burning, as well as miscellaneous structural fires. In addition, the chemical agents that are used to fight large naturally occurring fires should be investigated to determine if they contribute significantly to the overall NH_3 emissions from fire.
	Additional analysis of the NH_3 emission rates from SCR and SNCR NO_x control units, as measurement data become available for new installations, should be conducted.
	A test program to measure the NH_3 emissions from the newer automobiles, including natural gas fired vehicles and new catalysts, should be initiated. The data used to support the emission factors in this report are from older automobiles (1960's and 1970's) that do not represent the current fleet.
	A test program to reexamine the emission factors for fuel oil and natural gas combustion should be initiated. NAPAP was the only inventory to include NH_3 emissions from fuel oil and natural gas. The existing data indicate that fuel oil and natural gas contribute more NH_3 emissions than coal combustion, but all of the research and data are dated.
Human Breath & Perspiration	The article on *Uncertainties in Current Estimates of Emissions of Ammonia in the United Kingdom* (Lee & Dollard, 1994)[7] indicates that further research on indoor NH_3 concentrations at a variety of locations is currently being undertaken and will be published in the near future. The research is believed to be on-going in the United Kingdom by D.S. Lee and D.H.F. Atkins.
Spills - Accidental Releases	Software has been developed for extrapolating data from the Coast Guard spill data base. This could be extended to produce county-level results. The majority of the NH_3 reported as spills is believed to be a result of refrigeration leaks and, therefore, factors for spills were not developed (otherwise it would result in double counting). The assumption that NH_3 emissions in this category are contributed primarily from refrigerant leaks should be verified.

Five research areas are recommended to enhance the quality of NH_3 emission factors presented in this report. The five research areas are:

- Investigate the recent global climate literature on NH_3 from undisturbed soils. Merge the literature on emission fluxes with new land use land cover data categories to develop emission factors for the biogenic plants- area and mobile source classification category.

- Investigate recent literature on NH_3 emissions from biomass burning. Integrate the data results with information in the U.S. on naturally occurring fires to develop emission factors for the U.S. Also, investigate any information on NH_3 emissions from the chemical agents used to fight these naturally occurring fires.
- Research the primary references for the animal husbandry emission factors, in order to provide more accurate linkages with the U.S. Department of Agriculture statistics. In addition, investigate the discrepancy in the emission factors for sheep presented by Asman (1992) and Denmead (1990).
- Develop temporal profiles for the larger NH_3 emissions categories. Specifically, investigate the seasonal nature of the animal husbandry and fertilizer application emissions.
- Confidence in the emission factors reported for the industrial categories of refrigeration, POTWs, and selective catalytic and non-catalytic reduction (for control of NO_x emissions), may be improved with additional research. Refrigeration contributes a significant portion of the NH_3 inventory (about 5%); however, this factor was developed based on a material balance. POTWs also contribute a significant amount of NH_3 (about 2%); however, additional research is ongoing in the United Kingdom and California that may improve the accuracy of this emission factor.

REFERENCES FOR SECTION 7

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APPENDIX A

CRITERIA FOR ASSESSING EMISSION FACTORS[1]

This appendix describes the criteria that were used to assess the quality of the NH_3 emission factors presented in this report. The purpose of the ratings is to provide a qualitative indication of the reliability of the emission factors. Criteria used to assess the emission factors are listed below.

A.1 DISCUSSION OF CRITERIA

Emission Factor Development Methods: Most emission factors are determined from either source tests, industry surveys, mass balances, or engineering estimates. The accuracy of these methods depends on several different parameters which change from one emission source to another.

- **Source Tests**: In source testing, samples are taken directly from the source emitting the pollutant. Accurate approved test methods should have been used whenever possible. If an unapproved method or an outdated method was used, the quality of the emission factor should be questioned.

- **Industry Survey**: In a survey, EPA submits a series of questions to a plant or site that is emitting the pollutant in question. The plant or site personnel voluntarily fill out and return the questionnaire to the surveyor. To obtain accurate information, the questions must be worded carefully so that the correct and desired information will be given. If consistent results are reported by the participants, the information may be considered accurate. To effectively assess the quality of an emission factor, the survey methodology should be known.

- **Engineering Estimate**: An engineering estimate is based on process information available to the engineer. The engineer makes several assumptions and other available information, he estimates an emission factor. This method of determining an emission factor is generally the most inaccurate. However, with adequate background information, an accurate estimate can frequently be made.

Size of Database: The emission factor becomes increasingly accurate as the database from which the factor was determined expands. Emission factors constructed on information from one source have less credibility than those from several sources.

Database Represents a Good Cross Section of Industry: An average emission factor should be determined from a cross section of the industry. A good cross section is related to the size of the database. However, a large database does not ensure a good cross section, and an excellent cross section is possible from a small database.

Age of Data: Some emission factors quickly lose credibility for the following reasons:

! The sampling and testing methods may have been proven invalid, and as better methods are developed, inherent flaws in previously used methods are discovered.

! Technological innovations occur in most industries on a regular basis. Consequently, the process parameters used when the emission tests were performed may differ significantly from those currently used in the industry. Control systems may be more efficient, fuel feed and production rates may differ, the composition of pollutants may be significantly different, etc. As a result, the old emission factor may no longer apply.

! New laws and regulations may be passed which would significantly affect the emissions from a source.

A.2 RATING SYSTEM

A rating system, analogous to the *AP-42* system, was developed to grade each emission factor. Due to the variability in the type of information in the reference used to assign emission factors, a good deal of subjective engineering judgement was used in giving each factor a grade.

Emission factors for each process were given a rating of A through E, with the A rating representing the more reliable emission factor and the E rating a less reliable rating.

A qualitative description of each rating is listed below:

A Rating

! Large database from surveys or source tests on several different studies was used.

! Database covers a cross section of the industry.

! Emission factors were determined by mass balance based on sound measurement.

B Rating

! Database is fairly large; however, it is not clear that it represents a good cross section of the industry.

! Emission factor was measured using valid test methods at the time the test was performed. However, tests have since been revised.

! Engineering estimate based on sound, accurate information.

C Rating

- Database consists of a few good sources.
- Data may or may not be representative of the industry.
- Engineering estimates based on accurate information. However, information is not extensive or complete.

D Rating

- Database is small. If one sample, it was a representative site.
- Database may not be representative of industry.
- Unapproved test methods may have been used.
- Engineering estimates are based on information where accuracy is questionable.

E Rating

- Database is small. Results conflict with each other.
- Any sources tested are not representative of the industry.
- Engineering estimates are based on very little reliable information.

The above ratings are referred to throughout this report in the discussion of specific emission factors.

REFERENCE FOR APPENDIX A

1. Warn, T.E., S. Zelmanowitz, and M. Saeger. *Development and Selection of Ammonia Emission Factors for the 1985 NAPAP Emissions Inventory*. EPA-600/7-90-014, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. June 1990.