

Article

Persistent Ammonia Volatilization Under Conservation Tillage and Slow-Release Fertilization

Shichun Zhang ^{1,*} , Wanqi Guo ¹, Xiaofei Liu ¹, Aizhen Liang ^{2,*}, Weiwei Chen ³ , Hongmei Zhao ¹, Xuewen Chen ², Jing Fu ³ and Dandan Huang ²

¹ Research Center for Regional Development and Environment, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China; guowanqi25@mailsucas.ac.cn (W.G.); liuxiaofei_lxf123@163.com (X.L.)

² Key Laboratory of Black Soil Conservation and Utilization, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China; huangdandan@iga.ac.cn (D.H.)

³ Key Laboratory of Wetland Ecology, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China

* Correspondence: zhangshichun@iga.ac.cn (S.Z.); liangaizhen@iga.ac.cn (A.L.); Tel.: +86-0431-8554-2314 (S.Z.); Tel.: +86-0431-82536089 (A.L.)

Abstract

Ammonia (NH₃) emissions from fertilized cropland are influenced by conservation tillage practices, yet the underlying mechanisms remain insufficiently understood in the black soil region of northeastern China. In this study, field observations were conducted in a maize cropland to compare NH₃ volatilization under conventional tillage, no-tillage, and straw incorporating treatments following application of urea and slow-release fertilizer. Results showed that compared with conventional tillage, no-tillage-straw mulching (T1) and ridge tillage-straw mulching (T3) treatments significantly reduced soil temperature while increasing soil moisture and decreasing the estimated soil resistance to NH₃ transport. These changes were accompanied by higher NH₃ emission factors (EFs) in the T1 and T3 treatments, although differences in EFs among tillage treatments were not statistically significant. Compared with urea, slow-release fertilizer delayed the occurrence of peak NH₃ volatilization and reduced cumulative NH₃ emissions by approximately 54%. Notably, measurements under slow-release fertilizer application revealed that elevated NH₃ volatilization persisted for more than 40 days after fertilization, indicating that conventional monitoring periods may underestimate cumulative NH₃ losses in conservation tillage systems using slow-release fertilizers. Overall, conservation tillage substantially altered soil environmental conditions associated with NH₃ volatilization, while fertilizer types strongly influenced the temporal dynamics and magnitude of NH₃ emissions. These findings provide useful insights for improving NH₃ emission monitoring, process understanding, and inventory estimation in conservation tillage systems.

Keywords: conservation tillage; no-tillage; black soil; slow-release fertilizer; ammonia emission potential; ammonia compensation point



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1. Introduction

To meet the growing food demand, global nitrogen (N) fertilizer consumption has exceeded 110 Tg N a^{−1} and continues to increase [1]. The intensive application of N fertilizers has led to ammonia (NH₃) volatilization accounting for up to 65% of nitrogen loss from croplands [2], resulting in a global nitrogen use efficiency (NUE) of only about

40% [3]. Once released into the atmosphere, NH_3 contributes not only to air pollution [4,5], but also poses serious detrimental effects to sensitive ecosystems through dry and wet deposition [6]. Although not regularly regarded as a typical greenhouse gas species, NH_3 was referred to as the “next CO_2 ” because of its high global warming potential and its indirect influence on radiative forcing by participating in the formation of aerosols [7].

Ammonia in soil originates from multiple sources, including the mineralization of organic nitrogen, nitrogen fertilizer application, and ammonia oxidation-reduction processes, among which the hydrolysis of nitrogen in fertilizers is one of the primary pathways [8,9]. In soil, aqueous ammonium ions ($\text{NH}_4^+(\text{aq})$), aqueous dissolved ammonia ($\text{NH}_3(\text{aq})$) and gaseous ammonia ($\text{NH}_3(\text{g})$) exist in a dynamic equilibrium that is regulated by NH_4^+ concentration, NH_3 concentration, solution pH, and temperature [10,11]. Gaseous NH_3 subsequently diffuses through the soil pore space to the soil surface and is emitted into the atmosphere. The volatilization flux is primarily driven by the NH_3 concentration gradient between the soil surface and the overlying air [12], while being modulated by environmental factors such as soil temperature, moisture, pH, and wind speed [8]. Therefore, natural and anthropogenic factors, including climate, soil type, tillage, straw management, and fertilization practices, can alter soil properties and soil–atmosphere interface conditions, thereby regulating nitrogen transformation and NH_3 volatilization.

Compared with conventional tillage, conservation tillage reduces soil disturbance and increases surface residue cover, thereby modifying soil properties and soil surface microclimate. These changes can potentially influence NH_3 production, transport, and emission processes. However, only a limited number of studies have targeted conservation tillage conditions [13–16], and they have reported inconsistent conclusions regarding the effects of conservation tillage on NH_3 volatilization. For example, some studies suggest that straw incorporation or deep placement of nitrogen fertilizer can reduce NH_3 volatilization by decreasing soil pH or enhancing the adsorption capacity for NH_4^+ [13,17]. In contrast, a research reported that surface application of nitrogen fertilizer under no-tillage conditions is more prone to ammonia volatilization because of greater exposure of fertilizer-derived nitrogen at the soil surface [16]. Meta-analyses have also shown that, while no-tillage and straw incorporation can improve crop yield and nitrogen use efficiency, they may simultaneously increase NH_3 emissions [18]. Collectively, these contrasting findings suggest that the impacts of conservation tillage on NH_3 volatilization depend on complex interactions among soil conditions, management practices, and environmental factors.

The inconsistent conclusions largely stem from the fact that existing studies have primarily focused on the effects of individual management practices on specific nitrogen transformation processes or NH_3 emissions, while lacking an integrated understanding of the pathways linking conservation tillage, changes in soil properties, nitrogen transformation, soil–atmosphere interface conditions, and net NH_3 volatilization. Key quantities such as soil NH_3 emission potential, NH_3 compensation points, NH_3 fluxes and NH_3 emission factors remain difficult to quantify and predict accurately [10,19–23]. This limitation has become increasingly important with the incorporation of bidirectional NH_3 exchange and compensation point schemes into regional air quality models (e.g., WRF-CMAQ), which have substantially improved simulations of atmospheric NH_3 concentrations, deposition, and ammonium aerosol formation [24,25]. However, reliable application of these models is still hindered by the poor constraint and parameterization of key variables, particularly soil NH_3 emission potential and NH_3 compensation points [10,19,23,26].

Northeastern China contains one of the world’s four major black soil regions but experienced severe soil degradation due to decades of intensive cultivation. To address this issue, the Chinese government launched the Action Plan for Conservation Tillage in the Black Soil Region of Northeast China (2020–2025) in 2020 (State Council of China, 2020 [27]). Within

a short period from 2020 to 2022, conservation tillage technologies were promoted and applied across more than 13 million ha (State Council of China, 2022 [28]). The widespread adoption of conservation tillage is therefore likely altering NH_3 emission processes and their regional patterns by changing soil structure, microclimatic conditions, and nitrogen cycling. However, studies on NH_3 emissions in Northeast China have mainly focused on emission measurements and nitrogen use efficiency under traditional tillage practices, optimized fertilization strategies, and the application of urease inhibitors [29–39], and the limited number of studies investigating conservation tillage have reported inconsistent results [14,32,33,40], therefore the effects of conservation tillage on NH_3 emissions remain insufficiently understood. For example, Chen et al. [40] reported that maize straw mulching under no-tillage promoted the transformation of mineral nitrogen into immobilized and organic nitrogen pools, thereby improving nitrogen use efficiency and maize yield, while straw return combined with urease or nitrification inhibitors also reduced nitrogen leaching [41]. Based on a nine-year conservation tillage experiment in Lishu County in Northeast China, Zhao et al. [14] found that no-tillage and straw return significantly reduced NH_3 emissions and that urease and nitrification inhibitors further enhanced the mitigation effect. In contrast, Yan et al. [33] observed no significant differences in NH_3 volatilization losses among urea application, controlled-release fertilizer application, and straw return treatments in black soil maize fields. Furthermore, although conservation tillage is expected to modify soil NH_3 emission potential and NH_3 compensation points through its effects on soil properties and nitrogen cycling, investigations from these perspectives are still lacking in this region.

In this study, soil NH_3 emissions were measured in maize cropland located in a typical conservation tillage region in Changchun, northeastern China. The objectives of the study were to: (1) characterize NH_3 volatilization under different conservation tillage practices using urea and slow-release fertilizer in a comparative field experiment; (2) investigate factors associated with NH_3 volatilization under conservation tillage. The findings of this study can contribute to the evaluation of the overall impact of conservation tillage practices and support the development of soil NH_3 volatilization models.

2. Materials and Methods

2.1. Site Description

This experiment was conducted in 2021 at the Changchun Agro-Ecological Experimental Station (43°59'55" N, 125°24'01" E) of the Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, located in Changchun, China (Figure 1). The soil at the experimental site is classified as black soil (Mollisol). The plow layer contains organic matter content (SOC) of 17.08 g/kg, total nitrogen (TN) 1.45 g/kg, available phosphorus (AP) 17.6 mg/kg, and available K (AK) 120.1 mg/kg [42]. The site has a temperate continental monsoon climate, with an average annual precipitation of 550 mm and a mean annual temperature of 4.8 °C. Precipitation is mainly concentrated in June, July, and August.

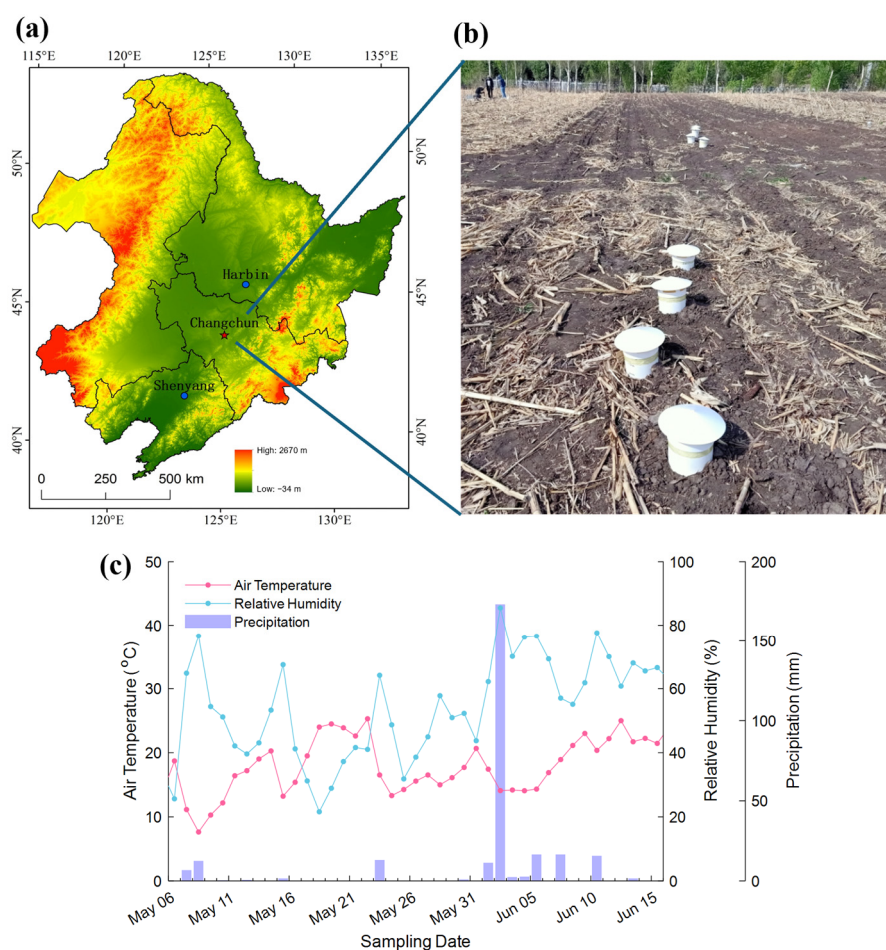


Figure 1. Location of the study site (a), layout of the PVC collectors in the experimental fields (b), and the daily variations in air temperature, relative humidity and precipitation during the field campaign (c). In panel (a), the red star indicates the study site, and the blue circles denote the other two major cities in the region.

2.2. Experimental Design and Treatments

The Changchun Agro-Ecological Experimental Station is a long-term experimental site for conservation tillage, encompassing ten treatment combinations of soil tillage, straw-mulching, and crop rotation. The experimental design follows a randomized complete block design with four replicates (i.e., four blocks). Four tillage treatments were established, including one conventional tillage treatment and three conservation tillage treatments: conventional tillage without straw incorporating (CK), no tillage with straw incorporating (T1), mouldboard plowing with straw incorporating (T2), and ridge tillage with straw incorporating (T3). All the four treatments were continuous maize cropping systems, differing only in soil tillage operations and straw-incorporating practices. These treatments were suitable for assessing differences in ammonia volatilization from fertilized soil under varying tillage systems and exploring their relationships with soil physicochemical properties.

In addition to tillage treatments, two types of fertilization, namely slow-release fertilizer and urea, were applied. A polymer-coated controlled-release compound fertilizer (25% N–8% P₂O₅–9% K₂O) was used as basal fertilizer and deeply applied at sowing with no additional fertilization during the growing season. A no-fertilizer control treatment (N0) was set up under the conventional tillage plots to quantify background soil NH₃ emissions.

Each treatment was replicated in four blocks, and the area of each plot was 5 m × 2.4 m. Detailed treatment codes and descriptions are provided in Table 1.

Table 1. Description of each treatment of the study.

Treatments	Tillage Type	Soil Manipulation	Straw Mulching	Fertilizer Type
N0 ¹	Conventional	Mouldboard Plow	Residual Removal	No Fertilizer
CK	Conventional	Mouldboard Plow ²	Residual Removal	Slow-Release Compound
T1	Conservation Tillage	No-Tillage	Straw Mulching	Slow-Release Compound
T2	Conservation Tillage	Mouldboard Plow	Straw Mulching	Slow-Release Compound
T3	Conservation Tillage	Ridge Tillage	Straw Mulching	Slow-Release Compound
CK-U	Conventional	Mouldboard Plow	Residual Removal	Urea
T1-U	Conservation Tillage	No-Tillage	Straw Mulching	Urea
T2-U	Conservation Tillage	Mouldboard Plow	Straw Mulching	Urea
T3-U	Conservation Tillage	Ridge Tillage	Straw Mulching	Urea

Note: ¹ N0 treatment was in the CK plots. ² Mouldboard Plow means approximately 20 cm deep fall moldboard plowing after maize harvest.

2.3. Measurement of Soil NH₃ Volatilization

Ammonia was collected using the ventilation method proposed by [43], which is suitable for controlled experiments at plot scales (Figure 1). Two circular sponge pads, each approximately 2 cm thick and 16 cm in diameter, after being rinsed in a phosphoric acid–glycerol solution were placed inside a PVC tube (16 cm in diameter and approximately 20 cm in height). The lower sponge was positioned 5 cm above the bottom of the PVC tube, while the upper sponge was near with the top of the tube. After a predefined exposure period (e.g., 1 or 3 days), the lower sponge was removed, immediately sealed in a plastic bag, and replaced with a freshly rinsed sponge. The upper sponge was replaced every 3–7 days depending on its moisture condition. All collected sponges were transported to the laboratory and stored in 500 mL plastic bottles for subsequent analysis.

The corn was sown on 6 May and the PVC tubes for ammonia collection were mounted in the afternoon of 7 May. Collection of the sponges was carried out on 9 May, 10 May, 12 May, 17 May, 25 May, 1 June, 8 June, and 15 June, respectively. For the slow-release fertilizer treatments, three PVC tubes were deployed within each plot (subplot) to account for within-plot spatial variability, and their measurements were averaged to represent a single observation per plot. For the urea treatments, one PVC tube was deployed per plot due to field operational constraints. In all cases, four replicated blocks were established, and the plot was treated as the experimental unit for statistical analysis.

To determine the amount of ammonia absorbed by the sponge samples, 300 mL of KCl solution was added to each plastic bottle containing field-collected sponges, ensuring the sponges were fully submerged. The bottles were shaken for 1 h, then allowed to settle. Once the soil-KCl suspension clarified, a portion of the supernatant was extracted and analyzed using a flow injection analyzer (TRAACS 2000, Bran & Luebbe, Norderstedt, Germany). If analysis could not be performed within 24 h, the suspension was filtered through filter paper and the filtrate was stored in a refrigerator for later analysis.

The daily ammonia flux (F_{daily} , kg N ha^{−1} d^{−1}), mean flux over the growing season (F_{mean} , kg N ha^{−1} d^{−1}), and cumulative ammonia volatilization (F_{cum} , kg N ha^{−1}) were calculated using the following equations:

$$F_{daily} = \frac{A_i \times 10000}{S \times D_i \times 0.99} \quad (1)$$

$$F_{mean} = \sum_{i=1}^n \left(\frac{A_i \times 10000}{S \times 0.99} \right) / \sum_{i=1}^n D_i \quad (2)$$

$$F_{cum} = \sum_{i=1}^n \left(\frac{A_i \times 10000}{S \times 0.99} \right) \quad (3)$$

where A_i is the amount of ammonia collected during the i th sampling (kg N), D_i is the corresponding sampling duration (days), S is the effective cross-sectional area of the collection device (m^2), and 0.99 is the ammonia recovery rate of the device [15,41].

2.4. Measurements of Soil Chemical and Physical Properties

Soil temperature and volumetric water content were measured using a Frequency Domain Reflectometry (FDR) sensor (FDS-200, Handan Development Zone Qing Yi Electronic Co., Ltd., Handan, China) during both the installation and collection of PVC tubes. Simultaneously, soil samples from a depth of 0–5 cm were collected using aluminum boxes ($5 \text{ cm} \times 5 \text{ cm} \times 3 \text{ cm}$) to determine volumetric and gravimetric water contents by weighing the samples before and after oven-drying at 105°C for 24 h.

Soil samples from the 0–5 cm depth across different plots were also collected to analyze ammonium (NH_4^+), nitrate (NO_3^-), and cation exchange capacity (CEC) under various treatments. After sieving and thorough mixing, 10 g of soil was extracted with 100 mL of 1 mol L^{-1} potassium chloride (KCl) solution. The mixture was shaken at 140 rpm for 1 h and then filtered through filter paper into vials. The concentrations of NH_4^+ , NO_3^- , and CEC were determined using a continuous flow analyzer (AutoAnalyzer 3, Seal Analytical Inc., Mequon, WI, USA).

In addition, 5 g of sieved soil was mixed with 25 mL of deionized water, and soil pH was measured using a pH meter.

2.5. Calculation of Soil Ammonia Emission Potential, Compensation Concentration and Soil Resistance

Soil NH_3 emission potential (Γ_s), defined as the molar ratio of dissolved ammonium ions (NH_4^+) to hydrogen ions (H^+), serves as a direct indicator of the dynamic equilibrium between NH_3 and NH_4^+ in the soil, thereby influencing ammonia volatilization. Based on the H^+ concentration derived from soil pH and the measured NH_4^+ concentration, Γ_s was calculated as follow [44].

$$\Gamma_s = \frac{[\text{NH}_4^+]}{[\text{H}^+]} \quad (4)$$

where $[\text{NH}_4^+]$ and $[\text{H}^+]$ are in $\mu\text{mol kg soil}^{-1}$.

The ammonia compensation points of soil (χ_c , μgm^{-3}) can be expressed as follow [23]:

$$\chi_c = \frac{A}{T} \cdot \Gamma_s \cdot \exp(-B/T) \quad (5)$$

where A and B are constants with values of 2.7457×10^{15} and 10,378, respectively, and T_s is the soil temperature (K).

Soil resistances (R_s , s m^{-1}) were calculated as

$$R_s = L/D \quad (6)$$

with

$$L = \frac{d_1}{e-1} \left[\exp \left\{ (1 - w_g/w_{sat})^{C_w} \right\} - 1 \right] \quad (7)$$

$$D = D_0 w_{sat}^2 \left(1 - \frac{w_{res}}{w_{sat}} \right)^{2+3b} \quad (8)$$

where L represents the estimated dry layer path length (m) as a function of relative soil water content. D is the reduced vapor diffusivity ($\text{m}^2 \text{s}^{-1}$) in the soil. The thickness of the top soil layer (d_1) is set to 1.75 cm. The parameter e is the base of the natural logarithm (≈ 2.71828), w_g and w_{sat} denote the volumetric water content and saturation volumetric

water content ($\text{m}^3 \text{m}^{-3}$) of the top soil layer, respectively. C_w is an empirical parameter that controls the concavity of the curve and is set to 5 to produce an exponential shape. D_0 is the molecular diffusion coefficient of water vapor in the atmosphere, which is fixed at $2.59 \times 10^{-5} \text{m}^2 \text{s}^{-1}$. The residual water content (w_{res}) is set to $0.01 \text{m}^3 \text{m}^{-3}$. The parameter b , representing the slope of the soil water retention curve, varies with soil texture and is assigned a value of 7.75 for silty clay loam, following Noilhan and Planton [45]. Further details can be found in Ran, et al. [46].

2.6. Statistical Analyses

Statistical analyses were performed using SPSS 26.0 (IBM Corp., Armonk, NY, USA). For the slow-release fertilizer treatments, three PVC collectors installed within each plot were treated as subsamples to account for within-plot spatial variability. Measurements from the three collectors were averaged to obtain a single plot-level value prior to statistical analysis. For the urea treatments, one PVC collector was installed per plot because the comparison between fertilizer types was not the primary objective of this study and the use of a single collector substantially reduced sampling effort and analytical costs.

In all cases, the plot (i.e., the replicate block) was considered the experimental unit, and four replicate blocks were used for each treatment. Therefore, four independent observations ($n = 4$) were used for statistical analyses. The no-fertilizer treatment (N0) was established only within the conventional tillage plots and served solely as a background reference; consequently, it was not included in statistical comparisons.

Because the primary objective of this study was to evaluate the effects of conservation tillage practices under each fertilizer regime, statistical analyses were conducted separately for the controlled-release fertilizer and urea treatments. One-way analysis of variance (ANOVA) was used to test differences among tillage treatments within each fertilizer type. When significant effects were detected ($p < 0.05$), treatment means were separated using Tukey's honestly significant difference (HSD) test.

3. Results

3.1. Dynamics of NH_3 Emission Flux and Cumulative NH_3 Emissions

Figure 2 shows the temporal dynamics of the soil NH_3 volatilization rate following the day of sowing and fertilization (6 May, denoted as d0; subsequent dates are denoted similarly). Although maize was sown as early as 6 May, the NH_3 volatilization rate was nearly zero during the first two sampling dates, 9 May (d3) and 10 May (d4) (Figure 2a, c). However, from 12 to 17 May, the volatilization rate increased sharply. For the slow-release fertilizer treatments (Figure 2a), the peak volatilization rate occurred on 26 May (d20), whereas for the urea treatments (Figure 2c), the peak appeared much earlier, between 12 and 17 May. In the urea treatments (Figure 2d), cumulative NH_3 emissions had largely stabilized by 15 June. In contrast, for the slow-release fertilizer treatments (Figure 2b), cumulative NH_3 emissions continued to increase throughout the observation period, indicating that appreciable NH_3 volatilization persisted for more than 40 days after fertilization.

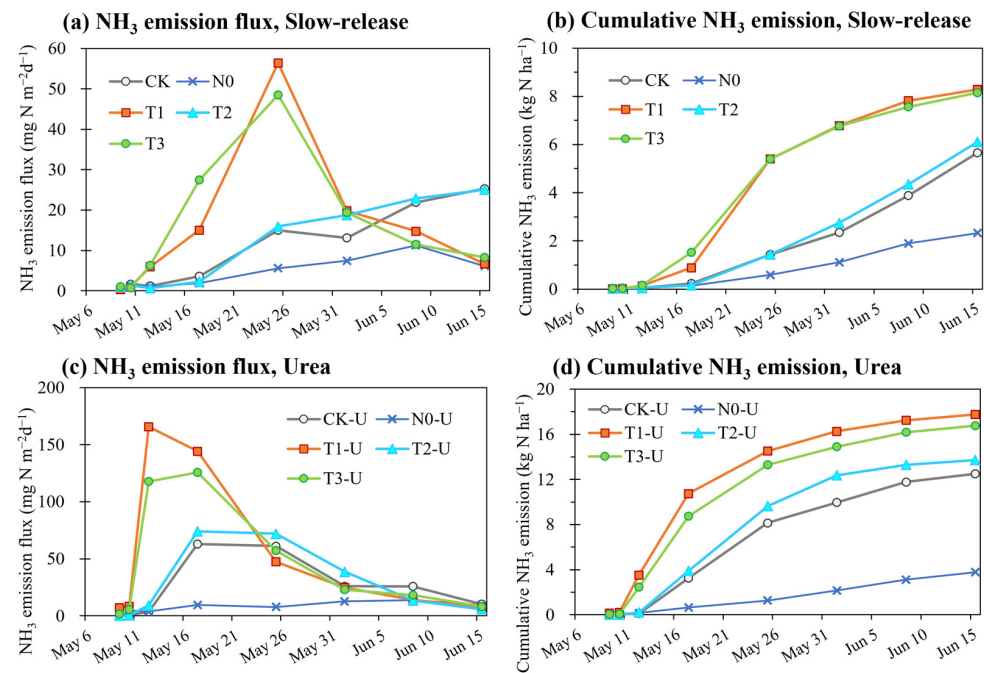


Figure 2. NH₃ emission flux rates for slow-release fertilizer (a) and urea (c), and cumulative NH₃ emissions for slow-release fertilizer (b) and urea (d) under different treatments over the sampling period.

3.2. Emission Factors

Figure 3 presents the NH₃ emission factors (EFs) under different tillage practices. Under both fertilizer types, the mean EFs of the conservation tillage treatments (T1, T2, T3 and their corresponding urea treatments T1-U, T2-U, T3-U) were generally numerically higher than those of the conventional tillage treatments (CK and CK-U). In particular, for the slow-release fertilizer treatments (Figure 3a), the EFs of the no-tillage with straw incorporating (T1) and ridge tillage with straw incorporating (T3) treatments exhibited the highest mean EFs among the four tillage treatments. However, one-way ANOVA followed by Tukey's HSD test indicated that the differences in EFs among the four major treatments (CK, T1, T2, and T3) were not statistically significant ($p > 0.05$). Therefore, these differences should be regarded as observed trends rather than statistically confirmed treatment effects.

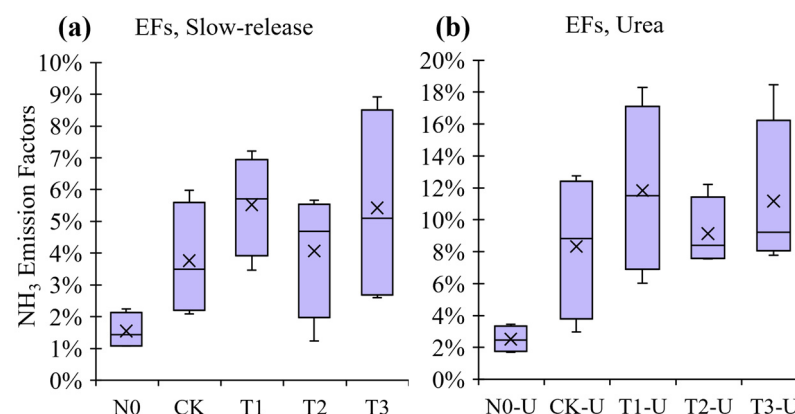


Figure 3. NH₃ emission factors under different treatments for slow-release fertilizer (a) and urea (b) applications over the sampling period. The box represents the interquartile range (IQR, 25th–75th percentiles), crosses represent arithmetic means, solid horizontal lines indicate medians, circles indicate individual non-outlier observations (inner points) displayed in the boxplots, and the whiskers extend to the most extreme observations within $1.5 \times \text{IQR}$.

4. Discussion

4.1. Factors Associated with Soil NH₃ Volatilization Under Conservation Tillage

As shown in Figures 2 and 3, the no tillage-straw mulching (T1) and ridge tillage-straw mulching (T3) treatments exhibited numerically higher NH₃ emissions and emission factors compared to conventional (CK) and mouldboard plow-straw mulching (T2) treatments. Although these differences in emission factors were not statistically significant (Table 2), they were accompanied by relatively higher NH₃ emission potentials (Figure 4a) and soil NH₄⁺-N concentrations (Table 2 and Figure 5b), suggesting that nitrogen availability may have contributed to the observed trends.

Interestingly, T1 and T3 exhibited numerically lower NH₃ compensation points (Figure 4b), significantly lower soil temperatures (Figure 5c) and slightly lower pH values (Figure 5a) than those for CK and T2, conditions that would generally be expected to suppress NH₃ volatilization. However, T1 and T3 treatments also showed noticeably higher soil water content (Figure 5d), and correspondingly lower soil resistance (Figure 5e). This combination suggests that enhanced gaseous transport under wetter soil conditions may have partly offset the inhibitory influences of lower temperature and pH, thereby contributing to the observed on NH₃ volatilization patterns.

Overall, conservation tillage altered several soil environmental variables associated with NH₃ volatilization, including soil temperature, soil moisture, soil resistance, and mineral nitrogen content (Table 2). In particular, two conservation tillage treatments (T1 and T3) exhibited soil temperatures approximately 3–5 °C lower, soil moisture contents about 5% higher, and estimated soil resistance values 53–57% lower than those under conventional tillage (CK). However, although the conservation tillage treatments generally showed a tendency of higher NH₃ emission factors than conventional tillage, these differences were not statistically significant in the present study.

Table 2. The cation exchange capacity (CEC), NH₄-N, NO₃-N, pH values, temperature (T_{soil}) and volumetric soil water content (VSW) of soils and NH₃ emission factors (EFs) under different treatments. Means followed by different lowercase letters indicate significant differences ($p < 0.05$, Tukey's HSD test) among tillage treatments within the same fertilizer type. Comparisons of letter groupings between the slow-release fertilizer and urea treatments are not applicable. The definitions of treatment abbreviations can be found in Table 1. Note the no-fertilizer treatment (N0) served solely as a background reference and consequently was not included in statistical comparisons.

Fertilizers	Treatments	CEC (cmol/kg)	NH ₄ -N (mg/kg)	NO ₃ -N (mg/kg)	pH	T _{soil} (°C)	VSW (%)	NH ₃ Emission Potential	NH ₃ Compensation Points (µg/m ³)	Soil Resistances (m/s)	EFs (%)
No Fertilizer	N0	26.3	13.1	20.5	6.58	22.3	14.5	777.7	4.54	679.7	1.6
Slow- release	CK	26.2	13.4 b	23.8	6.50	22.7 a	12.7 c	653.2	3.39	921.9 a	3.8
	T1	26.9	17.9 ab	29.7	6.43	17.3 c	18.2 a	787.4	2.44	430.2 b	5.5
	T2	26.4	12.7 b	20.1	6.56	22.5 a	13.1 bc	705.4	4.45	852.9 b	4.1
	T3	26.0	19.5 a	27.6	6.38	19.6 b	17.8 ab	756.9	2.84	399.2 b	5.4
Urea	CK-U	26.2	12.5 b	22.5	6.49	22.9 a	12.5 c	628.8 b	3.57	939.6 a	8.3
	T1-U	27.3	17.5 ab	28.2	6.42	17.5 c	18.2 a	914.9 ab	2.96	432.7 b	11.8
	T2-U	26.9	12.0 b	19.0	6.51	22.7 a	12.9 bc	623.9 b	3.65	880.9 ab	9.1
	T3-U	26.6	19.2 a	26.1	6.39	19.9 b	17.6 ab	1028.6 a	3.39	415.5 b	11.2

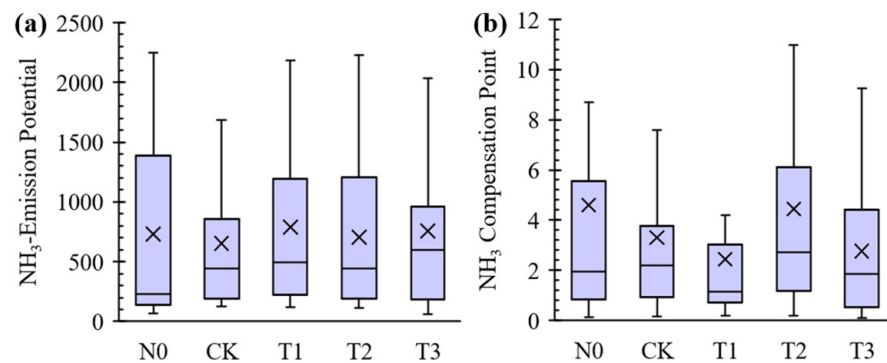


Figure 4. NH₃ emission potential (a) and compensation point (b) under different treatments for slow-release fertilizer applications. The box represents the interquartile range (IQR, 25th–75th percentiles), crosses represent arithmetic means, solid horizontal lines indicate medians, and the whiskers extend to the most extreme observations within $1.5 \times \text{IQR}$.

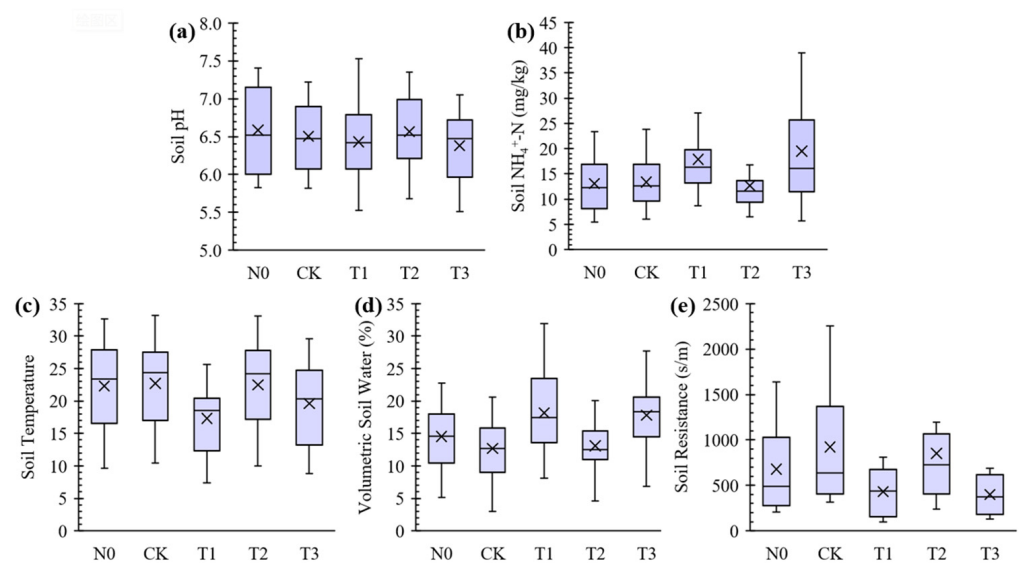


Figure 5. Soil pH (a), NH₄⁺ (b), temperature (c), volumetric water content (d) and resistance (e) for slow-release fertilizer applications. The box represents the interquartile range (IQR, 25th–75th percentiles), crosses represent arithmetic means, solid horizontal lines indicate medians, and the whiskers extend to the most extreme observations within $1.5 \times \text{IQR}$.

Several mechanisms proposed in previous studies may contribute to this pattern. First, no-till provides an undisturbed soil rhizosphere, reducing the likelihood of N fertilizer leaching into soil cracks [47], thereby retaining more N in the topsoil as a reservoir for NH₃ volatilization. Second, no-tillage with straw retention markedly increased soil water content in the topsoil compared to conventional tillage [48], substantially decreasing soil resistance to NH₃ volatilization. Third, no-till and/or straw-incorporating have been shown to increase urease activity by enhancing soil organic matter and providing a more stable environment for microorganisms [49,50]. Lastly, plant residues themselves may exhibit relatively high NH₃ emission potentials [51]. However, these mechanisms were not directly evaluated in the present study and therefore should be regarded as possible explanations rather than definitive conclusions.

The present results further illustrate the complexity of the effects of conservation tillage on NH₃ volatilization. Previous studies have reported contrasting responses of NH₃ emissions to conservation tillage practices. For instance, a meta-analysis study [18] reported that conservation agriculture overall decreases NH₃ emissions in maize systems, with straw-incorporating reducing emissions by 12% and no-till increasing them by only

2.4%. The mechanisms in those studies may involve higher carbonaceous substrates from straw promoting microbial assimilation of N [14], or lowered soil pH enhancing NH_4^+ adsorption [17]. These discrepancies likely reflect differences in site-specific conditions, such as soil properties, climatic properties, and residue management practices, and fertilizer placement methods. In the present study, conservation tillage significantly altered soil moisture, soil temperature, soil resistance, and mineral nitrogen availability, all of which are factors associated with NH_3 volatilization. The results therefore support the view that the net response of NH_3 emissions to conservation tillage depends on the combined influence of multiple interacting environmental and management factors, rather than on any single process alone.

4.2. Temporal Patterns of NH_3 Volatilization Under Slow-Release Fertilizer and Urea Application

Marked differences were observed in the temporal patterns of NH_3 volatilization between the slow-release fertilizer and urea treatments. Under the urea treatments, NH_3 volatilization rates increased rapidly after fertilization and reached their maximum values ($56.39 \text{ mg N m}^{-2} \text{ d}^{-1}$ for T1 treatment) 5 days after sowing. In contrast, For the slow-release fertilizer treatments, the peak NH_3 volatilization rates ($165.62 \text{ mg N m}^{-2} \text{ d}^{-1}$ for no-tillage T1 treatment) occurred much later, 18 days after sowing. This indicates that the slow-release fertilizer delayed the occurrence of peak NH_3 emissions and distributed nitrogen release over a longer period, resulting in a smoother the emission pattern that may better match the crop nitrogen demand.

Another notable finding was the prolonged duration of NH_3 emissions under the slow-release fertilizer treatments. For the urea fertilizer treatments, the cumulative volatilization of NH_3 stabilized at the end of the sampling period (d40), while for the slow-release fertilizer, the cumulative NH_3 emissions continued to increase, especially for the conventional (CK) and Mouldboard plow-straw mulching (T2) treatments (Figure 5). This result suggests that appreciable NH_3 volatilization persisted for more than 40 days after fertilizer application under slow-release fertilizer management. Such prolonged emissions imply that monitoring programs restricted to the first three or four weeks after fertilization may underestimate cumulative NH_3 losses from slow-release fertilizer systems. Therefore, longer observation periods may be necessary when quantifying NH_3 emissions, developing emission inventories, or evaluating mitigation strategies involving slow-release fertilizers.

The delayed emission peak observed in this study was more pronounced than that reported in previous studies. For example, Zhao's research [52] showed that the peak of NH_3 emission rates occurred 7 days later than conventional N fertilizers. The longer delay in the current study may related to the rain events and relatively low temperatures occurring shortly after sowing and fertilization (Figure 1), which could have slowed nitrogen release and NH_3 production during the early stages of the experiment.

In addition to altering the temporal pattern of emissions, slow-release fertilizer substantially reduced cumulative NH_3 losses. Our results show that the slow-release fertilizer treatment reduced as much as 54% of the accumulation NH_3 emissions as compared to the urea treatments. This reduction is likely attributable to the gradual release of nitrogen from the slow-release fertilizer, which better synchronizes nitrogen supply with crop demand and thus minimizes unnecessary nitrogen losses, thereby reducing NH_3 volatilization. The results here are consistent with those of other studies, for example, Zhao et al. [52] reported a reduction of 51% to 91% in accumulated NH_3 emissions from slow-release fertilizer as from urea and Hu et al. [53] reported a substantially lower NH_3 emission factor under subsurface application of slow-release fertilizer than under conventional fertilization practices.

4.3. Implications for Mitigating NH_3 Emissions

The present study showed that conservation tillage can substantially modify soil environmental conditions associated with NH_3 volatilization. Although no significant differences in emission factors were observed between conservation tillage and conventional tillage, no tillage straw-mulching treatment (T1) and ridge tillage-straw mulching (T3) showed significantly higher soil moisture, lower soil temperature, and reduced estimated soil resistance, creating conditions more favorable for NH_3 volatilization. This suggests that conservation tillage may alter the relative importance of environmental controls on NH_3 volatilization and should therefore be considered when developing agricultural NH_3 emission inventories and mitigation strategies.

Application of slow-release fertilizer resulted in 54% lower NH_3 emissions than urea and delayed the occurrence of peak emissions. These characteristics may help improve the synchronization between nitrogen release and crop nitrogen demand, thereby reducing the risk of rapid nitrogen loss following fertilization. Therefore replacement of urea with new generation of fertilizer should be recommended in order to get higher N use efficiency and lower N loss through soil volatilization and other path such as leakage. However, the prolonged NH_3 emission period observed under slow-release fertilizer application also suggests that monitoring periods should be sufficiently long to capture total NH_3 losses and avoid underestimation of cumulative emissions.

In addition to fertilizer type, fertilizer placement depth may represent an effective management option for mitigating NH_3 volatilization. In this study, the depth of fertilizer application is 5 to 10 cm, such depth helped reduce NH_3 volatilization. The research by Qiao et al. [35] also showed that NH_3 volatilization rates decreases as the depth of fertilizer application increases, with NH_3 loss from volatilization decreasing from 21.68% to 2.49% as the depth of N fertilization application from surface application to in-depth application at 9 cm. Collectively, these results suggest that combining slow-release fertilizers with appropriate fertilizer placement practices may provide an effective approach for reducing agricultural NH_3 emissions.

4.4. Limitations and Perspectives

Although clear differences in soil environmental conditions were observed among treatments, the differences in NH_3 emission factors among the treatments were not statistically significant. This may partly reflect the inherent spatial variability of field NH_3 emissions and the limited number of experimental replicates. Consequently, the present results should be interpreted as evidence of treatment-related trends rather than definitive proof of treatment effects. Additional multi-site and multi-year studies with larger sample sizes would help further evaluate the impacts of conservation tillage on NH_3 volatilization.

Another limitation is that NH_3 were measured within the PVC collectors, whereas the soil physiochemical properties were measured using the samples collected adjacent to, rather than within, the collectors. Although these measurements likely reflected similar environmental conditions, some uncertainty remains regarding the direct correspondence between the measured soil properties and NH_3 fluxes.

Besides, although long fragments (i.e., >10 cm) of returned straw were present in the field, only shorter straw pieces (i.e., <10 cm) could be covered within the PVC collectors. Therefore the whole influences of returned straw on soil NH_3 volatilization may not have been fully captured. In the future, other open style measurements methods, i.e., micrometerological methods, or larger chambers, should be used to strengthen the reliability regarding the mechanisms underlying soil NH_3 volatilization.

The prolonged NH_3 emissions observed under the slow-release fertilizer treatments also suggest a limitation of the current monitoring period. Under the slow-release fertilizer

and mouldboard plow (CK and T2), the NH_3 volatilization still remained elevated after 40 days after sowing, indicating that cumulative emissions may have been underestimated. Future studies should therefore extend monitoring periods when evaluating NH_3 emissions from slow-release fertilizer systems.

Furthermore, NH_3 volatilization represents only one pathway of nitrogen loss. Previous studies in northeastern China have reported trade-offs between NH_3 and N_2O emissions under conservation tillage and straw-returning practices [32,54]. Therefore, future research should simultaneously evaluate multiple nitrogen loss pathways, including NH_3 volatilization, N_2O emissions, nitrate leaching, and crop nitrogen uptake, to provide a more comprehensive assessment of the environmental consequences of conservation tillage.

Finally, this study was conducted in a typical black soil (mollisol) region characterized by enrich organic matter. However, in the current study, the related variables such as SOC, soil organic matter, and soil aggregate were not measured. These factors may influence nitrogen transformation and NH_3 volatilization and should be incorporated into future studies to improve understanding of the mechanisms underlying NH_3 emissions under conservation tillage.

5. Conclusions

This study evaluated NH_3 volatilization from fertilized soil under different conservation tillage practices and fertilizer types in a typical black soil region, northeastern China. The objectives were to characterize NH_3 volatilization under conservation tillage, compare NH_3 emission patterns between slow-release fertilizer and urea, and identify factors associated with NH_3 volatilization.

The results showed that although NH_3 emission factors under conservation tillage treatments were generally higher than those under conventional tillage, the differences among tillage treatments were not statistically significant. Nevertheless, conservation tillage significantly altered several soil environmental variables associated with NH_3 volatilization. Compared with conventional tillage, the no tillage-straw mulching (T1) and ridge tillage-straw mulching treatments (T3) exhibited soil temperatures approximately 3–5 °C lower, soil moisture about 5% higher, and estimated soil resistance values 53–57% lower than those under conventional tillage (CK).

Marked differences were observed between slow-release fertilizer and urea applications. Compared with urea, slow-release fertilizer delayed the occurrence of peak NH_3 volatilization and reduced cumulative NH_3 emissions by approximately 54%. More importantly, appreciable NH_3 volatilization persisted for more than 40 days after fertilization under the slow-release fertilizer treatments, indicating that short-term monitoring may underestimate cumulative NH_3 losses from such systems.

Overall, the results suggest that both tillage practices and fertilizer type can influence soil environmental conditions and NH_3 emission dynamics. The prolonged NH_3 emission period observed under slow-release fertilizer application highlights the importance of extended monitoring periods when quantifying agricultural NH_3 emissions. Future studies should further evaluate conservation tillage effects using larger sample sizes, longer observation periods, and more comprehensive measurements of nitrogen transformation processes and multiple nitrogen loss pathways.

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