



Distribution of ammonia in hydrosphere and atmosphere: A review

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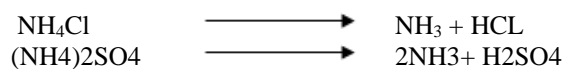
Abstract

Ammonia (NH₃) is an alkaline gas comes from both natural and anthropogenic sources, with agriculture being the primary source. Non-agriculture sources of ammonia include catalytic converters, organic material composting, and industry. Ammonia pollution is caused by excess levels of ammonia in hydrosphere and atmosphere and leads to eutrophication, acidification of soils and the synthesis of fine particulate matter in the atmosphere

Keywords: ammonia, EPA, ammonia pollution, alkaline gas, particulate matter

Introduction

Ammonia (NH₃) is an alkaline gas that is extremely reactive and soluble. It comes from both natural and anthropogenic sources, with agriculture being the primary source, such as manures, slurries and fertilizer application. Ammonium salts are rapidly decomposed in the presence of strong bases and heat, which lead to the formation of ammonia. Ammonium salts are thermally unstable and disintegrate rather readily when heated, for example:



The name of important Ammonium salts are: Ammonium chloride (NH₄Cl), ammonium sulphate (NH₄)₂SO₄, and ammonium nitrate NH₄NO₃. They are mostly utilized as nitrogen fertilizer (Malovanyy *et al.*, 2016) [5]. Ammonia is produced via the breakdown and volatilization of urea. Emissions and deposition differ over space, with “emission hotspots” associated with high-density intensive farming methods. Additional sources of ammonia emissions in agriculture include biomass burning and fertilizer production. Non-agriculture source of ammonia include catalytic converters in gasoline cars, landfills, sewage treatment plants, organic material composting, combustion, industry, and wild creatures and birds. (Sutton *et al.* 2000, Wilson *et al.* 2004) [4]. In Asia, the great majority of poultry, mainly chicken, ducks and geese are generally fed dispersively by farmer's families for egg laying. The emission factor was taken from Klaassen's paper (1991) [32], as 0.32 kg NH₃ head-1 yr-1. Human respiration and excretion are sources of NH₃ with an emission factor of 0.3 kg NH₃ person-1 yr-1 (Klaassen, 1991) [32]. In many places of the world, there is an ammonia oversupply. This contains both gaseous or molecular ammonia (NH₃) and compounds containing the ammonium ion (NH₄⁺), with the sum of both ammonia forms denoted as NH_x. Since the advent of the Haber- Bosch process (Haber, 1920), it has been possible to generate ammonia in huge quantities at a reasonable cost. The widespread use of ammonia and its derivatives as agricultural nitrogen fertilizers, in particular, has significantly increased ammonia emissions into the atmosphere, resulting in a variety of environmental hazards (Smil, 2001, Sutton and fowler, 2002, Erisman, 2004,

Erisman *et al.*, 2007) [4, 14]. They include eutrophication of semi-natural ecosystems, acidification of soils and the creation of fine particulate matter in the atmosphere. More than half of the world's ammonia is currently produced in four countries: China, USA, India and Russia. The largest emitters of ammonia in Asia are China and India. (Zhao *et al.*, 1994) [23]. Global human-induced emissions, which are dominated by nitrogen additions to croplands, increased by 30% over the past four decades to 7.3 (4.2–11.4) teragrams of nitrogen per year (Tian *et al.*, 2020) [19]. Demand for ammonia is projected to rise nearly 40% by 2050, driven by demand for fertilizers in Africa, Latin America, the Middle East and South-East Asia (www.weforum.org/reports/the-net-zero-industry-tracker/in-full/ammonia-industry accessed on 20 May 2023)

Impact of Ammonia in our surrounding

NH₃ gas neutralise sulfuric acid (H₂SO₄), nitric acid (HNO₃), and hydrochloric acid (HCl), producing ammonium sulphate (NH₄)₂SO₄, ammonium bisulfate (NH₄HSO₄), ammonium nitrate (NH₄NO₃), and ammonium chloride (NH₄Cl) aerosols (Baek and Aneja, 2005; Aneja *et al.* 2009) [31]. These processes are substantially controlled by the ambient air temperature, relative humidity, sun radiation, and precursor gas concentration (Baek *et al.*, 2004). NH₃ predominantly interacts with H₂SO₄ to generate sulphate aerosols at low concentrations.

The production of NH₄NO₃ is preferred over the neutralisation of H₂SO₄ by NH₃. Good correlation between NH₄⁺ and SO₄²⁻, NH₄⁺ and NO₃⁻, and NH₄⁺ and Cl⁻ concluded that most of the chemical components of PM_{2.5} could be (NH₄)₂SO₄, NH₄NO₃ and NH₄Cl. The produced ammonium salts are the major components of smog aerosols, affecting the opacity of the atmosphere and the earth's radiation budget.

Ammonia is a naturally occurring substance in the environment. Ammonia will destroy aquatic life even at extremely low quantities. As lightning strikes and rain falls on the earth, a small amount of ammonia is produced. Yet, the most majority of ammonia is created by bacteria in water and soil as a by product of the plant and animal waste decomposition. It can be found in relatively low harmless amounts in soil, air, and water and serve as a nitrogen source

Excess ammonia can produce eutrophication and acidification in semi-natural for environments, which can lead to changes in species composition and other negative

consequences (Bobbink *et al.*, 2010^[3]; Krupa, 2003^[28]; Pitcairn *et al.*, 1998; Sheppard *et al.*, 2008; Van den Berg *et al.*, 2008; Wiedermann *et al.*, 2009)

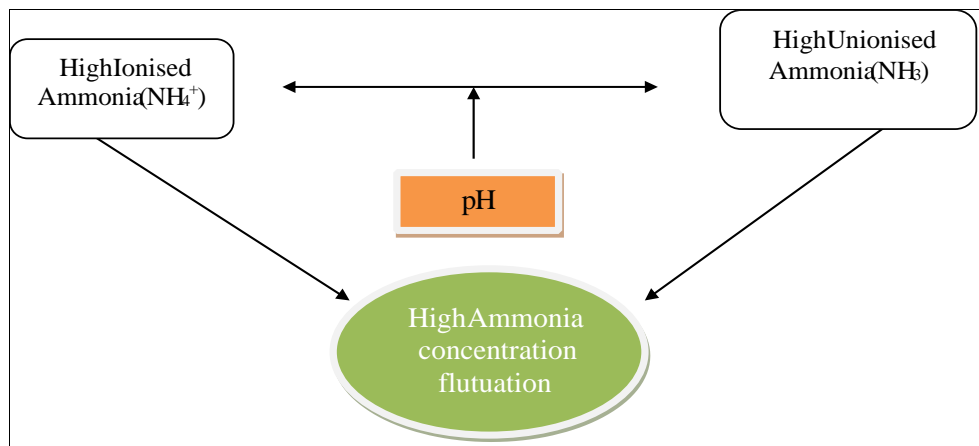


Fig 1: Impact of Ammonia fluctuation due to pH

Ammonia undergoes numerous complicated metabolic reactions in soils and water. These reactions are collectively referred to as the nitrogen cycle. Ammonia manufactured for use in commercial fertilizers as well as other industrial purposes. Gas exchange with the atmosphere, forest fires, organic waste decomposition, Human and animal waste (B. Yaron *et al.*, 1996)^[11].

Effect of Ammonia in Hydrosphere

Ammonia is a specific risk in the interaction of water with other chemical components. An increase in ammonia toxicity can result from a variety of environmental conditions, specifically pH and temperature. Ammonia levels in groundwater do not exceed 0.2 mg per litre under natural conditions. Ammonia levels were found to be higher in humic layers (3 mg/l). Ammonia toxicity has a significant impact on surface water quality. NH_3 and NH_4^+ are nutrients and excessive deposition of these components to oligotrophic ecosystems might lead to shift of plant species to more nitrophilic ones (Bobbink *et al.* 1992)^[27]. Adverse effects on vegetation occur when the rate of foliar uptake of NH_3 is greater than the rate and capacity for *in vivo* detoxification by the plants. Most to least sensitive plant species to NH_3 are native vegetation > forests > agricultural crops. While NH_3 uptake in higher plants occurs through the shoots, NH_4^+ uptake occurs through the shoots, roots and through both pathways (Krupa 2003)^[28]. Increased atmospheric N deposition is known to be able to reduce biodiversity in natural and semi-natural ecosystems. N deposition is predicted to be the third greatest driver of biodiversity loss on the global scale, after land use and climate change (Xiankai *et al.*, 2008)^[22]. Substance concentration that exceeds environmental quality guidelines can harm and kill aquatic life. In the EIFAC report a concentration of 25 $\mu\text{gN/l}$ of un-ionized ammonia is considered the maximum that fish can tolerate over a long period. In order to avoid any physiological damage, however, this level ought to be lowered to 20 $\mu\text{gN/l}$ (Arillo *et al.*, 1981)^[24]. Wet deposition of NH_4^+ to large areas, such as countries, can be approximated very simply from measurements at a small number of sites. Because of the widely scattered local NH_3 sources, dry deposition of NH_3 has a significant geographical variability. This discrepancy is due to the low source height of NH_3 sources, the

potentially high dry removal rates of NH_3 , the limited dry-deposition velocity of aerosol NH_4^+ , and the comparatively fast conversion rate of NH_3 to particulate NH_4^+ (Asman *et al.*, 1998)^[29]. When we compare NH_x deposition from dry, wet (precipitation), and cloud interception, we can conclude that cloud water interception provided more nitrogen (70%) than wet or dry deposition (Aneja *et al.*, 1998)^[20]. The recognition of this concern has resulted in the establishment of legislation in the European Union aimed at protecting the environment, specifically water from chemical pollution. (Bennion & Battarbee, 2007)^[6].

Different sources of ammonia includes

Direct Source includes nitrogenous wastes excretion of animals where as indirect sources include runoff from agricultural fields, nitrogen fixation, and air deposition. When ammonia levels in water are high enough, aquatic species struggle to expel the toxicant, resulting in toxic accumulation in internal tissues and blood, and potentially death. Ammonia toxicity in aquatic animals can be influenced by environmental conditions such as temperature and pH. (P. Verma and J.K. Ratan 2020)^[7]

EPA

EPA is a United State Agency for environmental protection. In 1976, the EPA released the first ammonia guidelines for aquatic life protection. The criteria were then modified 1985 and 1999 to reflect advanced knowledge. The suggested aquatic life criteria for ammonia in 1999 were based on the most sensitive endpoints available at the time. The acute criterion was on the bases of data of toxicity of salmonid fish and the chronic criteria was on the bases of data of bluegill sun fish toxicity. In 2003 EPA discovered that fresh water mussels were sensitive to ammonia and it becomes bases of new toxicity research. Afterwards EPA started to updating the 1999 criteria with this new piece of information. In April 2013, the EPA published updated ammonia guidelines that are nationally relevant, taking into consideration the most recent toxicity data for fresh water species such as unionid mussels and gill-breathing snails. The 2013 criteria contain Scientific feedback on the draught ammonia standards from 2009 and supersede the EPA's previously suggested 1999 criteria. J. Beaman *et al.*, 2013)^[9].

Effect of Ammonia on Atmosphere

Nitrogen compound emissions have a significant impact on air quality due to the human need for energy and food, leading to the emission of nitrogen oxides and agricultural emissions (Aneja *et al.*, 2001) ^[21]. Atmospheric Nitrogen species exist in the form of gases, vapours (hydrated gas molecules), and particles both solid and liquid. These are nitrogen oxides (NO_x, which are composed of nitric oxide, NO, and nitrogen dioxide, NO₂), ammonia (NH₃) and nitrous oxide (N₂O), peroxy-acyl nitrates (the most studied of which is peroxy-acetyl nitrate, or PAN), nitric acid (HNO₃), ammonium (NH₄⁺), and other inorganic and organic nitrates (NO₃s). (J. Colls & A. Tiwary, 2009) ^[8]. The volatilization of decomposing livestock waste is widely recognized as the largest of NH₃ emissions to the atmosphere, with losses from agriculture plant canopies, particularly following the use of N fertilizers, being the second significant source. (Behera *et al.*, 2013, R.H. Fox *et al.*, 1986) ^[10, 12]. There are many sources of ammonia emission, few are described below:

Agricultural emission of ammonia poses three important environmental challenges

- Stench- Ammonia releases strong and unpleasant smell led to disturbance to residents living nearby large scale animal rearing facilities.
- Habitability- High concentration of ammonia is detrimental to mammals (including humans). As a result, in breeding facilities controlling environmental ammonia levels is the top most priority.
- Quality of air –the deposition of fine particles through ammonia.

During the discussion, Henry Tyrrell (USDA) provided an overview of the major agricultural sources of ammonia, which are mostly caused by intensive animal husbandry operations such as dairy operations and beef cattle, hog, and poultry rearing facilities. Just around 10% of the nitrogen in beef cow feed is converted to meat; the remainder is eliminated in faeces (30%) N and urine (60%) N. Dairy cattle are slightly more efficient, although approximately 35% of the total N is still lost through urine. Although 90% of the nitrogen in lagoon- stored manure volatilizes, the N in urine is highly volatile, and much of it winds up in the atmosphere. When agricultural statistics are considered, the volumes of ammonia emitted become really frightening. James Ferguson (University of Pennsylvania) discussed possible changes to livestock production practices that could reduce NH₃ emissions from dairy businesses by reducing protein content in feed other possible solutions were by inhibiting urease and volatilization of NH₃ by acidifying it for the reduction of conversion of NH₃ from urea.

According to EPA data, the majority of ammonia emissions from swine operations come from barns (50%) with smaller quantities coming from lagoons (37%) and spraying animal faces (13%). Pierce and Bender recently provided estimates of ammonia emissions from cattle operations in the United States. Their estimations were based on USDA agricultural statistics and Battey *et al.*, emission coefficients.

On-Road Automobile Ammonia Emissions

The increasing use of three-way catalysts on cars has also led to increasing emissions of ammonia (NH₃) from vehicle exhausts, caused by the reducing conditions inside the

catalytic converter, particularly when the engine is cold. The different deposition rates of different gases mean that similar contributions to N deposition are likely for NH₃ and NO₂, and there will be additional N deposition from HONO that could be as large as for the other two gases (Cape, J. N., *et al.* 2004). In a study NH₃ is deposited more rapidly than other trace gases, such as ozone, sulfur dioxide or nitrogen dioxide (Duyzer 1994) ^[25]. Ninety-five percent of automobile in the United States are fitted with three-way catalysts to limit nitrogen oxide pollution, these catalysts reduce hydrocarbon, carbon monoxide (CO), and nitrogen oxides (NO_x) emission by constantly cycling the air- to- fuel ratio in the engine between oxidation and reduction conditions. The catalyst may also create ammonia in reducing circumstances. The EPA has initiated a restricted study of the dynamics of ammonia generation by instrumenting and driving an automobile on the road to identify ammonia as a function of operating modes. The EPA is particularly interested in ammonia generation during computer-controlled fuel enrichment and is still looking into real-time sensors. They have just done a little static testing and a few on road measurements so far. Table 2 and a recent research by Becker *et al.*

(1999) ^[13] provide more information on ammonia emissions from particular automobiles.

Table 1: Vehicles fitted with catalysts emit ammonia.

Data Source	Ammonia Emissions (gm./mi)
EPA Trends Report	0.1
1981 Buick	0-0.2
1983 OMS Average	0-0.5
1984 Volkswagen	0-0.14
1993 Chevrole Lumina	
Parking Lot	0.03-0.14
Route I-40	0.24

Ammonia Pollution

Ammonia pollution is caused by a by product of agriculture and industry which are ammonia (NH₃), a nitrogen and hydrogen molecule. Ammonia emissions from crops contribute significantly to atmospheric NH₃ pollution (15–20% of the total NH₃ emission (Asman *et al.*, 1998) ^[29]. There are many sources of ammonia such as ammonia gas emitting by rotting slurry from agriculture and fertilizer plants, while nature sources include burning coal mines of Jharia, and seabird guano, the Caustic Lake Natron. Ammonia gas in reaction with many other gases forms ammonium salts which are harmful for breathing. High ammonia concentrations can harm the human eyes, throat, respiratory tract, and other organs, causing bronchitis, pneumonia, pulmonary edema, even coma and shock, and offering non-carcinogenic dangers to the human body (de la Hoz *et al.*, 1996) ^[36]. Ammonia gas when falls on ground it degrades the quality of soil, it totally change its chemical properties. For instance, degrading the circumstances needed by peat land sphagnum moss and heathers. Many activities are responsible for ammonia pollution whether they are natural or anthropogenically (cause by human) generated, they are given below:

Ammonia generation from two sources through agriculture about 70% of the global emission is through agriculture in which 2/3rd is from livestock waste and 1/3rd is from fertilizers due to anthropogenic activity, one is through Artificial Fertilizer. Through the use of fertilizer as slurry is

manufactured in such a way that it is highly nutritious. They may consist of nitrogen bases compounds such as ammonium (NH_4^+) which is homology to organic manure and released in biosphere in the form of ammonia through volatilization or run off into water and get enters into hydrosphere. (V. Smil.;2001) ^[14] and the second way is through Livestock waste. Because of the use of nutrient dense feeds by farmer, live stock waste is rich in high amount of nitrogen. In animals manure about 80% of the nitrogen can be found in th form of ammonium (NH_4^+) which further converts through volatilization into ammonia (NH_3):



Our ocean is not unspoiled; all waste in the ocean when decompose liberate about 15% of the global emission of ammonia into the seawater. Surface levels can emit this by volatilization into atmosphere, which rises with strong wing, high temperature, rough waves and high acidity. (F. Paulot, *et al.*, 2015) ^[15].

Another natural cause for the emission of ammonia gas is wildfires when biomass combustion results into release of a lot of chemicals in which ammonia is also included. The most ammonia is released when tropical forest biomass is burned, such as in the Amazon Basin. (Sever, 2020) ^[16].

In engines catalytic converters reduces toxic chemical emissions, but as a consequence, ammonia is generated. This caused by the operation of the three way catalytic converter. Modifications such as lower exhaust temperatures and higher air- to- fuel ratios in newer automobiles have reduced ammonia emissions. (Y. Xin, 2023) ^[17].

Other sources of ammonia emission are caused by the volatilization of human waste, wild animal waste, and decomposition (J.F. Lamarque *et al.*, 2011) ^[18]. The correlation between air temperature and ammonia concentration. The NH_3 concentration was measured over a 1-year period at a heathland site in the center of the Netherlands [Duyzer *et al.*, 1989]; an analysis of these observations revealed that 40% of the variance in the ammonia concentration could be explained on the basis of the correlation with air temperature. This relationship can be understood on the basis of increased emission from animal manure at higher temperatures. Moreover, manure spreading is restricted in periods with low temperatures. There was also a correlation with wind speed, which showed that at this rather remote site the ammonia concentration was low at high wind speeds and high at low wind speeds. This analysis shows that it is important to use a resistance layer model with parameterization to estimate annual fluxes rather than average values for the deposition velocity and the concentration in air [see Hicks *et al.*, 1985]. A strong influence of surface wetness and the temperature was found. The temperature effect is probably related to the reduced solubility of ammonia at higher temperatures

Solutions

Ammonia emissions are also a significant component of PM_{2.5} reduction, and the social benefits much outweigh the costs involved. Ammonia emission reductions would thus be a cost-effective complement to nitrogen oxide and sulphur dioxide limits. Nitrogen emissions to the atmosphere cost an estimated 23.3 million years of life in 2013, resulting in a 420 billion US dollar yearly welfare loss

due to premature mortality. The marginal abatement cost of ammonia emissions is just 10% of the global abatement cost of nitrogen oxides, emphasising the importance of ammonia reduction (Gu *et al.*, 2021) ^[37]. There are several ways for reducing ammonia emission from atmosphere as well as lowering concentrations of ammonia in water. In studies it was showed that all tannin-based powders reduced the pH and ammonia released. When flavonoid-based powders were used, reductions in ammonia solution and cattle slurry were more than 75% and 95%, respectively (Sepperer, *et al.* 2020) ^[33]. The most promising practises were then tested in the field with a wind tunnel and an FTIR gas analyzer. The results revealed that with any type of mineral or organic fertiliser, closed-slot injection reduced NH_3 emissions. In comparison to surface broadcast, injected treatment of ammonium nitrate or organic fertilisers reduced NH_3 loss in maize by 75% and 96%, respectively, and in winter wheat by 87% and 98%. Injection was chosen as the most promising technology to support because it was already available to farmers (Mencaroni, *et al.* 2021) ^[34]. An ammonia level in the air is low as 5ppm can be recognized by odour. An average person can detects ammonia by odour at around 17ppm. Depending on its concentration, ammonia (NH_3) in drinking water can be beneficial or hazardous. One of the most successful strategies for removing ammonia from contaminated water is the use of biosorbents. Biosorption is a simple, cost-effective, and ecologically sound way of removing ammonia from water. Most people can taste ammonia in water at levels of about 35ppm. Measuring the capacity of biosorbents to remove ammonia from water has global importance due to their more availability and lower cost of the biosorbent materials. In a study by Dey *et al* 2022 percentage removal of ammonia from water by three different biosorbents was in the following order: Orange peels> Coconut wire waste> Tea waste. The biosorption is an effectual and eco-friendly process for the removal of ammonia ions from the wastewaters due to its easy design and fast operation (Dey *et al.* 2022) ^[35]

Conclusion

Ammonia (NH_3) is an alkaline gas that is extremely reactive and soluble. It comes from both natural and anthropogenic sources, with agriculture being the primary source. Ammonia pollution is caused by ammonia (NH_3), nitrogen and hydrogen molecule from agriculture and fertilizer plants, burning coal mines and many other sources. Ammonia release into the biosphere through volatilization or run off into water. In most countries around the world, there are currently no regulations or incentive programmes in place to reduce NH_3 emissions, in contrast to regulations for other primary gaseous pollutants such as SO_2 , NO_x , and volatile organic compounds (VOCs), despite the fact that all of these pollutants contribute to PM mass loading, visibility degradation, acidification and eutrophication. The nitrogen emissions from beef and dairy cattle are a major environmental issue, with only 30% of the energy converted to meat and 60% to urine. The EPA is interested in ammonia generation during computer-controlled fuel enrichment and is still looking into real-time sensors. The quantification of NH_3 emissions from agricultural point and nonpoint sources, as well as their 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-toparticle conversion to fine particles are all ongoing research efforts. A number of research and review papers have addressed critical topics linked to NH₃ emissions into the atmosphere at global, regional, and local scales, including emission sources, fate through atmospheric chemistry, and deposition on terrestrial bodies, throughout the previous two decades. There is need to address ammonia reduction processes by chemicals and natural ways. Monitoring and modelling of ammonia should be combined with other researches.

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