



Research Article

AMMONIA VOLATILIZATION LOSS FROM APPLIED NITROGEN FERTILIZERS IN VARIOUS SOIL

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Abstract: Despite nitrogen fertilizers has long been a critical component in agriculture it is associated with low nitrogen use efficiency. The low nitrogen use efficiency is attributed to various nitrogen losses such as ammonia volatilization, denitrification, leaching, and runoff. Among the various ways of nitrogen losses, ammonia Volatilization is a major nitrogen loss from agricultural soil. Large amount of volatilizing NH_3 contributes to high N load in the environment. N loss due to ammonia volatilization depends upon several factors such as environmental condition, type of N fertilizers used, soil chemical properties, microbiological activity and soil types. The information on ammonia volatilization with respect to soil types are very rare. This review, therefore presents the volatilization losses from various soil including the effect of soil properties and climate and the methods to reduce it. This may be more helpful on fertilizer management and to reduce nitrate pollution in soil.

Keywords: Nitrogen, Volatilization, Ammonia, Urea

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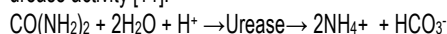
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Introduction

Increasing agricultural productivity is an urgent need for feeding the growing population. For optimal development and production, plants require 21 basic elements. Nitrogen (N) is the single most significant nutrient that influences crop development and output. As a result, nitrogen fertilisers have long been an important component in agriculture, accounting for more than half of the world's food output [1,2]. The low N-use efficiency is linked to a variety of N losses, including ammonia volatilization, denitrification, leaching, and runoff, among others [3]. However, the degree of N loss caused by various methods varies depending on environmental circumstances and management approaches used [4]. Among the different nitrogen loss mechanisms, ammonia volatilization is a significant nitrogen loss from agricultural soil. Ammonia volatilisation is a chemical process that happens at the soil surface when ammonium from ammonium-containing fertilisers is transformed to ammonia gas, with high pH accelerating the rate of volatilization. The N losses ranged from 10 to 60% of the N applied [5]. Through atmospheric transit and deposition mechanisms, a large amount of volatilizing NH_3 leads to a high N load in the environment. Continuous and excessive N loads eutrophicate the environment, causing ecosystems to suffer from a variety of consequences, including acidification [6], eutrophication of surface water [7], and changes in biodiversity [8]. Among nitrogeous fertilisers, urea is the most commonly and widely used in India, with around 31 million metric tonnes utilised annually, accounting for 83 percent of total N fertiliser usage in the nation. The urea-N efficiency is quite poor, often about 30–40%, and in certain circumstances much lower [9]. Though the N loss due to ammonia volatilization depends upon environmental condition and type of N fertilizers used, the information on ammonia volatilization with respect to soil types are very rare. Therefore, literature has been searched on nitrogen losses with due importance to ammonia volatilization and one assembled, discussed in soil wise and presented. This may be more helpful on fertilizer management and to reduce nitrate pollution in soil.

General reaction of urea N fertilizer in soil

The conversion of urea [$\text{CO}(\text{NH}_2)_2$] to plant available ammonium (NH_4^+) may occur only when urea dissolves in soil solution and the soil enzyme urease acts to liberate plant-available NH_4^+ . As a by product, bicarbonate ions (HCO_3^-) can combine with hydrogen ions (H^+) to generate carbon dioxide (CO_2), which then diffuses into the environment. The consumption of H^+ elevates soil pH by releasing positive-charged H^+ from the soil and allowing one negative charge to emerge for every H^+ released. This, together with other negative charges in the soil, can then absorb the majority of the NH_4^+ released. A part of the NH_4^+ that stays in the soil solution may be transformed to ammonia (NH_3), and this percentage increases as the pH rises. The urea component may migrate from the application site to the urease enzyme, which is mostly linked with soil colloids [10]. This urea transport is performed by molecular diffusion or water mass flow. Once urea comes into contact with soil urease, the rate of urea hydrolysis is determined by (i) the amount of active urease molecules and (ii) the parameters influencing urease activity [11].



N volatilization in various soil

Grassland soil

Indian grasslands/grazing fields are considered vulnerable ecosystems and are classified as class IV and V in terms of land capabilities. However, these grassland resources are important to the country's agricultural economy since they are used as pasture/forage supplies for cattle. They are also related with the livelihoods of thousands of people as grasses, which are used as fuel, shelter, and for a variety of traditional activities. However, estimates of grasslands and grazing resources in India range from 3.7 to 12 percent of total area [12] and get nitrate and/or ammonium ions from applied fertiliser. The two ions, however, differ in their response in soil and the process by which they are absorbed by plant roots. Nitrate is not adsorbed by colloidal material (clay and organic matter) in the soil,

therefore it is mobile in the soil solution and easily available to plant roots, but it is also subject to leaching and denitrification losses. Ammonium, on the other hand, is held via cation exchange sites on clay and organic materials. As a result, ammonium ions are less mobile than nitrate, less accessible to roots, and less prone to loss. Although ammonium is progressively transformed to nitrate by the nitrification process and moves mostly by mass flow with the passage of water and somewhat by diffusion, ammonium flows primarily by diffusion and just little by mass flow. [13]. Plants grown in solution culture use both ammonium and nitrate ions, however plants often take up nitrate more quickly than ammonium and show stronger growth responses to nitrate. Grasses, on the other hand, frequently assimilate more ammonium than nitrate when the two ions are provided in equal proportions. The volatilization loss of nitrogen in grassland soil varied from 4.2 to 36 % with mean of 19 % depends on the rate of fertilizer application and type of soil. However, the rate of volatilization increases with increasing doses of fertilizer application as proved by many scientists as in [Table-1].

Table-1 Ammonia volatilization losses from several grassland soil

SN	Rate of N applied (kg N ha ⁻¹)	Mean N volatilised (%)	Reference
1	180	22.8	[42]
2	15-200	17.6	[43]
3	50	36	[44]
4	30-150	26.7	[45]
5	25	7.5	[46]
6	23-536	11.6	[47]
7	70-437	17.7	[48]
8	90	17.8	[49]
9	70-280	28.1	[50]
10	80-120	19.3	[51]
11	150	4.2	[52]
Mean		19	

Flooded Soil

Plants receive N mostly as ammonium (NH₄⁺) in the wetland habitat because it requires less energy to digest into amino acids than nitrate [14]. As a result, the intensity of Ammonia volatilization losses in flooded soil is lower in acid soil and higher in alkaline soil [15]. However, the use of carbon dioxide by algae and other aquatic biota for photosynthetic activities raises floodwater pH, resulting in significant N losses due to ammonia volatilization in wetland ecosystems (Broadbent 1978). Ammonium fertilisers dissolve directly to NH₄⁺ ions, whereas urea may disintegrate to yield NH₄⁺ ions via catalytic hydrolysis [16]. Ammonium ions are weakly linked to water molecules and convert to non-ionized ammonia (NH₃), which can escape as a gas. Ammonia volatilization losses in wet soil range from zero to over 60% of applied N [17]. The pH and temperature of the floodwater, algal and aquatic weed development, crop growth, and soil qualities all influence ammonia volatilization (De Datta 1987). Nitrogen losses from fertiliser dispersed into flood water over fertile clay were as high as 20% of the fertiliser applied, although losses varied depending on water pH, nitrogen source, rate, duration, and manner of application. Due to the non-conductive nature of algal development and the pH of less than 6.8, NH₃ volatilization losses in an acid clay are consistently less than 1% of the total N applied. The application of N fertiliser at depths of 10-12 cm in the soil decreases NH₃ volatilization losses to less than 1% of the total N applied. Mac-Rae and Ancajas (1970) [18] recorded losses of volatile NH₃ from flooded soil as 1 percent of the ammonium sulphate and up to 19 percent of the urea applied within 7 weeks, at rates of 50 and 200 kg N/ha. Ventura and Yoshida (1977) [19] evaluated NH₃ volatilization losses from various N sources on a flooded clay soil and found that NH₃ losses occurred mostly during the first 9 days following N application. When the pH of the soil was reduced below 7.4, the losses were minimal. Furthermore, N losses of 3.8 percent from ammonium sulphate and 8.2 percent from urea were detected on the 21st day of sampling when broadcast at a rate of 100 kg N/ha. When N fertiliser was mixed into puddled soil, ammonia volatilization losses were cut in half. Vlek *et al.* (1980) [20] discovered that despite absorption into the soil, 50-60% of the urea was detected in the floodwater for three soils with cation exchange capacities ranging from 16.2 to 49.2 meq per 100 g. This floodwater urea was discovered to be hydrolyzed at the soil-floodwater interface. Only a small portion (20%) of the

ammonium produced was kept by the soil, with the balance detected in the floodwater as ammoniacal N. The deep application of fertiliser in puddled soil, regardless of the season or year in which the rice is farmed, is one of the greatest ways to minimise significant ammoniacal N loss.

Table-2 Ammonia volatilization losses from different flooded rice soil

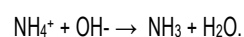
SN	Season	N applied as Urea (Kg N/ha)	Ammonia volatilization (kg/ha)	% of N loss as ammonia volatilization	Ref
1	March - Nov	403	145.6	36.1	[53]
2	March - Nov	162	32.1	19.8	[53]
3	Late June - Sep	240	63.5	26.5	[54]
4	Late June - Sep	240	44	18.33	[54]
5	Late April - Mid July	195	20.8	10.67	[55]
6	Late-July to Late-Oct	195	21.9	11.23	[55]
7	Nov to Mid-may	80-100	0.4-19.7	0.5-19.7	[56]
8	Mid-May to Oct	80-100	1.36-14.6	1.7-14.6	[56]
9	June to Nov	120	22.8	19	[57]
10	June to Nov	120	23.4	19.5	[58]
11	June	100	9.4	9.4	[59]
12	June	200	17.9	9	[59]
13	June	300	50	16.7	[59]
14	June	350	47.9	13.7	[59]

Calcareous soil

The ammonium compounds applied to the surface of a calcareous soil can react with solid state CaCO₃ and form Ca-precipitates of (NH₄)₂CO₃. This converted (NH₄)₂CO₃ decomposes into NH₄OH and CO₂. The CO₂ is lost from solution at a faster rate than NH₃ thereby producing additional OH⁻ ions. Consequently, more solution NH₄⁺ becomes electrically balanced by OH⁻ which would favour NH₃ loss. Fenn *et al.* (1981) [21] found that the surface soil pH was constant at about 8.3 in calcareous sand despite an increase in the urea application rate from 110 to 1100 kg/ha N. This suggests that the elevation of pH associated with urea hydrolysis may be buffered by the precipitation of CaCO₃ in calcareous soil. As much as 32% of urea-N applied can be lost by volatilization from calcareous soil [22]. The relative savings of urea-N were much higher in low CaCO₃ soil (approximately 70%) than in the highly calcareous soil (approximately 30%) [23]. Studies indicated that the potential loss of NH₃ was greatest with urea, intermediate with UAN solution and least with ammonium (NH₄) salts on non calcareous soil but greatest with ammonium Sulphate and much less with urea or ammonium nitrate on calcareous soil. Gasser (1964) [24] also reported higher losses from ammonium sulfate than from urea on a calcareous soil. Fenn and Kissel (1973) [25] also reported much higher losses of N under ammonium sulfate than ammonium nitrate on a calcareous soil. They also concluded that ammonium salts which react with calcium carbonate and form products of low solubility which resulted more ammonia losses. Application of ammonium sulphate produced chemically equivalent amounts of Ca and Mg whereas urea precipitate Ca and Mg. The amount of Ca and Mg precipitation is increased with decreasing NH₃ losses. Precipitation of divalent cations enhanced adsorption of NH₃ on soil cation exchange sites, thereby reducing upward movement of NH₄⁺ and subsequent reduction of NH₃ losses. The release of Ca from reaction of ammonium sulphate with CaCO₃ enhanced upward movement of NH₄⁺ and increased NH₃ losses. Many investigation reported volatilization loss of N from calcareous soil applied with urea and ammonium sulphate and is presented in [Table-3] and [Table-4]. The ammonia loss was 16.43% from urea and 28.83% from ammonium sulphate in different calcareous soil.

Arid soil

The chemical reaction accounted for the loss of significant amounts of NH₄⁺ from the N fertilizers applied to agricultural soil in arid and semi-arid regions [26] are as follows. When soil pH exceeds 7.0, ammonia gas is formed by the deprotonization of NH₄⁺, viz.:



The effect of applied-N (urea) on interdependence of ammonia volatilization and nitrification were studied in twelve arid soil by Aggarwal (1998) [27] and observed that ammonia volatilization from applied urea was affected by the threshold N concentration in soil (Vi).

The values of V_i ranged from 50 in sandy soil to 250 $\mu\text{gN/g}$ in clay soil. Ammonia volatilization was not detected when the threshold N concentration is below 25 $\mu\text{g N/g}$ applied-N in all the soil. However, the minimum concentration of applied-N required for ammonia volatilization (V_i) was 50 $\mu\text{g N/g}$. The volatilization losses were minimum in arid soil.

Table-3 Percent of ammonia loss in Calcareous soil from Urea

SN	Form of N applied	Amount of N applied	Lost $\text{NH}_4\text{-N}$	Ref
		(kg N/ha)	(Percent of N applied)	
1	Urea	46	6	[24]
2	Urea	46	10	[24]
3	Urea	25	21.9	[23]
4	Urea	50	21.7	[23]
5	Urea	100	20.9	[23]
6	Urea	200	10.6	[60]
7	Urea	184	23.9	[61]
Mean			16.43	

Table-4 Percent of ammonia loss in Calcareous soil from Ammonium sulphate

SN	Form of N applied	Amount of N applied	Lost $\text{NH}_4\text{-N}$	Ref
		(kg N/ha)	(Percent of N applied)	
1	Ammonium sulphate	46	8	[24]
2	Ammonium sulphate	46	7	[24]
3	Ammonium sulphate	140	40	[62]
4	Ammonium sulphate	280	41	[62]
5	Ammonium sulphate	140	45	[62]
6	Ammonium sulphate	280	36	[62]
7	Ammonium sulphate	415	56	[63]
8	Ammonium sulphate	200	13.98	[60]
9	Ammonium sulphate	400	12.5	[61]
Mean			28.83	

Ammonia volatilization from problem soil

Saline soil

The influence of soil salinity on NH_3 and N_2O emissions is little known, despite the fact that saline soils are extensively dispersed and continuously extending their area globally. However, laboratory research on the effects of salinity levels on ammonia volatilization losses from surface applied urea nitrogen (N) at three salinity levels, namely 4, 8, and 16 dSm^{-1} , indicated that volatilization losses were mostly determined by soil salinity and soil type. The gaseous losses of NH_3 increased as salinity rose. Peak N volatilization losses occurred between days 2 and 5, and then dropped dramatically over the next seven days with very little loss. The cumulative loss of N over 21 days of incubation was lower (approximately 28 and 35 percent of additional urea-N) in the control condition and higher (about 44 and 35 percent) in the highest salinity condition (16 dSm^{-1}) [28]. Field experiments with three soil salinity levels (S_0 = non-saline, S_1 = 1.0 dS m^{-1} and S_2 = 5.0 dS m^{-1}) with two N fertilizer (urea and ammonium sulphate) showed that all the salinity levelled soil significantly increases cumulative NH_3 volatilization losses by 40.0 to 92.2%, respectively ($p < 0.05$).

The N_2O emissions under the application of either urea or ammonium sulphate, at the soil salinity level of 1.0 dS m^{-1} was significantly greater than those at both 0 and 5.0 dS m^{-1} salinity levels ($p < 0.05$). The correlation showed that the NH_3 flux was an exponential function with respect to soil ammonium ($\text{NH}_4\text{-N}$) concentration and the N_2O flux displayed a linear relationship with soil nitrite ($\text{NO}_2\text{-N}$) concentration which accumulated to a much greater degree under the salinity level of 1.0 dS m^{-1} . The more the NH_3 volatilization in saline conditions, the greater the urea hydrolysis, nitrification, and suppression of soil $\text{NH}_4\text{-N}$ adsorption capability. Increased N_2O emissions were attributed to accumulated soil $\text{NO}_2\text{-N}$ generated by salinity imbalances, which limit nitrite and ammonia oxidation. It has also been established that saline soil has a significant capacity to generate NH_3 and N_2O emissions at the same time [29].

The constant fraction of N lost with increasing application rate is due to the inherent basic soil pH. Overrein and Moe (1967) [30] discovered that the higher the application rate, the longer the time of elevated soil surface pH at the granule location. Li *et al.* (2019) [31] discovered that NH_3 volatilization losses from saline soil were substantially higher than those from non-saline soil when N was applied. McClung and Frankenberger (1985) [32] discovered that three types of salt mixed

soil significantly promoted NH_3 volatilization, while Akhtar *et al.* (2012) [33] discovered that NH_3 volatilization from saline soil was 1.4 to 6.0 folds greater than that from control soil and increased proportionally to soil salinity. After fertilization, saline water irrigation produced more NH_3 volatilization than freshwater irrigation [34]. The data presented in [Table-5] clearly indicates that the percentage of ammonia volatilization enhanced with increasing salinity level in various location as discussed above.

Table-5 Ammonia volatilization losses from different saline soil

SN	EC(dSm^{-1})	% of ammonia volatilization	References
1	4	28-35	[28]
2	16	35-44	[28]
3	1	40-65	[31]
4	5	89-92	[31]

Saline-sodic soil

Saline-sodic soils are characterized with an EC_e of $>4 \text{ dS m}^{-1}$ and ESP of >15 . Thus, both soluble salts and exchangeable Na^+ are high in these soils. Since electrolyte concentration is high, the soil pH is usually < 8.5 and the soil is flocculated.

Table-6 Ammonia volatilization losses from different saline-sodic soil

SN	pH	EC	SAR	% loss
1	7.97	4.36	23	4.9
2	7.78	5.23	17.7	3.41
3	8.13	6.87	56	29.2
4	8.02	8.37	42.8	14.16
5	8.35	9.54	38.6	13.85
6	8.6	8.32	60.1	36.02
7	8.71	12.53	81.7	54.47
Mean				22.29

The table reveals that the N loss in soil with a pH of 8.71 and a SAR of 81.7% was 54.47 percent higher than in soil with a pH of 7.78 and a SAR of 17.7. (3.41 percent). Ammonia volatilization rose significantly as soil SAR increased. According to reports, the composition of the cations on the exchange complex influences ammonia volatilization from soil. Martin and Chapman (1951) [35] discovered larger ammonia losses in Na-saturated soil than in Ca and Mg-saturated soil, owing to higher pH values in Na-saturated soil. Similarly, Sharma *et al.* (1992) [36] found that increasing the exchangeable salt percentage of the soil enhanced ammonia leakage. Therefore, relatively higher pH of salt affected soil due to high sodium on exchange complex was also one of the major factors responsible for higher ammonia losses. The data on [Table-6] indicated that the ammonia losses progressively increased with increase in pH or SAR of the soil and showed highly significant correlation with the pH ($r = 0.88^{**}$) and SAR ($r = 0.98^{**}$) of the soil. The average ammonia losses from all the seven soils were 22.29 percent which were comparable in magnitude to that report of Ernst and Massey (1960) [37] and Fenn and Kissel (1973) from alkaline soil (25% or more).

Acid soil

The increase in the proportion of urea-N loss with increasing application rate is consistent with many reports for acidic soil [38]. In the case of acid soil, the slower rate of urea hydrolysis may be due to lower microbial activity. In acid laterite and acid sulphate soil, urea hydrolysis is continued till the fourth week. Acid sulphate soil maintained the highest amount of N as urea upto 4 weeks of incubation, which imply that the urea hydrolysis is slowest in acidic soil. Low ammonification rate in acid soil resulting in the retention of N in ammoniacal form which is confirmed with the findings of Siddappa and Rao (1971) [39] and Sarigumbu *et al.* (1978) [40]. More than 30% of urea-N applied to the surface of a residue-covered, acidic soil was volatilized as NH_3 [41].

Conclusion

The nitrogen loss is around 65% of the applied fertilizer and only 5 % alone is utilized by the crops. Though the nitrogen utilization is less, it is available to agricultural crops as nitrate and ammoniacal forms. They enter into the crops through the process of mass flow and diffusion respectively [64, 65].

The major process of nitrogen losses is ammonia volatilization, denitrification, leaching and runoff *etc.*, though the ammonia volatilization varied from 7.5 to 36 % and 0.5 to 36.1% in grass land and flooded soil it was more alkali soils than acidic soils. The ammonia volatilisation depends upon the pH, temperature and ESP of the soil besides the rate, source, time and method of application. The growth of the algae and aquatic biota increases the flood water, pH and leads to substantial losses of N by ammonia volatilization. Among the various types of N fertilizers, the ammonium sulphate releases less amount of gaseous loss of N than other fertilizer. However in calcareous soil the ammonium sulphate releases more gaseous ammonia than urea which precipitates calcium and magnesium and favours the adsorption of ammonia in soil exchange sites. The ammonia volatilization losses of N can be curtailed by 50% by incorporating N fertilizer with the puddled soil. Ammonia volatilization can be reduced by placing fertilizers below the soil surface. This reduces the risk of ammonia volatilisation because it reduces the ammonia/ammonium solution concentration at the soil surface. Split application of fertilizers also reduces losses. Co-application of fertilizers with acidifying agents also reduces the risk. The most efficient way of reducing loss is by coating urea with suitable coating materials.

Application of research: Reducing the ammonia volatilization loss is the ongoing topic of interest in soil fertility research. A better understanding of the chemical reactions in various soils will be helpful to find new strategies to reduce the loss which is covered in this article.

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