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Review

Urea application in soil: processes, losses, and alternatives—a review

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Abstract

Urea is the most used fertilizer because of its significance on world food security but it is also the toughest fertilizer to manage. It is readily available to the plant and it is vulnerable to loss in various ways, causing environmental pollution and huge economic losses. Urea application requires a sound knowledge for its effective management, which will increase its availability to plants and reduce possible losses. Ammonia (NH_3) and oxides of nitrogen (N) pollute the environment, and nitrate (NO_3^-) leaching alters the aquatic ecosystem, which lowers the nitrogen use efficiency (NUE) of applied urea. Nitrate-contaminated drinking water causes human and animal health risks, whereas the emission of nitrous oxide (N_2O) in the atmosphere is significant to ozone layer depletion and climate change. This review discusses the processes in the soil after urea application in the soil–plant system, which includes the loss mechanisms, and the significant factors affecting the N availability and losses. This review also shows that the judicial management of urea in soil–plant systems and maintaining the best management practices and technologies ensure sustainable agricultural development and decrease the risk of environmental contamination. Finally, the review summarizes the potential mechanisms of the applied urea in the soil with their mineralization and loss pathways and delivers the scientific reference to achieve sustainable crop production and reduce the risk of N losses.

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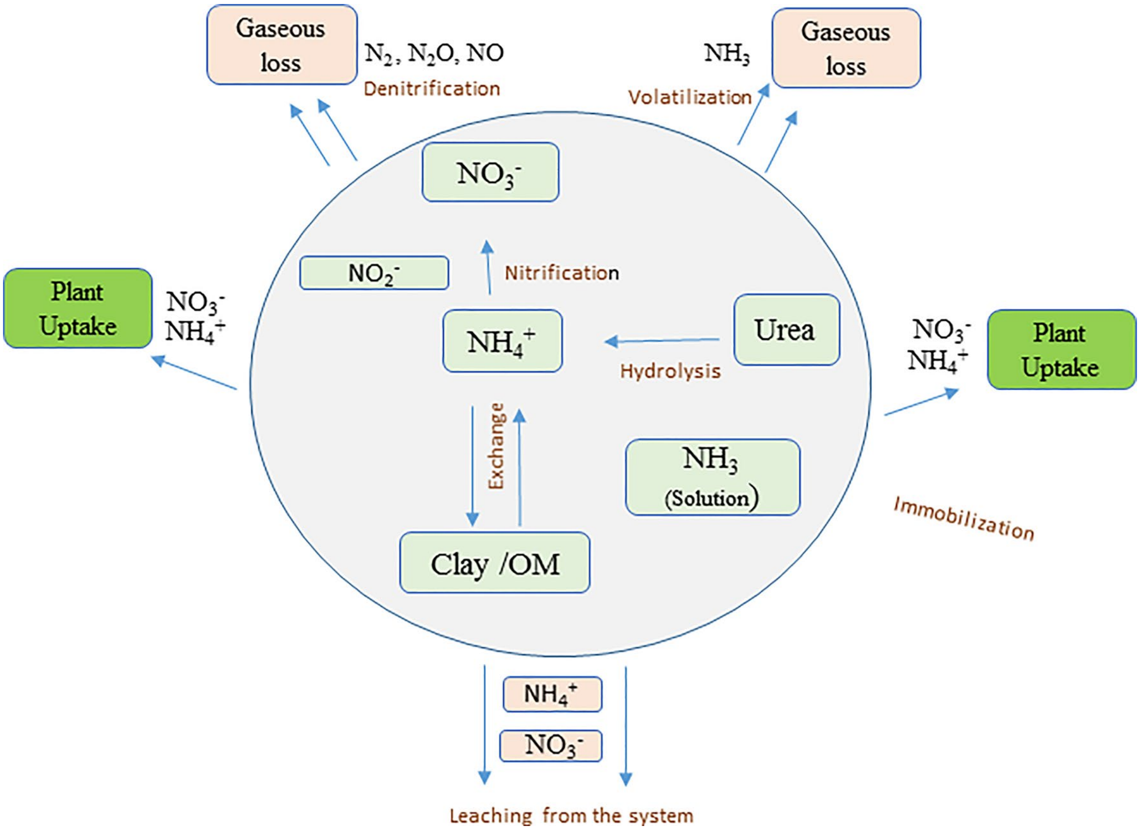
Graphical Abstract



Keywords Urea · NH_3 · N_2O · Nitrate leaching · NUE

1 Introduction

Urea is the most widespread and user-friendly and the most significant nitrogen (N) fertilization source globally [87] and covers 73.4% of all N fertilizers use in the world [69, 178]. But, the frightening problem related to the urea fertilizer is its huge nitrogen loss (20–60%), low nitrogen use efficiency (NUE) (30–40%) which was reported to be 10–50% in corn [117]. The agricultural system is the primary source of greenhouse gas (GHGs) emissions, and more than half of applied urea to the soil is lost through gaseous and leaching loss resulting in low NUE [85, 178]. The surface application of urea is the principal anthropogenic cause of gaseous emissions in agriculture.

Defective application techniques, unnecessary application, irregular distribution, periodic variation, climatic interference, and soil factors stimulate losses of applied urea, which leads to lower NUE and increases the crop production cost, and disruption of the natural crop ecosystem. The N losses through gaseous and leaching mainly rely on the speed and amount of urea hydrolysis, N mineralization, and the amount of urea in soil. Soil water content is one of the significant factors that starts the urea hydrolysis process [2] which maintain the total N content in soil, and affects the N mineralization and loss processes [50]. Faster rate of hydrolysis stimulates greater urea mineralization, and higher soil moisture content increases the hydrolysis and the mineralization processes of urea. Alternatively, fast urea hydrolysis, slow down gaseous N losses as it dispersed the applied urea and NH_4^+ in the sub-soil layer [88]. Generally, the volatilization of NH_3, emission of N_2O, and N leaching increase with the increase of the urea applications rate [5, 111, 114].

Therefore, there is a need to reduce GHGs emissions and increase NUE along with cost optimization for sustainable crop production due to the severe impact of GHGs emissions on crop production and environmental contamination [46].

However, N losses can be minimized if urea hydrolysis is fast so that the ammonium cations (NH_4^+) will be distributed uniformly throughout the soil profile [63, 129].

2 Forms of urea fertilizers

Various forms and formulations of urea are available in the market, such as granules, pellets, prills, crystals, and solutions (Table 1). Urea briquettes, urea super granules, and ammonium nitrate liquid (UAN-28%N) are also used in agriculture [96]. Most of the solid forms of urea contain a more or less similar amount of N. The size and weight of each solid urea may vary according to the manufacturer. Urea solutions have different N content depending on their formulation.

In addition, the typical urea is modified according to the specific objectives and to reduce loss potentiality and increase efficiency by coating and smeared with inhibitors or enzymes. Urea is coated with chemical, biochemical, or organic materials to enrich its quality [49, 214]. The commonly used coated urea are superphosphate-coated urea, sulfur-coated urea, and polyethene-coated urea [75]. Controlled-release urea and slow-release urea fertilizers are other types of urea that also modify typical urea by using inhibitors or enzymes.

Urea super granules are used in the root zone to increase its release time. It also reduces N losses and application frequency. Urea ammonium nitrate reduces loss potentiality during the mineralization process and enables mechanical surface or subsurface application. The coated urea and urea with inhibitors also slow down the hydrolysis process and control possible losses. Urea super granules coated urea, urea with inhibitor, or slow-release urea slow down the urea mineralization process, creating insufficient N availability to meet the crop demand. The N losses from their application could slow down, but total losses may be high. Liquid urea (e.g., UAN) enables faster hydrolysis to scatter inside the soil profile, which increases the N adsorption by the soil aggregates. These processes reduce the N loss potentiality and ensure immediate N availability to meet the current crop demand.

3 Problems related to urea applications

Urea is the most used fertilizer globally, having a significant impact on crop production to ensure food security. However, it also has some harmful effects on soil, the environment, and human health. Specifically, the loss of N from applied urea as N_2O is a corrosive greenhouse gas (GHG), while NH_3 gas pollutes the air. Nitrate leaching contaminates groundwater and causes eutrophication on surface water [171, 209]. Urea may be the possible reason for soil pollution, nutrient imbalance, acidification, and salinization [211].

Volatilization loss from the application of N fertilizers is widespread and harmful. Nevertheless, surface application of granular urea occurs more in the form of NH_3 volatilization when it is applied in no-till soil conditions. In addition, about 30% of applied N is lost through volatilization when broadcasted on sandy soils [55, 83]. The produced NH_3 gas creates adverse effects on seed germination and seedling development [19]. Furthermore, ammonia volatilization creates economic problems resulting in lower crop production and environmental contamination in the long term [167]. Ammonia gas loss also can be minimized with the effects of other nutrients like S, Cu, B, etc. [45]

Nitrogen leaching loss decreases crop growth, development, and NUE, polluting the surface and groundwater. Leaching is more problematic in light-textured upland soil [141]. During the denitrification process, nitrate (NO_3^-) is reduced to nitrite (NO_2^-), and later nitrite (NO_2^-) is reduced to nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2). Every step

Table 1 General forms of urea

SL No.	Urea formulation	Condition	% N (app.)	Particle size/briquette	References
1	Urea (typical)	Solid granule	45–46	Diameter: 2–4 mm	[185]
2	Prilled urea	Solid free-flowing	46	Diameter:1–2.8 mm	[185]
3	Urea super granule (UGS)	Solid	46	Three sizes: 0.9 g, 1.8 g or 2.7 g	[76]
4	Urea ammonium nitrate (UAN)	Liquid	28–32	–	[79]
5	High NRG-N (HNRGN)	Liquid	27	–	[192]

is catalyzed by specific enzymes and emits N oxides, which are corrosive gases and a reason for ozone layer depletion [125, 133, 143].

Split application of N fertilizers can increase the uptake capacity of crops, and the substrate concentration in soil solution for nitrification or denitrification can be minimized over a single application. The N losses from applied liquid N fertilizer (e.g., UAN) result in 25% and 27% less N loss as NH_3 volatilization and N_2O emission, respectively, than granular urea [60, 184]. Calcium ammonium Nitrate (CAN) resulted in higher crop yield [133]. Application of liquid urea increases N availability, uptake, NUE, protein content, and grain yield of cereals as plants found more available N in the soil to uptake [192].

Moreover, liquid urea reduces N loss from the soil-crop system by adsorbing it onto soil aggregates. The liquid urea application reduces the NH_4^+ concentration in the soil by dispersing the NH_4^+ into the soil profile and decreasing the NH_4^+ concentration in the soil. Increased urea application frequency with lower doses can lower the NH_4^+ concentration in soil compared to a single application [127, 129]. These mechanisms reduce the N loss potential and increase the N crop uptake potential of applied N [128]. Besides, some controlled released urea fertilizer reduces N losses (NH_3, N_2O) ensuring higher N concertation (NH_4^+,NO_3^-) and higher crop yield [98, 110].

3.1 Soil pollution

Soil fertilized with urea in excess of the optimum dose has higher potential risk of soil pollution. The long-term and unnecessary application of urea has harmful effects on soil chemical and biological properties, which reduces its fertility, and reduces the diversity and activities of the soil microbes [82, 116, 156]. Urea fertilization also causes soil acidification [146]. Though the surrounding soil pH increases immediately after urea application, frequent use of urea in the same field in the long term increases soil acidity. This is more prevalent in soil that is moderately acidic (pH 5–6). The higher soil acidity hampers the biological processes of soil. In addition, excess N in soil may reduce soil carbon content and alter the soil nutrient balance [122].

Soil pollution from applying N fertilizers can be minimized by increasing the uptake efficiency of crops and controlling N losses during mineralization. Split N application significantly increases the crop's N uptake potential, leaving less residual N in the soil and decreasing the possible N losses. Liquid urea is more eco-friendly with efficient uptake, and about 19% higher NUE. Moreover, liquid urea is superior in terms of N uptake, NUE, and yield compared to the other two liquid (UAN and High NRGN, a commercial liquid N fertilizer) fertilizers [71, 120, 192].

3.2 Environmental disruption

The environmental disruption through the agricultural system has now become a great concern. Urea application has significant effects on GHGs emissions, i.e., carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) from agricultural soils [159]. The agricultural sector emits the highest amount of (98%) ammonia (a potential air pollutant), and it is estimated that about 35% is from the application of nitrogen fertilizer [47]. In addition, more than 50% of applied urea is lost through NH_3 volatilization [115]. Agriculture also accounts for 60% of global anthropogenic N_2O emissions, and agricultural soils are their major source [77]. Nitrous oxide is a persistent and harmful GHG whose global warming potential is 265 times than CO_2 [77]. The nitrates from urea applications pollute surface and groundwater. The urea pollution promotes the ocean algae to manufacture a lethal poison called "Domoic acid". This Domoic acid causes various mass deaths of several marine animals and birds [33].

3.3 Health hazard

Nitrate pollution is common in surface and sub-surface water around the cropping areas. Frequent and dense rainfall, and flood irrigation are the main ways to carry nitrate to water which leads to the water contamination. Water contamination is positively correlated with the cropland percentage in a region. High levels of nitrate are harmful to the reproductive and respiratory system, spleen, thyroid, and kidney of children and adults in humans. It is also corrosive to infants [198]. In addition, higher nitrate concentration in drinking water may cause a higher risk of diseases such as diabetes, spontaneous abortion, gastric cancer, methemoglobinemia, and many more [64, 73]. Frequent and continuous contact of urea with the skin can be the cause of dermatitis. A harmful carcinogenic material, "nitrosamines", is produced in spinach and lettuce leaves fertilized with a high level of urea [157].

4 Processes involving urea in the soils

Urea transformation after application to soil involves several processes and steps [7]. It starts with urea hydrolysis, in which urea absorbs water and reacts with urease enzyme in the soil, and is transformed quickly to $(NH_4)_2CO_3$, and later dissociates to NH_4^+ and HCO_3^- ions. The produced NH_4^+ undergoes a chemical reaction to produce NH_3 under alkaline conditions ($pH > 7.5$) or a biological process called nitrification, which converts it to NO_3^- [15]. The NO_3^- can be used by the plants or leached down or undergoes a denitrification process which transforms NO_3 to N_2O and finally N_2 gas (Fig. 1).

Nitrogen dynamics and losses depend on the transformation of urea. Mineralization and nitrification improve N availability to the plant; however, volatilization, leaching, immobilization, and denitrification increase temporary or permanent N removal from rhizospheres.

$$\underset{\text{(Hydrolysis)}}{NH_2 - CO - NH_2 \rightarrow}\ \underset{\text{(Nitrification)}}{\overset{\text{Volatilization }(NH_3)}{NH_4^+}}\ \overrightarrow{\text{(Denitrification)}}\ NO_3^- \downarrow \rightarrow \underset{\text{Leaching}}{N_2O \uparrow} \rightarrow N_2 \uparrow ..$$

Optimum soil moisture content speeds up urea hydrolysis and reduces NH_3 volatilization loss. The soil moisture accelerates the hydrolysis and defuses the applied urea faster into the soil layer, reducing N loss. Clayey soil can adsorb more NH_4^+ and, therefore, reduce the amount of NH_4^+ available for nitrification. A leaching process can lose nitrate, or it can undergo denitrification. Nitrification and denitrification are both processes driven by soil microbial enzymes. The activities of these enzymes increase with the increase of soil organic carbon (SOC), cation exchange capacity (CEC), and clay content of soil [72]. Application method affects urea transformation. The surface broadcast of granular urea may lead to NH_3 volatilization from the soil surface after hydrolysis. In the case of sub-surface application of urea, the NH_3 volatilization loss decreased by 20–45%, while the nitrogen recovery efficiency increased by 26–93%, and the nitrogen agronomic efficiency and corn yield by 31–51%, and 5–11%, respectively [111]. On the other hand, the use of liquid nitrogenous fertilizer can reduce N losses. The NH_3 volatilization loss was 35–50% lower in liquid N fertilizer (e.g., UAN) than in granular urea. The nitrogen losses in UAN application are less in clay soil than in sandy soil [16, 204]. Surface and deep placement of UAN minimized the leaching loss of applied N in corn cultivation in poorly drained claypan soils [173]. Higher nitrate concentration in the soil promotes higher denitrification [165]. Therefore, liquid urea, which distributes quickly throughout the soil profile, can decrease denitrification by reducing the local nitrate density in the soil. The processes of urea transformation in the soil are described below.

4.1 Urea hydrolysis

Urea hydrolysis is the first process in urea transformation. The urea applied to the soil absorbs water and reacts with the soil urease enzyme, transforming to $(NH_4)_2CO_3$. This compound later dissociates to NH_4^+ and CO_3^{2-} ions. The hydroxyl ions released from the CO_3^{2-} ions increase the soil pH close to the hydrolysis site. The pH increase in the local soil site promotes NH_3 volatilization as well.

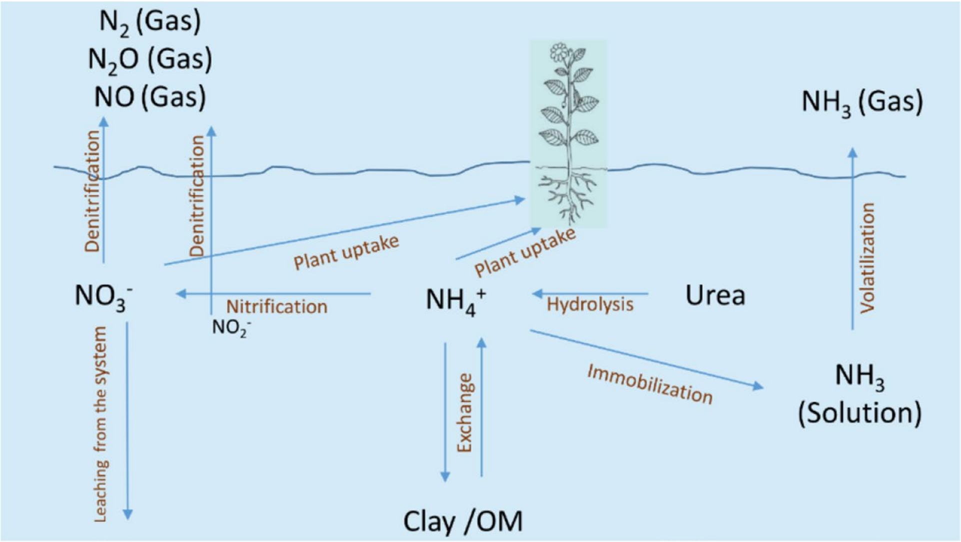


Fig. 1 Urea transformation in an ecosystem after Tung et al. [183]

The following equations represent the urea hydrolysis process.

$$NH_2 - CO - NH_2 + 2H_2O \rightarrow (NH_4)2CO3 \rightarrow 2NH_4^+ + CO_3^{-2},$$

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+,$$

$$CO_3^{-2} + H_2O \rightarrow HCO_3^- + OH^-,$$

$$H^+ - soil + NH_4^+ \leftrightarrow NH_4^+ - soil + H^+.$$

The ammonium ions are formed and adsorbed by the soil clay minerals whose ready for crop uptake or further transformation. The carbamate is transformed to HCO_3^- and increases soil acidity (Fig. 2).

Urea can be hydrolysed by the urease enzyme within 4–7 days in a warm soil temperature with optimum soil moisture content [88]. Urease activity depends on urea concentration in soil which varies from 0.5 to 1.3 mol/L [25]. Urease activity also depends on soil pH, temperature, soluble SOC, total N, and CEC [37]. The optimum pH for maximum hydrolysis is > 6.5 in 5 °C to 40 °C. Weather variation, soil management, and soil properties affect urease activity in the soil. The urease activity decreases with increase in soil moisture (from field capacity moisture content) [4, 113].

The first hydrolysis of urea decreases the diffusion time for urea and NH_4^+ deeper while applied on the soil surface, which reduces the local NH_4^+ concentration and increases the adsorption by the soil particles. The split application reduces the urea and NH_4^+ concentration in soil compared to a single application having a higher opportunity for urease activity and diffusing quickly inside the soil layer.

4.2 Soil factors affecting urea hydrolysis

The physicochemical properties of soil and environmental parameters affect the rate of urea hydrolysis. The factors include, e.g., soil microbial properties, temperature, moisture content, soil type, N quantity in soil, and soil pH [29, 40, 93, 191]. Among these factors, the most influential are the moisture content, temperature, and N quantity in soil [43, 103, 203]. In addition, the urease enzyme is the key catalyst for urea hydrolysis. The urease activity in soil is significantly associated with soil pH, temperature, moisture, organic matter content, and rate of urea applied [6, 11, 136, 145].

The granular urea application prevails higher ammonium concentration, which increases local soil pH temporarily. The higher soil pH promotes higher NH_3 volatilization. On the other hand, the dry situation reduces ammonium diffusion in the soil and thus increases NH_3 volatilization [204].

4.2.1 Soil pH

The soil pH is an important factor that affects the physical, chemical, and biological properties of soil. The soil pH promotes the chemical and biological properties of soil that control hydrolysis of applied urea. The rate of urea hydrolysis increases with the increase in soil pH [3, 30] because H^+ ions are absorbed, and HCO_3^- ions are released into the soil

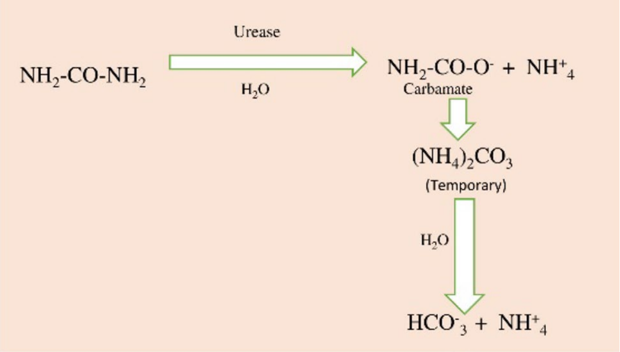


Fig. 2 Urea hydrolysis pathway after Konieczna et al. [97]

solution [88]. The highest hydrolysis was recorded at pH 8.0, but it varies in different soil and climatic conditions [3]. Six to seven is the optimum pH range for maximum urea hydrolysis due to the higher activity of the urease enzyme [89]. At the pH value 5.5–8.5, the rate of urea hydrolysis increases with the increase of urea concentration applied to soil, but at the pH over 9.5, the urea hydrolysis rate decreases with the increasing urea concentration. Nevertheless, the high urea concentration reduces the urease activity because of substrate inhibition or urease denaturation in high soil pH [25, 164].

The pH in the locality of a granule or liquid droplet of urea can be significantly higher than the adjoining soil as urea hydrolysis increases pH by capturing H^+ ions from the soil solution. This pH rise is very short because the produced NH_4^+ is rapidly transformed to NO_3^- and lowers the soil pH, yet this short time pH rise increases NH_3 volatilization loss [81]. The soil pH affects the ionic nature of urease enzymes required for hydrolysis to conjugate with acid and base. These mechanisms decline at the high soil pH and deactivate urease. The higher clay content of the soil increases urease stability from deactivation by adsorption into its surface, but very high clay content reduces its affinity to the substrate [164].

The application of liquid urea can reduce the substrate concentration in soil, which stabilize the soil pH. A higher application frequency at a lower rate also lowers the substrate concentration than at a higher rate and lower application frequency. Loamy soils have more potential for higher hydrolysis than very clayey soils.

4.2.2 Soil temperature

Soil temperature significantly promotes urea hydrolysis, and the rate of urea hydrolysis is increased with the increase in soil temperature [101, 155, 203], but after 70 °C, urea hydrolysis decreases sharply because of thermal deactivation of urease enzymes [130, 188]. At a temperature above 15 °C, the urea hydrolysis rate is faster and slows down under 8 °C [204]. At temperatures above >70 °C, the urea hydrolysis continues very slowly [20]. The rate of urea hydrolysis was 5.4 times higher at 28 °C than at 4 °C. Relatively higher soil temperature helps dissolve urea in water to be diffused in a deeper soil layer. Moreover, soil microbial activity remains high at optimum soil temperature, which increases the urease enzyme content in the soil.

The urease enzyme activity depends on the soil temperature, which affects the hydrolysis of solid urea. Liquid urea is previously hydrolyzed and readily scatters in the soil profile, which has less potential to be lost during application. Split urea application at a lower dose provides lower urea density that can disperse quickly inside the soil layer than higher dose sole urea application, as more elevated dense urea requires more water to be dissolved and hydrolyzed.

4.2.3 Soil texture

Soil texture determines several chemical and biological properties of soil. Urease activity is correlated with the clay content of soil [101]. Clayey soils usually contain higher OM and moisture and maintain higher urease activity and a sound urease synthesis environment. The higher soil moisture and urease enzyme encourage the applied urea to be diffused quickly in the soil profile. The clayey soils also have higher CEC, which can adsorb more NH_4^+, which prevents the further transformation of NH_4^+. On the other hand, light-textured soils have a higher potential for NH_3 volatilization due to their low CEC, low moisture content, high porosity, and relatively higher temperature than clayey soils [86]. The NH_3 volatilization loss was doubled in sandy loam than in clay loam soils due to lower water content potential and lower urease activity [54].

The coarse-textured soils dried fast, promoting the upward movement of applied N fertilizer and water to the soil surface as moisture evaporates. In this way, urea and NH_4^+ accumulate close to the soil surface and increase concentration. The loss can be affected by the capability of applied N fertilizers to be diffused at far from the application point [27, 31]. Liquid urea applications disperse quickly from the soil surface, decreasing loss potential during hydrolysis.

4.2.4 Soil moisture content

Soil moisture content is a vital factor that significantly affects urea hydrolysis. Being hygroscopic, urea absorbs water from an aqueous solution or gaseous form of water [190]. After being applied to the soil, the dissolution of urea starts immediately as urea is easily soluble (1080 g/L at 20 °C) in water. The urea dissolution and hydrolysis rate will be slow under low soil moisture content conditions [4]. The increase in soil moisture of dried soil can increase the rate of urea hydrolysis [188]. On the other hand, water-saturated soil decreases the soil air and gaseous interchange reduces the urease activities, and delays the rate of urea hydrolysis [13, 43]. Other researchers described that the urea hydrolysis constant decreased by 13.9–28.7% when the soil moisture content increased by 60–100% of the field capacity [106].

The soil moisture helps urea to be defused quickly inside the soil profile and decreases the local soil pH by decreasing the NH_4^+ concentration at the application point, which can lower the NH_3 formation. A dry situation reduces the NH_4^+ diffusion in the soil and, as a result, increases NH_3 formation in soil solution, increasing NH_3 volatilization potential [204].

4.2.5 Urea concentration in soil

The urea hydrolysis process is influenced by the concentration of urea applied to the soil [130]. Generally, the concentration of urea applied in soil ranges from 0.01 M to 10 M. The urea hydrolysis increases with an increase in urea concentration up to the saturation of urea by the urease enzyme [34, 180, 205]. After that, urea hydrolysis is negatively correlated with the N quantity in soil for the degeneration of urease at high urea concentration [104, 107]. The urease activity mainly promotes urea hydrolysis of applied urea, and the hydrolysis is maximum at the urea density below 0.5 M and begins to decrease at the density over 6 M [23, 90]. The fast hydrolysis promotes lower NH_3 volatilization loss as it diffuses quickly into the soil layer [215].

Granular urea application increases the ammonium concentration at the application point and quickly increases the local soil pH, even in acidic soils. This increased soil pH encourages to formation of higher NH_3 in the soil [204].

The liquid urea decreases the substrate concentration by dispersing rapidly inside the soil profile. The higher application frequency at the lower dose of urea reduces its concentration than a single application at the higher dose.

4.3 Nitrification

The biotic oxidation of NH_4^+ to NO_3^- is called nitrification. It is one of the essential processes for maintaining soil N content and losses. Nitrification also affects the NUE of urea fertilizer. The immobile NH_4^+ is converted to unstable NO_3^- by microbial process, and NO_3^- is misplaced from the soil system through denitrification and leaching [100, 177]. The vigorous nitrification rates in nitrogen-saturated soil occur due to various environmental issues, such as unbalancing soil buffering capacity, acidification, nitrate leaching to water, and emission of GHGs to the environment [152]**.** The nitrification changes the applied urea about how much is taken up by crops and how much contaminates the environment. Ammonium nitrification is a mechanism that follows two steps. Firstly, the ammonium or ammonia is transformed to nitrite (NO_2^-) by obligate autotrophic bacteria (*Nitrosomonas*) and in later to nitrate (NO_3^-) by obligate autotrophic bacteria (*Nitrobacter*). This process is a biological process.

$$2NH_4^+ + 3O_2 \overset{Nitrosomonas}{\rightarrow} 2NO_2^- + H_2O + 4H^+,$$

$$2NO_2^- + O_2 \overset{Nitrobacter}{\rightarrow} 2NO_3^-.$$

The complete nitrification process can be written as

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H_2.$$

During nitrification, hydrogen ions (H^+) are released, resulting in soil acidification, while most of the $NH_4{}^+$ is transformed to NO_3^- [182]. This soil acidification controls the diversity and population of nitrifying microbes in soils. Nitrate dominates in aerated soils and is ready for plant uptake or consumed by the soil microbes. Excess NO_3^- in the soil may be the possible source of NO_3^- loss through leaching. The soil particles have poorly adsorbed the nitrate due to their repulsion of each other [38].

The rates of nitrification are significantly affected by the soil properties (e.g., physical, chemical, and biological) soil pH, and water content. The maximum nitrification occurs at the field capacity water content but in case of wetter or very dry conditions of soils than field capacity water content, the nitrification rate is slower. Furthermore, the rates of nitrification vary depending on the amount and variety of nitrifying micro-organisms in the soil, substrate density, and availability of oxygen [137, 170]. Light-textured soils stimulate greater nitrification due to their higher oxygen potentiality than heavier soils. The lesser substrate density lowers the nitrification rate. Consequently, faster of hydrolysis urea diffuses the $NH_4{}^+$ inside the soil, reducing the spatial $NH_4{}^+$ density and, therefore, low nitrification. Moreover, synchronized application of urea to crop N uptake can decrease the substrate density concentration in the soil.

4.3.1 Factors affecting nitrification

Several (biotic and abiotic) factors are liable for the rate and quantity of NH_4^+ that undergoes the nitrification mechanism. The factors are pH, moisture content, temperature, oxygen availability, and substrate density in the soil solution. The nitrification mechanism greatly depends on the diversity and density of the nitrifying micro-organisms [100, 170]. The nitrification rate also depends on the soil nutrient status, allele-pathic chemicals, and crop species grown in an agricultural system [152]. In addition, seasonal and temporal oscillation affects the population of nitrifying organisms and net nitrate formation in soils. This phenomenon is more common in tropical climatic conditions.

4.3.1.1 Density of ammonium in soil The amount of NH_4^+ available in the soil system relies on the rate of urea hydrolysis, distribution, method of urea application, and the gaseous NH_3 loss. The net nitrate formation is positively correlated with the NH_4^+ in the soil. The more available NH_4^+, the more nitrification. However, very high NH_4^+ or NH_3 concentrations in soil may decrease the rate of nitrification due to the restriction of *Nitrobacter* activity [100, 124]. On the other hand, some coated urea (e.g.,: humate-coated urea) maintained higher NH_4^+ concentration without raising the NO_3^- concentration compared to typical urea form in soil [98].

The clay minerals and the biological NH_4^+ immobilization can fix the NH_4^+ and reduce the amount available NH_4^+ for nitrification. Plant uptake of NH_4^+ from the soil solution also reduces concentration, and these mechanisms may slow the nitrification process [152]. Liquid N fertilizer (e.g., UAN) application had higher NH_4^+ and lower NO_3^- concentration than that of granular urea. In liquid N fertilizers application, the concentration of NH_4^+ is less compared to granular urea where it is applied, which can decrease the nitrification process [194]. Liquid urea can disperse rapidly inward soil profile that can reduce the NH_4^+ concentration in the application point. In addition, multiple applications of urea in lower doses may decrease local NH_4^+ concentration in soil, thus reducing the nitrification rate.

4.3.1.2 Population density of nitrifying *bacteria* Nitrification is a microbial oxidation process where nitrifying organisms play the main role. Nitrification is wildly variable on the density and diversity of the nitrifying population in the soil. The higher the diversity and quantity of the nitrifying population, the higher the nitrification potential. A large number of these bacteria are available in agricultural soils and supply sufficient enzymes as needed. Ammonia oxidizing bacteria are actively involved with the enzyme as ammonia monooxygenase. The rate of nitrification is positively correlated with the population density of nitrifying microbes [26, 100, 175]. The activities of nitrifying organisms depend on the substrate concentration along with various soil and environmental parameters, such as soil moisture content, pH, temperature, and oxygen availability.

Soils with higher OM content and air have a higher potential to contain more nitrifying bacteria, while arid or water-saturated soils have less potential for nitrifying bacteria. In tropical soils, nitrifying bacteria are more functional; thus, the rate of nitrification is high. The nitrification rate will be low, while the activities of nitrifiers will be low. Moreover, the nitrifiers activities will be restricted while substrate concentration is limited. In that case, fast hydrolysis and rapid distribution of urea or $NH_4{}^+$ inside the soil profile decrease its concentration at the point of use.

4.3.1.3 Soil texture Soil texture influences nitrogen mineralization of soil because it controls several physical, chemical, and biological properties of soil, along with organic materials distribution and aeration. The higher clay content of soil can absorb more NH_4^+ ions, promoting a faster nitrification rate. Moreover, the growth rate of nitrifying microbes is also proportional to the soil particle surface area where the $NH_4{}^+$ ions are held. Sandy soil has a lower adsorb capacity for $NH_4{}^+$ ions, but it has more aeration [61, 176, 177].

The availability of NH_4^+ ions to nitrifying microbes for nitrification depends on the $NH_4{}^+$ fixation capability of soil clay particles and the competition of other cations. In this situation, nitrification is less complex than balancing CEC [150, 197]. The nitrification rate can be minimized by decreasing $NH_4{}^+$ absorption by the soil colloids while the uptake potential of a crop will be high. The increased application frequency can increase the NUE of a crop.

4.3.1.4 Soil pH Soil pH is a vital soil parameter because most of the physical, chemical, and biological processes are controlled by the soil pH value. The soil pH affects the rate of nitrification significantly. The optimum pH range for nitrification is 4.5–7.5 [65]. During nitrification, soil pH decreases, which reduces the ammonia volatilization loss.

The nitrification is faster at soil $pH \geq 6.0$, slower at $pH \leq 5.0$, and too slow at soil $pH \leq 3.8$. In acidic soil, most ammonia prevails in the NH_4^+ form, which is not appropriate to be oxidized by ammonia monooxygenase [179, 182]. In these conditions, the rate of nitrification depends on the survival of acid-tolerant nitrifiers strains in the soil [99]. During urea hydrolysis, the local soil acidity decreases temporally and thus higher nitrification. The temporally increases in soil pH depend on the local urea density at an application point. This short-time pH rise can be minimized by applying previously hydrolyzed urea (e.g., aqueous urea) and or split application than a single application of granular urea.

4.3.1.5 Soil OM content The rate of nitrification depends on the diversity and population of soil microorganisms. On the other hand, the diversity and microbes population depend on the soil organic matter quality, particularly on the C/N ratio of the soil, and the C/N ratio regulates the ability of microbes to carry on the nitrification process. A high C/N ratio in the soil promotes microbial immobilization of ammonium, which lowers the rate of nitrification [151, 177]. The optimum nitrification rate occurs in soil with a C/N ratio of about 10, and higher ammonium immobilization occurs at a higher C/N ratio. Lower nitrification and higher ammonium immobilization occur in grassland and forest soil since the C/N ratio is usually more than 100 [177, 182, 187].

Soil OM content increases soil's physical, chemical, and biological properties, facilitating soil aeration and microbial activity, thus higher nitrification. Light-textured soil has a lower potential to contain OM than clayey soil. Moreover, moist soil has the potential to preserve more OM than dry soil.

4.3.1.6 Soil moisture content Soil moisture content is an essential factor of soil nitrification because it has significant effects on soil properties. The maximum growth and diversity of nitrifying bacteria are recorded at the optimum moisture content, and the maximum rate of nitrification occurs in field capacity moisture content [65]. The nitrification rate is slow when soil moisture is more than field capacity. The nitrification is abruptly slow in dry soils but continues at the permanent wilting point [26].

The soil aeration also affects the rate of nitrification and nitrate stability. In this water-saturated condition, soil pores are filled with water, and the nitrification rate is stopped or near zero due to the absence of oxygen [152]. Seasonal variation, density, and distribution of rainfall promote the soil moisture content. Optimum moisture content promotes the diversity and distribution of nitrifying microbes in the soil. The microbial activity widely varies with the wet and dry periods of the soil. The net nitrification is significantly correlated with the density of nitrifying microbes [100]. Moreover, soil moisture content promotes substrate dispersion in the soil and increases NH_4^+ absorption by the clay minerals. Slow nitrification may be possible while N fertilizers are applied in a split rather than a single application. The split application also increases the NUE of a crop.

4.3.1.7 Soil temperature Soil temperature is a crucial factor that promotes the rate and amount of nitrification as it controls the activities of nitrifying bacteria. The quantity, diversity, and functions of these bacteria mostly depend on the soil temperature [10] And the most functional temperature for nitrifying bacteria ranges from 25 °C to 35 °C [66, 152, 177]. The nitrification rate is the highest at the optimum temperature and slower at lower than 5 °C but still occurs at − 1.5 °C [162].

Dry soil has a higher potential to be hot than moist soil. Moreover, water-saturated soil is in relatively lower temperatures than the soil with field capacity moisture content. The aqueous solution of urea (e.g., aqueous urea) can increase soil moisture and decrease soil temperature.

4.4 Ammonia (NH_3) volatilization

Ammonia is a corrosive GHG that causes environmental degradation along with its loss reduces NUE, hence, increasing crop production costs [144]. The agricultural sector emits the highest (98%) NH_3 volatilization, and 35% is estimated from nitrogen fertilization [47]. In addition, more than 50% of applied urea is lost through NH_3 volatilization [115]. Urea, ammonium sulphate, ammonium nitrate, and UAN are N fertilizers that are all vulnerable to NH_3 volatilization [35].

As a gas, NH_3 is likely to be volatilized to the atmosphere when present in the soil, water, or manure and shows a significant affinity to water. The basic determinants of volatilization rate are NH_3 reactions in water. The process of NH_3 volatilization [163, 189] is as follows.

$$NH_4^+\ (absorbed) \leftrightarrow NH_4^+(in\ solution) \leftrightarrow NH_3 \overset{to\ atmosphere}{\uparrow}\ (in\ solution) \leftrightarrow NH_3 \overset{to\ atmosphere}{\uparrow}\ (gas\ in\ solution).$$

The ammonia volatilization rate can be controlled with the withdrawal and dispersion of NH_3 in the air and by NH_4^+ density alteration or NH_3 in soil (Fig. 3). The driving force of NH_3 volatilization is the partial pressure variance of NH_3 between the liquid phase and the surrounding atmosphere [48].

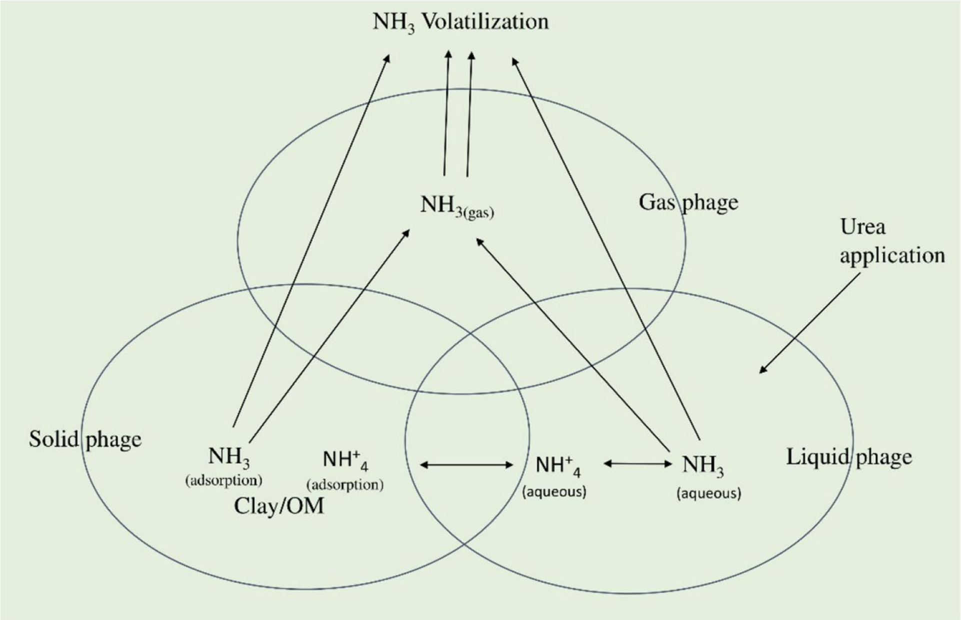


Fig. 3 Mechanisms of NH_3 volatilization after Liang et al. [109]

The instant contact of urea granules to the soil aggregates increases the adsorption of NH_4^+ to the soil solution, which significantly lowers the NH_4^+ transformation to volatile NH_3 of applied N in the presence of adequate moisture [166]. Similarly, Cabezas et al. [24] stated that an appropriate amount of moisture in the soil affects the NH_3 volatilization loss from top-dressed urea by reducing the hydroxyl ions concentration, which is responsible for the transformation of NH_4^+ to volatile NH_3^+. Thus, NH_3volatilization slows down when soil provides adequate moisture for urea hydrolysis and diffuses inside the soil particles.

4.4.1 Factors affecting NH_3 volatilization

Nitrogen losses as NH_3 volatilization from surface-applied NH_3 or NH_4^+ forming N fertilizers are stimulated by various soil, environmental, and fertilizer management factors [35]. In the soil, ammonia is adsorbed and desorbed from the soil particles, OM, and water that control the NH_3 liberation to the environment. Soil organic matter has more potential nature to retain NH_3 than soil particles, but clay minerals adsorb more NH_3. In acidic conditions, NH_3 is absorbed more by clay particles, but under a strong alkaline situation, NH_3 is adsorbed by the soil organic fraction. Generally, clay soils adsorb more NH_3 than sandy soil as it has a higher surface area. Moisture content influences this mechanism [126].

The amount of ammonium transformed to NH_3 also greatly depends on the soil pH and moisture content and in alkaline soils ($pH > 7.0$) is more vulnerable than natural to acidic (pH 5.0–7.0). The local soil pH increases during urea hydrolysis, which will increase NH_3 volatilization. The pH rise depends on the soil buffering capacity and density of urea. Soil moisture content decreases urea density by diffusing the urea/ammonium into the soil layer [48]. Besides, higher soil moisture content decreases NH_3 concentration in soil solution, which decreases the gaseous NH_3 liberation to the environment.

Ammonia volatilization is also affected by environmental factors such as frequency and distribution of rain, drought, air velocity, snowdrops, etc., along with the N fertilizers' source, time, and method of application. Topdressing or side dressing of granular urea increases the vulnerability of NH_3 volatilization loss. Moreover, the split application of urea [196] and UAN application [80, 184] significantly reduce NH_3 volatilization loss from soil.

4.4.1.1 Concentration of NH_4^+ in soil The ammonia volatilization mostly depends on the NH_4^+ concentration in the soil solution and application rate of urea. Usually, the higher the NH_4^+ concentration, the higher the NH_3 gas volatilization. A higher urea application rate also promotes higher NH_4^+ concentration, and more NH_3 volatilization loss will occur. Moreover, nitrification and denitrification rates, crop uptake, and many other factors influence the NH_4^+ and NH_3 concentrations in soil [26]. Higher $NH_4{}^+$ concentration in soil solution increases the conversion rate to NH_3 and the NH_3 concentration in the soil solution. The higher the NH_3 concentration in the soil, the solution encourages more ammonia gas to the environment [62].

In addition, higher NH_4^+ concentration increases the local soil pH and promotes higher NH_3 volatilization. The fast hydrolysis of urea will lower NH_3 volatilization loss as the urea is defused quickly into the soil [215]. If a high density of NH_4^+ remains on the soil surface longer, more NH_3 will be lost from applied urea.

4.4.1.2 Rate of urea hydrolysis The higher rate of urea hydrolysis decreases NH_3 volatilization loss by decreasing local NH_4^+ concentration. Fast hydrolysis diffuses NH_4^+ in a deeper soil layer from the surface. By increasing diffused time, the NH_4^+ is more concentrated and increases the soil pH and, thus, greater NH_3 gas volatilized [88].

Various soil and climatic factors affect the rate and amount of urea hydrolysis. The concentration of NH_4^+ in soil depends on the rate of urea hydrolysis and the soil water content. The concentration of NH_4^+ in the soil increases with a decrease in urea hydrolysis rate and at lower soil water content. The transformation of NH_3 from NH_4^+ depends on the NH_4^+ concentration in the soil solution. Higher NH_3 concentration in soil solution promotes higher NH_3 volatilization [35].

Many other processes and factors affect NH_3 concentration in the soil solution, such as nitrification, denitrification, plant uptake, irrigation, and rainfall, which promote to liberating of NH_3 to the environment. Liquid urea fertilizers (e.g., UAN) or urea in solution are hydrolyzed faster than previously hydrolyzed and defuse and disperse rapidly inside the soil, so less is lost as NH_3 volatilization. The risk of NH_3 volatilization loss can also be minimized by splitting the urea fertilizer application depending on the uptake potential of the plant.

4.4.1.3 Soil pH High soil pH promotes the transformation of NH_4^+ to NH_3 in the soil solution. The soil pH around the granules increases during urea hydrolysis by forming ammonium carbonate [78]. The alkaline soils (pH > 7) are more susceptible than acidic to neutral soils (pH 5–7) to NH_3 volatilization loss. The increase in soil pH increases the transformation rate of NH_4^+ to NH_3 in the soil solution, while the greater NH_3 concentration in the soil solution liberates more NH_3 to the atmosphere. Moreover, the NH_3 volatilization rate increases proportionally with the increase in soil pH by affecting the equilibrium between NH_4^+ and NH_3 in the soil solution. The NH_3 volatilization rate increased from 0.1 to 1, 10, and 50% by increasing soil pH from 6.0 to 7.0, 8.0, and 9.0, respectively [48].

Soil buffering capacity maintains pH stability, and clayey or OM-rich soil, which has a higher buffering capacity, decreases NH_3 volatilization compared to light-textured, which has low buffering capacity. Moreover, acidic to neutral soil (pH 5–7) may have low NH_3 volatilization loss, while alkaline soils (pH > 7) are more susceptible to having high NH_3 volatilization [35]. The higher availability of OH^- in soil solution accelerates the transformation of NH_4^+ to NH_3 according to the reaction:

$$NH_4^+ + OH^- \rightarrow NH_3 \uparrow + H_2O.$$

Hydrolysed urea of fast urea hydrolysis reduces the rate of pH rise by decreasing the ammonium carbonate concentration in soils soil solution while applying N fertilizers as a split application reduces NH_4^+ concentration in soil compared to a single application; therefore, less NH_3 volatilization loss will occur [196]. Liquid N fertilizers (e.g., UAN) contain dissolved NH_4^+, which can rapidly diffuse in the soil profile, and the concentration of ammonium carbonate/NH_4^+ will be lower. Consequently, NH_3 volatilization loss is lower when a liquid form of N fertilizers is used than solid N fertilizers [78, 80, 184].

4.4.1.4 Soil temperature Soil temperature essentially controls urea hydrolysis rates and maintains sound microbial activities after urea application. Higher soil temperature promotes higher rates of NH_4^+ transformation to NH_3 in the soil system [118]. High temperature and high soil pH cause NH_3 volatilization to proceed at higher rates because of their combined effects on increasing the concentration of NH_3 dissolved in the soil solution [81]. Moreover, the urea solubility is increased by the increased soil temperature and, therefore, more NH_3 volatilization. In the field condition, the rate of NH_3 volatilization varies depending on the variation in the daily soil temperature. However, the transformation period of NH_4^+ to NH_3 is prolonged at relatively lower temperatures [62]. The highest NH_3 volatilization occurs during the period of maximum daily temperature, and normally, the NH_3 volatilization risk increases at a temperature above 20 °C [26, 35].

In addition, the soil temperature affects NH_4^+ adsorption, the transformation of NH_4^+ to NH_3, and greater NH_3 volatilization. At temperatures over 15 °C, the urea hydrolysis rate starts to be faster, and this raises the local NH_3 concentrations and speeds up NH_3 volatilization [204]. While the temperature increases from 5 °C to 25 °C and from 25 °C to 45 °C, the NH_3 volatilization potential will be two- and three-fold, respectively [67]. At lower soil temperatures, the rate of NH_3 volatilization is low. Ammonia still volatiles from the soil surface even in cold or frozen conditions during the time of fertilizer application [35]. Light-textured soils have a higher potential to be warmer than clayey soils, and soils with relatively lower moisture content have a higher potential to be warmer than moist soils. Urea ammonium nitrate of liquid urea application can increase the soil moisture content and reduce the soil temperature.

4.4.1.5 Soil moisture content The concentrations of NH_4^+ or NH_3 in soils depend upon the soil moisture content, and lower moisture content promotes a higher concentration of NH_4^+ or NH_3, causing higher NH_3 volatilization loss [26]. Ammonium ions will be highly dispersed in soil with high moisture content ensuring lower NH_4^+/NH_3 concentrations than in dry soils. Urea broadcast on wet surfaces will have a high rate of hydrolysis, and the downward movement will be decreased because the soil pore spaces are filled with water. The NH_4^+ concentration will be higher and thus increase NH_3 volatilization [35]. In the case of very low soil moisture content, the urea dissolution and hydrolysis rates are lower resulting in slower NH_3 gas loss [4]. Field capacity moisture content facilitates the downward movement of NH_4^+ during urea hydrolysis and lowers NH_4^+ or NH_3 concentration on the soil surface, thus, NH_3 volatilization reduces.

Irrigation and precipitation wash the urea into the soil, maintain a lower NH_4^+ concentration, and reduce NH_3 gas volatilization from applied urea [14]. The application of anhydrous ammonia below the soil surface reduces NH_3 volatilization loss due to rapid dispersion inside the soil profile [168]. Liquid urea is previously hydrolyzed, and the $NH_4{}^+$ ions disperse rapidly into the soil profile, reducing local NH_4^+ and NH_3 concentration, thus low NH_3 volatilization. Split application of N fertilizers also has lower local NH_4^+ and NH_3 concentrations than sole application.

4.4.1.6 Physicochemical properties of soil The volatilization loss of NH_3 massively relies on the soil texture, which is controlled by the soil buffering potentiality as soil texture is a vital indicator of soil clay quantity and CEC. The cation exchange reactions of soil preserve NH_4^+ ions on the clay and OM surfaces by electrostatic attraction. This mechanism stores NH_4^+ in soil and keeps NH_4^+ concentration in soil solution low. The higher clay and OM content represent higher CEC, which indicates high NH_4^+ retention by the clay aggregates, which can prevent future transformation to NH_3. Urea application at higher frequency but at lower doses lowers NH_4^+ concentration in the soil, thus reducing NH_4^+ transformation to NH_3 [26, 142, 196].

Higher soil buffering capacity can resist an increase in the pH of soil, hence, light-textured soils which with lower CEC and less OM content have lower buffering capacity; therefore, urea is vulnerable to soil pH rise and will have higher NH_3 volatilization loss [35, 199]. Usually, he ammonia volatilization potential in clayey soil is lesser than that of sandy soil, which has lower CEC. Clayey soil also has a higher potential to contain more water than sandy soil [68]. Liquid N fertilizer increases the soil water content, which promotes faster hydrolysis and rapid NH_4^+ diffusion inside the soil, which lowers the NH_4^+ concentration and, therefore, lowers the possibility of NH_3 volatilization. Soil aeration does not influence NH_3 transformation but helps to liberate NH_3 from the soil; for example, wind velocity increases the liberation of NH_3 from the soil.

4.5 Nitrate leaching

Leaching of N is the most critical N loss passageway it is estimated more than 19% of N applied to soil leaches out from crop production systems worldwide, contaminates water, and creates economic and environmental problems [178, 212, 213]. Nitrogen leaching decreases crop nutrient availability, growth, and NUE. Leaching of N is more in light-textured upland soil [141]. The leached nitrate quantity from a field relies on the nitrate concentration of a soil solution. Besides, rainfall distribution, irrigation system adopted, and soil texture play a significant role in nitrate leaching, while the concentration of nitrate in a soil solution depends on the N application rates, nitrification and denitrification processes, plant uptake, etc. [26]. Being the same charged, nitrate ions repel by the soil particles, and leach down by following three principal processes convection, dispersion, and diffusion combination. Usually, the nitrate lets out through either the mass flow of soil water (convection), diffusion among the soil aggregates, or the substrate movement from higher concentration to relatively low concentrate water (diffusion). Though, one of the processes may be more dominant, yet all three mechanisms are active collectively in the most common agricultural systems [26, 121]. Controlled release sometimes resulted in lower leaching loss and contained more residual mineral N than optimum urea application in the rice production system which ensured higher grain yield [110].

Nitrates are transformed from NH_4^+through nitrification catalyzed by ammonia-oxidising bacteria. The rate of NO_3^- formation depends on the various soil factors, such as soil pH, moisture content and fertility status, and the maximum rate of nitrification at the field capacity moisture content [65]. The conditions favorable for nitrification increase nitrate leaching while plant uptake and denitrification decrease nitrate concentration in the soil solution, thus reducing the risk of nitrate leaching. The clayey soil with higher CEC adsorbs more NH_4^+ ions on its surfaces; therefore, they have a lower NH_4^+ concentration in the soil solution. The liquid urea application reduces the NH_4^+ concentration in the soil by dispersing the MH_4^+ into the soil profile and decreasing the $NH_4{}^+$ concentration in the soil. In addition, the increase in urea application frequency with lower doses lowers the NH_4^+ concentration in soil compared to a single application. These mechanisms reduce the rate of nitrification and ensure less nitrate concentration in soil solution, therefore, decreasing the potential of nitrate leaching.

4.5.1 Factors affecting N leaching

Several factors such as soil properties, climatic conditions, and crop management during crop production affect the leaching loss of N from applied urea. The nitrate leaching loss is facilitated by the NO_3^- concentration in the soil solution and water movement in the soil profile. The nitrate concentration depends on the N application rate, denitrification, and nitrification [26]. Sprinkler irrigation increases nitrate adsorption by 152% more than flood irrigation due to less water movement and a lower leaching rate. In addition, higher rainfall [8, 44] and excess or higher urea application rate significantly increase N leaching loss [114, 208]. The higher or excess N application rate increases the concentration of NO_3^- in soil, and higher water movement in the soil profile increases the leaching loss of nitrate. The nitrogen leaching is high, while the light-textured soil experienced more tillage operations.

Faster hydrolysis of applied urea and slower transformation of $NH_4{}^+$ to nitrate reduce N leaching loss due to the higher adsorption [215]. Moreover, the appropriate rate and timely application of urea increase crop uptake potential and reduce N leaching loss [54, 186]. When applied at the right time and position, the economically optimum dose of urea significantly reduces the leaching of N due to optimum synchronization between crop N demand and uptake, thus improving NUE [132]. However, Shapiro et al. [160] did not find any benefits of the subsurface application of urea ammonium nitrate (UAN) over broadcast surface application. Still, there is a relationship between the N application rate and the rate of N leaching [210]. Besides, various soil factors affect nitrate leaching, such as crop root system, earthworms, freezing and thawing, and alternate wetting and drying may create surface connecting macro soil pores that increase leaching loss from the soil–plant system. Biological immobilization and crop uptake of nitrate reduce the nitrate concentration in the soil, thus decreasing the leaching loss rate.

4.5.1.1 Urea application rate and NO_3^- concentration in soil The nitrate concentration in soil solution mainly affects its leaching loss as the nitrate leaching loss is positively correlated with the rate of N fertilizer application [74, 114]. Physical and biological processes in soil and plant N uptake ability maintain the NO_3^- concentration in soil solution. The quantity of nitrate that remains in the soil solution relies on the amount of N fertilizer applied and other soil and environmental parameters that promote the nitrification and denitrification rate in the soil [26]. The higher urea application increases the NH_4^+ concentration in the soil and increases the nitrification rate, enabling higher nitrate concentration, which promotes higher leaching loss. However, higher plant N demand and uptake ability decrease N leaching potential.

Liquid N fertilizers ensure lower NH_4^+ concentration by dispersing in soil and reducing nitrification. Clayey soil adsorbs more NH_4^+ ions and checks to increase NH_4^+ concentration in soil solution. The lower NH_4^+ concentration decreases the rate of nitrification; thus, nitrate leaching decreases significantly. Besides, fast hydrolysis decreases NH_4^+ concentration in soil and slows down the rate of nitrification.

4.5.1.2 Nitrogen adsorbing capacity of soil Soils have different capacities to hold the NH_4^+ and NO_3^- that prevent N leaching loss. Soils with high clay content adsorb significant amounts of NH_4^+ and lower the NH_4^+ concentration in the soil solution, reducing the nitrification rate. The lower rate of nitrification decreases the nitrate concentration in soil solution. The concentration of NH_4^+ and NO_3^- in soil solution decreases by the plant uptake, which lowers nitrate leaching.

Soil clay particles adsorb the cations (e.g. NH_4^+) and lower the NH_4^+ concentration in soil solution [131]. Moreover, the OM content of the soil increases the total N-holding capacity of the soil and reduces the nitrate concentration in the soil solution [102]. Ammonium adsorbing capacity depends on the NH_4^+ addition or NH_4^+ forming fertilizer application and bounding to the interlayers of clay minerals. The NH_4^+ ions that enter into the interlayers of clay minerals stay out of nitrification and thus remain safe to be leached-out. This NH_4^+ adsorbing mechanism may vary due to the variation of the soil type, soil mineralogical properties, and agro-climatic situations of a soil–plant system. For example, NH_4^+ holding into the 2:1 clay minerals protects from entering water into the lattice, where adsorption occurs, reducing NH_4^+ concentration in soil solution [94, 134].

Liquid urea is hydrolyzed previously and dispersed rapidly inside the soil profile increases the N adsorption capacity of the soil. A split application of N also increases the adsorption capacity of a single application. The adsorption capacity of NH_4^+ decreases concentration in soil solution and reduces the rate of nitrification. A lower rate of nitrification decreases nitrate concentration in soil and decreases the risk of nitrate leaching.

4.5.1.3 Distribution and frequency of rainfall Total leaching loss of urea is correlated with the water intrusion from soil [193]. This percolation typically depends on the quantity and distribution of rainfall and the method of irrigation practiced. The high rainfall affected areas suffered more NH_4^+ and NO_3^- leaching in relation to aired or temperate regions [9, 26]. Raining immediately after urea fertilizer application stimulates N leaching from the active plant root zone. The optimum use of urea fertilizer and effective irrigation lessened N leaching from 48 to 5% [59]. Huge rainfall raises the downward flow of water, which carries soluble ions from the soil. This water flow is higher in the sandy soil with a relatively lower water holding capacity, and lower CEC allows to easy drain out of the water with free ions in relation to clayey soil.

The nitrate leaching may increase 13 times depending on rainfall variability by controlling denitrification. In addition, under anaerobic conditions, the nitrate for denitrification is mostly limited due to the anaerobicity of soil is not favorable for nitrification and nitrate content controls the nitrogen turnover rate in soil [58]. The sandy soil is more likely to drain out of water inside the soil than clayey soil in intensive and frequent rainfall-prone areas. The higher nitrate concentration increases nitrate leaching through excess rainwater. The lower NH_4^+ concentration reduces the nitrate leaching by lowering the nitrification rate in the soil. Liquid urea promotes higher hydrolysis, and rapid dispersion inside the soil profile enables lower NH_4^+ concentration and lowers the nitrification rate. A split application lowers substrate concentration more than a single application. The lower nitrate concentration decreases nitrate-leaching loss from soil.

4.5.1.4 Properties of soil Soil properties significantly control the leaching of N from the soil. Nitrogen leaching losses are generally more significant in light-textured sandy soil than in finer-textured clayey soil. The clayey soil has a higher water-holding capacity, slower water movement, and higher denitrification potential. The leaching loss from silt loam soil was five times higher than from clay loam soil [140]. The higher CEC of soil reduced cumulative N losses by holding NH_4^+ from the nitrification process. The higher clay-content soil has a lower potential for N mineralization and relaxes organic N reversal [172]. The efficient drainage mechanism increases the nitrate leaching loss as it ensures faster transportation from source to sink. A good drainage system improves soil aeration conditions, which increases nitrification and decreases denitrification resulting in more nitrate prevailing in soil solution [158].

In addition, the nitrate leaching potential increases in the soil having lower water holding capacity, higher porosity, and higher soil permeability. Puddling rice cultivation reduces leaching potential by forming an impermeable layer below the plough layer (plough pan). Nitrate leaching also fluctuates with the depth of the "Vadose Zone" in a cropping system. Lower nitrate concentration decreases leaching loss. A lower rate of nitrification decreases nitrate concentration in solution, which decreases in lower NH_4^+ concentration. The lower NH_4^+ can possible fast hydrolysis and rapid dispersion of NH_4^+ in the soil profile.

4.5.1.5 Agronomic practices Agronomic practices influence the N leaching loss from the soil–plant system. The lower leaching loss occurs in arable cropland than in ploughed pasture and land cultivated with horticultural crops due to shallow plant root systems and higher soil permeability [39, 200]. Usually, the risk of nitrate leaching is low in wetland rice cultivation systems due to the formation of plough pans [26]. Appropriate irrigation promotes crop growth by increasing crop N uptake and fruitfully decreasing the N leaching loss potential. For example, Hahne et al. [59] recorded that fertilizer applied at an optimum rate and appropriate irrigation decreased leaching losses by 5–48%. Gheysari et al. [52] reported 25 kg/ha nitrate leaching loss from optimum irrigation, which was 47 kg/ha from a field with excessive irrigation. On the other hand, flood irrigation may cause drainage and increase the N leaching risk more than sprinkler irrigation.

When N fertilizers are applied above the optimum dose required for economic yield, a significant amount of N will be leached out due to excess nitrate in the soil solution [56]. Besides, higher N-fertilizer inputs, intensive crop cultivation, short life, or shallow roots of crops contribute to low NUE and increase the risk of nitrate leaching. In addition, higher nitrogen availability above crop uptake capacity or crop demand increases N leaching potential. On the other hand, the efficient N uptake mechanisms of the crops with an extensive rooting system decrease leaching loss. When the N uptake ability is high, the leaching loss potential in the soil-crop system will be lower.

Split application of N corresponding to the crop uptake potential significantly reduces nitrate leaching loss as it decreases the substrate concentration in the soil solution. For example, double or triple splits of N application increase N uptake efficiency considerably, leaving less nitrate in the soil through leaching than a single application [51, 195]. Liquid urea application allows fast hydrolysis and promotes NH_4^+ dispersion throughout the root zoon, thus decreasing the local NH_4^+ concentration and slowing the transformation to NO_3^-. This increases the uptake ability of the crop and reduces the leaching potential.

4.6 Denitrification

Denitrification is a very crucial process for N loss from a soil system. Under aquatic systems or anaerobic conditions, nitrate undergoes the denitrification process which is carried out by facultative denitrifies when oxygen availability is less than 0.50 mg/L [139]. The key requirements for denitrification are the availability of nitrate, lack of oxygen, and the presence of a continuous energy supply for the denitrifiers [18]. The denitrification rates are also influenced by soil pH and temperature [23, 201]. Denitrification occurs faster in neutral or slightly alkaline soils under water-saturated soil conditions at 25 °C. In acidic soil conditions ($pH < 4$) and low temperatures, the rate of denitrification is very low [21].

$$2NO_3^- \overset{\text{nitrate reductase}}{\rightarrow} 2NO_2^- \overset{\text{nitrite reductase}}{\rightarrow} 2NO \uparrow \overset{\text{nitric oxide reductase}}{\rightarrow} N_2O \uparrow \overset{\text{nitrous oxide reductase}}{\rightarrow} N_2 \uparrow . \tag{1}$$

During the denitrification process, nitrate (NO_3^-) is reduced to nitrite (NO_2^-), and later nitrite (NO_2^-) is reduced to nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2) (Eq. 1). Specific enzymes catalyze every step in the process. The first step is carried out by nitrate reductase and later nitrite reductase, nitric oxide reductase, and finally nitrous oxide reductase. In each step, the gaseous product may be emitted into the atmosphere or reduced again. The most significant part of the gas completes the whole reduction pathway by forming N_2. This process is fully anaerobic and microbes-driven [147, 165]. The N_2O emissions patterns are affected by N management patterns and soil texture. The single N application and low N uptake potential of the crop are liable for the most significant N_2O emission, whereas N application with irrigation water over the cropping season results in lower N_2O emission [105].

Clayey soil is more vulnerable to denitrification due to lower substrate movement and higher potential to be anaerobic. Besides, higher soil CEC repels nitrate to soil solution, therefore higher NO_3^- in the soil solution, which can undergo further denitrification under favorable conditions. Granular urea promotes higher denitrification resulting in about 23.8% higher N_2O loss due to rapid nitrification and about 5.3% yield loss compared to slow-released urea [154, 201]. Liquid urea (e.g., UAN) application reduced denitrification and decreased 27% nitrous oxide emission compared to granular urea fertilizer in corn cultivation. The higher local density of granular urea promoted higher nitrification and increased the nitrate concentration in the soil, thus, higher denitrification [60]. Split application of N fertilizers can increase the uptake capacity of crops, and the substrate concentration in soil solution for nitrification or denitrification can be minimized over a single application. Furthermore, the fast hydrolysis potential of the aqueous urea solution can lower the substrate concentration in the soil solution by dispersing inside the soil profile.

4.6.1 Factors affecting denitrification

The main prerequisites of microbial denitrification are the availability of nitrate, lack of oxygen, and source of organic energy for denitrifying microbes. Other factors include soil pH, temperature, nitrate concentration, presence of SOC, specific enzyme inhibitors, and water saturation [49, 95]. In addition, some of the other factors that affects the denitrification process indirectly are aquatic vegetation for OC source and the rate of nitrification which influences substrate concentration [70].

The main factors affecting denitrification are described below.

4.6.1.1 Nitrate (NO_3^-) concentration Higher nitrate content in the soil increases the rate of denitrification in submerged or saturated soils [1, 165]. The N application rate considerably increased the total N_2O emission from the soil by increasing substrate concentration and promoting the denitrification process [133, 161, 202].

Nitrate concentration in the soil can be reduced by applying coated urea, which mineralized slowly resulting in lower N_2O loss [98]. Overuse of N fertilizers initiates soil acidification which increases the rate of denitrification [181]. The concentration of NO_3^- in soil depends on NH_4^+ concentration and rate of nitrification. When the urea transformation processes are more frequent, the denitrification rate will be high, and N_2O emissions will be higher [84, 112, 169].

Clayey soil reduces substrate movement, increases local substrate concentration, and also increases the anaerobic potential of the soil, thus, increasing the denitrification rate. A side dressing of optimum N fertilizers and higher N uptake capacity of the crop reduces the substrate concentration in the soil. Split application of N fertilizers and fast hydrolysis of aqueous urea can decrease NO_3^- concentration in soil solution by decreasing $NH_4{}^+$ concentration and nitrification rate; therefore, the denitrification rate will be reduced.

4.6.1.2 Soil texture

Soil texture influences denitrification in the soil as the finer soil is more susceptible to oxides of N as it controls many soil physicochemical parameters affecting the rate of nitrification and denitrification. The clayey soil has a higher potential to be saturated by water, which speeds up denitrification and increases the gaseous emissions [108]. The higher CEC of clayey soil repels the nitrate ions in the soil solution, increasing its concentration and speeding up denitrification. Davidsson and Stahl [36] have recorded a higher denitrification rate in peat soil than in sandy loam soil. Poorly drained soil has a higher denitrification rate than well-drained soil due to its higher potential to be anaerobic. Besides, fertile soil has a higher denitrification rate due to higher substrate concentration than less-fertile soil [57]. Soil cultivation also influenced N_2O emissions by increasing the denitrification rate by increasing nitrification. The arable land emitted less N_2O because of lower carbon variability than grassland soil [108].

Liquid fertilizers (e.g., UAN) are easy-flowing in light-textured soil, with less potential for denitrification than in fine-textured soil. Besides, rapid substrate dispersion inside the soil layer (e.g., aqueous urea application) effectively decreases its concentration and thus, reduces the nitrification rate and eventually the denitrification. Split application of N fertilizers also lowers the risk of fast-increasing substrate concentration in soil than a basal or single application and, therefore, reduces the denitrification.

4.6.1.3 Soil pH

The rate of denitrification is significantly affected by soil pH. The denitrification rate is slow in acidic conditions (pH 3.6–4.8), very slow at pH < 4.1, and undetectable at the soil pH < 3.6. The faster rate of denitrification occurs at soil pH between 8.0 and 8.6, but N loss by denitrification will be non-significant at the soil pH < 5.0 [22]. Nitrous oxide production would be the main product of denitrification at pH 4.0 [95]. So, acidic soils with a pH of less than 5 have lower denitrification rates than typical agricultural soils having a pH of around 6 [66]. On the other hand, the low pH value reduces the transformation of N_2O to N_2, which increases N_2O concentration in soils [28].

The denitrification process increases soil pH, and the increased soil pH would increase the ratio of N_2O/N_2 emission [84, 149]. Furthermore, the increasing pH in the soil solution affects the N_2O to N_2 emission. Consequently, the acidic soil experiences a lower rate of denitrification [66, 149, 181]. The denitrification rate will be lower if nitrification remains lower and crop N uptake is vigorous, which lowers the substrate concentration in the soil solution. The split application of N fertilizers and instant dispersion of aqueous urea ensure lower substrate concentration in soil and decrease denitrification rate, thus improving the N uptake capacity of crops.

4.6.1.4 Soil OM content

Soil organic matter (OM) plays a significant role in the denitrification and emission of N_2O as it controls the microbial activity and population in the soil. The required organic carbon for microbial growth and activity is provided by the OM of soil [26]. The nitrous oxide emission relies on the microbial metabolism responsible for sustaining anaerobic conditions in soil [174]. The nitrate concentration and high moisture content in soils promote denitrification and emission of N_2O in the presence of sufficient OM in soil [148]. Soils with high OM content have a higher potential to have more nitrifying and denitrifying bacteria, which promote NH_4^+ transformation and N_2O emission. Nitrate denitrification, which is carried out by heterotrophic microbes, occurs when the organic compound is present for the growth of the microbes. Therefore, the quantity and nature of OM available in the soil are also crucial during denitrification. For example, the denitrification process is not detectable at low OM content but measurable after adding crop residues or glucose [21]. Furthermore, adding carbon sources such as glucose, methanol, sodium acetate, cellulose, starch, plant materials, and stover increases the denitrification rate under anaerobic conditions [165].

Clayey soils have a higher potential to hold higher moisture to be saturated and contain more OM than sandy soils. The higher moisture content decreases OM decomposition and preserves higher OM content in the soil. The denitrification rate will be lower when NO_3^- concentration is low, though there are optimum OM and availability of soil moisture. The lower nitrification rate decreases the NO_3^- concentration in soil solution. Fast urea hydrolysis and rapid dispersion of $NH_4{}^+$ inside the soil profile reduce the substrate concentration in the soil solution and, therefore, lower the nitrification and denitrification rates. Increased application frequency with lower dose N fertilizers also decreases the substrate concentration in soil solution, thus a lower denitrification rate.

4.6.1.5 Soil moisture content Soil moisture content is one of the driving factors of denitrification. Higher soil moisture content leads to poor aeration and makes the soil anaerobic, which promotes denitrification and increases N_2O emissions. On the other hand, higher precipitation carries the urea to the deep soil layer resulting in more NH_4^+ in the deep soil layer by the hydrolysed urea [207]. The denitrification rate will be faster, and the emission of N_2O will be higher in water-saturated soil than in soil with lower moisture content [12, 22, 53]. On the other hand, the increased denitrification rate decreases the N_2O/N_2 ratio in the soil. Denitrification is an enzyme-oriented process, and the enzyme synthesis is affected by oxygen, NO_3^- and NO_2^- concentration in soil solution. Therefore, it affects the denitrification rate and relative fraction of N_2O and N_2 formation [32, 119]. Increased soil moisture content increases the N_2O reductase in soil. A higher amount of N_2O reductase enzyme in the soil increases the denitrification rate but decreases the N_2O/N_2 ratio in soil solution [123]. The denitrification rate significantly increases while the soil moisture content exceeds the critical moisture level [92]. The denitrification rate increased sharply while 60% of soil pore space (PS) was filled by water and reached its maximum rate at 90% PS filled by water [42].

Clayey soil has a high moisture-holding capacity with a higher potential to be anaerobic and therefore has a high denitrification potential, thus having more N_2O emission than sandy soil. Furthermore, clayey soils possess poorly drainage conditions that increase denitrification potential than well-drained sandy soils. However, lower substrate availability reduces the rate of denitrification and lowers the emission of N_2O. If any urea fertilizer or application method modification can decrease the substrate concentration in soil, then the denitrification rate would be low and, thus, lower N_2O emission.

4.6.1.6 Soil temperature The denitrification rate is significantly affected by soil temperature. Higher soil temperature promotes the growth and metabolism of denitrifies which increases the denitrification process [153]. A suitable temperature range for denitrification is between 25 °C to 35 °C [17] and the denitrification rate increases with the increase in soil temperature. When the temperature increased from 6 °C to 21 °C, the denitrification rate increased 10 to 20-fold [135]. The denitrification rate is slow at < 4 °C, slower at < 2 °C, and very slow at 0 °C but continuing [41, 165]. At low to very low temperatures, a large amount of carbon substrate is required by the denitrifies to continue the denitrification process. The seasonal variation in soil temperature causes the rate of denitrification and the cumulative amount of N_2O emission to fluctuate [206]. Denitrification is affected more by the extreme temperature in non-irrigated dry soil than in irrigated soil [91].

Usually, light-textured soil maintains a relatively higher temperature than fine-textured soil, and light-textured soil has a lower potential to be anaerobic. Therefore, the denitrification rate in anaerobic light-textured soil will be higher than in fine-textured soil. The denitrifies activities increase with the increase of soil temperature, and the linear relation remains between the temperatures 4–25 °C. The rates of the enzymatic procedures increase with the rise of temperature if other factors such as substrate or moisture are not limited [138]. Therefore, the denitrification rate can be minimized by decreasing the substrate concentration in the soil solution. Liquid urea is an aqueous solution that decreases substrate concentration by distributing throughout the crop root zone, which may reduce the denitrification rate.

5 Conclusions

Urea is the common N source of the plant and plays an important role in ensuring world food security and it also has a significant contribution to the environmental disruption. The agricultural system is the primary source of greenhouse gas emission, and more than half of applied N to the soil as urea is lost through gaseous and leaching loss resulting in low NUE. The surface application of urea is the principal anthropogenic cause of gaseous emissions. Splits or aqueous watery urea solution application to soil may improve the soil N adsorption, plant uptake and reduce the possible risk of losses. Faulty application methods, excessive use, uneven distribution, seasonal variation, climatic interference, and edaphic factors promote loss of applied urea, which causes low NUE and increases the cost of crop production, and disruption of the natural ecosystem.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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