

Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies

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Abstract Gaseous ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. In addition, it is a major component of total reactive nitrogen. The largest source of NH_3 emissions is agriculture, including animal husbandry and NH_3 -based fertilizer applications. Other sources of NH_3 include industrial processes, vehicular emissions and volatilization from soils and oceans. Recent studies have indicated that NH_3 emissions have been increasing over the last few decades on a global scale. This is a concern because NH_3 plays a significant role in the formation of atmospheric particulate matter, visibility degradation and atmospheric deposition of nitrogen to sensitive ecosystems. Thus, the increase in NH_3 emissions negatively influences environmental and public health as well as climate change. For these reasons, it is important to have a clear understanding of the sources, deposition and atmospheric behaviour of NH_3 . Over the last two decades, a number of research papers have addressed pertinent issues related to NH_3 emissions into the atmosphere at global, regional and local scales. This review article integrates the knowledge available on atmospheric NH_3 from the literature in a systematic manner, describes the environmental implications of unabated NH_3 emissions and provides a scientific basis for developing effective control strategies for NH_3 .

Keywords Ammonia · $\text{PM}_{2.5}$ · Global emissions · Atmospheric chemistry · Dry deposition · Wet deposition

Introduction

About a century ago, Fritz Haber developed a process to convert essentially inert gaseous N_2 into biologically active forms that could fertilize food production, allowing increases in production capable of supporting a much larger population (Erisman et al. 2007; Sutton et al. 2008; Reis et al. 2009). Humans gradually learned to convert gaseous N_2 into forms that could sustain food production for a large population. However, the addition of excess anthropogenic nitrogen (N) compounds to the atmosphere remains a matter of great concern to human health and the environment (Krupa and Moncrief 2002; Aneja et al. 2008). Important N gases that are emitted by human activities are oxides of nitrogen (NO_x), nitrous oxide (N_2O) and NH_3 . Of these gases, NH_3 is emitted by a large number of sources, such as volatilization from animal waste and synthetic fertilizers, biomass burning (including forest fires), losses from soils under native vegetation and agricultural crops, emissions from human excreta and fossil fuel combustion (Olivier et al. 1998; Zhang et al. 2008; Aneja et al. 2012). Research on atmospheric NH_3 was started a long time ago, when Justus von Liebig, a German professor, reported that about 27 kg/ha of free fertilizer was obtained through wet deposition from the atmosphere (Von Liebig 1827; Erisman et al. 2007). Although this estimate of wet deposition of NH_3 was subsequently proved to be inaccurate, the findings from Liebig nevertheless gave a new perspective to the global biogeochemical NH_3 cycles.

The need to sustain food production to meet the demand for growing populations will lead to the increased agricultural emissions of NH_3 with perturbations of the global biogeochemical NH_3 cycle (Aneja et al. 2001; Aneja et al. 2008; Aneja et al. 2009). The phenomena involved in the

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atmospheric cycle of NH_3 are complex in nature. It is therefore necessary to get insights into the complex, multi-faced environmental cycle of NH_3 from a broad perspective. As illustrated in Fig. 1, NH_3 released from anthropogenic and natural sources participates in the atmospheric reactions (e.g. gas-to-particle conversion) gets transported by winds, and returns to the surface by wet and dry deposition processes, leading to adverse effects on the environment and increased public health risks.

The existence of gas-phase NH_3 and its interaction with the other trace chemical species in the atmosphere has been recognized since the last century. Being the only primary basic/alkaline gas species in the atmosphere, NH_3 plays an important role in determining the overall acidity of precipitation, cloud water and airborne particulate matter (PM or aerosols) (Shukla and Sharma 2010; Xue et al. 2011; Behera et al. 2013). Ammonia and ammonium (collectively abbreviated as NH_x) are also nutrients (because they fertilize plants), which undergo dry and wet deposition in the areas downwind of their major sources (Asman 1995; Sutton and Fowler 2002). However, more anthropogenic input of N to the environment may lead to eutrophication of terrestrial and aquatic ecosystems and thus threaten the biodiversity (Aneja et al. 1986; Asman et al. 1998; Galloway et al. 2003; Erisman et al. 2005).

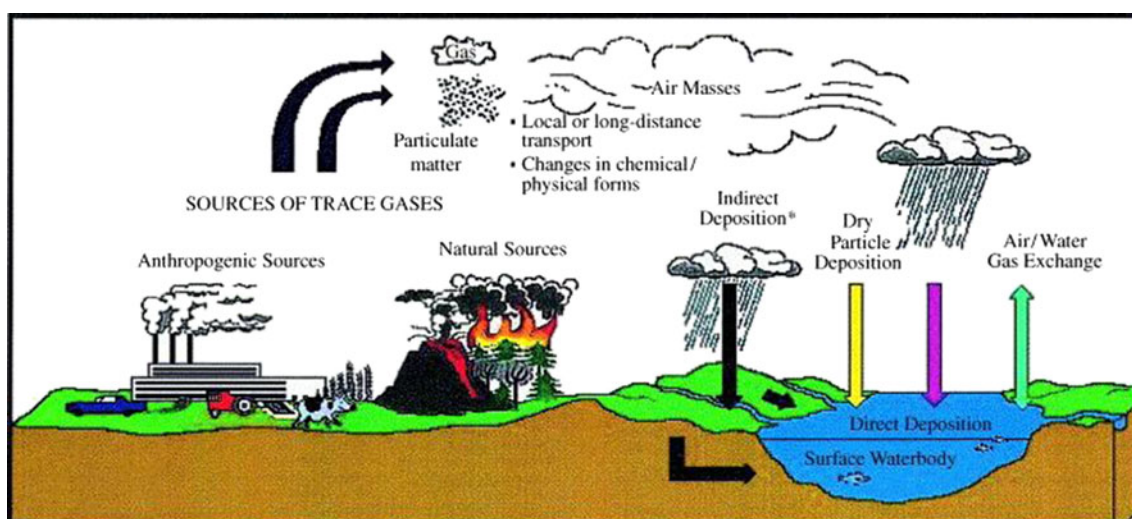
In recent years, the sources, transport and fate of atmospheric NH_3 have been widely studied due to its role in global climate change. For example, sulfate (SO_4^{2-}) and nitrate (NO_3^-) aerosols have important effects on global radiation budgets because of their ability to scatter the incoming solar radiation, act as cloud condensation nuclei and indirectly increase cloud lifetime (Charlson et al. 1990; Bauer et al. 2007; Myhre et al. 2009). In summary, NH_3 is a critical N

compound that alone has a major effect on the global biogeochemical N cycle, atmospheric reactions leading to particulate formation, climate change, health effects and more lasting cascading effects in the ecosystem.

There are currently no regulations or incentive programs in most countries around the world for reductions in NH_3 emissions. Compared with regulations for other primary gaseous pollutants such as SO_2 , NO_x and volatile organic compounds (VOCs), extensive control measures have not been taken to mitigate emissions of NH_3 despite the fact that all these pollutants make similar contributions to PM mass loading, visibility degradation and/or acidification/eutrophication. Current research efforts related to NH_3 include the quantification of its emissions from agricultural point and nonpoint sources and its temporal and spatial variations, re-emission in high emission/deposition areas, the atmosphere-biosphere exchange of NH_3 and its effect on vegetation, the quantification of landscape processes, low-level dispersion processes, the primary and secondary emissions of PM, and the gas-to-particle conversion to fine particles.

Over the last two decades, a number of research and review papers have addressed the key issues related to NH_3 emissions into the atmosphere at global, regional and local scales, including emission sources, fate through atmospheric chemistry and deposition on terrestrial bodies. Given such a wealth of knowledge available from the literature, there is a need to integrate these research efforts under one unifying theme and provide a clear understanding of pertinent issues related to NH_3 emission sources, its atmospheric transformation processes and deposition onto terrestrial bodies.

With the goal in mind, this comprehensive review article aims at bringing together the following information in a systematic, integrated manner with the organizational structure as:



* Indirect deposition is direct deposition to land followed by runoff or seepage through groundwater to a surface waterbody.

Fig. 1 Atmospheric emissions, transport, transformation and deposition of trace gases. Adapted from Aneja et al. (2001)

“Introduction” section summarizes the significance of atmospheric NH_3 from a broad perspective. “Emissions of NH_3 into the atmosphere” section discusses various fundamental processes associated with emissions of NH_3 along with the information on regional and global NH_3 emissions from all responsible sources. “Atmospheric chemistry of NH_3 ” section describes atmospheric chemical transformations of NH_3 with other important chemical constituents to assess its fate and transport under different conditions. “Deposition of NH_3 on terrestrial bodies” section describes the estimation methods of dry deposition and wet deposition of NH_3 on various terrestrial bodies and the description on effects of NH_3 on vegetation and forests. “Concluding remarks” section presents an overall summary and conclusion of this review paper. The compiled data on emission factors and its selection procedure will help the scientific community engaged in air quality modeling to generate and study spatial and temporal distributions of NH_3 on local to global scales. Several aspects of complex atmospheric chemistry involving NH_3 can be studied through chemical transport modeling by using the compiled data in this paper. In addition, the syntheses on various methods to estimate deposition rate on terrestrial bodies will help the modeling community to develop their own deposition models.

Emissions of NH_3 into the atmosphere

The main causes of NH_3 emissions are the production and use of ammoniacal fertilizers and the large population of domestic animals. Due to more demand for meat for consumption, animal production has been increased considerably resulting in a rapid rise in the number of domestic animals. For example, it has been observed that between 1960 and 2000, the human population roughly doubled, while the number of domestic animals roughly tripled during the same time (Oenema 2006). It is expected that the increases in the numbers of domestic animals will be relatively large in developing countries (Gerber et al. 2005; Oenema 2006). Currently, the global production of fertilizers is approximately 100 million metric tons of N year^{-1} , compared to approximately one million metric tons only 40 years ago (Aneja et al. 2001). The world average fertilizer use in 2005 was 96 kg/ha of agricultural land, ranging from 0.2 (Myanmar) to 2,656 kg/ha in Kuwait (Earth Trends Data 2010).

Global emissions

Important studies related to global NH_3 emissions include those of Schlesinger and Hartley (1992), Dentener and Crutzen (1994), Bouwman et al. (1997) and Olivier et al. (1998). Estimates of NH_3 emissions from the studies of Schlesinger and Hartley (1992), Dentener and Crutzen (1994) and Bouwman et al. (1997) are presented in Table 1. From the

estimation of Bouwman et al. (1997), it can be inferred that the anthropogenic sources contribute about 80 % of global NH_3 . Therefore, there is a critical need to review emissions of NH_3 from various anthropogenic sources in detail, so that effective control strategies can be formulated to reduce such emissions.

In addition to the above studies on NH_3 emissions, the NitroEurope research project (Sutton et al. 2007; <http://www.nitroeurope.eu>) is focused on updating N balances from local to regional scales, and the Emissions Database for Global Atmospheric Research (EDGAR; <http://edgar.jrc.ec.europa.eu/>) provides global past and present-day anthropogenic emissions of NH_3 by country and on spatial grid; the database of EDGAR is openly accessible. The above peer-reviewed studies on emission estimates were done for the years 1989–1990. To get the recent emission estimates of NH_3 from various sources, it becomes necessary to have an update estimate for development of control strategies. We used the database of EDGAR (<http://edgar.jrc.ec.europa.eu/>) to arrive at precise interpretations and arguments.

Table 1 Global estimate of NH_3 emissions from various sources (in million tons $\text{NH}_3\text{-N year}^{-1}$) (Source: Bouwman et al. 1997)

Source	Ammonia emission (million tons $\text{NH}_3\text{-N year}^{-1}$)		
	Schlesinger and Hartley 1992 ^a	Dentener and Crutzen 1994	Bouwman et al. 1997
Cattle including buffaloes	19.9	14.2	14.0
Pigs	2.0	2.8	3.4
Horses/mules/asses	1.8	1.2	0.5
Sheeps/goats	4.1	2.5	1.5
Poultry	2.4	1.3	1.9
Wild animals ^b	— ^d	2.5	0.1
Total animals	32.3	24.5	21.7
Synthetic fertilizers	8.5	6.4	9.0
Undistributed ecosystems	10.0	5.1	2.4
Croplands	— ^d	— ^d	3.6
Biomass burning including biofuels	5.0 5.0	2.0 2.0	5.7 5.7
Human excrement	4.0	— ^d	2.6
Sea Surface	13.0	7.0	8.2
Fossil fuel combustion	2.2 ^c	— ^d	0.1
Industry	— ^d	— ^d	0.2
Total emission	75.0	45.0	53.6

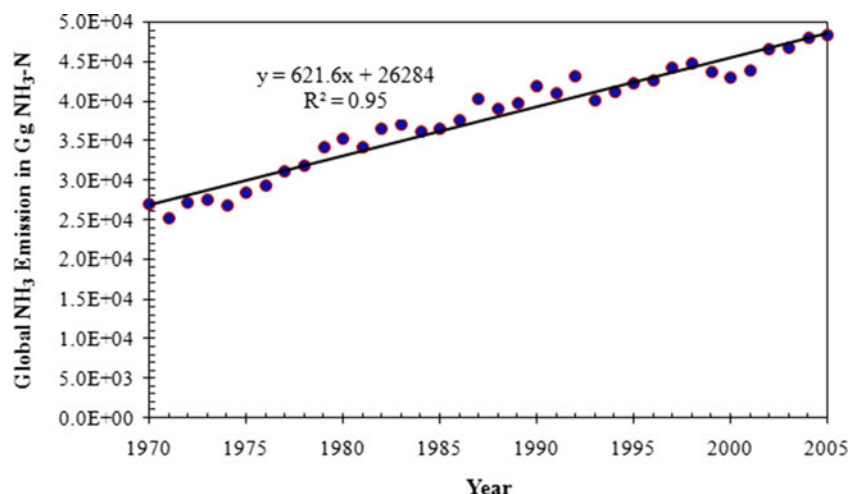
^a Values are reported in 10^{12} g N

^b Schlesinger and Hartley (1992) included the estimate for wild animals in undisturbed ecosystems

^c Mainly coal combustion

^d Data not available

Fig. 2 Global year-wise NH_3 emission trends. Dataset was compiled from EDGARv4.1; <http://edgar.jrc.ec.europa.eu/>, 2010



The methodology for EDGARv4.0 is based on calculation of emissions using a technology-based emission factor and spatial allocation of emissions on a $0.1^\circ \times 0.1^\circ$ grid resolution. Figure 2 shows the trends of global emission of NH_3 on a year-wise basis. It can be observed that NH_3 emission increased from 27,000 Gg $\text{NH}_3\text{-N}$ in 1970 to 48,400 Gg $\text{NH}_3\text{-N}$ in 2005, and the rate of NH_3 emission increase is equivalent to 621.6 Gg $\text{NH}_3\text{-N}/\text{year}$.

Figure 3 shows the global annual emissions from important sources for the years 1970, 1975, 1980, 1985, 1990, 1995, 2000 and 2005. The sources are classified as: (1) energy sector, which includes fuel combustion and fugitive emissions from fuel, manufacturing industries and construction, all forms of transport, residential sectors, etc., (2) industrial

processes (non-combustion) and product use, which cover production of minerals and chemicals, (3) agriculture sector consisting of livestock manure management and application of manure on field, (4) agriculture sector comprising application of synthetic fertilizers, (5) Savanna and agricultural waste burning, (6) forest and grassland fires and (7) other waste handling.

From Fig. 3, the following conclusions have been drawn: (1) the contribution of the energy sector, including all combustion and non-combustion processes, varies from 4.4 % (1,180 Gg $\text{NH}_3\text{-N}$ in 1970) to 8.3 % (4,030 Gg $\text{NH}_3\text{-N}$ in 2005), (2) the contribution of the livestock population (emission from manure management and its application on fields) varies from 42.3 % (11,400 Gg $\text{NH}_3\text{-N}$ in 1975) to 34.1 %

Fig. 3 Global year-wise NH_3 emission trends. Dataset was compiled from EDGARv4.1; <http://edgar.jrc.ec.europa.eu/>, 2010

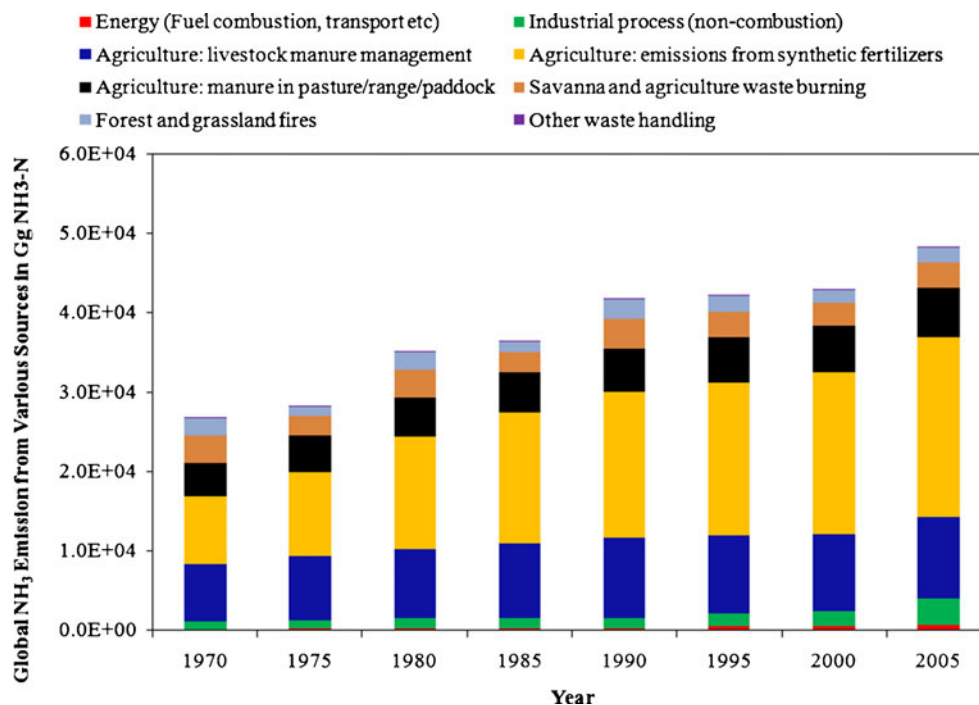


Table 2 Global estimates of anthropogenic NH₃ emissions in 2005 (Gg NH₃-N year⁻¹)

Source/subsector	Total	Canada	USA	Mexico	Rest C. America	South America	Africa	OECD-Europe	Central Europe	Turkey	Ukraine+	Russia+	Middle East	India+	China+	Rest of Asia	Oceania
Total	48,354.3	668.2	3,586.7	785.6	405.6	5,360.4	5,567.7	4,333.2	1,386.8	708.5	492.1	1,187.1	816.8	5,541.4	11,109.8	5,470.6	933.8
Energy: fuel combustion and fugitive emission from fuels	761.0	29.4	299.3	18.0	7.9	48.2	22.2	119.2	13.5	2.1	2.1	14.5	26.6	41.4	32.2	66.4	18.0
- Public electricity and heat production	102.7	2.0	20.3	3.4	2.8	5.1	3.2	25.2	2.6	0.3	0.6	6.4	9.4	3.2	5.6	11.6	1.0
- Other energy Industries	11.5	0.2	0.4	0.4	0.0	0.7	0.3	1.6	0.4	0.1	0.1	0.8	1.2	1.0	2.1	2.0	0.2
- Manufacturing Industries and Construction	145.3	7.4	28.7	1.6	3.3	24.9	3.5	16.2	3.1	0.6	0.4	1.1	4.2	24.9	6.2	16.3	2.9
- Road transportation	459.9	19.7	249.0	12.3	1.1	16.2	4.6	73.6	6.5	0.6	0.9	5.9	11.7	2.5	10.1	31.4	13.8
- Other transportation	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
- Residential and other sectors	41.6	0.1	0.9	0.3	0.7	1.3	10.6	2.6	0.9	0.5	0.1	0.3	0.1	9.8	8.2	5.1	0.1
Industrial process (non-combustion) and product use	3,268.3	9.1	34.4	1.2	10.1	239.1	548.7	25.6	77.3	4.0	19.5	15.3	127.7	453.4	859.1	842.6	1.2
- Production of minerals	37.6	0.0	9.9	0.3	0.0	0.3	0.6	4.7	2.2	0.8	0.6	2.3	0.6	1.6	12.8	0.6	0.3
- Production of chemicals	3,230.7	9.1	24.5	0.9	10.1	238.8	548.1	20.9	75.1	3.2	18.9	13.0	127.1	451.8	846.3	842.0	0.9
Agriculture (including Savanna burning)	42,271.2	589.9	3,217.6	750.9	374.5	4,241.4	4,319.4	4,160.8	1,292.9	701.7	466.8	1,031.5	661.8	5,034.9	10,209.9	4,343.9	873.3
- Manure management ^a	10,288.7	215.8	1,148.2	185.8	95.1	801.8	345.7	1,937.6	610.9	302.4	234.7	552.5	57.8	434.0	2,222.2	1,100.4	43.8
- Direct soil emission ^b	22,486.7	336.9	1,668.1	364.5	159.4	1,618.4	754.1	1,958.9	629.0	344.2	194.2	411.6	405.9	3,709.5	7,363.4	2,250.9	317.7
- Manure in pasture/range/paddock	6,207.2	33.1	383.0	166.6	88.0	1,448.3	1,459.9	255.9	40.6	38.6	31.0	54.1	193.6	753.7	613.8	245.6	401.4
- Savanna burning	2,576.2	0.0	0.8	19.5	20.9	220.2	1,731.1	0.0	0.0	0.0	0.0	0.0	0.0	8.8	3.3	477.9	93.7
- Agricultural waste burning	712.4	4.1	17.5	14.5	11.1	152.7	28.6	8.4	12.4	16.5	6.9	13.3	4.5	128.9	7.2	269.1	16.7
Land use change and forestry	2,035.9	39.1	31.1	15.5	13.1	831.5	677.4	20.6	2.9	0.6	3.7	125.8	0.2	8.7	8.2	216.2	41.3
- Forest fires	1,740.1	29.6	11.8	15.4	13.1	810.1	635.1	0.1	0.0	0.0	0.0	30.4	0.0	5.8	0.8	178.3	9.6
- Grassland fires	295.8	9.5	19.3	0.1	0.0	21.4	42.3	20.5	2.9	0.6	3.7	95.4	0.2	2.9	7.4	37.9	31.7
Wastes	17.9	0.7	4.3	0.0	0.0	0.2	0.0	7.0	0.2	0.1	0.0	0.0	0.5	3.0	0.4	1.5	0.0
- Other wastes handling	17.9	0.7	4.3	0.0	0.0	0.2	0.0	7.0	0.2	0.1	0.0	0.0	0.5	3.0	0.4	1.5	0.0

Source: Table 2 was compiled from the raw data from the data base of EDGAR "EC-JRC/PBL. EDGAR version 4.1. <http://edgar.jrc.ec.europa.eu/>, 2010"; 1 Gg=10⁹ g; Ukraine+: Belarus, Republic of Moldova, Ukraine; Russia+: Armenia, Azerbaijan, Georgia, Russian Federation; India+: Afghanistan, Bangladesh, Bhutan, India, Sri Lanka, Maldives, Nepal, Pakistan

^a Manure management from livestock

^b N-fertilizer use

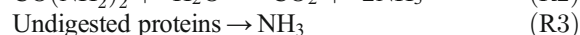
(16,500 Gg $\text{NH}_3\text{-N}$ in 2005), (3) the synthetic fertilizer application contribution varies from 31.8 % (8,570 Gg $\text{NH}_3\text{-N}$ in 1970) to 46.5 % (22,500 Gg $\text{NH}_3\text{-N}$ in 2005) and (4) biomass burning, including Savanna and agricultural waste burning, forest and grassland fires, contributes from 21.5 % (5,810 Gg $\text{NH}_3\text{-N}$ in 1970) to 11.0 % (5,320 Gg $\text{NH}_3\text{-N}$ in 2005). Overall, the agriculture sector contributes 80.6 %, followed by biomass burning at 11.0 %, and the energy sector including industries at 8.3 % of total global NH_3 emissions in 2005.

Table 2 shows the spatial distribution of NH_3 emissions from various sources in 2005; the total emission of NH_3 is 48,400 Gg $\text{NH}_3\text{-N}$. About half of the global emission comes from Asia (Table 2). About 85 % of the total global emission is related to food production, which includes domesticated animals, use of synthetic fertilizers, crops and agricultural waste burning. For the region comprising the USA, South America, Europe, Russia and Asia, agriculture contributes more than 70 % of the total global NH_3 emission. Large regions in Asia use synthetic fertilizers, which contribute about 60 % of the global emission for this source category, accounting for about 30 % emission of the total emissions in Asia (Table 2).

Sources

Animal livestock

Processes involved in NH_3 emission from domestic animals N is excreted in the form of urea (in mammals) or uric acid (in birds), i.e. through urine discharge of livestock and poultry, and in the form of urea, NH_3 and organic N in animal feces. The microbial and physico-chemical processes that give rise to NH_3 emissions are well understood and described in literature (e.g. Bussink et al. 1994; Groot Koerkamp et al. 1998a,b; Casey et al. 2006). Overall, it can be stated that the potential sources for NH_3 vaporization are from the decomposition of urea, uric acid, $\text{NH}_3/\text{NH}_4^+$ and undigested proteins. The processes responsible for NH_3 emissions from the animal livestock manure can be summarized as reactions R1 to R6, and equations Eq. (1) and Eq. (2).



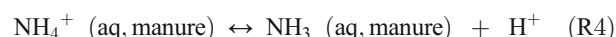
The uric acid is being decomposed by microbial action (by enzyme uricase) with oxygen and water to produce carbon dioxide and NH_3 (R1). Urea is degraded through urease activity performed by the urease enzyme (produced by micro-organisms commonly present in manure) to produce carbon dioxide and NH_3 . Undigested proteins are decomposed by both uricase and urease enzymes+bacterial metabolism to produce NH_3 (R3).

From the modeling aspects for estimating the volatilization rate of NH_3 from livestock manure, it can be deduced that NH_3 volatilization from livestock manure is proportional to the difference between the NH_3 concentration at the surface of the manure and the concentration in the air above the surface, which is governed by Eq. (1):

$$E = k(C_{\text{manure}} - C_{\text{air}}) \quad (1)$$

where E is the volatilization rate of NH_3 (grams per square meter per second), k is the diffusion coefficient for NH_3 in air (meters per second), C_{manure} is the NH_3 concentration at the manure surface (grams per cubic meter) and C_{air} is the NH_3 concentration in the atmosphere above the manure surface (grams per cubic meter).

The concentration at the surface of the manure (C_{manure}) depends on the chemical equilibrium between aqueous NH_4^+ (NH_4^+ (aq, manure)) and aqueous NH_3 in the manure (NH_3 (aq, manure)) (R4):



The $\text{NH}_4^+/\text{NH}_3$ equilibrium depends on the ionic strength of the solution, i.e. the dissociation constant (K_a) of reaction R4, given by the expression Eq. (2):

$$K_a = [\text{NH}_3] [\text{H}^+] / [\text{NH}_4^+] \quad (2)$$

where $[\text{NH}_3]$, $[\text{H}^+]$ and $[\text{NH}_4^+]$ are molar concentrations of the respective compounds. The equilibrium between $[\text{NH}_3]$ and $[\text{NH}_4^+]$ depends on pH and temperature as shown in Fig. 4.

The formation of gaseous NH_3 in manure depends on the equilibrium between NH_3 (aq, manure) and gaseous NH_3 (NH_3 (g, manure)) in the manure, which is governed by Henry's law for dilute systems (R5).

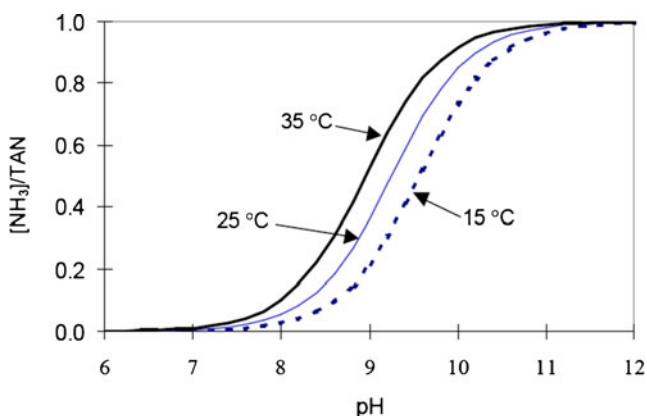
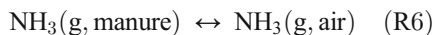


Fig. 4 Effect of pH and temperature on equilibrium between NH_4^+ and NH_3 in aqueous solutions. Adapted from Arogo et al. 2002

The volatilization of NH_3 from manure (NH_3 (g, manure)) into the air (NH_3 (g, air)) can be expressed as (R6):



Stages of NH_3 emissions from livestock

NH_3 emissions arise from urine patches on grazed pastures, excreta deposited onto the floors of housing facilities, manure held in storage and volatilization during the application of manure onto fields. The stages involved in NH_3 evaporation from livestock waste can be termed as various N compartments in which the loss of NH_3 takes place. The studies by Oenema et al. (2005; Oenema 2006) are of particular interest for this review article, as they discuss various stages of the processes involved in the livestock farming system, and N losses in these processes. Figure 5 demonstrates the N cycling and losses in a livestock farming system with four N compartment stages, i.e. (1) livestock, (2) manure, (3) soil and (4) crop; thick arrows present the major N flow within the system, thin arrows present the N inputs and outputs in useful products and dotted arrows present the N losses and percentages indicating the range of estimated transfer of N from one compartment to the other compartment and the range of estimated N losses (Oenema 2006). The following conclusions can be made about the stages of NH_3 emissions from the livestock systems: (1) grazing and mixed systems, and crop and animal production are connected locally, (2) land-less livestock systems encompass only two compartments, i.e. livestock and animal manure, where manure production occurs in one place and disposal manure occurs in another, (3) only a small fraction of N in animal feed is retained in milk, meat and eggs, and (4) the greater part (55–95 %) is discharged by the animals.

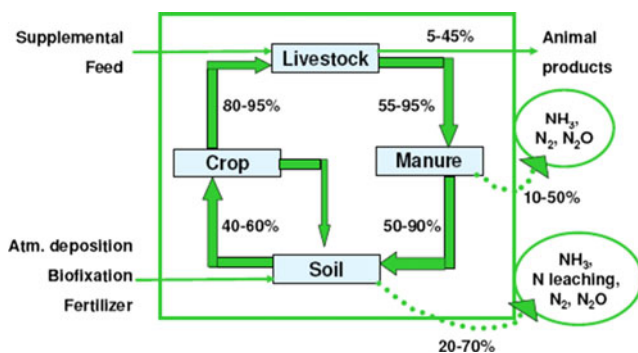


Fig. 5 Nitrogen cycling and losses in a livestock farming system with four N compartments, i.e. livestock, manure, soil and crop. Adapted from Oenema (2006) as modified

Factors affecting emissions of NH_3

Characteristics of manure

The NH_4^+ concentration in the manure is decreased by the dilution of the manure with soil or water resulting in less emission of NH_3 . In addition, if there is more water content in the manure, then the waste will percolate to the ground resulting in less evaporation of NH_4^+ and a high dry matter content of the manure decreases infiltration into the soil resulting in more evaporation of NH_4^+ (Rotz et al. 2005). Stevens et al. (1992), in their experimental study, have observed that 50 and 75 % reductions in NH_3 volatilization are possible, with about 85 and 100 %, respectively, of water dilution with manure. The fact of the issue is that manure characteristics/composition and the potential for volatilization of NH_3 depend on the species and breed of farm animals, the housing system and the diet composition (Nicholson et al. 2004; Hristov et al. 2011).

Diet patterns

Bouwman et al. (1997) confirmed that protein requirements for maintenance are proportional to the metabolic weight of the animal, whereas growth, lactation, pregnancy and production of eggs are additional protein requirements. Later, Conelly and Chaiken (2000) inferred that animals used for labor and grazing that travel long distances to collect their feed need additional energy, and thus have a higher feed and protein intake. Ferguson et al. (1998) observed that the reduction in crude protein causes equilibrium NH_3 gas concentration to reduce NH_3 emissions by about 31 %. Gates et al. (2000) subsequently reported that the reduction of NH_3 emissions could be about 90 % through diet protein reduction. As per Casey et al. (2006), the differences between the Gates et al. (2000) and Ferguson et al. (1998) studies were basically due to different in litter moisture content and number of flocks. Gates et al. (2000) worked with significantly drier litter (16 to 25 %) than Ferguson et al. (1998) (50 to 60 %), and took measurements over a period equivalent to the raising of three flocks using the same litter, while the Ferguson et al. (1998) data are from one flock only (Casey et al. 2006).

Rotz et al. (2005) have developed a model that predicts nutrient requirements, feed intake, growth and manure excretion for all animal groups making up a beef herd, and they evaluated the model predictions by comparing their model with other accepted models and production data. The N excretion rates for different subclasses of cattle, buffalo and camels are normally calculated using standard feeding tables and standard values for the N content of animal products (Medhammar et al. 2012). Table 3 presents N excretion by livestock from compound feeds. It may be seen that dairy cows, followed by camels and buffalos, discharge more N

excreta in comparison with other animals. The reason may be due to more diet quantity, protein intake and/or less efficiency in the digestive systems of these animals; similar observations were also made by Lucy (2001).

Types of livestock

The selection of emission factors is important for emission estimation from the livestock sources for a specified region. NH_3 emission factors for animals in an animal production operation represent the sum of the annual mean emission rates from housing, manure storage/treatment and land application of manure. The emission factors are commonly expressed as mass/year/animal; e.g. for dairy cows, kilogram NH_3 /year/dairy cow. Earlier studies have estimated NH_3 emissions from livestock in Europe and the USA (Bouwman et al. 1997; Van Der Hoek 1998; Misselbrook et al. 2000; USEPA 2002; Battye et al. 2003). In the US emission inventory, the emission was computed using a process-based model, which takes into account different animal sizes, husbandry practices and waste management practices (USEPA 2002). Some research groups have also presented NH_3 emission inventories in Asian regions (Zhao and Wang 1994; Lee and Park 2002), but these

studies have relied on emission factors based on animal-farming conditions in European countries (Asman 1992, European Environment Agency EEA (1999), because they did not have enough information on Asian-specific emission factors.

Table 4 presents findings of earlier studies (e.g. Buijsman et al. 1987; Battye et al. 2003) on emission factors of NH_3 from livestock through animal waste management, and their applications on the fields. From a climatic location point of view, temperature correction is essential for selection of NH_3 emission factors. Recently, Aneja et al. (2012) used temperature correction based on emission factors for the Indian region, derived from Steenvoorden et al. (1999), as given in Eq. (3):

$$\text{EF} = 0.9e^{0.062t} \quad (3)$$

where EF is the emission factor in grams N/animal/day and t is the temperature in degree Centigrade.

Housing/manure management system

De Bode (1991) measured NH_3 emissions equivalent to 5–15 % of total N over 180–250-day storage periods from circular tanks. Nicholson et al. (2004) observed that the emission rate for cattle slurry stored over changes with time to assess seasonal trends of emission; For example, it is different in winter and summer seasons. In general, livestock manure is stored in the forms of liquid, slurry and solid, which depend on the manure management system. Animal feces mainly contain organic N that mineralizes very slowly to produce NH_3 , suggesting that the NH_3 volatilization potential of fresh feces is relatively low in buildings (Bussink and Oenema 1998; Arogo et al. 2002). However, during long-term storage for buildings with under-floor storage, organic N compounds are degraded anaerobically, leading to an increase in NH_4^+ concentration in the manure (Arogo et al. 2002). Therefore, NH_3 emission from livestock depends on storage or flooring type, type of wastes, duration and time of the waste storage (Rotz 2004; Hristov et al. 2011). Cattle are commonly housed in tie stall barns, free stall barns and open feedlots. In practice, there are a number of housing systems, which differ with respect to the use of bedding and the storage of cattle excretions. Bussink and Oenema (1998) mentioned that NH_3 losses per housed cow increase in the order: cubicle houses < free stall with straw yard < open housing with solid or slatted floors.

Swine are produced in the housing system, either on a deep-litter system or slatted system. In a deep-litter system, bedding such as straw or sawdust is used to absorb and cover urine and feces. In a slatted housing facility, a slatted floor allows fecal and urine excretions to drop into a pit below the floor for removal. In a common poultry housing system, laying hens are kept in high-rise battery cage systems, where

Table 3 N excretion by livestock from compound feeds

Reference →	N excretion rate (kg animal ⁻¹ year ⁻¹)		
	Webb (2001) ^a	Bouwman et al. (1997) ^b	
Regions → Animal category ↓	England and Wales	Developed countries ^c	Developing countries ^d
Dairy cows	106	80	60
Non-dairy cows	61 ^e	45	40
Buffalo	— ^f	45	
Camels	— ^f	55	
Horses	— ^f	45	
Sheep	6.4 ^g	10	
Pigs	15.9 ^h	9	
Poultry	0.9 ⁱ	0.5	

^a Total N excreted by each animal per year including N derived from grass feeds

^b Data under categories considered

^c Developed countries include regions under Europe, the former USSR, North America, Australia and New Zealand, Israel and Japan

^d Developing countries include regions under Latin America, Oceania excluding Australia and New Zealand, Africa and Asia excluding the former USSR

^e Only for beef cows category

^f Indicates that no estimates or measurements were available

^h The data are the average four subcategories

ⁱ The data are taken from the N excretion from compound feeds and are the average of the six sub categories

Table 4 Summary of the published NH₃ emission factors for livestock

References	Country/region	Emission factors ^a for livestock (kg NH ₃ animal ⁻¹ year ⁻¹)									
		Dairy cow	Non-dairy cow	Buffalo	Sow pig	Finishing pig	Goat	Sheep	Camel	Horses	Poultry
Buijsman et al. 1987	Europe	18		– ^e	2.8		– ^e	3.1	– ^e	9.4	0.3
Asman 1992	Europe	23.1		– ^e	5.3		– ^e	1.9	– ^e	12.5	0.3
Sutton et al. 1995b	England & Wales	21.1		– ^e	5.2		– ^e	1.0	– ^e	– ^e	0.3
Sutton et al. 1995b	Scotland	18.7		– ^e	5.3		– ^e	1.0	– ^e	– ^e	0.3
Sutton et al. 1995b	North Ireland	20.1		– ^e	5.5		– ^e	1.0	– ^e	– ^e	0.3
Bouwman et al. 1997	Developed countries ^b	24.8	9.4	10.5	4.8		0.7	0.8	12.9	9.2	0.2
Bouwman et al. 1997	Developing countries ^c	21.1	9.8	10.5	4.8		1.1	1.2	12.9	10.5	0.2
Van der Hoek 1998	Europe	28.5	14.3	– ^e	16	6.4	1.3	1.3	– ^e	8.0	0.5
Misselbrook et al. 2000	UK	26.5	6.8	– ^e	5.2	4.8	– ^e	0.7	– ^e	– ^e	0.3
Bowen and Valiela 2001	USA	22.7		– ^e	7.3		– ^e	4.4	– ^e	– ^e	0.3
Hutchings et al. 2001	Denmark	22.8	7.2	– ^e	9.5	3.5	– ^e	1.9	– ^e	9.2	0.3
Battye et al. 2003	USA	28	10.2	– ^e	16.4	6.4	– ^e	1.3	– ^e	8.0	0.3
Aneja et al. 2012 ^d	India	5.2		4.1	1.8		1.3	1.7	8.5	8.5	0.1

^a Include the emission from the animal waste management system to their application on the field

^b Developed countries include regions under Europe, the former USSR, North America, Australia and New Zealand, Israel and Japan

^c Developing countries include regions under Latin America, Oceania excluding Australia and New Zealand, Africa and Asia excluding the former USSR

^d Includes the emission factors only for the animal wastes management system (i.e. excluding the land application)

^e Indicates that no estimates or measurements were available

manure is collected either on a conveyor belt or dropped into a storage pit or pile below the cages. The excreted manure is often removed annually, resulting in a long-term storage in the housing system causing more NH₃ emissions. In some cases, broilers and turkeys are raised in deep-litter systems, in which birds are raised on old litter for 1 year or longer before the entire house is cleaned out. Between clean-outs, only caked litter is removed at the end of the grow-out, and fresh bedding may be added to the litter (Xin et al. 1996; Arogo et al. 2002).

Meteorological and other factors

The observations by the experiments of Sommer et al. (1991) can be summarized as: (1) NH₃ emissions after 6 h were exponentially related to temperature ($r^2=0.841$), but the correlation weakened with time after slurry application, (2) an increase in NH₃ volatilization with increasing water vapor pressure deficit was considered to be an effect of temperature and (3) the NH₃ emissions rate increased when wind speeds increased up to 2.5 m/s, and no consistent increase in NH₃ emissions was found when the wind speed increased from 2.5 to 4 m/s.

Groot Koerkamp and Elzing (1996) observed that the concentration of TAN in litter found in aviary houses was approximately 4 % higher per 0.1 pH units, per °C per 10 g per kg water content. As per Groot Koerkamp and Elzing (1996), NH₃ emissions from litter can be reduced by maintaining a

high dry matter content and a low pH or low temperature, which minimize the degradation rate of organic N, resulting in a reduction in the volatilization of NH₃. However, control of pH and temperature may not always be possible or acceptable in aviary houses. Elzing and Monteny (1997) noticed that for repeated (daily) applications of feces and urine, there was an increase in the maximum NH₃ emission; however, a steady state was reached after 7 to 8 days, indicating that urease activity reached a constant level.

In the experiments on exploring various options to reduce NH₃ emissions from cubicle house, Kroodsma et al. (1993) observed that urea decomposition and NH₃ emission start within 30 min on manure-covered floors wetted with urine, and a maximum rate is reached shortly afterwards. Ogink and Kroodsma (1996) found that flushing with water reduced NH₃ emissions by 14 %, and that flushing with formaldehyde solution reduced emissions by 50 %. The reason for the greater reduction with formaldehyde could be due to the fact that formaldehyde reduces urease activity and also binds directly to NH₃. Braam and Swierstra (1999) found that high levels of urease activity could be expected to develop on all types of floor, and that only strategies for removing or deactivating urease present on the floor were likely to result in reduced NH₃ emissions.

Table 5 summarizes the findings of earlier studies related to the factors affecting NH₃ emission from various livestock

housing and manure management systems. It is not possible to directly compare all the emission rates because of the differences in housing, diet, management and periods of measurement. However, the overall conclusions drawn in this review (Table 5) can be enumerated as follows: (1) reducing excreted N by reducing protein diets or improved balance of amino acids will result in fewer NH_3 emissions, (2) higher emitting surface area in the housing leads to more NH_3 emissions, (3) frequent manure removal through belt transport, scrape and/or flush will reduce NH_3 emissions, (4) additions of acidifying materials, enzymes and biological additives will reduce NH_3 emissions, (5) emission of NH_3 is greater in summer than winter due to higher temperatures in summer, (6) losses of NH_3 from slurry stored in open tanks and lagoons are much larger than those from slurry stored in closed (underground) pits, (7) losses of NH_3 from slurry and FYM stored outside increase with an increase in temperature and surface area, and with the duration of storage, (8) more straws in the housing

increase NH_3 loss due to higher temperatures in the housing system and (9) a high moisture content of FYM may reduce NH_3 losses due to reduced gas exchange.

Synthetic fertilizers

As a major contributing source, the application of synthetic N fertilizers is known as a key driving force in the atmospheric biogeochemical cycle of NH_3 . Table 6 presents the global use of synthetic N fertilizers with their formula and N contents. It is obvious that urea constitutes the highest global consumption of total fertilizers (i.e. 56 %), and it also contains a higher N content (i.e. 47 %). In developing countries, more than 50 % of the N fertilizer used is in the form of urea (IFA 2012). Ammonium bicarbonate (NH_4HCO_3) is mostly used in China. NH_4HCO_3 is a highly volatile compound. Urea is less volatile than NH_4HCO_3 , and therefore, in the soil, urea is first

Table 5 NH_3 emission from various types of livestock housing system

Reference	Country/ region	Species	Floor facility/manure management system	NH_3 EF ^a (g NH_3 /animal unit/day)
Bjorneberg et al. 2009	USA	Dairy cow	Open-lot with solid manure removal	40–250
Bluteau et al. 2009	Canada	Dairy cow	Tie stall with gutter system	11.3 to 18.2 ^b and 5.47 ^c
Cassel et al. 2005	USA	Dairy cow	Open-lot with scrape pile system	19 to 143
Zhang et al. 2005	USA	Dairy cow	Various (mostly scrape)	7.5 to 47.5
Snell et al. 2003	Germany	Dairy cow	Free-stall with scraped system	38.9 to 40.3
Snell et al. 2003	Germany	Dairy cow	Sloped straw-yard	85.4
Snell et al. 2003	Germany	Dairy cow	Pen with boxes	57.1
Van Duinkerken et al. 2005	Netherlands	Dairy cow	Free-stall with slatted floor	17.0 to 65.3 ^d
Demmers et al. 2001	UK	Dairy cow	Cubicle; slurry with scraped floor	24.1
Demmers et al. 2001	UK	Beef cow	Straw beds	8.2
Groot Koerkamp et al. 1998a	Europe	Dairy cow	Litter based	1.3–23.4
Groot Koerkamp et al. 1998a	Europe	Dairy cow	Cubicle based	23.7–29.9
Groot Koerkamp et al. 1998a	Europe	Beef cow	Litter based	6.3–11.6
Groot Koerkamp et al. 1998a	Europe	Beef cow	Slatted	8.3–16.5
Groot Koerkamp et al. 1998a	Europe	Pigs	Litter based	7.3–31.1
Groot Koerkamp et al. 1998a	Europe	Pigs	Slatted	7.8–17.5
Demmers et al. 1999	UK	Finish pig	Fully slatted	128.5
Nicholson et al. 2004	UK	Layer poultry	Weekly belt scrapping	96.1
Nicholson et al. 2004	UK	Layer poultry	Daily belt scrapping	37.9
Nicholson et al. 2004	UK	Layer poultry	Deep pit	107.9
Nicholson et al. 2004	UK	Layer poultry	Belt scrapped	78.7
Nicholson et al. 2004	UK	Layer poultry	Stilt house	40.7
Nicholson et al. 2004	UK	Broiler poultry poultry	Litter (straw)	58.3
Nicholson et al. 2004	UK	Broiler poultry poultry	Litter (wood shavings)	29.1

^a EF for emission factor and an animal unit corresponding to 500 kg body mass

^b For summer and fall estimates

^c For winter months estimates

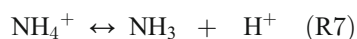
^d For low and high dietary ruminally degradable protein, respectively

converted to NH_4HCO_3 by the enzyme urease, which takes about 2–3 days.

Mechanism involved in NH_3 emission from fertilizer applications

NH_3 emissions from applied fertilizers follow the transport of NH_3 from the surface of an ammoniacal solution (either within the soil surface or plants) to the atmosphere (Singh and Nye 1986a; Van der Molen et al. 1990; Sommer et al. 2004). The rate of NH_3 emission is determined by the concentration gradient and resistance to NH_3 transport between the surface and the atmosphere as controlled by atmospheric transport processes, the chemical composition of the solution and transformations of TAN ($\text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$) in the soil and plants (Sherlock and Goh 1984; Sommer et al. 2004). The transportation of NH_3 gas takes place through two fundamental fluid layers, i.e. the laminar layer at the liquid–air interface by molecular diffusion and the turbulent layer to the free atmosphere by turbulent diffusion.

The instantaneous rate of NH_3 loss (F_v) may be given by the following equation:



$$F_v = K_b \times (\chi - \text{NH}_{3,a}) \quad (4)$$

where K_b is a bulk transfer coefficient, χ is the partial pressure of NH_3 in the air at the soil/plant–air interface and $\text{NH}_{3,a}$ is the partial pressure in the free atmosphere. The transfer coefficient depends on wind speed and atmospheric stability. χ can be determined by the concentration of TAN and equilibrium processes in the solution:

$$[\text{NH}_{3,L}] = \frac{\text{TAN}}{1 + 10^{(0.09018 + 2.729.92/T - pH)}} \quad (5)$$

$$\chi = [\text{NH}_{3,L}] \times 10^{1.477.7/T - 1.69} \quad (6)$$

where $\text{NH}_{3,L}$ is the concentration of NH_3 in the solution, and T is the temperature ($^{\circ}\text{K}$).

Nye and co-workers have predicted NH_3 volatilization from urea application through a mechanistic modeling approach and validated the model with experimental results, and have subsequently also investigated the aspects of sensitive analysis of their developed model. Singh and Nye (1986a) developed a mechanistic model that combined the process of NH_3 volatilization with the simultaneous transformation and movement of urea and its products in soil. For the system of surface application of urea to soil columns, Singh and Nye (1986b) measured concentration profiles of urea, ammoniacal nitrogen, soil pH and the losses of NH_3 by volatilization, and then compared these measured values with the model-predicted values. Singh and Nye (1986c) examined the sensitive analysis of the model developed by them previously (Singh and Nye 1986a) and confirmed that the proportion of N lost as NH_3 from surface-applied urea is very sensitive to the initial pH of the soil, its pH buffer capacity, the rate of urea application and the soil urease activity. For a detailed procedure of the model development, including derivation of continuity equations, boundary conditions, estimation of NH_3 volatilization and methods for numerical solutions, Singh and Nye (1986a) can be referred.

Kirk and Nye (1991a) expanded the model developed by Singh and Nye (1986a) for estimation of NH_3 volatilization after considering the effects of steady-state water movement

Table 6 List of fertilizers mostly used with the global consumption amount in 2010

Fertilizer type	Chemical formula	N Content (%)	Global consumption ^a (Tg N year ⁻¹)	% consumption of total ^b
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	21	3.4	3.3
Urea	$(\text{NH}_2)_2\text{CO}$	47	56.8	55.8
Ammonium nitrate	NH_4NO_3	35	5.0	4.9
Calcium ammonium nitrate	Mixture of NH_4NO_3 , CaCO_3 , MgCO_3	28	3.2	3.1
Anhydrous ammonia	NH_3	82	3.7	3.6
Nitrogen solutions	Mixture of $(\text{NH}_2)_2\text{CO}$, NH_4NO_3 , H_2O	28 to 32	5.0	4.9
Other straight N	NH_4HCO_3	18	7.3	7.2
Diammonium phosphate	$(\text{NH}_4)_2\text{PO}_4$	19	7.0	6.9
Nitrogen phosphorous and potassium	N-P-K	17	8.5	8.3
Other nitrogen and phosphorous	N-P	31	1.9	1.9
Total			101.8	100.0

^a Source of information: IFA 2012 (<http://www.fertilizer.org/ifa/ifadata/search>)

^b Percentage consumption of each fertilizer is calculated with respect to the total consumption (i.e. 101.8); Other straight N fertilizer includes NH_4HCO_3 ammonium bicarbonate in China

by drainage or evaporation when the soil does not dry out to any great extent. Kirk and Nye (1991b) expanded the model by Singh and Nye (1986a) for estimation of NH_3 volatilization after considering the effects of transient-state water evaporation when the soil surface dries significantly. Kirk and Nye (1991b) concluded that the dry layer results in increased gaseous NH_3 diffusion through the soil, and thereby increases the flux of NH_3 across the soil surface and the neutralization of H^+ ions generated by volatilization.

Factors affecting NH_3 emission from fertilizer application

Type of fertilizer

NH_3 emission depends on a mechanism for the destruction of the complex molecules of fertilizers in the hydrolysis process. The N contents are also different for different fertilizers (Table 6). Therefore, NH_3 emission varies from fertilizer to fertilizer. NH_4HCO_3 is a highly volatile compound. NH_3 emission from NH_4HCO_3 application is greater than from urea application on the field. The selection of these factors plays a key role in the development of the NH_3 emission inventory in a specified region or country.

Values of NH_3 emission factors from synthetic N fertilizers are typically expressed as a percentage of N applied that volatilizes as NH_3 . Some earlier studies have reported empirical relations for NH_3 volatilization rates as functions of wind speed, soil pH and soil moisture content (e.g. Kirk and Nye 1991a, b). Some studies also developed mathematical models to estimate emission factors under varying parameters (e.g. Singh and Nye 1986a, b). The major challenge for the use of these empirical relations or models is the collection of large amounts of data. To overcome this and other problems, Battye et al. (1994) have proposed and used average emission factors for each type of fertilizer to develop the emission inventory.

Table 7 presents the emission factors of NH_3 from different fertilizer applications based on previous studies (e.g. Buijsman et al. 1987; Misselbrook et al. 2004; Aneja et al. 2008). According to Battye et al. (1994), Asman (1992) provided the most up-to-date and reliable factors for most types of fertilizer.

Soil properties

Soil surface roughness enhances NH_3 emission after application of fertilizers on the field. A possible reason could be that soil surface roughness increases the turbulence in the pores of the soil, leading to an increase in friction velocity, and as a result, exchange between the soil surface and the atmosphere takes place. This exchange between the soil surface and the atmosphere helps the surface NH_3 to be better mixed and dispersed in the near atmosphere (Bajwa et al. 2008). The initial NH_3 emission rates after fertilizer application will tend to be larger from small plots than big fields, and to decline

faster due to the fact that TAN has been reduced because of the larger emission during the first few hours. The NH_3 loss rate declines after 5–10 days due to an increase in the volume of soil water through rain leaching into the soil, being absorbed into the soil and, as a result, reducing the volatilization of TAN (Haynes and Williams 1992). Sommer and Ersbøll (1996) used a sigmoidal model to relate cumulated loss of NH_3 from urea and days from application, and showed that for loamy soils, half of the total loss of NH_3 occurs 2–7 days after urea application.

NH_3 emission from a soil-applied fertilizer containing TAN is a function of dissolved NH_3 in equilibrium with the atmosphere either directly or through soil pores (Reynolds and Wolf 1987; Sommer et al. 2004). According to the dissociation of NH_4^+ and Henry's constant [Eqs. (5) and (6)], the emission is related to the concentration of TAN and H^+ ($\text{pH} = -\log[\text{H}^+]$). As a result, doubling the TAN concentration will double NH_3 emission, whereas doubling the H^+ concentration will halve NH_3 emission. With an increase in water content of the soil, the rate of hydrolysis is increased (Reynolds and Wolf 1987). Air humidity enhances hydrolysis of fertilizers due to the hygroscopic nature of the fertilizers. As a result, NH_3 emission is significant from fertilizer application on dry soil under high air humidity (Reynolds and Wolf 1987).

Meteorological conditions

The transfer coefficient depends on wind speed and atmospheric stability [Eq. (4)]. So, with an increase in wind speed, it is expected that the higher wind speed, along with higher temperatures, will increase NH_3 emission from applied fertilizers (McGarry et al. 1987). However, on days with lower solar radiation, the increase in wind speed will lead to reduced soil and plant surface temperatures and thereby the emission potential of the solution. The dependency of wind speed cannot be specific, as Bussink et al. (1994) have previously reported that NH_3 emissions from manure applied to fields have shown that NH_3 emissions are not always related to wind speed. Schjoerring and Mattsson (2001) demonstrated that a light shower in dry soil can lead to acceleration of the dissolution of the fertilizer granules and increase the NH_3 volatilization from soil. However, heavy rain will reduce the volatilization of NH_3 from soil, and Bouwmeester et al. (1985) also reported that 20 mm of rain is sufficient to reduce NH_3 volatilization significantly.

Biomass burning

N, as an essential ingredient of proteins, is present in all biomass. For example, the average concentration of N in wood is about 0.1 % (Battye et al. 1994; Sutton et al. 2000). This N is in a "reduced" chemical state, typically as amides ($\text{R}-(\text{C}=\text{O})-\text{NH}-\text{R}'$), and amines ($\text{R}-\text{NH}_2$). Under poor mixing conditions during

Table 7 Summary of NH₃ emission factors from fertilizer application

Reference → Country/region → Fertilizer type ↓	NH ₃ emission factors (NH ₃ loss as % of N contents)					
	Buijsman et al. 1987 Europe	Asman 1992 Netherlands	Zhao and Wang 1994 China (Asia)	Bouwman et al. 1997 Global context	Misselbrook et al. 2004 ^e UK	Aneja et al. 2008a ^f USA
(NH ₄) ₂ SO ₄	15	9.7	— ^g	8	2.9	9.7
(NH ₂) ₂ CO	10	18.7	12.1	15 ^a 25 ^b	12.4	18.2
NH ₄ NO ₃	10	2.5	— ^g	2	1.5	2.5
Calcium ammonium nitrate	2	— ^g	— ^g	2	— ^g	— ^g
Anhydrous NH ₃	10	1.2	— ^g	4	— ^g	1.2
Nitrogen solutions	— ^g	3.0	— ^g	2.5	— ^g	3.0
NH ₄ HCO ₃	— ^g	3.0	— ^g	20 ^c 30 ^d	1.3	3.0
NH ₄) ₂ PO ₄	5	4.8	— ^g	5	— ^g	4.8
N-P-K	— ^g	4.8	6.1	4	— ^g	4.8
Other N-P	— ^g	— ^g	— ^g	3	— ^g	— ^g

^a Temperate zones^b Tropical zones^c China, temperate zones^d China, tropical zones^e Average of arable and grassland^f Aneja et al. (2008a) expressed NH₃ volatilization in terms of kilograms NH₃/Mg nitrogen^g Data not available

biomass burning, the biomass N can be released as NH₃. Denmead (1990) developed an NH₃ budget for Australia and included a method for estimating NH₃ emissions from biomass burning that is dependent upon an emission ratio for NH₃ relative to the increase in CO₂. Denmead (1990) concluded that biomass burning may contribute 1/16 to 1/6 of the NH₃ released in Australia. Schlesinger and Hartley (1992) compiled a global budget for atmospheric NH₃ in which they estimated that biomass burning may contribute up to 12 % of the total annual global flux. The biomass burning includes the sources from burning during forest clearing, savanna burning, agricultural waste burning and combustion of bio-fuels for energy purposes.

Natural ecosystem

Emissions of NH₃ from natural ecosystems occur from soils (under natural vegetation) and directly from natural vegetation. A number of organisms present in soils decompose organic matter and release NH₃ or N compounds that readily hydrolyze to NH_y (NH₃ and NH₄⁺). In equilibrium conditions for a natural ecosystem, NH₃ fluxes occur from above the ground and/or from below the ground. This means that NH₃ fluxes are related closely to biological activity in the soil. NH_y generated below a depth of several centimeters from the

surface may remain in the system, while that produced at or near the surface is vulnerable to loss (Woodmansee 1978). It is also evident that 10 cm depth of topsoil, approximately 50 % (±20 %) of the N mineralization occurs and is present as NH_y, which is vulnerable to loss by volatilization (Trumbore et al. 1995). The NH₃ emitted from the soil surface may be absorbed by plant leaves. Denmead et al. (1976) showed that virtually all NH₃ emitted by the soil was reabsorbed or deposited in the canopy. Dense canopies may absorb NH₃ effectively, as gaseous transport is much faster through stomata than through the soil matrix, and the leaf area of a dense canopy is often much greater than the soil area below the vegetation (Burkhardt et al. 2009). Furthermore, deposition to the canopy can be enhanced in the presence of dew or rainwater on leaves.

In addition to emissions from the soils under natural vegetation, the canopy may also act as a source of atmospheric NH₃. Langford and Fehsenfeld (1992) showed that under circumstances of high atmospheric NH₃ concentrations, vegetation acts as a sink for NH₃, and at low atmospheric NH₃ concentrations, vegetation can release NH₃ into the atmosphere. The primary driver of NH₃ exchange is the difference between the atmospheric NH₃ concentration and the average concentration in the ecosystem canopy, both of which vary with time and space (Sutton et al. 1995b; Asman et al. 1998; Fowler et al. 2009). Within the

canopy, several sources and sinks combine together to determine the average NH_3 concentration in the canopy, including exchange with plant tissues through stomata, with leaf cuticles and with decomposing leaf litter and the soil surface (Sutton et al. 1998; Fowler et al. 2009).

The atmospheric concentration at which plants neither gain nor lose NH_3 is defined as the canopy compensation point. Plants assimilate NH_3 when the atmospheric concentration is higher than the canopy compensation point, and plants emit NH_3 when the atmospheric concentration is lower than the canopy compensation point. The compensation point is strongly dependent on temperature, NH_4^+ concentration of the canopy, NH_3 deposition to leaf cuticles and pH of the soil (Schjoerring et al. 1998). Therefore, the net emission from the soil–vegetation complex depends on the soil equilibrium concentration, the turbulent transport through the canopy, the compensation point and the exchange between the plant leaves and the atmosphere. It should be noted that the net NH_3 fluxes would depend on the difference between the canopy compensation point and the atmospheric concentration. This canopy compensation point accounts for both bi-directional stomatal exchange and deposition to leaf cuticles (Nemitz et al. 2001). One of the key points to be noted about the NH_3 compensation point is that it depends on the net solubility of NH_3 in aqueous solution, which is largely dependent on its equilibrium with NH_4^+ . Overall, the exchange of NH_3 between the atmosphere and the land surface is controlled by both atmospheric and land surface processes and can thus be bi-directional. Whether emission or deposition occurs depends on the N status of the ecosystem.

Sea surface

The emission of NH_3 from the sea surface is the bi-directional exchange of NH_3 between the atmosphere and the sea surface (similar to the compensation point). Normally, seawater NH_4^+ is in equilibrium with dissolved NH_3 . $\text{NH}_{3(\text{air})}$ later tends to a sea–air equilibrium concentration $[\text{NH}_{3(\text{eq})}]$, within the scalar roughness height, following Henry's law (Barret 1998). If $\text{NH}_{3(\text{eq})}$ exceeds surface layer air concentrations $\text{NH}_{3(\text{air})}$, then NH_3 emission from the sea surface takes place. The emission of NH_3 from sea surfaces can be described by the theory reported by Barret (1998), and the expressions are given below.

The proportional interdependence of the concentration of aqueous NH_3 $[\text{NH}_{3(\text{aq})}]$ and gaseous partial pressure $P_{\text{NH}_{3(\text{g})}}$ can be expressed through the Henry's law constant H_{NH_3} , in Eq. (7):

$$H_{\text{NH}_3} = \frac{[\text{NH}_{3(\text{aq})}]}{P_{\text{NH}_{3(\text{g})}}} \quad (7)$$

where $[\text{NH}_{3(\text{aq})}]$ is the molar concentration of aqueous NH_3 in moles per liter. $P_{\text{NH}_{3(\text{g})}}$ is the partial pressure of gaseous NH_3 in atmosphere.

The formulation used to calculate $[\text{NH}_{3(\text{eq})}]$ on the sea surface is given in Eq. (8):

$$[\text{NH}_{3(\text{eq})}] = \frac{[\text{NH}_4^+(\text{aq})]}{RT \times H_{\text{NH}_3} \left(\frac{1}{\alpha} + \frac{10^{-\text{pH}}}{\beta \times K_{\text{NH}_4^+}} \right)} \quad (8)$$

where $[\text{NH}_{3(\text{eq})}]$ is the NH_3 concentration in sea–air equilibrium (moles per cubic meter). $[\text{NH}_4^+(\text{aq})]$ is the NH_4^+ concentration on sea surface (moles per cubic meter). R is the gas constant ($8.0275 \times 10^{-2} \text{ atm L mol}^{-1} \text{ K}^{-1}$). T is the temperature of the sea water ($^\circ\text{K}$). H_{NH_3} is the Henry's law coefficient (moles per liter per atmosphere). α is the activity coefficient of NH_3 in water. β is the activity coefficient of NH_4^+ . pH is the pH in sea water. $K_{\text{NH}_4^+}$ is the dissociation constant for NH_4^+ (moles per liter), in the reaction where NH_3 is hydrolyzed to form NH_4^+ and OH radical.

Energy sector

Very few studies (e.g. Bouwman et al. 1997; Sutton et al. 2000; Battye et al. 2003) are concerned about NH_3 emissions from the energy sector, including fuel combustion, industrial process (non combustion sources) and transport sectors. However, the emission estimates reported by these studies are of fairly low accuracy. The reason may be: the energy sector is being treated as a minor source for NH_3 emission, in comparison with the dominant source of agricultural emissions (animal waste and fertilizer application). Sutton et al. (2000) attempted to estimate NH_3 emission from various industries and vehicles in the UK. Similarly, Battye et al. (1994) proposed emission factors for industries and vehicles in the USA.

Transport sector

The contribution of vehicles to non-agricultural NH_3 emissions has been considered to be negligible up to 1995 (Sutton et al. 1995b; Perrino et al. 2002). Recent studies, however, have shown that NH_3 concentration in urban environments has increased significantly due to over-reduction of NO_x in catalytic converters in automobile exhaust, and also in industrial and power station control systems (Sutton et al. 2000; Perrino et al. 2002). According to the technical report of 2011 of the European Environment Agency (EEA 2011) on emission inventories, road transport is estimated to contribute 2 % to total NH_3 emissions, industrial processes 1 % and waste decomposition 1 %, with the remaining percentage being attributable to agriculture from activities such as manure storage, slurry spreading and the use of synthetic nitrogenous fertilizers (Reche et al. 2012). Although vehicles form a minor part of global emissions, they have significant local NH_3 emissions (Fraser and Cass 1998; Kean et al. 2009). For

example, after conducting measurements in a roadway tunnel, Fraser and Cass (1998) concluded that the contribution of motor vehicle emissions had risen from 2 to 15 % of the total NH_3 emissions in the Los Angeles area since the introduction of catalysts. Road side measurements in the UK, USA and Europe have shown strong links between NH_3 emissions and traffic (Perrino et al. 2002; Cape et al. 2004; Kean et al. 2009).

The reasons for the growing concern over NH_3 emissions from vehicles at the urban level are: (1) the introduction of gasoline-powered vehicles equipped with three-way catalytic converters (TWCs) and (2) diesel-powered vehicles adopting the selective catalytic reduction (SCR) system (Heeb et al. 2006; Pandolfi et al. 2012). In TWC vehicles, NH_3 is the product of NO reduction on the catalyst surface which, beyond the formation of molecular N_2 , leads to NH_3 in motor vehicle exhaust. In SCR vehicles, NH_3 is used as a reagent and supplied to the catalyst system by the injection of urea into the exhaust, which then undergoes thermal decomposition and hydrolysis to form NH_3 .

For automobiles, the emissions generally depend on the air-to-fuel (A/F) ratio. Under lean conditions, lower combustion temperatures lead to lower NO_x emissions. However, a very high A/F ratio engine can cause misfires leading to high hydrocarbon emissions. Therefore, the present trends of the implementation of catalytic abatement under any A/F conditions for pollutants have been rising to comply with the legislation limits. The objective of reduction in NO_x has been achieved through automotive exhaust under lean conditions, i.e. $\text{A/F} > 14.7$, compared with the stoichiometric feed ($\text{A/F} = 14.7$) of a traditional gasoline-fuelled engine; e.g. the polluting components are abated using TWC or SCR. The introduction of catalytic reductions to the automobile sector was started in the 1980s and increased in the 1990s, which was generally attributed to their requirement for a stoichiometric A/F ratio to achieve best performances. However, there are other factors that substantially contribute to the drawbacks of catalytic reductions, such as the increase in vehicle weight due to the implementation of security systems, the generalized use of vehicle air conditioning and emission of NH_3 into the atmosphere, etc.

Increased road traffic with a larger volume of on-road vehicles has also been recognized as an important source of NH_3 , but its release from vehicles is not yet regulated (Battye et al. 2003; Pandolfi et al. 2012; Reche et al. 2012). The percentage of vehicles equipped with TWCs in the USA has increased from less than 10 % in 1981 to more than 75 % in 1993, suggesting that the introduction of this type of converter has significantly influenced on-road NH_3 emissions (Perrino et al. 2002).

Heeb et al. (2006) investigated the efficiency of the catalytic reduction of NO and the selectivity towards reduction of NH_3 . Post-catalyst NH_3 emissions strongly depend on velocity and acceleration and vary by two orders of magnitude from 1 to 170 mg km^{-1} . Table 8 presents emission factors for pre-

and post-catalytic NO and NH_3 . From this table, it could be concluded that post-catalyst NO emissions were lowest when NH_3 formation was most intense, and vice versa. This complementary behavior indicates that a TWC can be operated in a way that causes either NH_3 or NO emissions to dominate. Reche et al. (2012) observed that winter levels of NH_3 were higher at traffic sites, suggesting a contribution from vehicle emissions, and that NH_3 levels decreased by 55 % with increasing distance (50 m) to the direct emissions from traffic.

Other sources

The other minor sources are identified as: (1) direct NH_3 emissions from humans, (2) wild animals and sea birds, (3) horses and pets and (4) sewage. NH_3 emissions from humans occur through human sweat, human breath, smoking and infant excretion. NH_3 emissions from human sweat were first suggested by Healy et al. (1970), when NH_3 levels were observed to be higher inside the room. It has also been reported that NH_3 emission from human breathing is less than from human sweat (Lee and Dollard 1994). The rate of emission from sweat depends on the geographical location, climate of the region and manual work. Therefore, it is expected that people staying in hot climates will emit more NH_3 through sweat and breathing. Martin et al. (1997) have measured NH_3 emissions from cigarettes and found a substantial NH_3 emission of 4.15 $\text{mg NH}_3\text{-N cigarette}^{-1}$. Sutton et al. (2000) emphasized that excretion of N from infants may be a significant contribution to NH_3 emissions since urine in nappies does not enter the sewage system and may hydrolyze, giving high indoor NH_3 concentrations.

The larger percentage losses of NH_3 can be found in housed animals than grazing animals. This may be due to the fact that a larger fraction of emission can be retained by soil and vegetation for smaller individual sources. Due to this reason, it is expected that NH_3 emissions from small dispersed wild animals or sea birds are negligible, with most emissions recaptured within plant canopies. However, the emissions may be significant from larger colonies of wild animals or sea birds.

Although horses are not generally used as agricultural animals for agricultural activities, some studies showed that horses have a significant NH_3 emission (e.g. 8 $\text{kg N animal}^{-1} \text{ year}^{-1}$; Buijsman et al. 1987). NH_3 emission from horses may come from competition horses, and the mechanism of emission is similar to that of the livestock used for agricultural purposes, but different in the quantity of emission, as factors affecting the emissions are not the same for both these categories. The processes involved in emission of NH_3 from pets (e.g. dogs, cats) are also similar to those of livestock farming. Like the livestock, the free roaming pets produce fewer emissions than the pets staying in houses.

Table 8 Mean pre- and post-catalyst NO and NH₃ emission factors (Source: Heeb et al. 2006)

Cycle, phase	Driving pattern	Mean velocity (km h ⁻¹)	NO pre-cat. (mg km ⁻¹)	NO post-cat. (mg km ⁻¹)	Conversion efficiency ^a	NH ₃ pre-cat. (mg km ⁻¹)	NH ₃ post-cat. (mg km ⁻¹)	Selectivity ^b	Mixing ratio ^c post-cat. (mol mol ⁻¹)
ECE	Urban ^d	19	1,170	260	0.78	4.7	48.9	0.086	0.3
EUDC	Extra-urban	62	1,890	5.8	>0.99	<1.5	53.8	0.049	16
BAB	Highway	119	3,160	7.3	>0.99	<1.0	65.5	0.036	16
Ra, I	Highway	112	2,680	7.6	>0.99	<0.7	73.6	0.048	17
Ra, II	Highway	97	1,990	10.5	>0.99	<0.6	49.8	0.044	8.4
Ra, III	Extra-urban	74	1,200	18	0.99	<0.7	22.4	0.032	2.2
Rb, I	Extra-urban	53	890	37.4	0.96	<1.2	23.5	0.046	1.1
Rb, II	Urban	33	1,090	20.7	0.98	<1.3	21.2	0.033	1.8
Rb, III	Stop-and-go	5	250	4.1	0.98	<1.5	64.3	0.45	28

ECE Economic Commission for Europe, EUDC European driving cycle, BAB German highway cycle, Ra and Rb Swiss real world cycles

^a The NO conversion efficiency of the TWC was calculated according to formula $1 - ((\text{NO}_{\text{post-cat.}})/(\text{NO}_{\text{pre-cat.}}))$

^b The NH₃ selectivity of the TWC was calculated according to formula $((\text{NH}_3 \text{ post-cat.}) - (\text{NH}_3 \text{ pre-cat.})) / ((\text{NO}_{\text{pre-cat.}}) - (\text{NO}_{\text{post-cat.}})) \times (m_{\text{r NO}}/m_{\text{r NH}_3})$.

^c The post-catalyst NH₃/NO mixing ratio was calculated according to formula $(\text{NH}_3 \text{ post-cat.}) / (\text{NO}_{\text{post-cat.}}) \times (m_{\text{r NO}}/m_{\text{r NH}_3})$

^d Affected by cold start

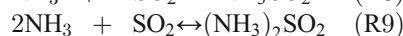
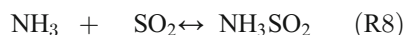
NH₃ emission from sewage normally comes from waste water treatment works through both the processes of: (1) anaerobic processes occurring in the treatment system and (2) spreading of treated sewage onto agricultural land. Harmel et al. (1997) found an average volatilization of 27 % N for digested sewage sludge with N content of 5.2 % of dry solids. Sutton et al. (2000) considered NH₃ emission under sludge injection as 75 % less than spreading. Munday (1990) concluded that nitrogenous emissions equate to 7.3 % of methane emissions, with 10 % of the emitted N being in the form of NH₃ from the landfill. According to Burton and Watson-Craik (1998), municipal refuse contains significant quantities of fixed N (0.5 % N). However, there is very little information available on gaseous emissions of NH₃ from landfills.

Atmospheric chemistry of NH₃

Reaction of NH₃ with SO₂ and SO₃

The products that could be formed from the reaction of anhydrous NH₃ with SO₂ have remained a subject of debate for a long period. Some researchers (e.g. Landreth et al. 1974; Meyer et al. 1980) have confirmed that the products depend on the molar ratio of NH₃ and SO₂ and the vapor pressure of these gases. At a stoichiometric ratio of 1:1, NH₃ and SO₂ react to produce a yellow solid (NH₃SO₂), in equilibrium with the vapor pressure of its components (reaction: R8; Meyer et al. 1980). At a stoichiometric ratio of 2:1, NH₃ and SO₂ produce a white solid (NH₃)₂SO₂, in equilibrium with the

vapor pressure of its components (reaction: R9; Landreth et al. 1974; Meyer et al. 1980). The reactions of anhydrous SO₂ and NH₃ gases leading to the formation of NH₃SO₂ and/or (NH₃)₂SO₂ are completely reversible. When the gas vapor pressure is sufficiently low, the solids dissociate into their original components; i.e. SO₂ and NH₃ (Meyer et al. 1980).



Benner et al. (1992) conducted a thorough designed investigation for the reaction of SO₂ with NH₃ under simulated cloud conditions and in thin water films. They observed that conversion of as much as 81 % of the SO₂ to SO₄²⁻ has occurred after 10 min of reaction when the initial concentrations of SO₂ and NH₃ were 1 ppm each and the relative humidity was 60 %. Under typical cloud conditions and in the presence of NH₃, the conversion of SO₂ to SO₄²⁻ will be completed in less than 5 min, indicating that the cloud system is the catalytic factor for SO₄²⁻ formation (Hansen et al. 1991).

SO₂ can be converted to sulfur trioxide (SO₃) in the atmosphere via the gas phase oxidation of SO₂ by OH and peroxy radicals; the subsequent reaction with atmospheric moisture produces H₂SO₄. Shen et al. (1990) found that the gas-phase reaction of NH₃ with SO₃ was faster than the gas-phase reaction of SO₃ with water by almost four orders of magnitude (rate constant of NH₃ and SO₃ is $6.9 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Under normal atmospheric conditions, the water concentration in the atmosphere is much higher than the concentration of NH₃ (at least six orders of magnitude; Renard et al. 2004).

As a result, SO_3 normally reacts predominantly with water and not with NH_3 under normal atmospheric conditions.

Reaction of NH_3 with H_2SO_4

H_2SO_4 condenses both onto preexisting particles and into new particles with partial neutralization by NH_3 (Swartz et al. 1999). The rates of SO_2 oxidation processes are influenced by atmospheric photochemistry and temperature. Photochemistry affects the rates of these oxidation reactions as some of the intermediate reactions may be photochemical in nature (Finlayson-Pitts and Pitts 2006). Upon reaction with NH_3 , H_2SO_4 is converted to $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4HSO_4 . The droplet phase reactions are important for the oxidation of SO_2 to SO_4^{2-} in the atmosphere. New particle formation by nucleation of gas-phase species significantly influences the size and number of tropospheric aerosols. The gas-phase reaction of NH_3 and H_2SO_4 can lead to three well-defined compounds, depending on the molar ratio of these two reactants; i.e. (1) NH_4HSO_4 when $\text{NH}_3:\text{H}_2\text{SO}_4=1$, (2) letovicite ($(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$) when $\text{NH}_3:\text{H}_2\text{SO}_4=1.5$ and (3) $(\text{NH}_4)_2\text{SO}_4$ when $\text{NH}_3:\text{H}_2\text{SO}_4=2$ (Scott and Cattell 1979; Renard et al. 2004). Among these compounds, $(\text{NH}_4)_2\text{SO}_4$ is the most stable form of solid in the atmosphere due to its low vapor pressure, and is predominantly present in the atmosphere as one of the components of $\text{PM}_{2.5}$ (Wang et al. 2006; Poulain et al. 2011).

Possible reactions involved under normal atmospheric conditions

Under normal atmospheric conditions, particulate SO_4^{2-} is a product of gas-to-particle phase reactions involving atmospheric oxidation of SO_2 by both homogeneous and heterogeneous processes. In the gas phase, the oxidation of SO_2 takes place by OH radicals that produce H_2SO_4 , which later condenses to form SO_4^{2-} . Table 9 presents possible reactions occurring in various pathways during formation of NH_4^+ salts in the atmosphere. It can be seen that the majority of aqueous phase reactions with SO_2 normally occur in cloud water, where SO_2 can be oxidized into SO_4^{2-} via several pathways reacting with dissolved ozone, hydrogen and organic peroxides, hydroxyl radicals and various oxides of N (Table 9).

As discussed in “Reaction of NH_3 with H_2SO_4 ” section, the formation of particulate SO_4^{2-} depends on availability of NH_3 . In the presence of surplus NH_3 , particulate $(\text{NH}_4)_2\text{SO}_4$ is formed through the neutralization transformation process. In any normal ambient conditions, NH_4NO_3 and NH_4Cl are formed via reversible phase equilibrium with precursor gases such as NH_3 , HNO_3 , and NH_3 and HCl , respectively (Table 9). The affinity of H_2SO_4 with the reaction with NH_3 is much larger than the affinity of HNO_3 and HCl with NH_3 . As a result, the available NH_3 is first taken up by H_2SO_4 to form $(\text{NH}_4)_2\text{SO}_4$, and the excess available NH_3 may then react with

HNO_3 and HCl to form NH_4NO_3 and NH_4Cl , respectively (Lin and Cheng 2007; Behera and Sharma 2011; Behera and Sharma 2012). Particulate NO_3^- is formed in the atmosphere through gas-to-particle conversion processes starting with NO_x and proceeding via HNO_3 formation (Table 9).

The reaction mechanism for the formation of HNO_3 depends on the duration of the day, which is decided by the meteorology. For example, during the daytime, the most important pathway of HNO_3 is the homogeneous gas phase reaction of NO_2 with the OH radical (R13), and during the night, the free NO_3 radical is the source of tropospheric HNO_3 (R19 and R20). NO_3 may either combine with NO_2 to form dinitrogen pentoxide (N_2O_5), which reacts with water on particles, fog or cloud water droplets to produce HNO_3 (Table 9), or it may form the acid by H-atom abstraction from aldehydes or hydrocarbons. When atmospheric HNO_3 is available, it has a tendency to react with alkaline species such as surplus NH_3 to form NH_4NO_3 . This reaction is believed to be the main source of fine particulate NO_3^- in urban air (Stockwell et al. 2000; Ianniello et al. 2011). A second pathway for particulate NO_3^- formation involves HNO_3 reacting with the sodium chloride (NaCl) in sea salt particles to form sodium nitrate (NaNO_3) aerosol, and to release HCl into the atmosphere. The mode of formation of NO_3^- depends on the concentration of NH_3 and existing sea-salt and crustal aerosols (Zhuang et al. 1999; Sharma et al. 2007). Pierson and Brachaczek (1988) reported that NO_3^- in fine mode ($\text{PM}_{2.5}$) is NH_4NO_3 and NO_3^- in coarse mode includes not only NH_4NO_3 but also NaNO_3 .

Overall, it can be summarized that under normal atmospheric conditions, the reaction between NH_3 and H_2SO_4 is preferred over reactions of NH_3 with HNO_3 and NH_3 with HCl . Due to their semi-volatile nature, formations of NH_4NO_3 and NH_4Cl are favored under conditions of higher relative humidity and lower atmospheric temperature; otherwise, these NH_4^+ salts can be reversed into their respective precursor gases. However, particulate $(\text{NH}_4)_2\text{SO}_4$ is a non-volatile and stable compound in equilibrium with its precursor gases (NH_3 and H_2SO_4).

After particulate formation and with the advantage of atmospheric lifetimes of the order of 1–15 days, NH_4^+ salts have the tendency to be transported and deposited at larger distances from emission sources, contributing to soil acidification, forest decline and eutrophication of waterways (Aneja et al. 2001, 2008, 2009). To study the behavior of these precursor gases under a multi-reaction system, Behera and Sharma (2011) estimated the degradation rates of NO_2 , SO_2 and NH_3 as: $\text{NO}_2=0.26\pm0.15\text{ h}^{-1}$, $\text{SO}_2=0.31\pm0.17\text{ h}^{-1}$, $\text{NH}_3=0.35\pm0.21\text{ h}^{-1}$, indicating that the reaction rate for the oxidation of NH_3 with H_2SO_4 is faster than the reaction rate for the oxidation of NH_3 with HNO_3 . The new findings from the chamber study of Behera and Sharma (2011) are that degradation rates of precursor gases are dependent on the initial molar

Table 9 Possible reactions for the pathways during formation of NH_4^+ salts in the atmosphere

Reaction details	Reaction number	Reference
$\text{NO}_{2(g)} + h\nu \rightarrow \text{NO}_{(g)} + \text{O}_{(g)}$	R10	Lin and Cheng 2007
$\text{NO}_{(g)} + \text{O}_{3(g)} \rightarrow \text{NO}_{2(g)} + \text{O}_{2(g)}$	R11	Lin and Cheng 2007
$\text{O}_{(g)} + \text{O}_{2(g)} \rightarrow \text{O}_{3(g)}$	R12	Lin and Cheng 2007
$\text{NO}_{2(g)} + \text{OH}_{(g)} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	R13	Lin and Cheng 2007
$\text{HNO}_{3(g)} + h\nu \rightarrow \text{OH}_{(g)} + \text{NO}_{2(g)}$	R14	Seinfeld and Pandis 2006
$\text{HNO}_{3(g)} + \text{OH}_{(g)} \rightarrow \text{H}_2\text{O}_{(g)} + \text{NO}_{3(g)}$	R15	Seinfeld and Pandis 2006
$\text{NO}_{2(g)} + \text{O}_{3(g)} \rightarrow \text{NO}_{3(g)} + \text{O}_{2(g)}$	R16	Seinfeld and Pandis 2006
$\text{NO}_{(g)} + \text{HO}_{2(g)} \rightarrow \text{NO}_{2(g)} + \text{OH}_{(g)}$	R17	Calvert and Stockwell 1983
$\text{NO}_{3(g)} + h\nu \rightarrow \text{NO}_{2(g)} + \text{O}_{(g)}$	R18	Calvert and Stockwell 1983
$\text{NO}_{3(g)} + \text{NO}_{2(g)} + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	R19	Calvert and Stockwell 1983
$\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(g)} \rightarrow 2\text{HNO}_3 + \text{M}$	R20	Calvert and Stockwell 1983
$\text{SO}_{2(g)} + \text{OH}_{(g)} + \text{O}_{2(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{SO}_{4(g)} + \text{HO}_{2(g)}$	R21	Bufalini 1971
$\text{SO}_{2(g)} + \text{O}_{(g)} + h\nu \rightarrow \text{SO}_{3(g)}$	R22	Bufalini 1971
$\text{SO}_{3(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{SO}_{4(g)}$	R23	Phillips et al. 1995
$\text{NH}_{3(g)} \leftrightarrow \text{NH}_{3(aq)}$	R24	Clegg and Brimblecombe 1989
$\text{NH}_{3(aq)} + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$	R25	Clegg and Brimblecombe 1989
$2\text{NH}_{3(g)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow (\text{NH}_4)_2\text{SO}_{4(s)} \text{ or } (\text{aq})$	R26	Finlayson Pitts and Pitts 2006
$\text{NH}_{3(g)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{NH}_4\text{HSO}_{4(aq)}$	R27	Finlayson Pitts and Pitts 2006
$\text{NH}_{3(g)} + \text{NH}_4\text{HSO}_{4(aq)} \rightarrow (\text{NH}_4)_2\text{SO}_{4(aq)}$	R28	Finlayson Pitts and Pitts 2006
$\text{NH}_{3(g)} + \text{HNO}_{3(g)} \leftrightarrow \text{NH}_4\text{NO}_{3(s)}$	R29	Finlayson Pitts and Pitts 2006
$\text{NH}_{3(g)} + \text{HCl}_{(g)} \leftrightarrow \text{NH}_4\text{Cl}_{(s)} \text{ or } (\text{aq})$	R30	Zhang et al. 2008
$\text{NH}_{3(g)} + \text{HNO}_{3(g)} \leftrightarrow \text{NH}_4^+ + \text{NO}_{3(aq)}$	R31	Mozurkewich 1993
$\text{NH}_{3(g)} + \text{OH}_{(g)} \leftrightarrow \text{NH}_{2(g)} + \text{H}_2\text{O}_{(g)}$	R32	Diau et al. 1990

ratio of $(\text{NH}_3)/(\text{NO}_2 + \text{SO}_2)$, which is indicative of NH_3 -rich and NH_3 -poor situations for eventual production of NH_4^+ salts, and that initial particulate concentration has more impact on degradation of precursor gases (Fig. 6). As a result, NH_3 -rich conditions in the ambient air always enhance the formation of SIA components of $\text{PM}_{2.5}$, and the role of the existing particle surface is very important to the transformation process.

Although studies of atmospheric acidity have focused primarily on H_2SO_4 and HNO_3 , there are situations in which HCl may make an appreciable contribution to airborne acidity. Besides the wet and dry deposition of HCl itself, a major sink for HCl is neutralization by gaseous NH_3 to form NH_4Cl aerosol. NH_4Cl can only exist in the atmosphere in the solid state when the relative humidity is lower than the deliquescent point, i.e. humidity is lower than 75–85 % (Pio and Harrison 1987a). Like NH_4NO_3 , NH_4Cl is unstable and can dissociate reversibly to NH_3 and HCl . The behavior of solid NH_4Cl is also remarkably similar to that of solid NH_4NO_3 . From these studies (Pio and Harrison 1987a, b; Allen et al. 1989; Matsumoto and Tanaka 1996), it can be concluded that NH_4Cl aerosols in both dry and aqueous phase evaporate faster than the corresponding NH_4NO_3 aerosols.

Equilibrium of NH_3 with HNO_3 and HCl to form aerosols

The dissociation constants of the equilibria depend on atmospheric temperature and relative humidity (Stelson et al. 1979; Stelson and Seinfeld 1982a,b; Pio and Harrison 1987a,b). Under conditions of high temperature and low relative humidity, particulate NH_4NO_3 and NH_4Cl are volatile, resulting in lower observed ambient levels of these particulate species. The validity of the equilibrium assumptions has been tested in several field measurements in the past (Doyle et al. 1979; Harrison and Pio 1983; Harrison and Msibi 1994). These studies established relationships between the thermodynamic equilibria with temperature and relative humidity. These results were also confirmed by model simulation theory of the latest study by Chang et al. (2011).

The analysis of such a multi-component system is a complex problem, particularly when attempting to build a predictive quantitative model of various species. Apart from temperature and relative humidity, these dissociation equilibria depend on the chemical composition of the aerosols and precursor gases (Mozurkewich 1993; Ansari and Pandis 2000). For example, in the gas–liquid phase equilibrium for an HNO_3 – H_2SO_4 – NH_3 – H_2O system, the partial pressure of gaseous HNO_3 depends on the liquid phase pH value and increases as the NH_3/SO_2 ratio in the

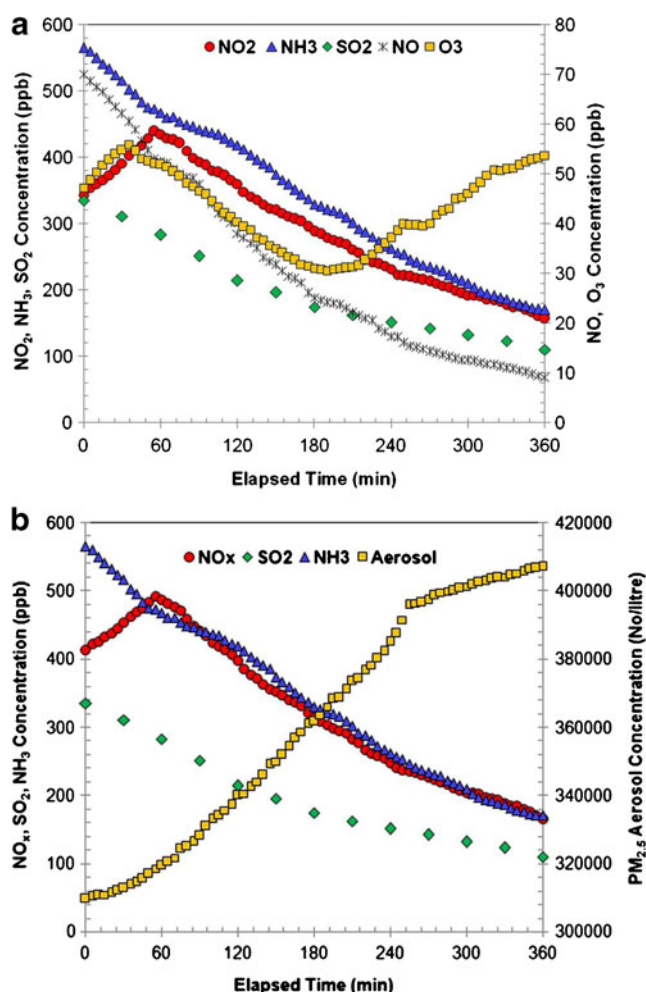


Fig. 6 Trends of precursors during a multi-reaction system: **a** trends of gaseous species during particle formation; **b** trends of NO_x , SO_2 , NH_3 and $\text{PM}_{2.5}$. Adapted from Behera and Sharma (2011)

liquid phase decreases (Tang 1980). As a result, excess NH_3 over that required for complete neutralization of H_2SO_4 facilitates the existence of particulate NO_3^- .

During the preliminary days of the study on the equilibrium of NH_4NO_3 , Doyle et al. (1979) and Stelson et al. (1979) carried out ambient air quality studies on this particular topic and observed that the calculated concentration products $[\text{NH}_3][\text{HNO}_3]$ were of a similar order to those inferred from the field measurements of gas phase concentrations. Therefore, the approaches for studying the chemical equilibrium of NH_4NO_3 can be done in two ways: (1) estimating the equilibrium parameters theoretically and/or (2) estimating equivalent equilibrium parameters through experimental results.

Stelson and Seinfeld (1982a, b) studied in detail the thermodynamic equilibrium of $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--NH}_3\text{--H}_2\text{O}$ system and formulated a temperature-dependent dissociation constant of NH_4NO_3 . Later, Allen et al. (1989) also validated the theory of Stelson and Seinfeld (1982a, b) in the measurement study. When sufficient $\text{NH}_3(\text{g})$ and $\text{HNO}_3(\text{g})$ are present at

temperatures above 5°C , the product of the partial pressures was found to be in rough agreement with the NH_4NO_3 dissociation constants recommended by Stelson et al. (1979), and consistently somewhat larger than the values recommended by Stelson and Seinfeld (1982a). However, the partial pressures tend to be considerably higher than expected from the dissociation constant at lower temperatures due to kinetic factors (Wexler and Seinfeld 1992).

As per Jaffe (1988), atmospheric measurements of NH_3 and HNO_3 do seem to show agreement with the one laboratory determination of the NH_4NO_3 equilibrium constants, extrapolated to ambient temperature. However, given the large uncertainty in these equilibrium constants at ambient temperature, it is not possible to assess the importance of this equilibrium in the atmosphere, and therefore, models which are very sensitive to this parameter should be treated with caution (Jaffe 1988).

Mozurkewich (1993) had given the formulation for computation of the dissociation constant of $\text{NH}_4\text{NO}_3(\text{aq})$ to $\text{NH}_3(\text{g})$ and $\text{HNO}_3(\text{g})$ as a function of temperature and either solution concentration or equilibrium relative humidity. For saturated solutions, these equations are consistent with the results for the solid, and for dilute solutions they are consistent with data on dilute solutions of $\text{NH}_3(\text{aq})$ and $\text{HNO}_3(\text{aq})$. For particles with radii less than $0.1\ \mu\text{m}$, the Kelvin effect has a substantial effect on the dissociation constant. However, particle size has little effect on the deliquescence point. The gas-to-particle equilibrium of NH_4NO_3 can be described by reactions R(29) and R(31), as presented in Table 9. Reaction R(29) corresponds to the gas-to-particle partitioning of dry NH_4NO_3 particles (Mozurkewich 1993). The dissociation equilibrium constant of NH_4NO_3 into HNO_3 and NH_3 (K_n) can be described by Eq. (9):

$$\ln(K_n) = 118.87 + \frac{24,080}{T} - 6.0254 \ln(T) \quad (9)$$

where K_n is the dissociation constant in ppb^2 and T is the ambient air temperature in Kelvin. The phase transition from a solid particle to a liquid drop occurs when the relative humidity reaches a certain critical value [deliquescence relative humidity, (DRH)] corresponding to the water activity of the saturated solution. For deliquescent particles (relative humidity, $\text{RH} > \text{DRH}$), the influence of RH should be considered. Therefore, for $\text{RH} < 99.7\%$, Reaction (R31) can be described by the following equation:

$$K_n^* = (P_1 - P_2(1 - a_w) + P_3(1 - a_w)^2) \times (1 - a_w)^{1.75} \times K_n \quad (10)$$

where P_1 , P_2 and P_3 are the denominations used for mathematical formulations derived in Mozurkewich (1993), and a_w

is the water activity approximation ($=RH/100$) that normally ranges from 0 to 1 (Topping et al. 2005; Kreidenweis et al. 2008). For details of the derivation of the formulations, Mozurkewich (1993) can be referred to.

In an ideal system, the phase transition depends on the nature of the particle and the existing condition of RH. For example, it can be seen that when RH increases, the transition from solid phase equilibrium (R29) to the aqueous phase (R31) takes place, provided the conditions of deliquescence depend directly on the ambient RH value compared with the DRH of the particle. When RH decreases, the transition from R31 to R29 depends on the ambient RH value compared with the efflorescence relative humidity (ERH). For example, at 298 K, pure $(\text{NH}_4)_2\text{SO}_4$ particles have a DRH of 80 % and an ERH of 35 %, while pure NH_4NO_3 particles have a DRH of 62 % and no ERH is observed (Martin et al. 2004; Seinfeld and Pandis 2006; Poulain et al. 2011). For RH values lying between the values of DRH and ERH, particles are in a metastable state and in this condition, the prediction of whether particles are in solid or liquid phase does not depend on the chemical composition of the particle only, but also on the RH history of the particles (Martin et al. 2004; Poulain et al. 2011).

In a recent study, Poulain et al. (2011) considered R31 and equation Eq. (10) to describe the dissociation equilibrium of NH_4NO_3 in an ideal system made of NH_3 , HNO_3 and H_2O . In the diurnal analysis, Poulain et al. (2011) observed that NO_3^- concentrations anti-correlated with K_n^* for all seasons. The decrease of NO_3^- concentration when K_n^* increases agrees with an increased conversion of particle phase NH_4NO_3 into gas phase HNO_3 and NH_3 during daytime.

To describe the thermodynamics of NH_4NO_3 under deliquescent conditions, the equilibrium constant of reaction R31 can also be expressed as describing the formation of NH_4NO_3 on deliquescent particles (K_{deliq}) instead of describing its dissociation constant (K_n^*). K_{deliq} can be calculated as follows:

$$K_{\text{deliq}}(T) = K(298) \exp \left[a \left(\frac{298}{T} - 1 \right) + b \left(1 + \ln \frac{298}{T} \right) - \frac{298}{T} \right] \times 10^{-18} \quad (11)$$

where $K(298)=3.35 \times 10^{16} \text{ atm}^{-2}$, $a=75.11$, $b=-13.5$ and 10^{-18} is a conversion factor that provides the same unit as K_n^* . A similar approach is used to describe the NO_3^- concentration in the ISORROPIA model by Nenes et al. (1998) and Fountoukis and Nenes (2007). With this approach, Poulain et al. (2011) have observed that the diurnal variation of K_{deliq} correlated with diurnal changes to NO_3^- concentrations during the day, the reason being that K_{deliq} describes the reverse mechanism of K_n^* . From these studies (Poulain et al. 2011; Sun et al. 2011), it could be inferred that the diurnal profiles of NO_3^- match their thermodynamic properties (K_n^* and/or K_{deliq}) well, resulting in an important evaporation of NH_4NO_3

during the day and a condensation process on preexisting particles during the night.

In the case of the formation of solid NH_4Cl , the same procedure for the equilibrium study of NH_4NO_3 can be applied. At humidity lower than 75–85 %, the particulate NH_4Cl exists in the solid phase in equilibrium with the gaseous products. However, due to a hysteresis phenomenon, the existence of liquid NH_4Cl aerosol droplets is possible at much lower humidity than thermodynamic equilibrium values, as has already been observed for various hygroscopic atmospheric aerosols. The theoretical equilibrium constant K_c in units of ppb^2 for solid NH_4Cl (reaction R30) can be calculated by a formula provided by Pio and Harrison (1987a), when the ambient relative humidity is below the respective DRH:

$$\ln K_c = 2.2358 \ln T - 2.13204 \times 10^{-4} T^{-1} + 65.4375 - 8.167 \times 10^{-3} T + 4.644 \times 10^{-7} T^2 - 1.105 \times 10^{-10} T^3 \quad (12)$$

After reviewing the ongoing studies in the area of equilibrium thermodynamics of NH_4NO_3 and NH_4Cl , this review paper suggests approaches on scientific data interpretation from the experimental results. To check the thermodynamic equilibrium conditions of a measured set of data on ambient air quality, one should first convert the units of measured NH_3 , HNO_3 and HCl into parts per billion. Next, the measured equilibrium constants for NH_4NO_3 and NH_4Cl can be estimated in units of ppb^2 by multiplying the levels of NH_3 with HNO_3 , and NH_3 with HCl , respectively. Then, the theoretical dissociation constants are calculated based on theories from existing literature (e.g. Stelson and Seinfeld 1982a, b; Pio and Harrison 1987a, b; Mozurkewich 1993). If the measured equilibrium constants are more than the theoretical values, then it is expected that formations of NH_4NO_3 and NH_4Cl occur in that locality. Sometimes, measured equilibrium constants are less than the theoretical values. However, significant levels of NO_3^- and Cl^- are observed in the ambient air. In this case, data should be segregated into two groups based on: (1) $\text{RH} < \text{DRH}$ and (2) $\text{RH} \geq \text{DRH}$. In category (1), the interpretation is a simple one following the measured and theoretical equilibrium constants; however in category (2), more attention should be given to determining the theoretical equilibrium constants under deliquescent conditions. Some studies can be referred to for details of the procedures of finding theoretical constants and their interpretations, along with ambient air quality status (e.g. Allen et al. 1989; Poulain et al. 2011; Ianniello et al. 2011).

Kinetic studies of NH_3 with H_2SO_4 , HNO_3 and HCl to form aerosols

In general, chemical kinetic studies are the basis for finding the rate and time of the formation of these chemical compounds through interaction of NH_3 with other acidic species. It may be

seen that only a few studies (i.e. Erisman et al. 1988; Harrison and Kitto 1992; Baek et al. 2004; Behera and Sharma 2012) have investigated the chemical kinetics responsible for the formation of NH_4^+ salts. The study by Erisman et al. (1988) is the first study that estimated the reaction rate constant for conversion of NH_3 to NH_4^+ . Later, Harrison and Kitto (1992) also examined the chemical kinetics for formation of NH_4^+ salts. Both Erisman et al. (1988) and Harrison and Kitto (1992) had estimated the chemical rate constant with a pseudo-first-order chemical kinetic approach, and the estimated rate constant includes conversion from all chemical reactions involving NH_3 .

Baek et al. (2004) considered all the individual reactions responsible for the formation of NH_4^+ salts, including $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , NH_4Cl , and estimated the reaction rate constants based on chemical kinetic approaches after deducing the empirical relations between initial concentration, final concentration and time responsible for reaction from the results of ambient air measurements in USA. In a recent study, Behera and Sharma (2012) have estimated the reaction rate constants for the formation of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and NH_4Cl from the experimental outcomes of a simulated outdoor environmental chamber under background concentrations of ambient air and direct sunlight in Indian conditions. Table 10 presents the reaction rate constants of the formation of these NH_4^+ salts from both these studies (i.e. Baek et al. 2004; Behera and Sharma 2012). These two studies were carried out under different conditions, one in the ambient air and another in the chamber study. However, the discrepancies in these two studies could be due to: (1) meteorological parameters, e.g. higher temperature and solar radiation in Indian conditions and (2) the existing particulate surface (due to higher levels of background particulate matter), which could play a significant role in enhancing the condensation process leading to the formation of these compounds. The new finding was arrived in kinetic study that the existing surface of the aerosol could play a significant role in the formation rates of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 .

Losses of semi-volatile ionic species during measurement

It has been concluded that NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4Cl are represented by the ions of SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ (known as SIA), which typically comprise 25–75 % of atmospheric $\text{PM}_{2.5}$ mass (Heitzenberg 1989; Pavlovic et al. 2006). The process of formations of SIA components of $\text{PM}_{2.5}$ can be summarized as: (1) SIA consisting of SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ are secondary in nature, (2) these are formed either by physical processes or chemical reactions, or by a combination of both these two processes, (3) processes such as nucleation, condensation and evaporation are categorized under physical processes, (4) chemical reactions of precursor gases such as H_2SO_4 , HNO_3 , HCl and NH_3 that can undergo the photochemical gas phase, aqueous-phase oxidation and particulate-phase processes are categorized as chemical

reactions. These transformation processes are dependent upon the meteorological conditions (temperature and RH) and the availability of NH_3 in the vicinity.

Previously, various field measurement studies (e.g. Harrison and Pio 1983; Chang et al. 1986) on concentrations of NH_3 , HCl and HNO_3 were performed, and it was observed that the concentration products of $[\text{HCl}][\text{NH}_3]$ and $[\text{HNO}_3][\text{NH}_3]$ were in agreement with theoretical model values predicted by thermodynamic equilibrium laws for NH_4Cl and NH_4NO_3 formations, respectively (as described in section “Equilibrium of NH_3 with HNO_3 and HCl to form aerosols”). In some other studies (e.g. Allen et al. 1989; Mehlmann and Warneck 1995), experimental products were different from theoretical predictions. The discrepancies occurred mainly at relative humidity below 60 % and above 90 %.

The above-mentioned studies also found that gas-particle equilibrium conditions were not attained instantaneously in the atmosphere at temperatures lower than 15 °C. The reason for such nonattainment of equilibrium could be: several minutes are required for achievement of the system of equilibrium. However, the discrepancies between the measured and theoretical equilibrium constants under higher temperature are a matter of concern. These discrepancies could be due to kinetic constraints in the system of equilibrium by the evaporation of NH_4^+ aerosols that have restricted to chemical reaction and mass transfer of particle evaporation. Therefore, the concept of artifacts in the measurement system arises under higher temperature for the measurement of semi-volatile particulate NH_4NO_3 and NH_4Cl .

During the measurement of ionic species, there will be losses from the filter samples for NH_4^+ , NO_3^- and Cl^- , if the artifact problems are not taken into account. As a result, significant under-reporting of levels of NH_4^+ , NO_3^- and Cl^- takes place in the measurement program of ambient air. The underestimation of the semi-volatile particulate NH_4NO_3 and NH_4Cl will tend to over-emphasize the importance of non-volatile particulate $(\text{NH}_4)_2\text{SO}_4$. For this reason, there is a need for representative and reliable methods for measuring the atmospheric concentrations of NH_4^+ , NO_3^- and Cl^- without disturbing atmospheric equilibrium conditions during sampling. Denuders for absorbing gases prior to particle collection, and back-up filters (nylon filter) for absorbing HNO_3 , HCl and NH_3 evaporated from collected particles, have been

Table 10 Reaction rate constants (cubic meters per micromole per second) for formation of ambient NH_4^+ salts

Compound	Baek et al. 2004	Behera and Sharma 2012
$(\text{NH}_4)_2\text{SO}_4$	1.14×10^{-4}	2.68×10^{-4}
NH_4NO_3	7.30×10^{-5}	1.59×10^{-4}
NH_4Cl	8.56×10^{-5}	5.16×10^{-5}

widely accepted as effective tools to avoid sampling artifacts (gas–particle and particle–particle interactions) and to correct for the evaporated particles with back-up filters. Several studies in the past (e.g. Baek and Aneja 2004; Pathak and Chan 2005; Ianniello et al. 2011; Behera and Sharma 2012) used the denuder techniques with back-up filters to measure these gaseous and particulate species.

Chow et al. (2005) observed that total evaporative NO_3^- losses ranged from <10 % during cold months to >80 % during warm months of the total particulate NO_3^- . Pathak and Chan (2005) observed that the percentage of NO_3^- loss was 36 %, and the percentage of Cl^- loss was 61 % in the NH_3 -rich samples. Ianniello et al. (2011) comprehensively investigated the losses due to artifact effects by using a denuder/filter pack system to collect inorganic and soluble $\text{PM}_{2.5}$ without interferences from gas–particle and particle–particle interactions in Beijing, China. Ianniello et al. (2011) observed evaporation losses from the Teflon filters to be 33.05, 23.65 and 34.71 % of the fine particulate NO_3^- , Cl^- and NH_4^+ , respectively, during the winter period, and 83.33, 74.64 and 53.07 % of the fine particulate NO_3^- , Cl^- and NH_4^+ , respectively, during the summer period.

Based on earlier studies (Baek and Aneja 2004; Pathak and Chan 2005; Yu et al. 2006; Behera and Sharma 2012) on the measurement of ions in $\text{PM}_{2.5}$ for gases and particles, we have summarized the methods of sampling and analysis to avoid the artifact effects. Two coated glass honeycomb denuders in series can be kept in the cartridge of filter pack to absorb the gaseous components of air (HCl , HNO_2 , HNO_3 , SO_2 and NH_3). The arrangement of denuders and filter packs from the direction of airflow should follow this sequence: (1) first denuder with sodium carbonate (Na_2CO_3) coating, (2) second denuder with citric acid coating and (3) a filter pack containing Teflon and nylon filters in series, which collects fine particles. Denuders should be cleaned and coated before the start of each experiment. The first denuder coated with 1 % glycerine and 1 % Na_2CO_3 in a 50 % mixture of methanol and ultra-pure Milli-Q water collects average gas concentrations of HCl , HNO_2 , HNO_3 and SO_2 . The citric acid denuder should be coated with 2 % citric acid in a 50 % mixture of methanol and ultra-pure Milli-Q water to capture NH_3 . The filter pack contains both a 47-mm diameter Teflon filter and a nylon filter. The nylon filter is installed above the Teflon filter to capture NO_3^- as HNO_3 , Cl^- as HCl and NH_4^+ as NH_3 , which are evolved from the front Teflon filter as a result of NH_4^+ salt dissociations (NH_4NO_3 and NH_4Cl).

The evaporation of volatile NH_4^+ salts from the fine particles collected on the front Teflon filter is due to fluctuations in temperature and relative humidity and/or a pressure drop across these filters, which perturb the gas–particle equilibrium. Water-soluble inorganic ions (NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , SO_4^{2-} and Cl^-) should be extracted from PTFE filters using ultra-pure Milli-Q water following the USEPA

reference method (USEPA 1999). The nylon filter should be extracted using a 5-mL 1.8-mM Na_2CO_3 /1.7-mM NaHCO_3 solution (anion IC eluent). The samples extracted from the PTFE and nylon filters should be ultrasonicated at a temperature of about 30 °C for 1 h and filtered through a 0.22- μm filter paper to remove insoluble matter. Chemical analyses of the extracted samples from the denuders, Teflon filters and nylon filters are carried out using Ion Chromatography instrument.

After analysis, total concentrations of NH_4^+ salts in $\text{PM}_{2.5}$ should be estimated as the sum of the measurements of both (1) on the Teflon filter for non-volatile fine particulate species (unevolved particulate species) and (2) on the nylon filter for volatile fine particulate species (evolved particulate species). The estimations for concentration of the species are given in the following equations:

$$[\text{NO}_3^-]_{\text{evolved}} = [\text{NO}_3^-]_{\text{N}} \quad (13)$$

$$[\text{Cl}^-]_{\text{evolved}} = [\text{Cl}^-]_{\text{N}} \quad (14)$$

$$[\text{NH}_4^+]_{\text{evolved}} = [\text{NH}_4^+]_{\text{N}} \quad (15)$$

$$[\text{NO}_3^-]_{\text{unevolved}} = [\text{NO}_3^-]_{\text{T}} \quad (16)$$

$$[\text{Cl}^-]_{\text{unevolved}} = [\text{Cl}^-]_{\text{T}} \quad (17)$$

$$[\text{NH}_4^+]_{\text{unevolved}} = [\text{NH}_4^+]_{\text{T}} \quad (18)$$

$$[\text{NO}_3^-]_{\text{fine}} = [\text{NO}_3^-]_{\text{unevolved}} + [\text{NO}_3^-]_{\text{evolved}} \quad (19)$$

$$[\text{Cl}^-]_{\text{fine}} = [\text{Cl}^-]_{\text{unevolved}} + [\text{Cl}^-]_{\text{evolved}} \quad (20)$$

$$[\text{NH}_4^+]_{\text{fine}} = [\text{NH}_4^+]_{\text{unevolved}} + [\text{NH}_4^+]_{\text{evolved}} \quad (21)$$

where subscripts N and T stand for nylon filter and Teflon filter, respectively. Thus, the total concentrations of the fine particulate Cl^- , NO_3^- and NH_4^+ can be determined without disturbing the partition equilibrium existing in the atmosphere between gaseous NH_3 , and the particulate NH_4Cl and NH_4NO_3 .

Role of NH_3 in formation of secondary inorganic aerosols

PM consists of many different types of particles covering a broad range of composition and size, and can be categorized into primary and secondary aerosols. Primary aerosols include automobile exhaust, sea spray and dust, which are emitted to the atmosphere directly from their sources. Secondary aerosols, which generally have diameters $d_p < 2.5$ or $10 \mu\text{m}$, are produced in the atmosphere from chemical reactions involving gases such as NO_x , SO_2 , VOCs and NH_3 . In many regions, secondary aerosol components represent a significant fraction of PM_{10} (particles with $d_p < 10 \mu\text{m}$) or $\text{PM}_{2.5}$ ($d_p < 2.5 \mu\text{m}$) (Chow et al. 1994; Pavlovic et al. 2006).

In this section, important findings of recent studies that are ongoing in various parts of the world are synthesized. The literature syntheses are made through modeling and experimental results of previous studies that show how NH_3 is responsible for the formation of SIA components of PM and may contribute disproportionately to fine PM. In Europe, secondary PM comprises 50 % or more of $\text{PM}_{2.5}$ (Erisman and Schaap 2004). In the Eastern United States, approximately half of the $\text{PM}_{2.5}$ has an inorganic chemical speciation that is composed of NH_4^+ , NO_3^- and SO_4^{2-} , and a very small amount of the inorganic $\text{PM}_{2.5}$ is attributable to direct emissions (USEPA 1996). Ansari and Pandis (1998) explained how the PM concentration behaves with respect to the precursor concentrations of SO_4^{2-} (or SO_2), total (gas+aerosol) NH_3 and total (gas+aerosol) HNO_3 using an inorganic aerosol equilibrium model, GFEMN. Ansari and Pandis (1998) concluded that the PM concentration level responds nonlinearly to SO_4^{2-} and shows an overall sensitivity to concentrations of NH_3 and HNO_3 .

Erisman and Schaap (2004) assessed the effects of various reduction strategies using a box model and the 3D LOTOS long-range transport model version 5.2, developed by TNO-MEP. Erisman and Schaap (2004) found from this modeling approach that secondary PM concentrations can be reduced effectively only if NH_3 emissions are decreased in much the same way as those of SO_2 and NO_x . Pavlovic et al. (2006) studied NH_3 emission, its concentrations and implications in the formation of PM, in Texas, USA and found that such a complex problem can only be solved by photochemical and thermodynamic modeling, which is an advanced and promising tool for modeling the typical atmospheric pollution system.

Luo et al. (2007) used a thermodynamic aerosol model in a three-dimensional chemical transport model to assess the role of NH_3 chemistry and the coarse mode natural aerosol in the global distribution of SO_4^{2-} , NO_3^- and NH_3 . Luo et al. (2007) compared the SO_4^{2-} , NO_3^- and NH_4^+ deposition between pre-industrial and present scenarios, and showed that the present NO_3^- and NH_4^+ deposition is twice the amount of pre-industrial deposition, and that the present SO_4^{2-} deposition is almost five times that of pre-industrial deposition. Sharma et al. (2007), Shukla and Sharma (2008) and Behera and Sharma (2010) used statistical analyses of a large data set of atmospheric constituents and fundamentals of atmospheric chemistry to show the formation of SIA in the atmosphere, particularly in Kanpur, India. Since prevailing atmospheric conditions (temperature, humidity, wind speed, etc.) responsible for SIA formation vary from day to night and from one season to another, the scientific explanations proposed by Sharma and co-workers are helpful in understanding seasonal and diurnal variations of SIA.

Wang et al. (2005) reported levels of water-soluble inorganic ions of $\text{PM}_{2.5}$ in Beijing, China, from 2001 to 2003. Wang et al. (2005) used a molar concentration balance method

to estimate the concentration of NH_4^+ salts from existing levels of ions (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Ca^{2+} and K^+). Wang et al. (2005) established that the ions existed mainly in the form of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , NaCl , KCl and CaCl_2 in $\text{PM}_{2.5}$, and that $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 were the predominant compounds among all identified NH_4^+ salts. Later, Wang et al. (2006) measured the levels of water-soluble inorganic ions of $\text{PM}_{2.5}$ in Shanghai, China during four seasons from 2003 to 2005. Wang et al. (2006) observed that the seasonal variation of ion concentrations was significant, with the highest concentrations observed in winter and spring and the lowest in summer and autumn.

Pinder et al. (2007) examined NH_3 emission control as a potential cost-effective strategy for reducing ambient inorganic $\text{PM}_{2.5}$ concentration in the Eastern United States and concluded that larger reductions in winter inorganic PM are achievable at a lower cost through controls on NH_3 emissions. The overall scientific convergence clearly suggests that NH_3 should be targeted for the effective reduction of $\text{PM}_{2.5}$. Moreover, Table 11 summarizes the levels of $\text{PM}_{2.5}$ along with NH_4^+ , NO_3^- and SO_4^{2-} in some important regions of the world. It could be concluded that a surplus amount of NH_3 is present in the atmospheres of the urban environments throughout the world, and forms SIA components of PM.

From Table 11, it may be observed that the levels of NH_4^+ are observed to be higher in the Asian regions (e.g. Lahore) than in the North American regions (e.g. New York). There are uncertainties over estimating the global emissions and spatial distributions of NH_3 and NH_4^+ , mainly due to lack of widespread ground-based air quality monitoring and insufficient data on fertilizer use and animal production. In addition, NH_3 is short-lived in the atmosphere, which makes ground-based measurement more difficult. To overcome these problems, European researchers made observations from space through an infrared sensor aboard a satellite to monitor the global distributions of NH_3 . Clarisse et al. (2009) used infrared spectra, obtained by the IASI/MetOp satellite, to map global NH_3 concentrations from space over the course of 2008. Clarisse et al. (2009) showed NH_3 hotspots after establishing discrepancies between the satellite-measured NH_3 levels and global NH_3 inventories estimated from models. A total of 28 hotspots for NH_3 emissions were identified around the world. Some high levels of atmospheric NH_3 were explained by fires in the mid-latitudes in South Siberia and Inner Mongolia, South America and East, West and South Africa (Fig. 7). Almost all the other hotspots were identified above agricultural regions of North America, Europe and Asia.

Deposition of NH_3 on terrestrial bodies

In general atmospheric phenomena, NH_3 can either be converted to NH_4^+ , or subjected to dry or wet deposition.

Table 11 Levels of PM_{2.5} and their secondary inorganic components in some of the regions of the world (micrograms per cubic meter)

City site	PM _{2.5}	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	Reference
Pearl River Delta, China	NA	9.2	7.2	24.1	Hu et al. 2008
Seoul, South Korea	72.5	5.2	12.6	9.4	Kang et al. 2004
Guangzhou, China	79.2	7.3	9.5	21.6	Tao et al. 2009
Seoul, South Korea	37.6	3.7	5.2	5.8	Heo et al. 2009
Beijing, China	168.0	12.5	14.2	20.8	Kim Oanh et al. 2006
Bangkok, Thailand	50.0	1.6	1.2	5.6	Kim Oanh et al. 2006
Milan, Italy	24.5	1.7	3.2	4.2	Lonati et al. 2008
New York, USA	13.4	1.9	2.0	4.3	Qin et al. 2006
Lahore, Pakistan	209	16.1	18.9	19.2	Biswas et al. 2008
Kanpur, India	136.0	9.4	5.2	19.4	Behera and Sharma 2010

NA data not available

Higher levels of NH₃ are found near emission sources that are confined to the lower tropospheric layer. It has been observed that horizontal concentration profiles show a decrease in concentrations with increasing distance from the source. For example, Erisman et al. (1987) have found a 50 % reduction in concentration at a 600-m distance from the source, while Asman et al. (1989) have found a 70 % reduction at a 4-km

distance from the source. Dry deposition is the process by which atmospheric pollutants are removed from the atmosphere without significant interaction with atmospheric moisture. Conversely, wet deposition of pollutants takes place through prominent interaction with atmospheric moisture, for example, in-cloud and below-cloud pollutant scavenging, pollutant removal by fog droplets or dew.

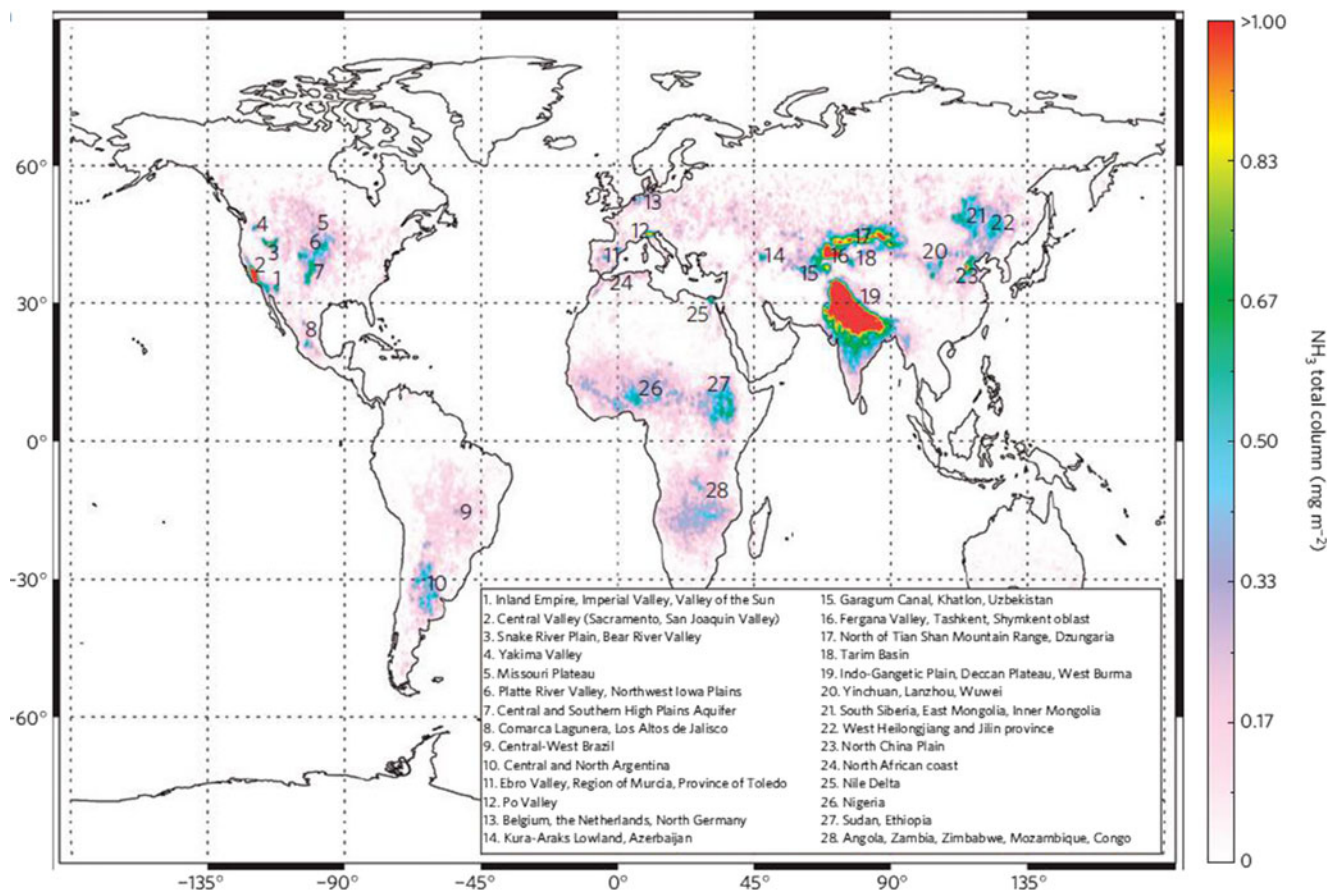


Fig. 7 Yearly average total columns of NH₃ in 2008 retrieved from IASI measurements on a 0.25° by 0.25° grid. Adapted from Clarisse et al. (2009)

Wet deposition of NH_3

The wet deposition process is complex, and involves reactions that occur both in-cloud and below-cloud between water droplets, gases and aerosols (Mizak et al. 2005). In in-cloud scavenging, the pollutant enters cloud droplets or ice crystals and takes part in their formation and growth phases, for example, via nucleation scavenging. When cloud droplets that contain pollutants collide with each other, this collision results in a precipitation event, removing the scavenged pollutants and bringing them down to the surface (Asman et al. 1998; Jylhä 1999). In below-cloud scavenging, pollutants adhere directly to falling precipitation. During wet deposition, three processes are responsible for the wet removal of NH_3 : interception, scavenging and transport to the surface. Interception occurs when NH_3 gas is brought into contact with condensed water, followed by scavenging by cloud water and raindrops through dissolution of NH_3 and deposition to the Earth's surface (Mizak et al. 2005; Seinfeld and Pandis 2006). The in-cloud scavenging of gaseous NH_3 is more efficient than the below-cloud scavenging because the contact time between the gas and the droplet is much longer in the cloud than in the one below it.

In-cloud scavenging

Aerosols containing NH_4^+ act as condensation nuclei at normal atmospheric conditions; however, NH_3 is a highly soluble gas. As a result, almost all NH_3 at the cloud level is dissolved instantaneously into cloud droplets. The rate of removal of NH_3 and NH_4^+ by in-cloud scavenging under such conditions is only determined by the rate at which the liquid water is removed from the cloud. In-cloud scavenging can be described with a scavenging ratio of about 1×10^6 (Asman and Janssen 1987). The in-cloud scavenging of NH_3 proceeds at about the same rate as the in-cloud scavenging of SO_4^{2-} aerosol particles which act as condensation nuclei (Asman 2001).

We present the formula for scavenging ratio by Liu et al. (1982) reported in Asman and Janssen (1987) as: $S_{ic} = 5,000 \times I^{-0.36}$, where I is the precipitation rate in meters per second. By selecting the values of rainfall rates as 1 and 2 mm h^{-1} , S_{ic} has been found to be 1.1×10^6 and 0.9×10^6 , respectively.

The in-cloud scavenging coefficient (A_{ic}) is given by Eq. (22):

$$A_{ic} = S_{ic} \times \frac{I}{H} \quad (22)$$

where I is the precipitation rate in meters per second and H is the height of the mixing layer (meters). At rainfall rates of 1 and 2 mm h^{-1} and a height of the mixing layer of 800 m, A_{ic} has been found to be 3.8×10^{-4} and 6.3×10^{-4} , respectively. Normally, NH_3 is emitted at or near ground level, and the cloud base is

generally a few hundred meters above the ground. This signifies that to a very near source, when the plume is under the cloud base, scavenging will occur at a much lower rate than at some distance from the source, where the remaining NH_3 is scavenged mainly by in-cloud processes.

Below-cloud scavenging

Mizak et al. (2005) have stated that below-cloud scavenging of gases is dependent on the proximity of the deposition location from the emitting source. During below-cloud scavenging, due to the large sizes of rain showers, the concentration of NH_3 in the drop will not have reached equilibrium with the NH_3 in the surrounding atmosphere by the time the drop reaches the ground.

The model of Asman (1995) estimates NH_3 concentration in the raindrop as a result of the following phenomena: (1) uptake of NH_3 gas at the drop surface and subsequent dissociation and liquid diffusion and (2) change in drop radius due to water evaporation.

The height of the cloud base from dew point can be estimated as Eq. (23):

$$Z_{base} = c_1 + d_1 \ln(RH(0)) \quad (23)$$

where $c_1 = -9,620 + 62.10T_a(0)$ and $d_1 = -5,254 - 13.43T_a(0)$. $T_a(0)$ is the temperature at ground level in K , $RH(0)$ is the relative humidity at ground level in percentage and Z_{base} is the height of cloud base in meters. Asman (1995) reported that the error made by using Eq. (23) instead of the results of the model is less than 5 %.

Best's distribution function is representative of observed distribution over a larger range of rainfall intensity than any other model under real atmospheric conditions. Therefore, Asman (1995) selected Best's distribution function for raindrop size distribution due to the reason for getting the smallest scavenging coefficient resulting a value closer to the actual value

Asman (1995) derived Eq. (24) to estimate the below-cloud scavenging coefficient λ_b :

$$\lambda_b = a \times I_{mm}^{bav} \quad (24)$$

where I_{mm} is the rainfall rate at ground level (millimeters per hour), $a = aa + bb D_g$ (NH_3 diffusivity in air) with $aa = a_0 + a_1 RH(0)$, $bb = b_0 + b_1 RH(0)$, $bav = bav_0 + bav_1 RH(0)$ and with the following values:

$$a_0 = 4.476 \times 10^{-5} - 1.347 \times 10^{-7} T_a(0),$$

$$a_1 = -3.004 \times 10^{-7} + 1.498 \times 10^{-9} T_a(0),$$

$$b_0 = 8.717 - 2.787 \times 10^{-2} T_a(0),$$

$$b_1 = -5.074 \times 10^{-2} + 2.894 \times 10^{-4} T_a(0),$$

$$bav0 = 9.016 \times 10^{-2} + 2.315 \times 10^{-3} T_a(0),$$

$$bav1 = 4.458 \times 10^{-3} - 2.115 \times 10^{-5} T_a(0).$$

Overall, the amount of NH_3 scavenged by the rainfall can be estimated using the concentration of NH_3 in the air below the cloud, the volume of the atmosphere affected by the rain and period of the rainstorm, temperature and relative humidity at ground level. Later, Aneja et al. (1998) have calculated the contribution of below-cloud scavenging to total NH_3 deposition as 15 %. For more details of the model and estimation of the scavenging ratio, Asman (1995) can be referred to.

From the studies by Asman and co-workers, other relevant studies (e.g. Aneja et al. 1998; Goncalves et al. 2000; Mizak et al. 2005) and the review by Renard et al. (2004), it can be summarized that wet deposition can be described by below-cloud and in-cloud scavenging coefficients. Close to the source, where the plume has not yet reached the clouds, scavenging is described by a precipitation rate-dependent below-cloud scavenging coefficient. At more than 30 km from the source, where the plume is fully mixed and in-cloud scavenging dominates, scavenging is described by a precipitation rate-dependent overall scavenging coefficient based on a scavenging ratio of 1×10^6 for both NH_3 and particulate NH_4^+ . At intermediate distances from the source, the scavenging ratio is a function of both below-cloud and in-cloud scavenging rates. The time-averaged wet removal rate is a function of the scavenging coefficient, the probability of precipitation, the average duration of the precipitation and the precipitation rate for each meteorological class for each wind direction.

Dry deposition of NH_3

The measurements of the surface–atmosphere exchange provide, at the simplest level, the mass exchange per unit area of surface, which may be ground, water or leaf area, per unit time (Fowler et al. 2009). The phenomenon of surface–atmosphere exchange is the result of contributions from several pathways. This transfer scheme can be simplified to vertical levels between a source and a sink. The most widely applied transfer scheme is a resistance analogue in which the flux of trace gas or particle is treated as an analogue of electrical current flowing through a simple network of resistances (Monteith and Unsworth 2007; Fowler et al. 2009).

Dry deposition over vegetation

The researchers had previously quantified the dry deposition velocity of NH_3 on vegetation through either of two approaches: modeling or experiments (leaf-level measurements and whole canopy measurements). The presence of

atmospheric moisture on the surface of the leaves of plants acts as a sink for atmospheric NH_3 . Therefore, the concept of dry deposition of NH_3 over the vegetation is a complicated phenomenon that can take place bi-directionally. To get an insight into the mechanism of this bi-directional exchange and the method estimation of dry deposition on vegetation, we present adequate descriptions in this section based on earlier studies.

Mechanism of bi-directional exchange

At atmospheric NH_3 concentrations below the compensation point, NH_3 is emitted from the leaves of plants. Depending on the concentration of NH_3 prevailing in the atmosphere, vegetation can be either a source or a sink for NH_3 . This bi-directional exchange of NH_3 between vegetation and atmosphere has become better understood in the past few years. The most widely known example of bi-directional exchange is CO_2 , which exhibits both deposition and emission fluxes due to photosynthesis and respiration, respectively. The recognition of bi-directional exchange of NH_3 requires modeling approaches to simulate the process for application in surface–atmosphere exchange schemes is illustrated in Fig. 8.

The dry deposition rate is normally expressed in the form of a deposition velocity. The deposition velocity is assigned by the unit of length per unit time, and is valid for the reference height z . This velocity varies with time and type of surface. During daytime, when the stomata of vegetation are often open, there is an uptake of water-soluble gases. Sunlight also warms the ground and creates vertical mixing of air. Both these processes enhance the deposition in daytime and decrease it during the night. Deposition velocities are divided into resistances in different regions (e.g. the lower troposphere, the laminar boundary layer, stomata, etc.). The resistances are further expressed as a function of various parameters such as roughness length, wind speed, latitude, season, time of day, etc.

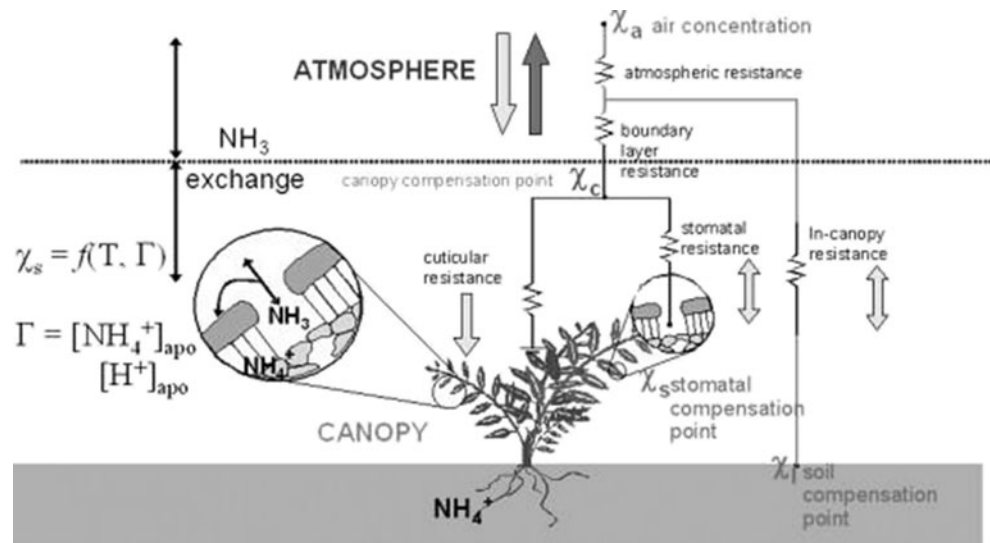
Estimation of dry deposition on vegetation

The inferential method based on the “big leaf multiple resistances approach” can be used for estimating the dry deposition fluxes of NH_3 (Wesely and Hicks 1977; Hicks et al. 1987; Sutton et al. 1995a). The deposition flux (F) (micrograms per square meter per second) of a nonreactive trace gas for which the surface is a sink under all ambient conditions is defined by Eq. (25):

$$F = -V_d \times X(z_{ref}) = -\frac{X(z_{ref})}{R_a + R_b + R_c} \quad (25)$$

where $X(z_{ref})$ is the trace gas concentration (micrograms per cubic meter) at the reference height z_{ref} (meters) and V_d

Fig. 8 A diagrammatic representation of bi-directional exchange, for NH_3 exchange between the atmosphere and vegetation. Adapted from Fowler et al. (2009)



denotes the dry deposition velocity (meters per second), which is the reciprocal of the sum of the turbulent resistance (R_a) (seconds per meter), the quasi-laminar or viscous boundary layer resistance (R_b) (seconds per meter) and the surface resistance (R_c) (seconds per meter) (Sutton et al. 1998; Trebs et al. 2006). The inferential method is valid for trace gases whose mixing ratio just above the soil and/or vegetation elements is zero. However, in the case of NH_3 , the scenario is different, as NH_3 can be deposited to and emitted from surfaces. Therefore, the canopy compensation point concentration, X_c (micrograms per cubic meter), should be considered in the estimation methodology (Nemitz et al. 2004). X_c represents a concentration analogue of R_c and is the air concentration at which competing chemical and biological consumption and production processes balance each other (i.e. the net flux is zero) (Sutton et al. 1995a; Trebs et al. 2006). X_c can be expressed as Eq. (26):

$$F = \frac{X_c - X(Z_{ref})}{R_a + R_b} \quad (26)$$

Sutton and co-workers investigated various model formulations for estimation of the bi-directional exchange of NH_3 . To be specific, a dynamic resistance model proposed by Sutton et al. (1998) can also be applied for prediction of the bi-directional surface-atmosphere exchange of NH_3 . Recently, Trebs et al. (2006) have estimated the dry deposition of NH_3 for a remote pasture site in the Amazon Basin based on in situ measurements, which were based in turn on the model of Sutton et al. (1998). Apart from uptake and emission of NH_3 via plant stomata, the dynamic model accounts for absorption of NH_3 by epicuticular water films under very humid conditions, and subsequent re-evaporation (capacitive leaf surface exchange). For details of the models for estimation of the dry

deposition of NH_3 on vegetation, refer to Sutton et al. (1995a) and Sutton et al. (1998). For application of this modeling approach to estimate the dry deposition velocity of NH_3 over vegetation, refer to Trebs et al. (2006).

Interestingly, Trebs et al. (2006) have concluded that by ignoring NH_3 emission from the vegetation surface, the annual net N deposition rate was estimated to be about $-11 \text{ kg N ha}^{-1} \text{ year}^{-1}$. However, on the other hand, if surface-atmosphere exchange of NH_3 could be considered bi-directional, the annual net N budget at the pasture site is estimated to range from -2.15 to $-4.25 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Trebs et al. 2006). Therefore, the model for estimation of dry deposition on vegetation should consider the bi-directional exchange of NH_3 .

Table 12 summarizes the estimated dry deposition velocity of NH_3 from some selective studies (e.g. Andersen et al. 1993; Aneja et al. 1986). From these studies, it can also be concluded that deposition velocities ranging from 0.4 to 1.5 cm s^{-1} are characteristic of annual plants of modest height and foliage crown development. Deposition velocities ranging from about 2.5 to 5.0 cm s^{-1} relate to forests.

Major factors responsible for dry deposition of NH_3 on vegetation are relative humidity, temperature, atmospheric conditions and hours of a day. The condensed atmospheric moisture deposited on the surface of leaves constitutes a potential sink for atmospheric NH_3 . As a result, the deposition of NH_3 increases with an increase in relative humidity. Erisman and Wyers (1993) have quantified the impact of the moisture deposited on leaf surfaces by considering the canopy water storage level of the forest. They have observed that a canopy saturated with water (e.g. after a rainfall) has a canopy water storage value exceeding 2 mm . However, a dry canopy has a canopy water storage value of less than 0.25 mm . The canopy saturated with water has less resistance to NH_3 deposition than the dry canopy. Therefore, the deposition velocities are at their maximum, averaging about 60 mm s^{-1} .

When the canopy is dry, the deposition velocity decreases exponentially with the decreasing humidity level. During nighttime, the NH_3 deposition on vegetation is lower compared with during the daytime duration. The deposition of NH_3 on vegetation during nighttime is generally influenced by both the physiological and meteorological characteristics of nighttime, compared with those of daytime (Renard et al. 2004). The physiological characteristics of plants have a greater influence during nighttime. The stomatas of plants close at night, thereby stopping the NH_3 uptake by plant tissues. From a meteorological point of view, the calmer air, lower temperature and therefore lower humidity during the night also affect the effectiveness of NH_3 deposition. For coniferous forests, Duyzer et al. (1992) found a clear maximum deposition velocity of NH_3 at midday (50 mm s^{-1}) and a minimum of about 28 mm s^{-1} during the night.

It is difficult to observe the effect of temperature and atmospheric conditions on NH_3 deposition under real field conditions and differentiate the effects of temperature from those of the relative humidity. Nevertheless, Aneja et al. (1986) attempted to find the concentration of NH_3 under well-controlled chamber experiments with whole canopy conditions at different temperatures. They found that the gas phase NH_3 concentration ranged from 90 to 1,400 ppbv, and changes in temperature from 12 to 30°C had negligible impact on the deposition velocity. However, at low temperatures, the decrease in physiological activities in plants led to a closing of the stomata and to a corresponding increase in resistance to NH_3 uptake, which resulted in deposition velocities below 5 mm s^{-1} (Erisman and Wyers 1993).

Dry deposition on forests

Forest covers approximately 9.4 % of the Earth's surface, or 30 % of the total land area. Although forests are classified primarily by trees, the concept of a forest ecosystem includes additional species such as smaller plants, fungi, bacteria and animals, as well as physical and chemical processes such as energy flow and nutrient cycling. However, a typical forest is

composed of the overstory (canopy or upper tree layer) and the understory. The understory is further subdivided into the shrub layer, herb layer and also the moss layer and soil microbes. Considering the case of Europe, about 30 % of the land area is forested (25 % is arable land and 17 % is used for pasture). The dry deposition of NH_3 on a forest is higher than on a meadow or a lake simply because its surface is rougher.

During the last two decades, detailed investigations of atmospheric N deposition have been conducted in the Netherlands, Germany, UK, Denmark and Sweden. The wet deposition of N is homogeneously distributed over the region, while the dry deposition of N varies considerably, though with a general decreasing gradient from Central Europe towards the North, away from industrial areas and areas of intensive agricultural activities (Andersen and Hovmand 1999). Andersen and Hovmand (1999) reported that the dry deposition of N compounds on forest ecosystems contributes one to two times the amount received from wet deposition in Denmark.

The turbulence above a forest is normally higher than over short vegetation at a certain wind velocity. Therefore, the deposition velocities are mainly determined by the turbulent transfer. The deposition rates are larger for a forest than for short vegetation. The factors that control the dry deposition are often conceptualized as resistance to transport for the various steps, and the total resistance to transport is considered as the sum of the resistances operating in series (Andersen and Hovmand 1999; Monteith and Unsworth 2007). The resistance to turbulent transfer (aerodynamic resistance) is named R_a , the resistance to transport through the laminar surface layer (sometimes named the laminar boundary layer), R_b , and the resistance to uptake at the surface (surface resistance), R_c . The sum of the resistance is the total resistance, $R_t = R_a + R_b + R_c$, the inverse of which is the deposition velocity, V_d .

Fog deposition

Fog or cloud deposition is an intermediate process, sometimes referred to as occult deposition, but mostly grouped with dry deposition (Ferm 1998). This process is fairly efficient, occurs

Table 12 Dry deposition velocity of NH_3 over vegetation

Plant/terrain	NH_3 conc. ($\mu\text{g}/\text{m}^3$)	V_d (cm s^{-1})	References
Spruce forest	0.47	2.60	Andersen et al. 1993
Alpine Tundra	3.80	0.40	Langford and Fehsenfeld 1992
Douglas Fir Forest	6.10	2.0 to 3.0	Duyzer et al. 1994
Forest	—	2.2	Van Aalst 1986
Douglas fir forest	—	2.7	Draaijers et al. 1989
Coniferous forest	—	3.6	Duyzer et al. 1992
Soyabean	59.00	0.61	Aneja et al. 1986
Snap bean	76.00	0.40	Aneja et al. 1986
Fescue	456.00	1.16	Aneja et al. 1986
Corn	190.00	0.31	Aneja et al. 1986

occasionally and depends strongly on the roughness of the receptor. The fog water content in the air is usually very low and the scavenging of pollutants rather efficient. Even if the deposition rate is low, the effect of the fog deposition can be severe because the droplets are so concentrated. In most places, the fraction deposited through fog is very small compared with the total deposition. Some places have, however, frequent fog events, for example the Po Valley in Italy. A more general example is mountain areas, where fog deposition can be the dominant process (Lovett et al. 1982).

Water bodies deposition

The mechanisms of dry deposition differ according to surface characteristics. The dry deposition on surfaces of natural water bodies depends on the mass transfer coefficient of NH_3 from the air-to-water phase. Renard et al. (2004) have summarized the estimation of the flux of removed NH_3 over a unit surface area of water using Eq. (30):

$$F = A[C_{\text{NH}_3}]_g V_d t \quad (30)$$

where $[C_{\text{NH}_3}]_g$ is the concentration of NH_3 in the air in micrograms per cubic meter; for NH_3 , $1 \mu\text{g m}^{-3} = 58.8 \text{ nmol m}^{-3} = 1.32 \text{ ppbv}$ ($\text{nmol} = \text{nanomole} = 10^{-9} \text{ mol}$), V_d is the dry deposition velocity in meters per second, t is duration of the event in seconds, F is the flux of deposited NH_3 in kilograms per square meter and A is the unit conversion constant ($=10^{-9}$). The dry deposition of NH_3 can be estimated by either the application of film theory or application of resistance, as explained in the previous section. Larsen et al. (2001) reviewed and compiled the published results of the deposition velocity of NH_3 over seawater (Table 13).

Shahin et al. (2002) conducted extensive measurements and analysis of dry deposition of NH_3 over water surfaces in Chicago. To determine the mass transfer coefficient, they applied film theory and a resistance model. In their first approach, diffusion is the driving force, which is directly proportional to the diffusion coefficient and to the thickness

Table 13 Dry deposition velocity of NH_3 over seawater (Source: Larsen et al. 2001)

Location	V_d (cm s^{-1})	References
Atlantic Basin	0.80–2.00	Quinn et al. 1996
Australia-Southern Ocean	0.83	Griffiths et al. 1999
NE Pacific	0.83	Quinn et al. 1988
North and Baltic Seas	0.80	Barrett 1998
North Sea	0.76	Asman 1995
Tampa Bay	0.70	Poor et al. 2001
North Sea	0.20–1.50	Lee et al. 1998

of the boundary layer, which is controlled by the wind speed to a large extent. Table 14 presents the estimates of dry deposition velocities of NH_3 over fresh water.

As explained in section “Sources” on ‘emission of NH_3 from sea surface’, NH_3 emission/deposition from the sea surfaces is like the bi-directional exchange between the sea surface and the atmosphere depending on the compensation point. The deposition can be through dry deposition or wet deposition. Duce et al. (1991) reported the global atmosphere-to-ocean deposition rates of a number of N species. Table 15 presents both flux and deposition values for major ocean regions and for the oceans as a whole. The deposition of NH_x is highest over the North Pacific ($5.9 \times 10^{12} \text{ gN year}^{-1}$) followed by the North Atlantic ($4.09 \times 10^{12} \text{ gN year}^{-1}$). The total NH_x deposition on different oceanic surfaces is $16.9 \times 10^{12} \text{ gN year}^{-1}$. Comparing this value of deposition with the total NH_3 emission from all sources, which is $53.6 \times 10^{12} \text{ gN year}^{-1}$ (Table 15), it can be concluded that the excessive growth of the anthropogenic NH_3 emission could impact the biodiversities of the oceanic bodies through eutrophication.

For modeling to estimate atmospheric N deposition fluxes of N, a recent study by Jung et al. (2012) can be referred to in order to estimate atmospheric inorganic N input via dry, wet and sea fog deposition on the oceanic surface. Jung et al. (2012) found that the contributions of dry, wet and sea fog deposition to total deposition flux for total inorganic N ($46 \pm 48 \mu\text{mol m}^{-2} \text{ day}^{-1}$)

Table 14 Dry deposition velocity of NH_3 on freshwater at different wind speeds (Source: Shahin et al. 2002)

Dry deposition velocities at the given wind speed ^a , cm s^{-1}						References
1	2	3	4	5	6	
0.69	0.96	1.23	1.5	1.77	2.04	Yi et al. 1997
0.22	0.43	0.64	0.85	1.06	1.27	Liss 1973
0.69	0.87	1.06	1.24	1.43	1.61	Munnich et al. 1978
0.22	0.48	0.78	1.12	1.50	1.93	Mackay and Yeun 1983
0.82	1.05	1.28	1.51	1.74	1.97	Penman 1948
1.14	1.64	2.14	2.64	3.14	3.64	Shahin et al. 2002

^a Wind speed in meters per second

Table 15 Nitrogen deposition to the oceans (Source: Duce et al. 1991)

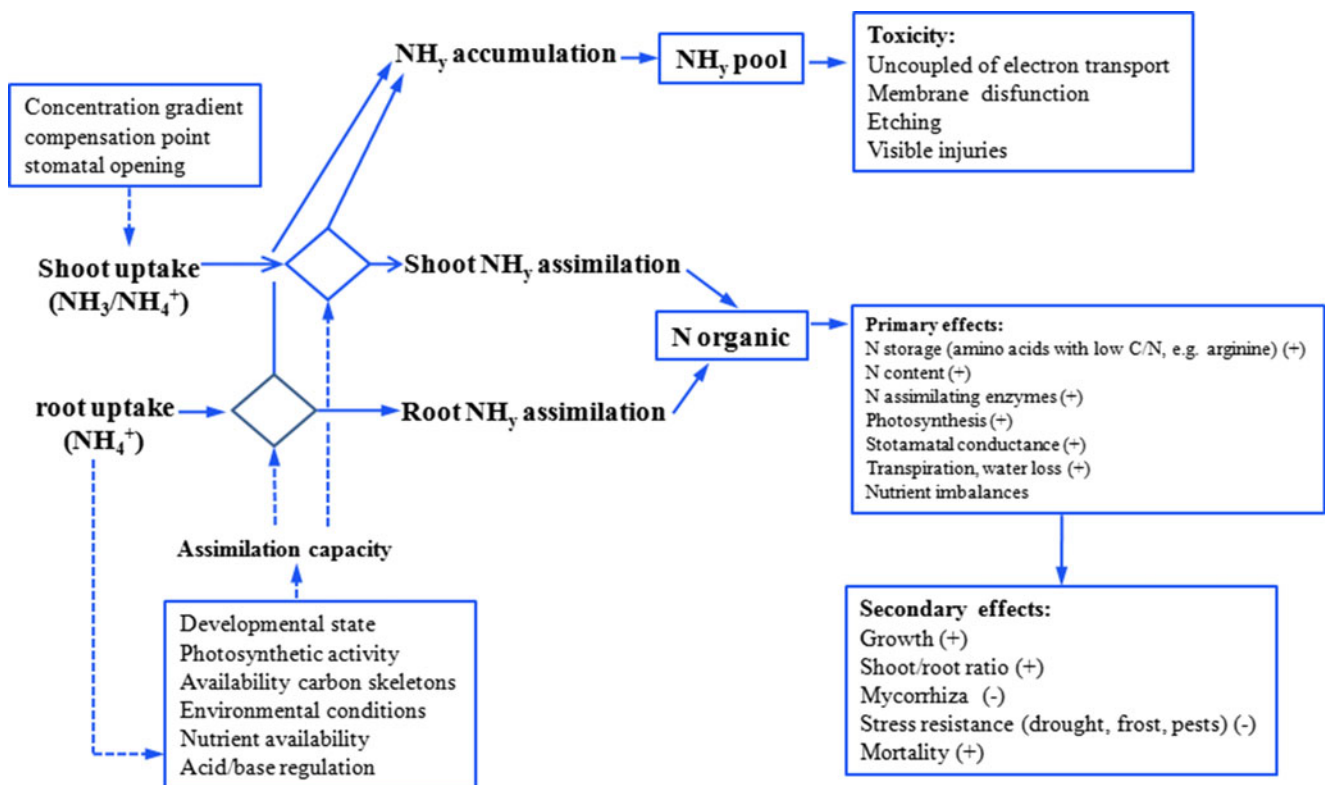
Species	Deposition type	North Atlantic	South Atlantic	North Pacific	South Pacific	North Indian	South Indian	Total
Nitrogen deposition, 10^9 gN year ⁻¹								
NH ₄ ⁺	Wet	2,740	610	4,050	1,900	1,170	970	11,400
NH ₄ ⁺	Dry	530	160	630	290	170	170	1,950
NH ₃	Wet	820	180	1,220	570	350	290	3,400
Subtotal		4,090	950	5,900	2,760	1,690	1,430	16,800
Nitrogen flux, mg N m ⁻² year ⁻¹								
NH ₄ ⁺	Wet	49	14	50	20	99	16	33
NH ₄ ⁺	Dry	9	4	8	3	15	3	6
NH ₃	wet	15	4	15	6	30	5	10
Subtotal		73	22	73	29	144	24	49

were 11, 72 and 17%, respectively, into the subarctic Western North Pacific Ocean during summer periods. This recent study has drawn attention to the consideration of sea fog for the study on deposition of N species to the oceanic surfaces.

Effects of NH₃ deposition on vegetation

Both anthropogenic NH₃ and NH₄⁺ are considered together as NH_y significantly influences N cycling in ecosystems (Fenn et al. 1998). Fangmeier et al. (1994) provided a comprehensive review on the effects of NH_y on vegetation. Later, Krupa (2003) also reviewed the same topic and mentioned the effects

of NH_y deposition on vegetation. The current knowledge of the effects of NH_y on plants is based on studies using a number of different approaches. These include experimental designs with artificial exposures to NH₃ or NH₄⁺, in controlled environment growth chambers, greenhouses, closed or open-top field chambers and chamberless field plots where the physical and the chemical (pollution) climate are not controlled. According to Fangmeier et al. (1994), and later mentioned by Krupa (2003), the effects of NH_y on plants depend on several processes illustrated in Fig. 9, which are: (1) uptake, (2) detoxification/assimilation, (3) development of injury when the amount of uptake exceeds detoxification, (4)


Fig. 9 Pathways and factors governing the effects of NH_y on plants. Adapted from Fangmeier et al. 1994, as modified

metabolic changes related to detoxification/assimilation and (5) growth of secondary effects following NH_3 uptake and successful detoxification.

In general, the assimilation capacity of the plant species normally determines the degree of injury. If the assimilation capacity is not sufficiently high to detoxify NH_3 , acute (visible) injuries may occur (e.g. Figs. 10 and 11). In the field, such observations were made mostly on trees on a local scale in the vicinity of NH_3 sources such as livestock farms, manure storages or fertilizer fabrication (Van der Eerden 1982). Conifers near livestock farms usually respond to NH_3 by needle necrosis, which usually starts at the tips of the oldest needles, subsequently progresses to needle loss and finally ends with the death of the tree. In the reviews of Fangmeier et al. (1994) and Krupa (2003), four types of visible NH_3 injuries on *Pinus sylvestris* are mentioned: (1) red or brown needle discoloration due to insufficient NH_3 detoxification, (2) yellowing of needles, occurring more frequently in older needles due to K^+ and/or Mg^{2+} deficiency, (3) yellowing of the youngest needles, most pronounced at the needle base due to extremely high arginine content and (4) occurrence of fungal or insect diseases due to nutrient imbalance of the plant.

Van der Eerden (1982) observed black spots on cauliflower (*Brassica oleracea*) and sharply bordered necrotic tips of older needles of *Taxus baccata* to be specific for NH_3 . However, in most cases, leaf injury from acute NH_3 concentrations may not be easily distinguished from symptoms caused by



Fig. 10 Row of table beet (*Beta vulgaris*) exposed to acute (relatively high) NH_3 concentrations due to an industrial malfunction. **b** Close-up of a table beet leaf showing acute response to NH_3 . Note the death of the leaf tissue (brown areas) between the veins. These symptoms are very similar to those induced by acute exposure to SO_2 . Adapted from Krupa (2003)

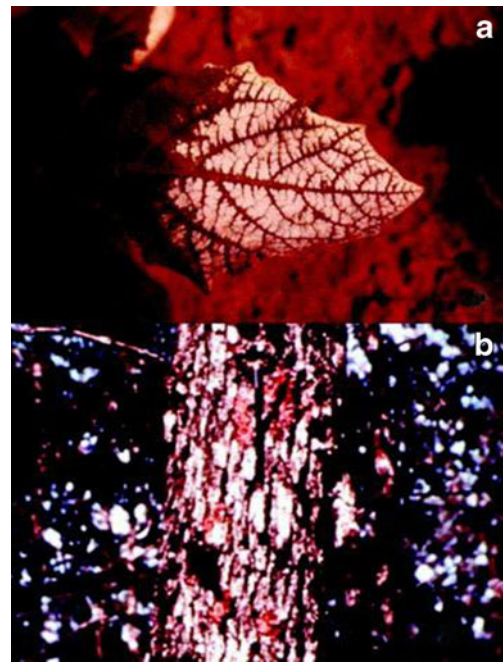


Fig. 11 Cherry tomato (*Lycopersicon esculentum* var. *cerasiforme*) showing acute response (white bleached areas between the veins) to NH_3 . **b** Epiphytic lichens on the trunk of an oak tree exhibiting purple coloration due to acute exposure to NH_3 . This response can be used as a biological indicator of NH_3 pollution. Adapted from Krupa (2003)

other stresses (Van der Eerden 1982). For more information on experiments yielding visible injuries, the reader can refer to Table 7 in Fangmeier et al. (1994). Fangmeier et al. (1994) can be referred to for the detailed description of these processes.

Effects of NH_3 deposition on forests and potential consequences for C sequestration

When N is applied directly to the canopy foliage, it becomes immediately available to promote photosynthesis and thereby leads to an increase in gross primary production (Spangenberg and Kölling 2004; Wortman et al. 2012). Dezi et al. (2010) found a positive relationship between net ecosystem production and N deposition that was mediated by the canopy N uptake. However, in the developed areas of Europe and North America, high N deposition has affected the health of forest ecosystems by causing several effects, including soil acidification, nutrient imbalance, decrease in productivity, forest decline and threats to the forest biodiversity (e.g. Chiwa et al. 2004; Gaige et al. 2007; Sievering et al. 2007; Xiankai et al. 2008; Wortman et al. 2012).

Eugster et al. (1998) reported that forests receiving high atmospheric N deposition may experience negative impacts on photosynthesis. The reason for this observation could be that the existing N loads exceed the nutrient critical loads by several kilograms N per hectare per year in all N-sensitive ecosystems. One example of areas showing such trends is some Swiss locations that are especially downwind of

populated and industrialized areas, or areas with high cattle density (Eugster et al. 1998). Chiwa et al. (2004) observed that almost all of the NO_3^- and NH_4^+ applied to canopy mist were absorbed by the canopy in low N treatments, and 30–35 % absorption in high N treatments. Spangenberg and Kölling (2004) reported that elevated N depositions will decrease biodiversity and change plant community structures, and thus affect ecosystem properties and processes (Spangenberg and Kölling 2004). Gaige et al. (2007) and Sievering et al. (2007) have shown that canopy N uptake can account for up to 80 % of N deposition and as much as 1/3 of the total N required during a growing season. N amendments that are directly applied to the soil are at increased risk of leaching out of the soil or becoming a nutrient source for soil microbes.

Xiankai et al. (2008) reviewed the science of the impacts of N deposition on forest biodiversity by emphasizing aspects of: (1) plant diversity, including arborous plants, understory plants and cryptogam plants, (2) soil microorganism diversity, (3) animal diversity, including underground soil fauna and aboveground herbivores. From Xiankai et al. (2008), it can be confirmed that N deposition could alter species diversity, and excessive N could reduce species diversity, such as richness and abundance, and even lose special species.

Spangenberg et al. (2004) studied the effects of high NH_3 emissions and N deposition on tree growth. They analysed the wood cores of 125 Norway spruces along a transect (800 m) from the forest edge to the forest interior, and the forest edge was exposed to a strong NH_3 emission source (a poultry farm, less than 50 m away). The atmospheric N bulk deposition, NH_3 concentration, soil solution concentration, soil nutrient content, foliar N concentration and C/N ratio of the humus layer were measured at five plots along the transect. Overall, Spangenberg et al. (2004) observed that the growth of N-influenced spruce trees increased. However, trees with excessive long-term N load appeared to lose increment after a long-term N impact.

Recently, Zhang et al. (2011) investigated the impact of enriched atmospheric NH_3 in combination with low and high N mediums on growth, total C and N accumulation and photosynthetic characteristics of two maize cultivars, i.e. SD19 (cult. 1) and NE5 (cult. 2) with low N and N high use efficiency, respectively. Plants were exposed to 10 and 1000 nl/L NH_3 fumigation for 30 days in open-top chambers. Under exposure to the low N medium, an increase of the atmospheric NH_3 concentration to 1,000 nl/L from the ambient level significantly ($P < 0.05$) increased dry matter (DM; by 18 % in cult. 1 and 14 % in cult. 2, respectively), total C and total N accumulation, net photosynthetic rate (P_n), stomatal conductance (G_s) and apparent quantum yield (AQY), but decreased intercellular CO_2 concentration (C_i) in both cultivars. In contrast, in the high N solution, enriched atmospheric NH_3 led to a decrease in DM, total C and total N accumulation, P_n , G_s and AQY, but an increase in C_i of cult. 2 only.

Dark respiration rate remained unaffected by the enrichment of NH_3 in each treatment. Therefore, appropriately enriched atmospheric NH_3 can improve the plant growth of maize by enhancing total C and total N, and photosynthesis in the low N medium. However, enriched NH_3 can reduce plant growth of maize by decreasing total C and total N, and photosynthesis in the high N medium. Table 16 presents the differential effects of enriched atmospheric NH_3 on photosynthesis parameters.

Catovsky et al. (2002) examined how seedlings in mixed conifer–broad-leaved forests in eastern North America differed in their growth and mortality responses to N availability. We reviewed the study by Catovsky et al. (2002) for assessment of the potential effects of N availability on forest dynamics mediated through seedling regeneration. The earlier successional broad-leaved species (yellow birch and red maple) consistently showed the greatest increases in biomass in response to N addition, while the most late successional of the broad-leaved species (sugar maple) and all the coniferous species did not grow significantly larger with increased N. N-induced changes at the community level arise from the combined effects of N on two distinct components of seedling regeneration: (1) growth in high light and (2) mortality in low light. Finally, Catovsky et al. (2002) revealed that N effects on both seedling growth in high light and seedling mortality in low light could change the overall forest structure and dynamics.

Nakaji et al. (2001) studied the effects of high N load on the growth, photosynthesis and nutrient status of *Cryptomeria japonica* and *Pinus densiflora* seedlings. In their experiments, 1-year-old seedlings were grown in brown forest soil treated with N as NH_4NO_3 at 0, 25, 50, 100 and 300 mg l^{-1} fresh soil volume, equivalent to 0, 28, 57, 113 and 340 kg N ha^{-1} . The net photosynthetic rate and the whole-plant dry mass of *C. japonica* seedlings were increased by the N treatment, whilst those of *P. densiflora* seedlings were significantly reduced by the highest N treatment. The reduction in the net photosynthesis of *P. densiflora* seedlings was mainly due to a depression of carboxylation efficiency accompanied by a decrease in concentration and activity of Rubisco in the needles. In *P. densiflora* seedlings, the needle concentrations of P and Mg were decreased and the concentrations of N and Mn were increased by the highest N treatment. The reductions in needle protein concentration and Rubisco activity were negatively correlated with the ratios of N/P and Mn/Mg in the needles. These results suggest that nutrient imbalances of these elements may be induced in *P. densiflora* seedlings grown under high N deposition. The study of Nakaji et al. (2001) confirmed that *P. densiflora* is more sensitive to high N deposition than *C. japonica*, and that the relatively high atmospheric N deposition to Japanese forest ecosystems may adversely affect the health of N-sensitive tree species such as *P. densiflora*.

As global concern over climate change continues to increase, there is an ongoing debate concerning how the

Table 16 Differential effects of enriched atmospheric NH_3 on photosynthesis parameters of SD19 (cult. 1) and NE5 (cult. 2) in the low and high N medium (Source: Zhang et al. 2011)

Treatment		P_n ($\mu\text{mol CO}_2/\text{m}^2/\text{s}$)	C_i ($\mu\text{mol}/\text{mol}$)	G_s ($\text{mol}/\text{m}^2/\text{s}$)	AQY ($\text{mol CO}_2/\text{mol}$)	R_d ($\mu\text{mol CO}_2/\text{m}^2/\text{s}$)
Low N (1.67 mmol/L) combined with different NH_3 concentration						
Cult.1	Control	16.18 \pm 0.89b	269.2 \pm 10.6 a	0.139 \pm 0.016 b	0.078 \pm 0.003 b	1.273 \pm 0.180 a
	EAN	20.63 \pm 1.55a	195.2 \pm 10.3 b	0.193 \pm 0.018 a	0.095 \pm 0.004 a	1.290 \pm 0.220 a
Cult.2	Control	25.02 \pm 2.52b	204.2 \pm 8.3a	0.175 \pm 0.014b	0.093 \pm 0.004b	1.638 \pm 0.120a
	EAN	28.70 \pm 2.33a	163.4 \pm 7.9b	0.225 \pm 0.016a	0.108 \pm 0.005a	1.636 \pm 0.180a
High N (5.00 mmol/L) combined with different NH_3 concentration						
Cult.1	Control	24.02 \pm 1.12a	179.3 \pm 8.8a	0.205 \pm 0.014a	0.099 \pm 0.002a	1.312 \pm 0.159a
	EAN	22.96 \pm 1.03a	188.3 \pm 8.7a	0.183 \pm 0.014a	0.091 \pm 0.003a	1.327 \pm 0.156a
Cult.2	Control	38.24 \pm 2.22 ^a	130.0 \pm 7.5 ^a	0.255 \pm 0.018 ^a	0.123 \pm 0.002 ^a	1.750 \pm 0.220 ^a
	EAN	33.17 \pm 2.03b	153.0 \pm 8.3b	0.212 \pm 0.016b	0.105 \pm 0.005b	1.744 \pm 0.250a

Data represent mean of ten replicates ($n=10$). Mean values followed by different lowercase letters within each column indicate significant differences at $P<0.05$ between enriched atmospheric NH_3 fumigation and control treatment with the same cultivar and N supply

C_i intercellular CO_2 concentration, *control* ambient NH_3 concentration (10 nl/L), G_s stomatal conductance, AQY apparent quantum yield, EAN enriched atmospheric NH_3 concentration (1,000 nl/L), P_n net photosynthetic rate, R_d dark respiration rate

interactions of biodiversity and N deposition influence ecosystem functioning and provision of ecosystem services, i.e. productivity and carbon sequestration. Changes in biodiversity will influence carbon sequestration by altering biomass and productivity. An increase in photosynthetic efficiency represents an increase in primary production in plants and, therefore, potentially results in an increase in carbon sequestration as plants take up CO_2 during photosynthesis (Wright et al. 2004; Wortman et al. 2012). However, it has been shown that the leaf life span is inversely related to productivity and leaf N content, which raises the question of whether an increase in photosynthetic efficiency simply speeds up the life cycle of leaves with little or no net effect for carbon sequestration (Wright et al. 2004). Wright et al. (2004) also argued that the indirect effect of a shorter leaf lifespan, which is associated with increased assimilation rates (and hence photosynthetic efficiency) and higher leaf N content, will increase leaf vulnerability to herbivory and physical hazards. This could result in a negative effect on carbon sequestration in the long term. However, in a recent study, Wortman et al. (2012) did not agree with the above facts. Therefore, the potential for increased C storage resulting from N deposition is widely debated.

A much-discussed study by Magnani et al. (2007) estimated that as much as 470 kg C per kg N could result from N deposition. Reay et al. (2008) defined the response of C sequestration to N input as 40–200 kg C per kg N, resulting in an additional 0.67 Pg C uptake by Northern Hemisphere forests each year due to total reactive N deposition. A further study by de Vries et al. (2009) concluded that carbon sequestration is in a range of 5–75 kg C per kg N for Northern Hemisphere forests, with a most probable range of 20–40 kg C per kg N. While the scale of additional carbon storage due to

N input may vary, N deposition plays an important role in understanding climate change influences (De Schrijver et al. 2008; Wortman et al. 2012). Overall, excessive N deposition can decrease biodiversity and influence ecosystem productivity, which may have positive or negative effects on carbon sequestration.

Concluding remarks

NH_3 is an important atmospheric constituent for a variety of reasons. At the global scale, of all the N species in the atmosphere and their deposition onto terrestrial vegetation and other receptors, NH_3 is considered to be the foremost. The major sources of atmospheric NH_3 are agricultural activities and animal feedlot operations, followed by biomass burning (including forest fires) and, to a lesser extent, fossil fuel combustion. NH_3 emission from road traffic has increased significantly in recent years, especially in urban areas, because of the use of catalytic converters in gasoline-driven automobiles. Besides providing insights into the emission of NH_3 from various sources, this review article also provides a clear understanding of the complex phenomena involved in the environmental cycling of NH_3 , and highlights several emerging issues that may enable further advances in our understanding of the role of NH_3 in (1) atmospheric chemistry, (2) the formation of secondary inorganic aerosols, (3) climate change and (4) ecological effects.

NH_3 from over-fertilization of plant life, industrial discharge, human and animal waste discharge, and traffic emissions can greatly add reactive N to the natural system, which may have an impact on air, water and soil quality. We have critically reviewed and integrated the information on NH_3

emissions into the atmosphere from sources such as volatilization of animal waste, usage of synthesis of fertilizers, biomass burning, soils under natural vegetation, agricultural crops, human excreta and waste, industrial processes and fossil fuel combustion in different regions throughout the globe. Overall, the agriculture sector contributes 80.6 % to the total global NH_3 emissions, followed by 11 % from biomass burning and 8.3 % from the energy sector, including industries and traffic. The regions with the highest emission rates are located in Europe, the Indian subcontinent and China, South America reflect the patterns of animal densities and the type and intensity of synthetic fertilizer uses. For the region comprising the USA, South America, Europe, Russia and Asia, agriculture contributes more than 70 % of the total global NH_3 emission. This reflects the patterns of animal densities (type and intensive production) and the use of synthetic fertilizer. The countries in these regions need to work together regionally or even globally to develop NH_3 emission abatement strategies.

Finally, it should be noted that the demand for energy generation and the need for food production, especially animal meat, to sustain growing populations could lead to unsustainable and irreversible changes to biogeochemical NH_3 cycles. However, gaps remain in the scientific understanding of NH_3 emissions and their subsequent fate. Nevertheless, it is imperative that we develop emission abatement policies based on the best available science to protect human health and lower environmental risks. Current scientific and technological knowledge must be translated into manuals and protocols for immediate implementation. Research ideas, specifically solution-oriented ones, i.e. Best Management Practices and engineered solutions, must be identified. Finally, it must be recognized that the complex issues of NH_3 management are inter-linked and often conflicting (e.g. control of NH_3 may control SO_4^{2-} and NO_3^- particles, but the absence of these particles may enhance global warming or acid rain), and that a holistic view must be taken of NH_3 management in the atmosphere, in order to optimize its effects.

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