frontiers | Frontiers in Soil Science

TYPE Original Research
PUBLISHED 26 January 2026
DOI 10.3389/fsoil.2026.1746042

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OPEN ACCESS

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RECEIVED 14 November 2025
REVISED 31 December 2025
ACCEPTED 02 January 2026
PUBLISHED 26 January 2026

CITATION
Zong H, Zou P, Sun Y, Li J, Wang C and Zheng W (2026) Controlled-release urea reduces nitrogen fertilizer-induced proton release: a column experiment. *Front. Soil Sci.* 6:1746042. doi: 10.3389/fsoil.2026.1746042

Controlled-release urea reduces nitrogen fertilizer-induced proton release: a column experiment

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Nitrogen (N) fertilization is a major driver of soil acidification, yet quantitative evidence on how controlled-release urea (CRU) alters H^+ production (H_{pro}) pathways remains limited. We conducted a 90-day soil column experiment using a calcareous fluvo-aquic soil collected from a 14-year long-term field site. Five treatments were established with four replicates: no N (CK), full- and high-rate CRU (CRF1 and CRF2), and full- and high-rate conventional urea (BBF1 and BBF2). Leachates were collected on days 7, 30, 60 and 90 and analyzed for inorganic N, major cations and anions. The H_{pro} was quantified using an input-output balance approach by separating the N-cycle component (associated with net NO_3^- export) and the carbonate-related C-cycle component (associated with net HCO_3^- export). Compared with conventional urea at the same N rate, CRU reduced cumulative NO_3^- leaching by 54.17% (CRF1 vs. BBF1) and 44.93% (CRF2 vs. BBF2), accompanied by lower base-cation losses. Total H_{pro} over 90 days decreased by 42.47% (CRF1 vs. BBF1) and 33.66% (CRF2 vs. BBF2). These results indicate that CRU mitigates fertilizer-induced acidification potential mainly by moderating nitrification-driven NO_3^- losses and associated charge-balanced cation leaching, thereby lowering the net H^+ load exported from the soil profile.

KEYWORDS

base cations, controlled-release urea, fertilization, proton generation, soil acidification

1 Introduction

Nitrogen fertilizers are extensively used in modern agriculture to sustain crop production. In 2017, China's croplands accounted for ~9% of the world's agricultural land but consumed ~30% of global N fertilizers (1). Excessive N inputs can disrupt elemental cycling and trigger multiple environmental problems, including eutrophication of water bodies (2) and increased N_2O emissions that enhance global warming potential (3). In addition, intensive N fertilization is widely recognized as a key driver of soil acidification across ecosystems and regions (4, 5).

In agroecosystems, fertilizer-induced soil acidification is closely linked to N transformations and N losses. Nitrification of fertilizer-derived NH_4^+ releases H^+, and when NO_3^- is not fully taken up by crops, it tends to accumulate and leach, often accompanied by the loss of base cations; this combined process increases the net H^+ load and reduces soil acid neutralizing capacity (ANC) (6). Long-term experiments and meta-analyses have consistently shown that N additions lower soil pH and promote base-cation depletion and NO_3^- leaching (7, 8). In calcareous soils, acid inputs may not immediately translate into large pH declines because carbonate buffering consumes H^+, but this buffering can drive carbonate dissolution, increase bicarbonate (HCO_3^-) export, and potentially accelerate losses of soil inorganic C (9, 10). Recent syntheses on urea behavior further emphasize that urea management strongly regulates nitrification intensity and NO_3^- leaching risk in soil-plant systems (11).

Because soil pH alone does not fully reflect the magnitude or sources of acidity-particularly in buffered calcareous soils-quantitative frameworks are needed to partition and compare acidification drivers (12). The H^+ accounting and element-budget approaches quantify acidification as the net balance of H^+-producing and H^+-consuming processes and link soil acidity change to charge-balanced fluxes of cations and anions (13). Simplified H^+ budgets for the N cycle can be constructed from external inputs of NH_4^+ and NO_3^- and their leaching outputs, without explicitly tracking each intermediate N transformation pathway. Such H^+-budget approaches have also been applied to diagnose acidification drivers across land uses and fertilized systems (14, 15). However, quantitative evidence remains limited regarding how fertilizer formulation (e.g., controlled-release vs. conventional urea) shifts the relative contributions of N-cycle and carbonate-related processes to net H^+ production (H_{pro}) and export in calcareous croplands.

Controlled-release fertilizers, especially controlled-release urea (CRU), are designed to synchronize N release with crop demand and thereby reduce N losses; recent reviews summarize rapid advances in controlled-release fertilizer technologies and their environmental implications (16). Nevertheless, most studies on CRU focus on yield, N use efficiency, or N loss pathways, while H^+-budget-based quantification of acidification potential remains scarce. We hypothesize that the slow-release pattern of CRU alters N transformation dynamics, moderates NO_3^- leaching and associated base-cation losses, and consequently reduces net H_{pro} compared with conventional urea at the same N rate. Therefore, using a laboratory soil-column experiment with calcareous fluvo-aquic soil, we aimed to (i) quantify H_{pro} associated with major substance-cycling processes under different fertilizer types and N rates, (ii) elucidate post-fertilization processes by analyzing soil-solution composition and elemental/ionic relationships, and (iii) determine how increasing N application enhances cation leaching and its coupling with NO_3^- export.

2 Materials and methods

2.1 Materials

This experiment is an extension of a long-term study on the evolution of fluvo-aquic soil fertility and the effects of different fertilization strategies, started in June 2008. The study is located in Huantai County, Shandong Province, China (117°59′21″E, 36°57′75″N). The region is characterized by a temperate continental monsoon climate, with an average annual temperature of 13.2°C and an annual average precipitation of 615.1 mm. The soil at the experimental site is fluvo-aquic soil, classified in the Chinese soil taxonomy system as Calcaric Ochr-Aquic Cambosols. The soil texture is classified as loamy soil, consisting of 14.03% clay particles, 12.49% sand particles, and 73.48% silt particles. The soil collection area was situated in a long-term fixed-position trial zone where N fertilizer had been omitted. Fertilization included the application of calcium superphosphate (16% P_2O_5) and potassium sulfate (50% K_2O). Before soil collection, the site had undergone 14 years of wheat-maize cropping, covering 28 crop cycles. Detailed information on the site and its management has been previously described by Zheng et al. (17). Soil samples were collected during the maize harvest season of 2022. Surface soil from the collection area was gathered using a soil auger and then thoroughly mixed. After removing roots, litter, and stones, the soil was sieved through a 2 mm mesh. The CRU used in this experiment was prepared by blending polymer coated urea (43% N) and polymer coatings of sulfur-coated urea (35% N) in a ratio of 5:2 based on N content, with a designed nutrient release period of 120 days. The specific nutrient release characteristic has been previously described by Zheng et al. (17). The CRU was manufactured by the National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources at Shandong Agricultural University, China. Other fertilizers used in the trial were uncoated, large granule urea.

2.2 Leaching experiment

Soil was packed into acid-washed PVC columns (Height = 43 cm, Diameter = 7 cm) at a bulk density of 1.2 $g{\cdot}cm^{-3}$, forming a 40 cm soil layer. The top of the soil columns was covered with perforated tin foil to keep darkness and allow airflow, while the bottom was filled with 120 g of quartz sand, wrapped in a nylon net with 0.2 mm pore size to prevent soil loss. These soil columns were then mounted on funnels connected to plastic bottles (Figure 1). The soil characteristics prior to the commencement of the experiment are summarized in Table 1.

The experiment consisted of five treatments, encompassing two types of fertilizers and two different application rates, with the application rates consistent with the annual fertilization levels used in field trials. The specific treatments were as follows: CK (non-N fertilized), CRF1 (CRU, 540 $kg{\cdot}hm^{-2}$), CRF2 (CRU, 810 $kg{\cdot}hm^{-2}$), BBF1 (conventional urea, 540 $kg{\cdot}hm^{-2}$), BBF2 (conventional urea, 810 $kg{\cdot}hm^{-2}$). Each treatment was implemented in four replicated soil columns.

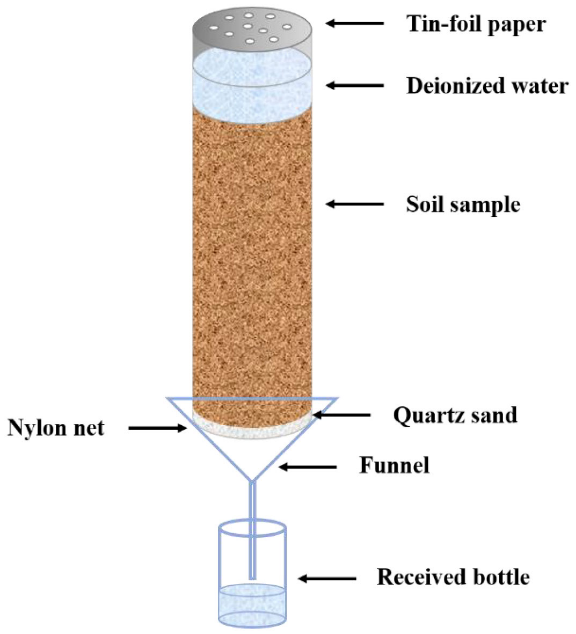

FIGURE 1
Soil column devices with an exploded diagram.

During the experiment, the interior of the soil columns was kept dark, and the leaching experiments were conducted at room temperature (25 ± 2°C). Following the filling of the soil columns, the soil moisture content was adjusted to field capacity using deionized water and maintained for 7 days before the addition of fertilizers. The fertilizers were applied in a localized manner at the center of the soil. The leaching phase of the experiment started 7 days after fertilization and continued with additional leaching events on the 30, 60, and 90 days. For each leaching event, a total of 200 mL deionized water was applied manually using a graduated cylinder in four successive aliquots (50 mL each). The next 50 mL aliquot was applied only after the previous aliquot had infiltrated. A piece of moistened filter paper was placed on the soil surface during water application to avoid disturbing the surface soil. Leachate was collected continuously after water addition and the collection was stopped when drainage ceased (i.e., no further droplets were observed).

TABLE 1 Chemical characteristics of the sampled soils.

Parameter	Units	Value
pH	–	8.35
Total N	$g{\cdot}kg^{-1}$	0.81
Organic Matter	$g{\cdot}kg^{-1}$	18.30
NO_3^--N	$mg{\cdot}kg^{-1}$	5.00
NH_4^+-N	$mg{\cdot}kg^{-1}$	4.10
Available Phosphorus	$mg{\cdot}kg^{-1}$	9.20
Available Potassium	$mg{\cdot}kg^{-1}$	112.50
Exchangeable Calcium	$cmol{\cdot}kg^{-1}$	17.89
Exchangeable Magnesium	$cmol{\cdot}kg^{-1}$	5.55
Exchangeable Potassium	$cmol{\cdot}kg^{-1}$	1.27
Exchangeable Sodium	$cmol{\cdot}kg^{-1}$	0.17
CEC	$cmol{\cdot}kg^{-1}$	24.88
$CaCO_3$	$g{\cdot}kg^{-1}$	9.08

2.3 Sampling and measurement

The collected leachate samples were stored at -20°C in the dark after adding 1 ml of chloroform and passing through a 0.45µm nitrocellulose filter. NO_3^-N and NH_4^+-N in the leachate were measured using ultraviolet spectrophotometry (UV2600, Shimadzu, Japan). The major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) were determined by inductively coupled plasma emission spectroscopy (ICAP7000, Thermo Fisher, USA), and the major anions (F^-, Cl^-, SO_4^{2-}) were quantified using ion chromatography (Dionex Aquion, Thermo Fisher, USA). HCO_3^- concentration was decided by acid titration.

2.4 Data evaluation

The acidity budget was calculated by summing the processes that produce H^+, such as fertilizer input and N transformations (14). The total H_{pro} was computed as follows:

$$H_{pro} = H_{pro,N} + H_{pro,HCO3} \tag{1}$$

$$H_{pro,N} = NH_4{}^+{}_{in} - NH_4{}^+{}_{less} + NO_3{}^-{}_{less} - NO_3{}^-{}_{in} \tag{2}$$

$$H_{pro,HCO3} = HCO_3{}^-{}_{less} - HCO_3{}^-{}_{in} \tag{3}$$

Where $H_{pro,\ N}$ represents the H^+ produced during N transformation processes, and $H_{pro,HCO3}$ is the H^+ produced from the net leaching of HCO_3^-. “in” denotes the input of elements, and “less” signifies the output of elements.

2.5 Statistical analysis

The column experiment was arranged as a completely randomized design with five treatments and four replicates. Data processing was performed using Microsoft Excel 2019 (Microsoft Inc., Redmond, WA, USA). For time-series variables measured at each leaching event (days 7, 30, 60, and 90), differences among treatments were tested using one-way analysis of variance (ANOVA) separately for each leaching event. Cumulative leaching amounts and calculated H_{pro} variables were analyzed using one-way ANOVA. When treatment effects were significant, mean separation was performed using Duncan’s multiple range test at $P< 0.05$. Statistical analyses were conducted using IBM SPSS Statistics 26 (IBM Corp., Armonk, NY, USA). Graphs were generated using GraphPad Prism version 10.0.2 (GraphPad Software, Boston, MA, USA).

3 Results

3.1 N leaching dynamics

In the four leaching events, the NO_3^- concentrations in the five treated leachates generally showed an increasing trend, while NH_4^+ concentrations exhibited a decreasing trend. However, the patterns of change varied among different treatments. The range of NO_3^- concentration in the leachate was from 19.73 mg·L^{-1} to 960.25 mg·L^{-1}, and that of NH_4^+ was between 0.02 mg·L^{-1} and 0.58 mg·L^{-1}. The CK treatment columns experienced the slightest variation in NO_3^- concentration, while the BBF2 treatment columns showed the most significant change. During the four leaching events, the most remarkable difference in NO_3^- concentration among treatments occurred in the fourth leach, with the concentration in the conventional urea leaching being significantly higher than that in the CRU treatments. The concentration in the BBF2 treatment columns was the highest, reaching 960.25 mg·L^{-1}, which is an increase of 189.55% compared to the CRF2 treatment columns, and the BBF1 treatment columns showed an increase of 192.27% compared to the CRF1 treatment columns. The first leaching event showed the highest NH_4^+ concentration among different treatments, although the differences were not significant except for the CRF2 treatment columns.

3.2 Cations leaching dynamics

The leachates had predominantly Ca^{2+} and Na^+ cations. The concentration of leached cations was significantly higher in the N-fertilized columns compared to the CK columns. The fourth leaching event showed the most pronounced difference in cation leaching across different treatment columns. The leaching characteristics of different cations varied. The concentration of Ca^{2+} in the leachates increased during the leaching events, peaking in the fourth leaching (Figure 2a). The CK treatment had

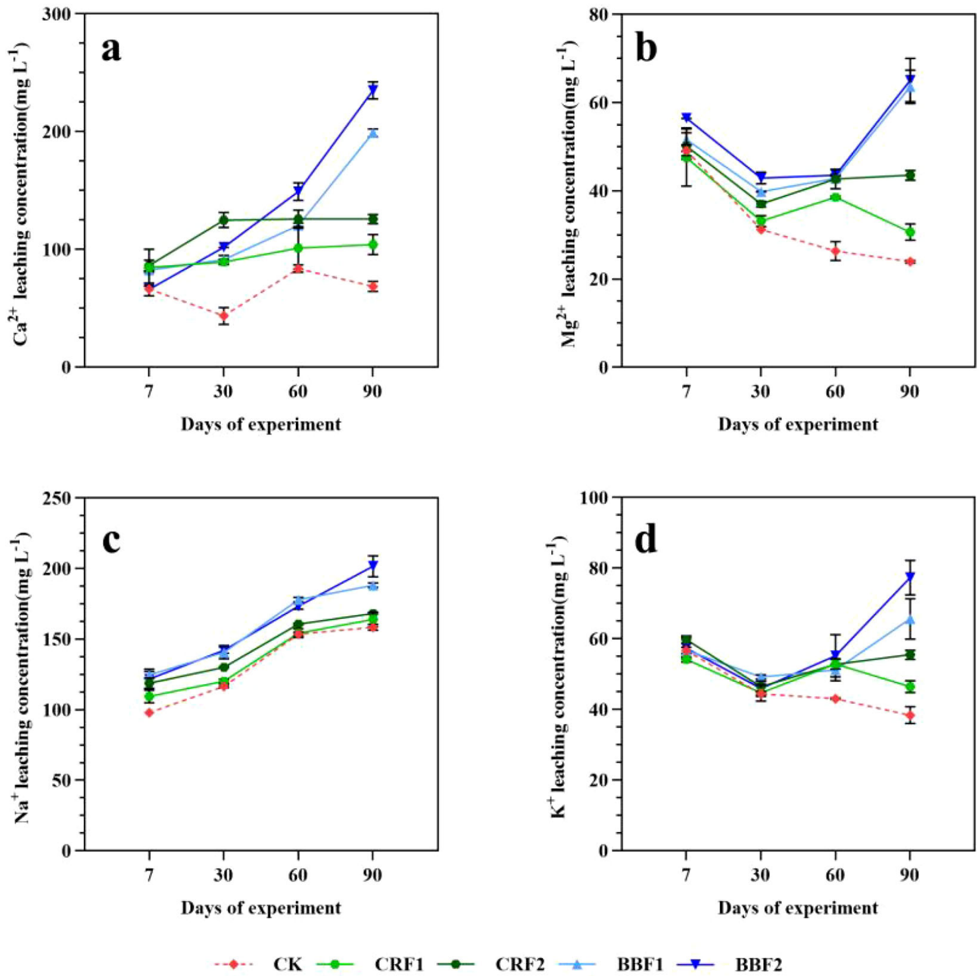

FIGURE 2
Changes in the concentration of BC (Ca^{2+}、Mg^{2+}、Na^+、K^+) over time and cumulative leaching under different fertilization treatments. **(a)** Concentration of Ca^{2+} leaching under various under different fertilization treatments; **(b)** Concentration of Mg^{2+} leaching under different fertilization treatments; **(c)** Concentration of Na^+ leaching under different fertilization treatments; **(d)** Concentration of K^+ leaching under different fertilization treatments. Values are means ± SD.

lower leaching amounts than the N treatments in the first three leaching events, but the leaching concentration characteristics of the N treatments were inconsistent. In the fourth leaching event, the concentration of Ca^{2+} ions were higher in the conventional urea treatment compared to the CRU treatment, and it increased with the amount of N applied. The concentration of Mg^{2+} ions in the leachate decreased and then increased (Figure 2b). This change was clear in the first and second leaching events in the CK treatment. During the four leaching events in the N treatments, the concentration of Mg^{2+} ions was higher in the conventional urea treatment than in the CRU treatment. It increased with the amount of N applied. The concentration of Na^{+} ions in the leachate gradually increased throughout the four leaching events, with the conventional urea treatment exceeding the CRU treatment (Figure 2c). The concentration of K^{+} ions in the leachate varied among treatments (Figure 2d). In the CK treatment, the ion concentration decreased during the leaching process, while in the N treatments, it initially decreased and then increased. Similarly, in the fourth leaching event, the ion concentration in the conventional urea treatment was higher than in the CRU treatment.

3.3 Anions leaching dynamics

The SO_4^{2-} and HCO_3^- were the primary anions found in all leachates, each exhibiting distinct leaching characteristics. The F^- concentration in the CK treatment columns was the highest during all four leaching events, increasing as leaching progressed and reaching its peak in the fourth event (Figure 3a). The CRF1 treatment columns had higher F^- concentrations in the N treatments than in the other treatments, peaking in the second leaching event. The Cl^- concentrations were highest in the first leaching event for all N treatment columns. The concentration initially decreased and then increased as the leaching process progressed. In contrast, the concentration decreased over time in the CK treatment columns (Figure 3b). The BBF1 treatment

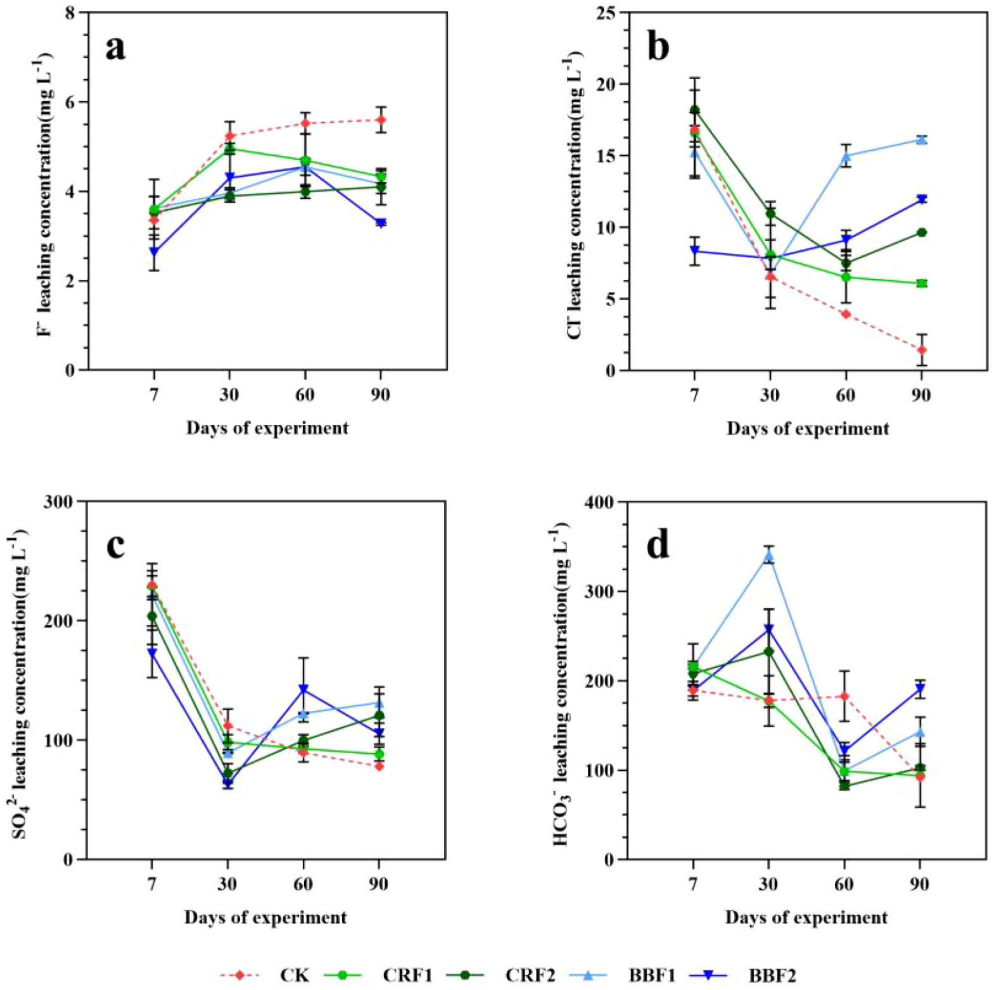

FIGURE 3
Changes in leachate concentrations of anions (F^-、Cl^-、HCO_3^-、SO_4^{2-}) over time under different fertilization treatments. **(a)** Concentration of F^- leaching under different fertilization treatments ; **(b)** Concentration of Cl^- leaching under different fertilization treatments; **(c)** Concentration of HCO_3^- leaching under different fertilization treatments; **(d)** Concentration of SO_4^{2-} leaching under different fertilization treatments. Values are means ± SD.

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columns showed the most significant changes throughout the cultivation period. The HCO_3^- concentration peaked in the CK treatment columns during the third leaching event. In contrast, the N treatment columns peaked during the second leaching event and showed significant differences. The concentration in conventional urea treatment columns was higher than in CRU treatment columns, with the most notable changes saw in the BBF1 treatment columns (Figure 3c). The SO_4^{2-} concentration peaked in the first leaching event in all treatment columns. Over time, the concentrations in the CK and CRF1 treatment columns decreased. The CRF2 and BBF1 treatment columns initially decreased and then increased. The BBF2 treatment columns experienced continuous fluctuations in SO_4^{2-} concentration (Figure 3d).

3.4 Element leaching intensity

Table 2 shows the cumulative leaching amounts of various ions in the leachates from different fertilization treatments. Throughout the cultivation period, leaching was predominantly composed of NO_3^-, ranging from 17.50 to 158.36 mg. The total leaching amount of NH_4^+ was significantly lower than that of NO_3^-, ranging between 0.10 and 0.13 mg. The CK treatment showed the lowest total NO_3^- leaching, while the fertilized treatments had significantly higher NO_3^- leaching than the CK treatment. The BBF2 treatment had the highest leaching amount, with an increase of 81.58% compared to the CRF2 treatment. The leaching amount in the BBF1 treatment increased by 118.18% compared to the CRF1 treatment. The differences in total NH_4^+ leaching among the treatments were not significant. The leaching flux of soil cations ranged from 132.28 to 196.23 mg. The CRF2 treatment showed a 12.04% increase over the CRF1 treatment, while the BBF2 treatment showed an 8.18% increase compared to the BBF1 treatment.

The different fertilization treatments affected the leaching amounts of base cations. The BBF1 treatment showed a 21.21% increase in leaching over the CRF1 treatment at the same N application rate, and the BBF2 treatment showed a 14.4% increase over the CRF2 treatment.

The leaching of F^- and Cl^- ions was influenced by different fertilization treatments and the amount of N applied. At the same fertilization level, the BBF1 treatment showed a 7.65% reduction in F^- ions compared to the CRF1 treatment, while Cl^- ions increased by 42.41%. Similarly, the BBF2 treatment showed a 5.08% decrease in F- ions compared to the CRF2 treatment, while Cl^- ions decreased by 24.38%. The leaching of HCO_3^- and SO_4^{2-} ions was influenced by different fertilization treatments, with conventional urea treatments resulting in higher leaching than CRU treatments. Compared to the CRF1 treatment, the BBF1 treatment showed an 11.13% increase in SO_4^{2-} ions and a 36.29% increase in HCO_3^- ions. Similarly, the BBF2 treatment showed a non-significant decrease of 2.97% in SO_4^{2-} ions compared to the CRF2 treatment but a significant increase of 16.47% in HCO_3^- ions.

3.5 Elemental input-output budget

The output of NO_3^- in the leachate showed a significant linear relationship with the amount of fertilizer applied. The columns treated with CRU and conventional urea showed a significant increase in NO_3^- output as the N application rate increased (P < 0.05, Figure 4). The highest NO_3^- outputs for both CRU and conventional urea treatment columns were seen at a fertilization rate of 810 kg·hm^{-2}, reaching 87.21 mg and 158.36 mg, respectively. The experiment resulted in outputs of 540 kg·hm^{-2} and 0 kg·hm^{-2} fertilization rates. The NH_4^+ output in the leachate from different

TABLE 2 Variations in leachate composition under different fertilization treatments.

(a) Inorganic N and base cations							
Treatments	NO_3^- (mg)	NH_4^+ (mg)	Ca^{2+} (mg)	Mg^{2+} (mg)	K^+ (mg)	Na^+ (mg)	BC (mg)
CK	17.50 ± 1.56 e	0.12 ± 0.01 a	31.48 ± 0.64 d	15.69 ± 0.17 e	21.92 ± 0.27 e	63.20 ± 0.60 d	132.28 ± 0.81 e
CRF1	61.32 ± 4.74 d	0.11 ± 0.00 a	45.50 ± 4.07 c	17.99 ± 0.53 d	23.78 ± 0.44 d	65.77 ± 0.62 c	153.04 ± 3.65 d
CRF2	87.21 ± 1.23 c	0.10 ± 0.01 a	55.54 ± 1.12 b	20.81 ± 0.47 c	25.75 ± 0.17 c	69.37 ± 0.46 b	171.47 ± 1.42 c
BBF1	133.79 ± 2.13 b	0.11 ± 0.01 a	59.16 ± 0.91 b	23.75 ± 0.54 b	26.74 ± 0.48 b	75.84 ± 0.63 a	185.50 ± 0.98 b
BBF2	158.36 ± 8.51 a	0.11 ± 0.01 a	66.24 ± 1.16 a	24.97 ± 0.66 a	28.30 ± 0.48 a	76.71 ± 1.68 a	196.23 ± 1.91 a

(b) Anions				
Treatments	F^- (mg)	Cl^- (mg)	SO_4^{2-} (mg)	HCO_3^- (mg)
CK	2.37 ± 0.02 a	3.45 ± 0.13 d	61.19 ± 1.11 ab	77.16 ± 4.53 bc
CRF1	2.11 ± 0.11 b	4.48 ± 0.51 c	61.08 ± 1.77 ab	70.41 ± 8.60 c
CRF2	1.86 ± 0.08 cd	5.56 ± 0.30 b	59.67 ± 5.25 b	78.14 ± 10.90 bc
BBF1	1.96 ± 0.04 bc	6.38 ± 0.29 a	67.88 ± 2.68 a	95.96 ± 4.54 a
BBF2	1.77 ± 0.12 d	4.47 ± 0.42 c	57.95 ± 5.60 b	91.01 ± 4.53 ab

*Values are mean ± SD Different letters indicate significant differences at P< 0.05 (one-way ANOVA followed by Duncan's test).

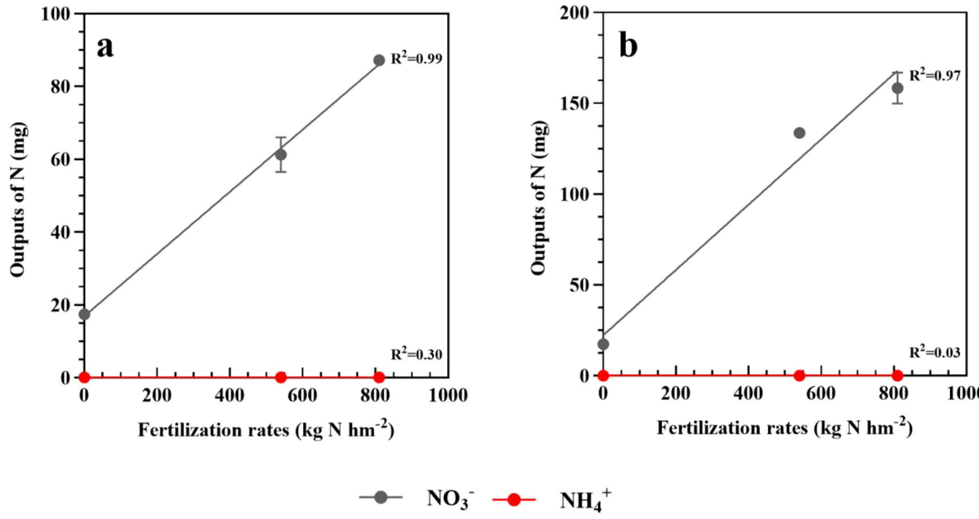

FIGURE 4
Relationship between fertilization rates and outputs of NO_3^- and NH_4^+ by leachate. **(a)** Controlled-release urea treatment; **(b)** Conventional urea treatment. Values are means ± SD.

treatment columns was minimal and did not show a linear relationship with the amount of fertilizer applied ($P > 0.05$).

The application of fertilizer has a significant impact on the output of base cations (K^+, Ca^{2+}, Na^+, and Mg^{2+}), as proved by the highly significant linear relationship ($P < 0.05$, Figure 5). The solid linear regression shows that N application increases the output of each base cation, with Ca^{2+} being the predominant base cation in the leachate and Mg^{2+} contributing the least. The correlation between base cations and NO_3^- leaching proves that these two substances are simultaneously leached from the soil column. The amount of both increases as the N application rate rises ($P < 0.05$, Figure 6).

3.6 Proton production in different fertilization treatments

The production of H^+ varied significantly among different fertilization treatments (Table 3). The H_{pro} ranged from 1.54 to 4.04 mmol and was influenced by both the type of fertilizer and the amount of N applied. The BBF2 treatment showed an increase in H_{pro} of 8.43% and 50.59% compared to the BBF1 and CRF2 treatments, respectively. The BBF1 treatment resulted in a 74.30% increase in H_{pro} compared to the CRF1 treatment, while the CRF2 treatment experienced a 25.50% increase over the CRF1 treatment.

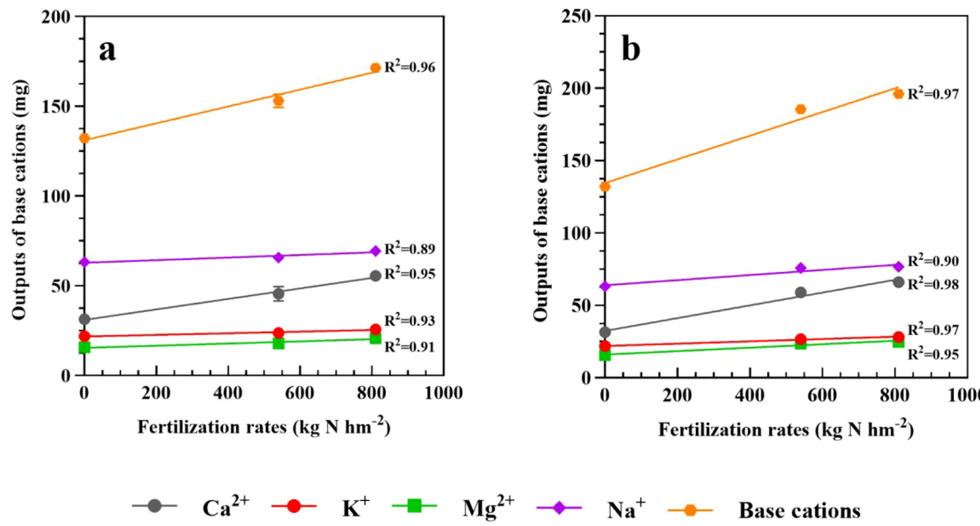

FIGURE 5
Relationship between fertilization rates and outputs of base cations (K^+, Ca^{2+}, Na^+ and Mg^{2+}) by leachate. **(a)** Controlled-release urea treatment; **(b)** Conventional urea treatment. Values are means ± SD.

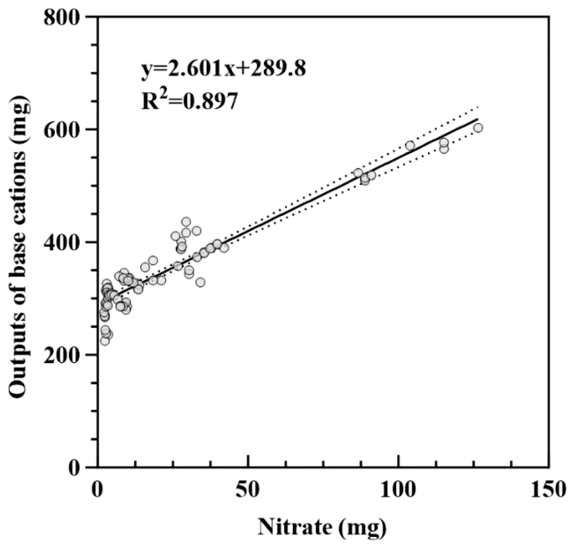

FIGURE 6
Relationship between concentrations of NO_3^- and concentrations of base cations (K^+, Ca^{2+}, Na^+ and Mg^{2+}) in leachate.

The proportion of H_{pro} from N and C cycling varied among the different fertilization treatments. In the CK treatment, the primary pathway of H_{pro} was through the C cycle, which accounted for 81.82% of the total H^+ produced. In both the CRF1 and CRF2 treatments, the C and N cycling proportions were nearly equal, with the C cycle accounting for 53.81% and 47.74% of the total H^+, respectively. In the BBF1 and BBF2 treatments, the N cycle was the dominant process, accounting for 57.78% and 63.06% of the total H^+, respectively.

4 Discussion

4.1 Conceptual basis of leaching-driven acidification potential in calcareous soil

Soil acidification is commonly defined as a decrease in the ANC of the soil inorganic phase (including the soil solution), rather than a pH decline alone (13). In managed ecosystems, changes in ANC are mainly driven by element cycling (especially N and C) and fertilizer-induced reactions that alter charge-balanced fluxes of anions and cations (18). In the present column experiment using a calcareous fluvo-aquic soil (initial pH 8.35), acidification processes related to Al and Mn redox cycling were expected to be minor compared with N- and carbonate-related processes. Therefore, we focused on the H^+ budget associated with the N cycle and the carbonate system.

The "H_{pro}" quantified here is derived from H^+ accounting based on input–output balances (Equations 1–3), and thus represents the net H^+ load (acidification potential) associated with solute export (e.g., NO_3^-, HCO_3^- and charge-compensating cations) during the 90-day incubation. It does not represent the instantaneous concentration of free H^+ in leachate, nor does it include gaseous pathways (e.g., NH_3 volatilization). This distinction is particularly relevant for calcareous soils, where carbonate buffering can maintain alkaline pH while ANC is still depleted through carbonate dissolution and cation losses. Accordingly, the HCO_3^--related term in our H^+ budget is best interpreted as consumption of alkalinity/ANC associated with carbonate dissolution and subsequent HCO_3^- export, rather than direct generation of free H^+ in leachate (19).

4.2 Nitrogen transformation pathways, temporal effects of CRU, and implications of NH_3 volatilization

Urea-derived N can affect acidity through coupled hydrolysis and nitrification processes (20). In calcareous soils, H^+ produced during nitrification and other reactions can be neutralized mainly by carbonate buffering, so the net acidification signal is often expressed as enhanced carbonate dissolution and increased export of Ca^{2+} and HCO_3^-, rather than as an accumulation of free H^+ in leachate (21). In the H^+ accounting framework, net N-related H_{pro} is governed by the imbalance between NH_4^+ and NO_3^- fluxes (15). In our plant-free columns, NH_4^+ leaching was very small and did not differ significantly among treatments, while NO_3^- dominated the leachate and increased strongly with N rate (Figures 7, 4, Table 2). This indicates that a substantial fraction of fertilizer N was nitrified and exported as NO_3^-, making NO_3^- leaching a key integrator of N-cycle acidification potential in this system.

At the same N rate, conventional urea caused markedly higher cumulative NO_3^- leaching than CRU (BBF1 vs. CRF1 and BBF2 vs. CRF2; Table 2), which translated into significantly higher Hpro,N and total H_{pro} (Table 3). This pattern supports a mechanistic explanation in which CRU reduces short-term (90-day) leaching-

TABLE 3 The production of H^+ in the N cycle and C cycle.

Treatments	NH_4^+ (mmol)	NO_3^- (mmol)	H_{proN} (mmol)	$H_{proHCO3}$ (mmol)	Total H^+ (mmol)
CK	0.01 ± 0.00 a	0.28 ± 0.03 e	0.28 ± 0.02 e	1.26 ± 0.07 bc	1.54 ± 0.07 e
CRF1	0.01 ± 0.00 a	0.99 ± 0.08 d	0.98 ± 0.08 d	1.15 ± 0.14 c	2.14 ± 0.10 d
CRF2	0.01 ± 0.00 a	1.41 ± 0.02 c	1.40 ± 0.02 c	1.28 ± 0.18 bc	2.68 ± 0.19 c
BBF1	0.01 ± 0.00 a	2.16 ± 0.03 b	2.15 ± 0.03 b	1.57 ± 0.07 a	3.72 ± 0.09 b
BBF2	0.01 ± 0.00 a	2.55 ± 0.14 a	2.55 ± 0.14 a	1.49 ± 0.07 ab	4.04 ± 0.20 a

*Values are mean ± SD Different letters indicate significant differences at P< 0.05 (one-way ANOVA followed by Duncan's test).

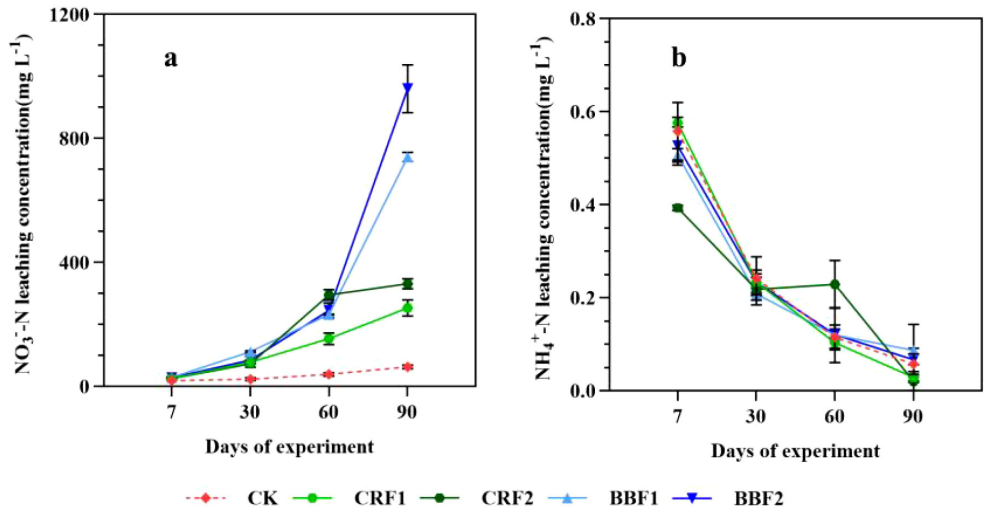

FIGURE 7
Changes in the concentration of N concentration under different fertilization treatments over time. **(a)** NO_3^- leaching concentration under various treatments; **(b)** NH_4^+ leaching concentration under various treatments. Values are means ± SD.

driven acidification potential by moderating NH_4^+ availability for nitrification and limiting NO_3^- accumulation during percolation events. In contrast, conventional urea provides a rapid NH_4^+ supply, which can sustain higher nitrification rates and promote NO_3^- build-up and flushing during subsequent leaching events. This interpretation is consistent with the very high NO_3^- concentrations observed in later leaching events, especially under BBF2 (Figure 7).

The CRU used in this study has a nominal release period of 120 days, whereas the incubation lasted 90 days. Therefore, part of the lower NO_3^- leaching and lower calculated H_{pro} under CRU likely reflects a temporal redistribution of N release and nitrification beyond the observation window. For this reason, our results should be interpreted as a reduction in net H^+ load exported via leaching during the 90-day period (i.e., reduced acidification potential within the incubation window), rather than definitive evidence that CRU decreases lifetime H^+ generation under all conditions. Nevertheless, within the same observation period, CRU consistently reduced NO_3^- export and the associated losses of base cations and HCO_3^- (Tables 2, 3), indicating a meaningful mitigation of short-term ANC depletion through leaching pathways.

Because the soil was alkaline, urea hydrolysis could increase NH_3 volatilization risk, particularly shortly after application. NH_3 volatilization was not measured in this study and could influence the N balance by removing fertilizer N before it is nitrified, thereby potentially lowering NO_3^- leaching and the calculated Hpro,N (22). Volatilized NH_3 may also contribute to off-site acidification after atmospheric transport, deposition and subsequent nitrification, which is not captured by a leachate-based H^+ budget (23). In our setup, fertilizer was placed within the soil rather than surface-applied, which likely reduced (but did not eliminate) volatilization. Given that BBF2 still exhibited the highest NO_3^- leaching and the highest calculated H_{pro}, treatment differences in this experiment were more strongly governed by N release patterns, nitrification, and leaching export than by any unquantified NH_3 losses. Therefore, NH_3 volatilization is considered a limitation that may affect absolute budgets, while the relative treatment ranking for leaching-driven acidity is expected to remain robust (24).

4.3 Coupling of NO_3^- export with base-cation leaching and depletion of buffering capacity

Nitrate is a mobile anion and its leaching is commonly accompanied by the leaching of charge-balancing cations. Consistent with this mechanism, we observed a significant positive relationship between NO_3^- and the major base cations (K^+, Ca^{2+}, Na^+ and Mg^{2+}) in leachate (Figure 6), and cumulative base-cation losses increased with N rate and were higher under conventional urea than under CRU at the same N rate (Table 2). Such co-leaching directly contributes to ANC depletion because base cations represent alkalinity that is removed from the soil exchange complex and soil solution (6). In calcareous systems, Ca^{2+} often dominates the leachate because carbonate dissolution and cation exchange can supply Ca^{2+} to maintain charge balance when NO_3^- is exported.

Controlled-release urea lowered NO_3^- concentrations in percolating water and thus reduced the driving force for charge-balanced cation export. This provides a coherent explanation for the observed coupling among lower NO_3^- leaching, lower base-cation leaching, and lower net H^+ load under CRU. Although plant uptake and residue recycling can partially return base cations to topsoil in field agroecosystems (13), the present plant-free columns isolate the soil-process component and demonstrate that fertilizer release pattern alone can substantially alter leaching-driven ANC losses.

4.4 Carbonate buffering, CO_2-driven dissolution, and HCO_3^- export in calcareous systems

Carbonate buffering can neutralize acidity generated by nitrification and other H^+-producing reactions. Thus, acid inputs can be expressed as enhanced carbonate dissolution and increased export of Ca^{2+} and HCO_3^- (18). In our experiment, conventional urea generally increased HCO_3^- leaching compared with CRU at the same N rate (Table 2), and the HCO_3^--related H^+ component differed among treatments (Table 3). Together with the greater NO_3^- and base-cation leaching under conventional urea, these results suggest that rapid N release intensified short-term acid loading, which in turn stimulated carbonate buffering reactions and associated solute export (9, 10). In contrast, CRU moderated NO_3^- export and reduced the magnitude of accompanying cation and HCO_3^- losses within 90 days, thereby lowering the net H^+ load and ANC depletion through leaching pathways during the incubation.

Overall, these results support a consistent conceptual model in which conventional urea produces a rapid N pulse that promotes nitrification, NO_3^- accumulation and flushing, and charge-balanced export of base cations and HCO_3^- (18, 20), whereas CRU spreads N supply over time, dampens NO_3^- peaks and associated solute losses, and consequently reduces leaching-driven acidification potential within the experimental period. Future studies extending the incubation beyond 90 days and/or including crop uptake and gaseous N loss measurements would help to determine the full-season and long-term implications for net H^+ budgets in calcareous croplands.

5 Conclusions

Controlled-release urea treatment significantly reduces acid production in soil. The main acid-producing processes in soil are the N and C cycles. During the N cycling process, acid production from CRU treatment is far lower than that from conventional urea treatment. In the N cycle, the H_{pro} under the BBF1 treatment is 118.18% higher than in the CRF1 treatment, and in the BBF2 treatment, it is 81.58% higher than in the CRF2 treatment. The output of base cations and NO_3^- in soil shows a linear relationship and increases with the amount of N applied. Mechanistically, CRU moderated NO_3^- export and the concomitant charge-balanced leaching of base cations, thereby lowering the net H^+ load exported from the soil profile during the 90-day incubation. The proportion of H_{pro} from the C and N cycles varies with different fertilization treatments. In the unfertilized treatment, the C cycle is the primary acid-producing process. As pH increases, this proportion decreases in fertilized treatments. In the CK treatment, the C cycle accounts for 81.82% of the total H_{pro}, while in the CRF1 and CRF2 treatments, the proportions are 53.81% and 47.74%, respectively, and in the BBF1 and BBF2 treatments, they are 57.78% and 63.06%. Overall, CRU reduced the calculated H_{pro} associated with solute leaching compared with conventional urea at the same N rate. These findings suggest that CRU can mitigate fertilizer-induced soil acidification risk via leaching pathways, while long-term field verification is still required.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material. Further inquiries can be directed to the corresponding authors.

Author contributions

HZ: Data curation, Writing – original draft. PZ: Writing – review & editing, Resources. YS: Resources, Writing – review & editing. JL: Data curation, Writing – review & editing, Formal Analysis. CW: Formal Analysis, Writing – review & editing, Funding acquisition. WZ: Project administration, Writing – review & editing, Funding acquisition, Resources.

Funding

The author(s) declared that financial support was received for this work and/or its publication. This work was financially supported by the National Key Research and Development Program of China (Grant No. 2022YFD170060502) and the Shandong Provincial Natural Science Foundation (Grant No. ZR2020QD113).

Conflict of interest

HZ and PZ were employed by.Kingenta Ecological Engineering Group Co., Ltd. YS was employed by China United Property Insurance Company Limited Shandong Branch.

The remaining author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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