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Mechanistic insights into the role of biochar, alum, and iron sulfate in nutrient retention and DOC-associated leaching from poultry litter-amended soils

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Introduction: Indiscriminate application of poultry litter (PL) often exceeds crop nutrient demand, resulting in nitrate (NO_3-N) and phosphate (PO_4-P) leaching to groundwater. Conventional amendments, i.e., alum and iron sulfate, effectively immobilize nutrients but may induce soil acidification. Biochar (BC), a carbon-rich byproduct, has emerged as a potentially sustainable alternative. However, a systematic comparison with established amendments is required, along with the role of manure-derived dissolved organic carbon (DOC) on nutrient leaching dynamics, before broader adoption.
Materials and methods: An *in-situ* pot experiment was conducted using coarse-textured soil in 24 leaching columns under open-field conditions with corn (*Zea mays*) as the test crop. Six treatments were evaluated: (i) soil without PL, (ii) soil with 20 t ha^{-1} PL (iii) soil with 20 t ha^{-1} PL + 10% BC-1 (w/w relative to PL), (iv) soil with 20 t ha^{-1} PL + 10% BC-2, (v) soil with 20 t ha^{-1} PL + 10% alum, and (vi) soil with 20 t ha^{-1} PL + 10% iron sulfate. Leachate samples across five natural rainfall events were analyzed for NO_3-N, PO_4-P, and DOC.
Results: In unamended PL-treated soil, NO_3-N and PO_4-P concentrations ranged from 0.53–51.5 and 3.88–20.5 mg L^{-1}, respectively. With amendments, NO_3-N concentrations ranged from 1.94–42.0 (BC-1), 1.72–39.2 (BC-2), 1.07–22.1 (alum), and 1.55–46.7 mg L^{-1} (iron sulfate), while PO_4-P concentrations ranged from 3.20–13.9, 3.18–13.6, 1.51–8.25, and 1.99–11.6 mg L^{-1}, respectively. Across, five rainfall events, amendments reduced cumulative average PO_4-P loading by 14.5% (BC-1), 33% (BC-2), 48% (alum), and 52% (iron sulfate) and NO_3-N loading by 37% (BC-2), 41% (alum), and 33% (iron sulfate), whereas BC-1 increased cumulative average NO_3-N loading by 10% compared to unamended manure soil. DOC exhibited significant positive correlations with NO_3-N ($r = 0.54$, $p < 0.05$) and PO_4-P ($r = 0.83$, $p < 0.001$). Grain yield was similar in unamended and BC-amended soils, significantly higher than alum- and iron sulfate-amended soils.
Conclusion: The role of amendments (BC-2, alum, and iron sulfate) was significant for PO_4-P retention. The NO_3-N retention was modest and influenced by crop growth stages, while PO_4-P loss was governed by rainfall amount.

KEYWORDS
dissolved organic carbon, leaching, nitrate, phosphate, poultry litter

1 Introduction

The global poultry industry has expanded rapidly over the past two decades, driven by rising *per capita* income and the adoption of modern production systems. In the United States, poultry is one of the fastest-growing agricultural sectors, contributing nearly 16% of global poultry meat production (Mottet and Tempio, 2017). However, this growth has also led to the generation of substantial quantities of poultry litter (PL), a heterogeneous waste byproduct rich in plant-available nutrients and organic matter (Ashworth et al., 2020). Land application of PL has traditionally been considered an effective strategy to enhance soil fertility and crop productivity. Yet, in poultry-dense regions, this practice is facing increasing regulatory scrutiny due to the long-term environmental consequences of excessive or indiscriminate litter disposal (Reddy et al., 2008; Bolan et al., 2010). While much of the current attention focuses on nutrient runoff into surface waters, the risk of groundwater contamination through leaching remains comparatively underexamined. Repeated manure applications can cause gradual nitrate (NO_3-N) leaching and the accumulation of phosphorus (P) throughout the soil profile (Huang et al., 2017). Excess P (legacy P) accumulating in the soil beyond crop uptake can cross the critical threshold known as the phosphorus saturation ratio (PSR), allowing it to leach in the form of dissolved P and pose a persistent threat to groundwater quality (Dari et al., 2018). Phosphorus saturation ratio (PSR) is a molar ratio of extractable P to extractable iron plus aluminum (Fe + Al). It suggests that soil rich in Fe and Al will have a greater P-sorption capacity and eventually release low P even at the same STP (soil test phosphorus) with a low PSR. Based on the analysis of 186 surface soil samples across diverse physiographic regions of the United States, Dari et al. (2018) identified a threshold PSR value of 0.10, above which water-soluble P concentrations increased sharply. Butler and Coale (2005) demonstrated that only 4 years of continuous manure application were sufficient to exceed the PSR threshold in surface soils (0–2 m) of the Atlantic Coastal Plains. McDowell et al. (2020) observed that once manure is over-applied, STP concentrations can exceed agronomic optima, requiring sufficient time to reach the environmental regulatory level, leading to a long legacy of P losses even if the balance is made negative to decrease STP concentrations. Unlike phosphate (PO_4-P), NO_3-N is even more mobile, with peak NO_3-N concentrations observed during the periods of low crop uptake (Nguyen et al., 2013). Moreover, the continuous mineralization of organic N in poultry-manured soil can sustain elevated NO_3-N concentrations long after manure application ceases, further extending the potential for nutrient loss. Given the historical over-application of PL in many U.S. agricultural regions, identifying effective soil amendments to reduce nitrate and phosphate leaching is critical for protecting water quality.

The use of chemical and organic amendments offers a cost-effective strategy for reducing nutrient mobility. Amendments containing Fe, Al, or Ca can bind with NO_3-N and PO_4-P, forming less soluble complexes through co-precipitation or sorption. For example, Alum (aluminum sulfate) has proven particularly effective, as Anderson et al. (2018) reported an 83% reduction in dissolved P in alum-treated soil cores compared to untreated controls, with manures applied at 9 t ha^{-1} for 20 years. Yan et al. (2014) further demonstrated that alum interacts not only with inorganic P but also with phytate, forming aluminum-phytate complexes with reduced solubility. Iron sulfate, another inexpensive amendment, is widely used to enhance microbial activity and reduce nitrogen losses in compost systems (Xiao et al., 2025). The acidifying effect of Fe- and Al-based amendments also reduces ammonia volatilization by converting NH_3-N into the less volatile NH_4^+-N form. However, in acidic soils (pH < 5.5) Al or Fe can show potential toxicity that limits plant growth and development (Bojórquez-Quintal et al., 2017). In recent years, Biochar (BC) has been increasingly recognized as an effective nutrient adsorbent due to its large surface area, internal porosity, and diverse functional groups (Laird et al., 2010). Bankole et al. (2025) observed that the co-application of wood-derived BC with poultry manure reduced cumulative NO_3-N and PO_4-P release by 32% and 17%, respectively, after 8 weeks. However, evidence from multiple studies indicates that BC's nutrient retention capacity can vary substantially depending on its feedstock and production conditions (Semida et al., 2019). Several studies have reported reductions in NO_3-N leaching ranging from 14% to 34% (Zhang et al., 2020); however, other research has found limited or negligible NO_3-N sorption potential in BC, highlighting inconsistencies in observed outcomes (Li et al., 2018). These discrepancies are due to the wide variation in feedstock types, pyrolysis conditions, and physicochemical properties of BC (Jindo et al., 2014). This highlights the need to compare BC with established amendments, such as alum and iron sulfate, to better understand their efficacy in retaining nutrients.

Dissolved organic matter (DOM), particularly dissolved organic carbon (DOC), plays a critical yet often overlooked role in nutrient mobility in manured soils (Tiefenbacher et al., 2020). It serves as a carbon source for heterotrophic microbial communities and may influence NO_3-N dynamics through denitrification in the unsaturated zone (Hussain et al., 2020). Organic acids in DOC can chelate Fe and Al oxides that normally bind dissolved P, eventually releasing PO_4-P into solution. Additionally, DOC competes with PO_4-P for adsorption sites on soil minerals, reducing P retention and enhancing co-leaching (Scott et al., 2015). Despite its central influence on soil biogeochemistry, the relationship between DOC and NO_3-N or PO_4-P leaching under conditions of heavy manure loading remains poorly understood. It is also essential to determine whether soil amendments intended to reduce nutrient leaching have unintended effects on grain yield and nutrient uptake in row crops such as corn.

To address these knowledge gaps, we conducted an *in-situ* experiment on a coarse-textured soil to evaluate the effectiveness of soil amendments in reducing NO_3-N and PO_4-P leaching, as well as their impact on corn grain yield and nutrient uptake. Corn was grown under natural rainfall conditions, and the selected amendments were applied in conjunction with PL. We hypothesized that DOC would exhibit a strong association with the mobility of NO_3-N and PO_4-P across treatments, and that amendments such as alum, iron sulfate, and BC would reduce cumulative nutrient losses while improving plant nutrient uptake and grain yield. Accordingly, the objectives of this study were to: (i) compare the efficacy of two BC (same feedstock) with alum, and iron sulfate in mitigating nutrient leaching; (ii) investigate the relationship between DOC, NO_3-N, and PO_4-P to assess their contribution to nutrient leaching potential in manured soils; and (iii) assess whether amendments intended to reduce nutrient losses also influence nutrient uptake and corn grain yield.

2 Materials and methods

2.1 Experimental site

The leaching experiment was conducted at the Bioresource Laboratory (32° 34′ 56″ north, 85° 30′ 17″ west) of the Department of Crop, Soil, and Environmental Sciences at Auburn University. The experimental site experiences maximum and minimum annual temperatures ranging from approximately 4 °C–32 °C with an average of 15 °C. The region receives an average annual precipitation of 1,364 mm, with March being the wettest month and October the driest.

2.2 Characterization of soil, PL, and BC

The composite surface soil (0–15 cm) was collected from a row crop farm in Lee County, Alabama. The soil was Marlboro loamy sand (Fine, kaolinitic, thermic typic Paleudults) (Soil Survey Staff, 2024), which naturally facilitates nutrient leaching due to coarse texture. Soils, after collection, were air-dried and sieved through a 10-mm sieve for the pot experiment to remove large stones, roots, and coarse debris while preserving natural soil aggregates. A 2-mm sieve was subsequently used for laboratory analyses. The soil particle size distribution was determined by the hydrometer method (Bouyoucos, 1962). Soil pH was determined in 1: 2 soil-water suspension (Jackson, 1973). The total C and N of the soil were determined by the dry combustion method using a CNS analyzer (Vario Max, Elementar, Germany) (Watson and Galliher, 2001). For total elemental analysis (P, K, Ca, and Fe), soil was digested with aqua regia (3.1, v/v HCl to HNO_3) (Quevauviller, 1998) and analyzed using ICP-OES (Agilent 5800 ICP OES). The extractable P and N were analyzed using Mehlich-3 (Mehlich, 1984) and 2 M KCl (Nelson, 1983) and determined by a flow injection analyzer (FIAlyzer-1000, FIA Lab, USA).

The PL used in this study was obtained from a commercial poultry farm in northern Alabama and represented a 2-year cleanout with pine shavings bedding. The collected PL was air-dried, ground, and passed through a 1-mm sieve to obtain a homogeneous sample. A subsample of this was analyzed for pH (Peters et al., 2003), total C, N and nutrients (Ca, Mg, Fe, and P) composition. The litter sample was digested using a nitric acid (HNO_3) - hydrogen peroxide (H_2O_2) procedure (USEPA, 1996) and analyzed by ICP–OES.

The BC used in this study was procured from a commercial vendor (Waste to Energy, Slocomb, Alabama, USA), produced from yellow pine wood using a continuous-flow pyrolysis system at 550 °C with a residence time of 10 min. Two BCs (BC-1 and BC-2) were procured from different production batches with identical feedstock and pyrolysis conditions. The pH of the BC samples was measured using a 1:20 (w/v) biochar-water suspension after shaking for 24 h at 130 rpm (Zheng et al., 2013). Total carbon, nitrogen, and nutrient concentrations were determined using the same analytical procedures applied to soil samples. The detailed morphological, physical, and chemical properties of BC-1 (including specific surface area, pore volume, pore diameter, and elemental analysis) were carried out by Kumar et al. (2025), while the corresponding characterization of BC-2 has been documented by Temi et al. (external/unpublished). For BC background information, this study supports their observations and findings as a reference.

2.3 Experimental design and treatments

The experiment utilized pots measuring 29 cm in upper diameter, 25.5 cm in lower diameter, and 35 cm in height, each fitted with columns designed to capture leaching during rainfall events. Each pot was first layered with gravel and then packed with soil to a height of 30 cm. Leachate collection columns were installed at the base of each pot to capture water percolating through the soil profile, allowing accumulated leachate to be collected after vertical drainage. Column caps were kept closed to prevent evaporation. A pictorial representation of the experimental setup is presented in Figure 1. A rain gauge was installed adjacent to the pots to record rainfall throughout the study. Twenty-four pots with attached leachate collection columns were arranged in a completely randomized design and replicated four times to represent six treatments: T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, and T6 = Soil + PL + Iron Sulfate. The recommended PL application rate for pasture and forage crops in north Georgia is 10 t ha^{-1} (Gaskin et al., 2010). To account for the historical overapplication of poultry manure in Alabama and to simulate the effects of legacy P, the PL application rate in this study was set twice as much as the recommended rate, i.e., 20 t ha^{-1}. Amendments (BC, alum, and ferrous sulfate) were applied at 10% (w/w) relative to PL. This rate was selected based on alum management guidelines for PL, which typically recommend application rates in the range of 5%–10% (w/w) depending on the litter characteristics and moisture content (Moore, 2023). However, in the present study, the upper end of this recommended range was intentionally used to represent a conservative, upper-bound mitigation scenario. While such a rate may not be fully field-realistic, it allows a clear assessment of the effectiveness of amendments on nutrient leaching under maximum stabilization conditions. The control treatment (T1) consisted of soil without manure application. The alum ($Al_2(SO_4)_3.18H_2O$, 99.5%) and iron sulfate ($FeSO_4.7H_2O$, ≥ 99%) used in the study were ACS grade and obtained from VWR International, USA.

2.4 *In-situ* pot experiment

Three seeds of corn (*Zea mays* var. DKC70-45) were planted (5 June 2025) per pot at a depth of 4–5 cm. No synthetic fertilizers or chemical inputs were applied to any pots. Two weeks after emergence, plants were thinned to maintain one uniform plant per pot. Life-saving irrigations were applied when the crop showed temporary wilting, and these were assumed to have a negligible influence on nutrient leaching because they met only the evapotranspiration demand. The plants were harvested 105 days after sowing. At harvest, above-ground plant biomass was separated into stems, husks, cobs, and leaves, and oven-dried at 60 °C–70 °C to a constant weight. Dry biomass was recorded, and grain weight was adjusted to a standard moisture content of 15.5%. Dried plant samples were submitted to Waters Agricultural Laboratory

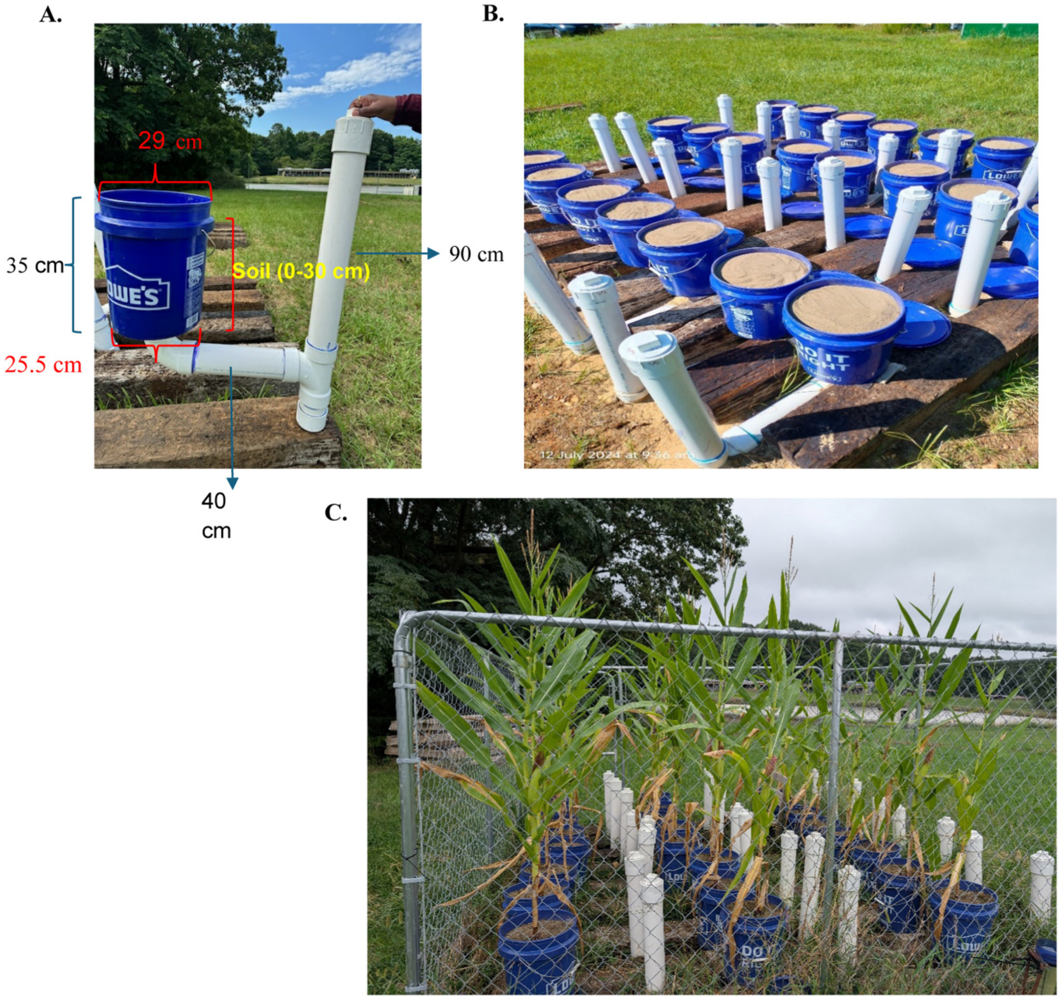

FIGURE 1
Overview of experimental setup **(A)** lysimeters, **(B)** arrangement of lysimeters in a completely randomized design, and **(C)** corn plants grown in the lysimeter.

(Georgia, USA) for nutrient analysis. Nutrient uptake for both above-ground biomass and grain was calculated by multiplying nutrient concentrations by the corresponding dry biomass.

2.5 Collection, processing, and analysis of leachate samples

The leachate samples were collected at pre-planting (1 day before planting; E1), early emergence (4 days after planting; E2), early vegetative (20 days after planting; E3), mid-vegetative (40 days after planting; E4), and reproductive (65 days after planting; E5) stages of the crop growth. During these events, the rain gauge recorded a total of 210, 51, 76, 19, and 108 mm of rainfall. The rainfall distribution across the experimental setup was uniform, suggesting that each pot received a similar amount. The rainfall was expressed as the cumulative rainfall between events. Each pot was hydraulically isolated and functioned as an independent unit (Figure 1), with no lateral water exchange between pots. Leachate was collected exclusively through the bottom drainage outlet that connected to individual leachate collection columns. During collection, the leachate volume was first recorded, and the samples were stored in HDPE bottles at 4 °C. The next day, the samples were filtered through a 0.45 µm filter paper using a vacuum filtration to obtain a clear filtrate. Then, PO_4-P and NO_3-N in the filtered sample were determined by the flow injection analyzer (FIAlyzer-1000, version 2.0, USA). The DOC of the samples was analyzed using a TOC analyzer (TOC-L, Shimadzu, Japan). The load of nutrients (g ha^{-1}) was calculated by multiplying the total volume of leachate by the nutrient concentration. The QC (quality control), LOD (Limit of Detection), and LOQ (Limit of Quantification) of the instrument were performed during sample analysis to determine the validity of the results.

2.6 Statistical analysis

Effects of treatments on NO_3-N and PO_4-P concentration in leachate, plant growth attributes, and plant nutrient uptake were evaluated using one-way Analysis of Variance (ANOVA) based on a Completely Randomized Design (CRD). In contrast, nutrient load data were analyzed using a two-way factorial design, with rainfall

TABLE 1 Basic physical and chemical properties of soil, poultry litter (PL), and biochar types (BC-1 and BC-2) used in the study.

Parameters	Soil	PL	BC-1	BC-2
pH	6.1 ± 0.35	8.39 ± 0.28	9.6 ± 0.25	9.5 ± 0.22
Texture	Loamy sand	-	-	-
Sand (%)	79.0	-	-	-
Silt (%)	17.0	-	-	-
Clay (%)	4.0	-	-	-
TC (%)	1.28 ± 0.12	28.5 ± 2.38	76.3 ± 4.55	72.2 ± 2.68
TN (%)	0.11 ± 0.02	3.51 ± 0.87	0.26 ± 0.04	0.20 ± 0.06
Ca (%)	0.15 ± 0.06	3.55 ± 0.45	1.97 ± 0.37	1.46 ± 0.45
Mg (%)	0.05 ± 0.04	0.85 ± 0.23	0.45 ± 0.16	0.28 ± 0.14
P (%)	0.15 ± 0.03	1.89 ± 0.19	0.14 ± 0.05	0.11 ± 0.03
Fe (%)	0.24 ± 0.13	0.29 ± 0.11	0.25 ± 0.12	0.36 ± 0.13
[a]Extractable P (mg kg^{-1})	103 ± 21	-	-	-
[b]Extractable NH_4-N (mg kg^{-1})	5.81 ± 1.25	-	-	-
Extractable NO_3-N (mg kg^{-1})	1.27 ± 0.87	-	-	-
[c]BET specific surface area (m^2 g^{-1})	-	-	91.6	256
[c]Ash content (%)	-	-	3.04 ± 0.33	Undefined

N = 3 observations were used to calculate the standard deviation.
[a]Mehlich 3 extractable.
[b]2 M KCl, extractable.
[c]The reported parameters for BC-1 and BC-2 were not measured in this study but were adopted from Kumar et al. (2025) and Temi et al. (unpublished), respectively, as the same feedstocks were used in both studies.

event as Factor A, treatment/amendment as Factor B, and their interaction (A x B) to determine their effects on average leachate nutrient loads. To evaluate the extractable nutrients in pre-sowing and post-harvest soil samples across different treatments, a two-way factorial statistical analysis was performed using soil sampling (pre-sowing and post-harvest) as factor A and amendments as factor B, and their interaction (A x B). The statistical analyses were conducted using the Windows-based R software GRAPES 1.1.0 (Gopinath et al., 2020). Differences among treatment means were assessed using Tukey's test (Tukey, 1991) at a 5% significance level.

3 Results

3.1 Characteristics of soil, PL, and BC

The physical and chemical characteristics of the soil are presented in Table 1. The soil was loamy sand with a slightly acidic pH (6.1). The total C and N contents of the soil were 1.28% and 0.11%, respectively. The total Ca, Mg, P, and Fe content in the soil was 0.15%, 0.05%, 0.15%, and 0.24%, respectively. The soil recorded an extractable (Mehlich-3) P of 103 mg kg^{-1}, while extractable (KCl) NH_4-N and NO_3-N were 5.81 and 1.27 mg kg^{-1}, respectively.

PL used in the study recorded an alkaline pH (8.39) (Table 1). Chemical analysis of the litter sample indicated that PL could serve as an important source of N (3.51%), P (1.89%), Ca (3.55%), and Mg (0.85%). The PL recorded a substantially higher carbon content (28.5%).

The two BC used in the study showed similar pH values in the alkaline range, while the mineralogical composition differed. The Total C, N, Ca, Mg, and P content was considerably higher in BC-1, while the Fe content and specific surface area were high in BC-2 (Table 1).

3.2 Trends in PO_4-P and NO_3-N concentration in leachate

Nitrate concentrations in leachate varied significantly across crop growth stages. The greatest concentrations occurred before planting (E1), while concentrations were lowest during active growth phases (E4 and E5) (Figure 2A). At E1, amendments significantly ($p < 0.05$) reduced (mean) NO_3-N compared to unamended soil (T2; 51.5 ± 7.41), 18% by BC-1 (T3; 41.99 ± 30.53), 24% by BC-2 (T4; 39.26 ± 23.64), 65% by alum (T5; 18.13 ± 13.58), and 9% by iron sulfate (T6; 46.70 ± 25.57). No significant differences were observed during E2-E4 between amendments. However, at E5, NO_3-N was highest in alum-amended soil (T5; 6.75 ± 3.79 mg L^{-1}), followed by iron sulfate (T6; 4.62 ± 3.51 mg L^{-1}), BC-1 (T3; 2.48 ± 2.30 mg L^{-1}), and BC-2 (T4; 1.72 ± 0.82 mg L^{-1}), with the lowest concentrations in control (T1; 0.80 ± 1.05 mg L^{-1}) and unamended soil (T2; 0.53 ± 0.68 mg L^{-1}). This suggests that unamended pots had already lost most NO_3-N through leaching or plant uptake, whereas amended soils released

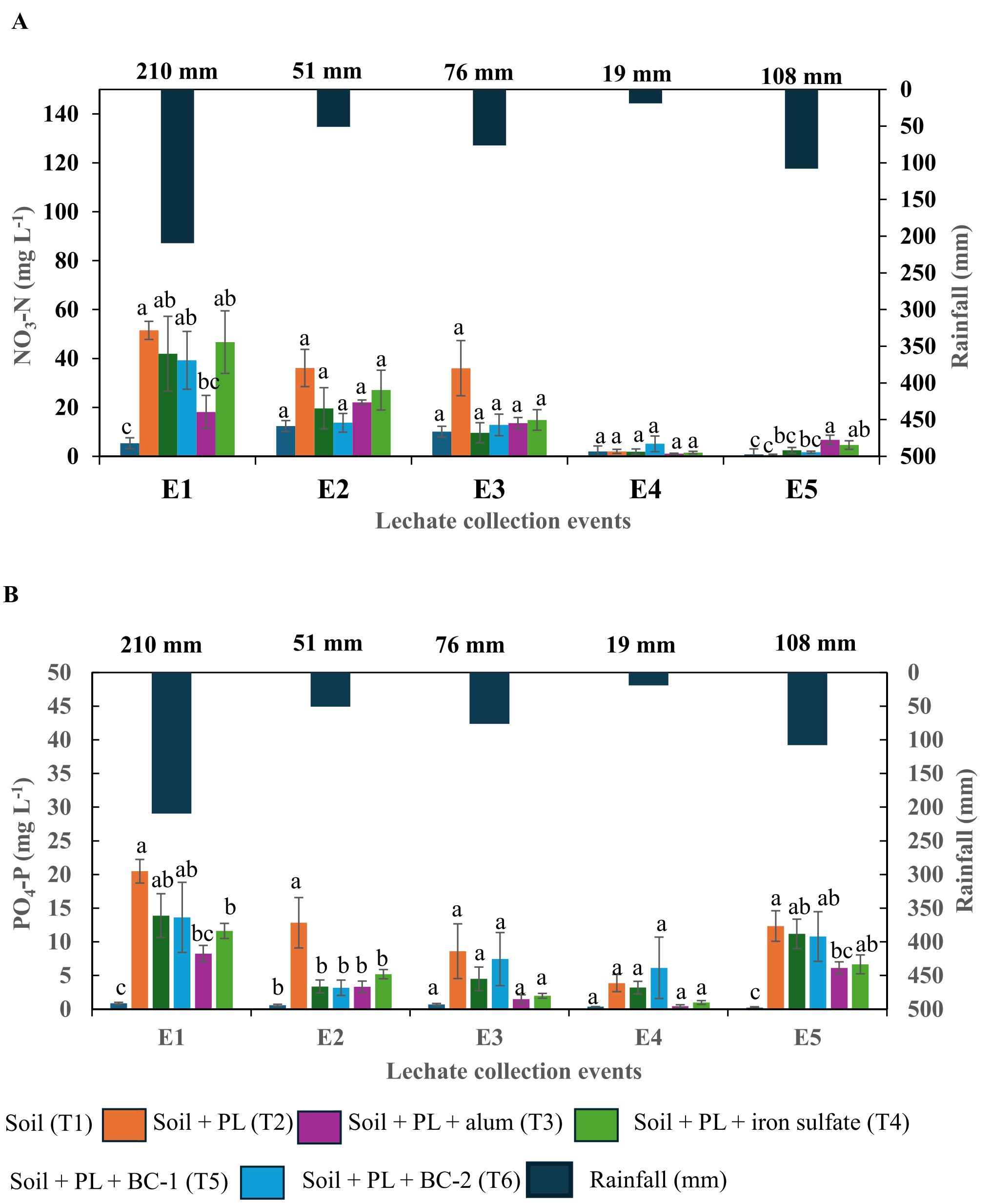

FIGURE 2
Average concentrations of **(A)** NO_3-N (mg L^{-1}) and **(B)** PO_4-P (mg L^{-1}) in leachate over five rainfall events (shown in secondary Y-axis). Bars represent means ± standard errors. Within each rainfall event (shown in secondary Y-axis), treatments with different letters differ significantly according to Tukey's test ($P \leq 0.05$). (PL = Poultry litter, BC = Biochar). E1 = 1day before planting, E2 = 4 days after planting, E3 = 20 days after planting, E4 = 40 days after planting, E5 = 65 days after planting.

nitrate more gradually. Across all sampling events, NO_3-N in T2 ranged from 0.53 ± 0.68 to 51.5 ± 7.41 mg L^{-1}, while BC-1, BC-2, alum, and iron sulfate treatments recorded lower ranges of 1.94 ± 2.15 to 42.0 ± 30.5 mg L^{-1}, 1.72 ± 0.82 to 39.2 ± 23.6 mg L^{-1}, 1.07 ± 0.44 to 22.1 ± 1.89 mg L^{-1}, and 1.55 ± 1.02 to 46.7 ± 25.6 mg L^{-1}, respectively. Control soils (T1) consistently exhibited the lowest concentrations (0.80 ± 1.05 to 12.4 ± 10.4 mg L^{-1}).

Phosphate concentrations also varied with rainfall distribution. At E1, BC-1, BC-2, alum, and iron sulfate significantly ($p < 0.05$) reduced (mean) PO_4-P concentrations by 32% (T3; 13.90 ± 6.49), 33% (T4; 13.64 ± 10.41), 60% (T5; 8.25 ± 2.44), and 43% (T6; 11.63 ± 2.23), respectively, compared to unamended (T2; 20.49 ± 3.50) soil (Figure 2B). Significant reductions ($p < 0.05$) also occurred at E2 and E5. Using amendments (BC-1, BC-2, alum, and iron sulfate) mean PO_4-P was reduced by 74% (T3; 3.37 ± 1.94), 75% (T4; 3.18 ± 2.28), 74% (T5; 3.33 ± 1.70), and 59% (T6; 5.20 ± 1.37) compared to the unamended (T2; 12.84 ± 7.48) pot at E2, and by 9% (T3; 11.18 ± 4.38), 13% (T4; 10.79 ± 7.37), 50% (T5; 6.11 ± 1.84), and 46% (T6; 6.66 ± 2.79) compared to unamended (T2; 12.35 ± 4.54) soil at E5 (Figure 2B). No significant differences were observed during E3 and E4. Across all events, PO_4-P in T2 ranged from 3.88 ± 2.55 to 20.5 ± 3.50 mg L^{-1}, while BC-1, BC-2, alum, and iron sulfate recorded lower

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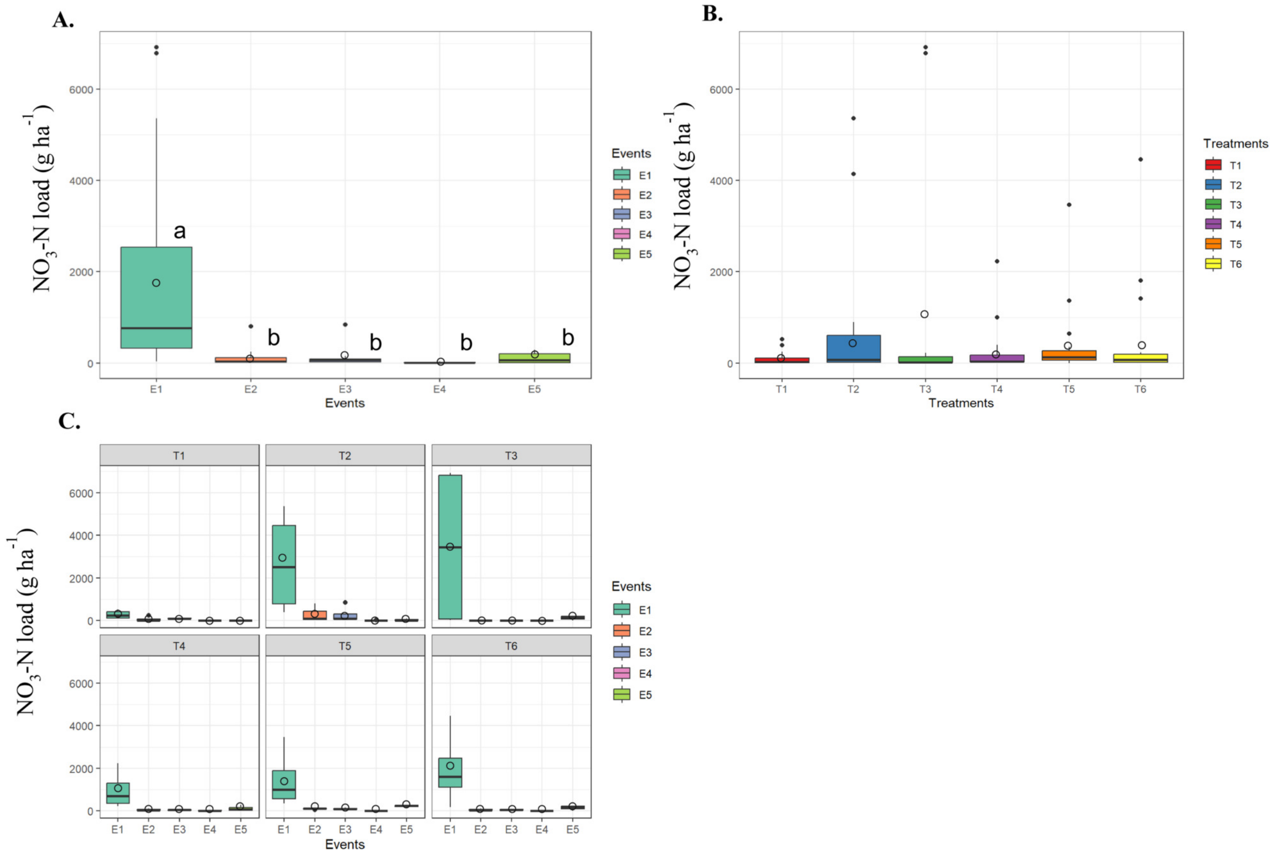

FIGURE 3
Box plots showing the effects of **(A)** rainfall events, **(B)** amendments, and **(C)** their interaction on mean NO_3-N load (g ha^{-1}). Rainfall events had a significant effect (DF = 4, F = 12.185, P < 0.001), whereas treatments (DF = 5, F = 1.304, P = 0.271) and their interaction (DF = 20, F = 0.904, P = 0.584) were not significant. Treatments were: T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, and T6 = Soil + PL + iron sulfate (BC = biochar; PL = poultry litter). Different letters denote significant differences at $P \leq 0.05$.

ranges of 3.20 ± 1.87 to 13.9 ± 6.49 mg L^{-1}, 3.18 ± 2.28 to 13.6 ± 10.4 mg L^{-1}, 1.51 ± 1.26 to 8.25 ± 2.44 mg L^{-1}, and 1.99 ± 0.72 to 11.6 ± 2.23 mg L^{-1}, respectively. Control soils (T1) consistently showed minimal leaching (0.25 ± 0.22 to 0.87 ± 0.29 mg L^{-1}).

3.3 Trends in PO_4-P and NO_3-N loads in the leachate

A series of boxplots (boxes represent 50% of the data, whiskers on either side of the box represent the maximum and minimum value, the dots outside the whiskers represent the outliers, the circles inside the box represent the mean and the lines within the box represent the median) was used to illustrate the effects of rainfall distribution and amendments on NO_3-N and PO_4-P leaching loads (Figures 3, 4). Nitrate losses varied significantly ($p < 0.05$) across rainfall events (Figure 3A), with the highest load occurring during the first event (E1; 1804 g ha^{-1}), followed by sharp reductions in subsequent events (E2: 96.4 g ha^{-1}; E3: 105 g ha^{-1}; E4: 9.4 g ha^{-1}; E5: 102 g ha^{-1}) indicating depletion of readily available N after the initial leaching. Rainfall distribution also significantly ($p < 0.05$) influenced phosphate losses (Figure 4A), with the first and last events producing the greatest PO_4-P loads (606 and 403 g ha^{-1}, respectively). Soil amendments significantly ($p < 0.05$) reduced PO_4-P loads (Figure 4B). BC-2 (T4), alum (T5), and iron sulfate (T6) lowered mean PO_4-P loads to 256, 210, and 183 g ha^{-1}, representing reductions of 35%, 47%, and 54% compared to unamended soil (T2; 378 g ha^{-1}). In contrast, BC-1 (T3) showed no significant reduction (397 g ha^{-1}), performing similarly to T2, indicating variability in BC effectiveness. This variability likely reflects differences in BC properties, as BC-1 had a lower specific surface area than BC-2 (Table 2), thereby influencing nutrient adsorption capacity. No significant effect of amendments was observed on nitrate load (Figure 3B). The interaction between rainfall amount and amendment type was not significant for both nutrients (Figures 3C, 4C). Supplementary information about the significance of different factors and their interaction on NO_3-N and PO_4-P load is presented in Supplementary Table S1.

3.4 Cumulative leaching loads of NO_3-N and PO_4-P

Cumulative nutrient load was calculated by summing the average loads of NO_3-N and PO_4-P across all five rainfall events during the corn growth cycle. Across all rainfall events, cumulative

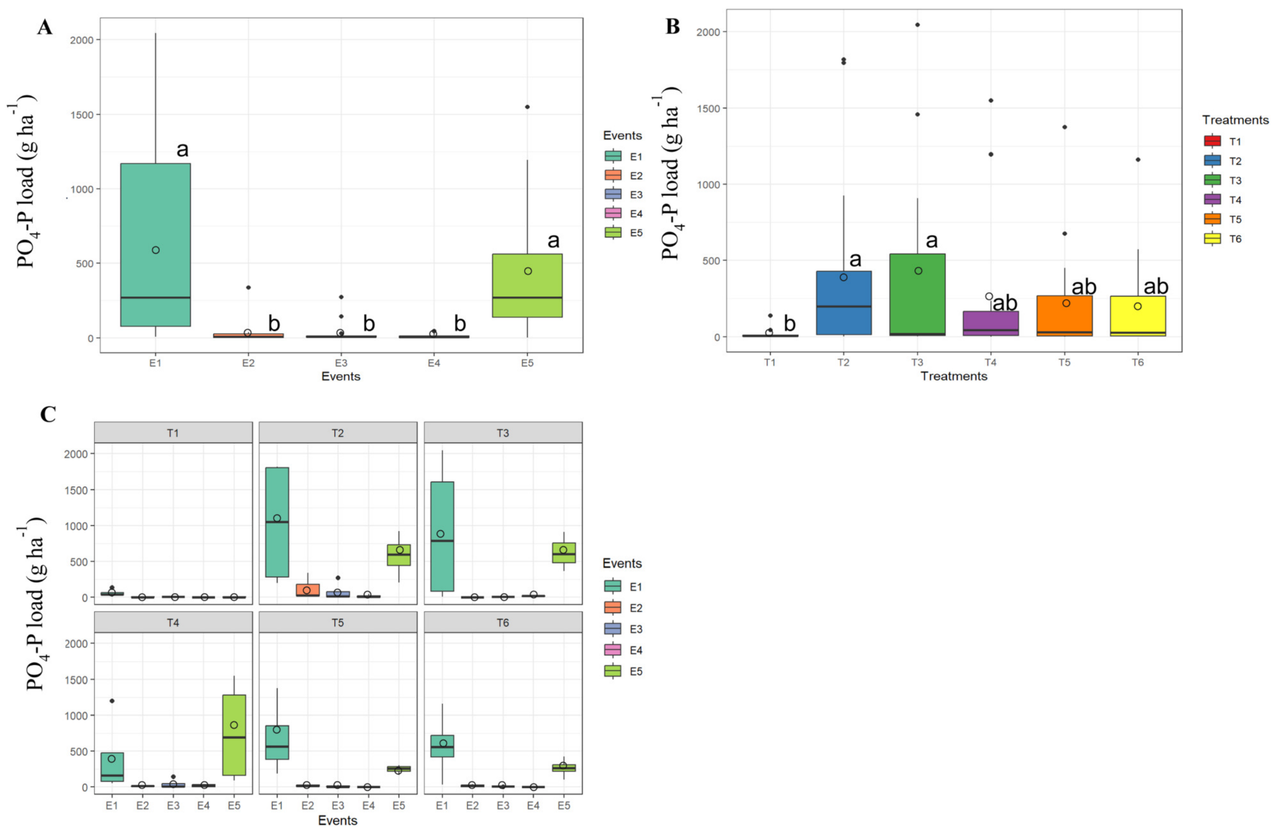

FIGURE 4
Box plots illustrating the effects of **(A)** rainfall events, **(B)** amendments, and **(C)** their interaction on mean PO_4–P load (g ha^{-1}). Two-way ANOVA indicated significant effects of rainfall events (Factor A: DF = 4, F = 12.694, P < 0.001) and treatments (Factor B: DF = 5, F = 2.548, P = 0.035), while the interaction between rainfall events and treatments (A × B) was not significant (DF = 20, F = 0.932, P = 0.550). Treatments were: T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, and T6 = Soil + PL + iron sulfate (BC = biochar; PL = poultry litter). Different letters denote significant differences at P ≤ 0.05.

NO_3-N loads were highest in BC-1 amended soils (T3; 3638 g ha^{-1}), followed by unamended (T2; 3306 g ha^{-1}), iron sulfate (T6; 2224 g ha^{-1}), BC-2 (T4; 2071 g ha^{-1}), and alum (T5; 1937 g ha^{-1}) (Figure 5). Cumulative PO_4-P loads were greatest in unamended soils (T2; 1828 g ha^{-1}), followed by BC-1 (T3; 1,563 g ha^{-1}), BC-2 (T4; 1,200 g ha^{-1}), alum (T5; 950 g ha^{-1}), and iron sulfate (T6; 872 g ha^{-1}). Control soils had minimal cumulative loads (74 g ha^{-1} PO_4-P and 471 g ha^{-1} NO_3-N).

3.5 Relationship between DOC and nutrient concentration in the leachate

Figure 6 illustrates the relationship between DOC and nutrient concentrations in leachate. Thirty samples were collected across five rainfall events, including six treatments at each event, and DOC values were plotted against corresponding nutrient concentrations. Dissolved organic carbon ranged from 15 to 531 mg L^{-1}, with an average of 158 mg L^{-1}. (Figure 6A) a strong positive correlation was observed between DOC and PO_4-P (r = 0.83, p < 0.001), and (Figure 6B) a moderate positive correlation with NO_3-N (r = 0.54, p < 0.05). These results indicate that elevated DOC levels are associated with increased nutrient leaching in coarse-textured soils.

3.6 Plant yield and nutrient uptake

Grain yield was highest in T2 (6,082 ± 451 kg ha^{-1}), followed by T4 (5,939 ± 406 kg ha^{-1}), T3 (5,647 ± 1,041 kg ha^{-1}), T5 (4,535 ± 503 kg ha^{-1}), and T6 (4,248 ± 1,625 kg ha^{-1}) (Figure 7). Above-ground biomass was greatest in T4 (6,612 ± 1,298 kg ha^{-1}), followed by T3 (6,318 ± 144 kg ha^{-1}), T2 (6,144 ± 557 kg ha^{-1}), T6 (5,699 ± 1,279 kg ha^{-1}), and T5 (5,557 ± 667 kg ha^{-1}); however, the differences in above ground biomass were statistically similar (p > 0.05). Soils receiving poultry litter (T2) produced significantly higher biomass and grain yield (p < 0.05) compared to soils without PL (T1). Grain yield was statistically similar among T2, T3, and T4, indicating that BC amendments maintained a similar yield and biomass, whereas alum and iron sulfate reduced yield but maintained biomass relative to T2, T3, and T4. The lower biomass and greater yield in T1 highlight the nutrient value of PL in enhancing corn productivity.

Nitrogen uptake in both above-ground biomass and grain was highest in T2, followed by T4. Treatments T3, T4, T5, and T6 exhibited similar N uptake in grain (Table 2), but all were significantly lower than T2, indicating that biochar, alum, and iron sulfate reduced N uptake compared to poultry litter alone. Phosphorus uptake in biomass was statistically similar across T2-T6, likely because soil test P levels exceeded the agronomic optimum,

TABLE 2 **Effect of different amendments on corn aboveground biomass[a] and grain nutrient uptake.**

Parts	Nutrient	Treatments					
		T1	T2	T3	T4	T5	T6
Above-ground biomass	N (kg ha^{-1})	61 ± 7.23^{b}	76 ± 3.40^{a}	46 ± 0.72^{c}	51 ± 8.90^{c}	45 ± 3.98^{c}	43 ± 8.52^{c}
	P (kg ha^{-1})	15 ± 1.16^{b}	22 ± 2.05^{a}	22 ± 0.87^{a}	23 ± 4.70^{a}	22 ± 2.96^{a}	22 ± 5.5^{a}
	K (kg ha^{-1})	52 ± 5.49^{cd}	92 ± 5.91^{a}	61 ± 2.80^{bc}	68 ± 13.7^{b}	45 ± 5.44^{d}	55 ± 11.9^{bcd}
	Mg (kg ha^{-1})	13 ± 1.26^{bc}	18 ± 0.92^{a}	10 ± 0.34^{d}	18 ± 3.35^{a}	10 ± 0.91^{cd}	13 ± 2.83^{b}
	Ca (kg ha^{-1})	36 ± 4.84^{b}	48 ± 2.80^{a}	19 ± 0.91^{c}	44 ± 7.85^{a}	23 ± 2.06^{c}	32 ± 6.87^{b}
	S (kg ha^{-1})	7.2 ± 0.85^{b}	13 ± 0.72^{a}	4.2 ± 0.07^{d}	5.5 ± 1.00^{c}	4.7 ± 0.37^{cd}	5.4 ± 1.10^{c}
	B (g ha^{-1})	87 ± 10.41^{c}	190 ± 14.8^{a}	97 ± 4.00^{c}	191 ± 33.5^{a}	99 ± 8.67^{c}	148 ± 30.3^{b}
	Zn (g ha^{-1})	322 ± 25.7^{a}	143 ± 9.95^{c}	173 ± 4.07^{c}	253 ± 46.7^{b}	224 ± 15.7^{b}	225 ± 45.1^{b}
	Mn (g ha^{-1})	372 ± 39.1^{bc}	442 ± 26.6^{ab}	248 ± 10.9^{d}	455 ± 82.9^{a}	278 ± 22.6^{d}	354 ± 73.6^{c}
	Fe (g ha^{-1})	242 ± 26.2^{c}	401 ± 16.8^{b}	402 ± 5.31^{b}	542 ± 108^{a}	343 ± 22.8^{b}	341 ± 66.2^{b}
	Cu (g ha^{-1})	44 ± 5.88^{a}	37 ± 1.87^{b}	16 ± 0.55^{d}	25 ± 4.57^{c}	18 ± 1.71^{d}	20 ± 3.92^{d}
Grain	N (kg ha^{-1})	13 ± 8.48^{c}	77 ± 5.68^{a}	69 ± 12.7^{ab}	76 ± 4.19^{a}	62 ± 6.89^{ab}	58 ± 22.1^{b}
	P (kg ha^{-1})	5.4 ± 3.53^{c}	34 ± 2.48^{a}	33 ± 6.04^{a}	32 ± 1.75^{a}	28 ± 3.07^{ab}	25 ± 9.59^{b}
	K (kg ha^{-1})	5.9 ± 3.77^{d}	40 ± 2.93^{a}	34 ± 6.35^{ab}	37 ± 2.05^{a}	29 ± 3.22^{bc}	26 ± 10.1^{c}
	Mg (kg ha^{-1})	2.2 ± 1.42^{c}	12 ± 0.90^{a}	12 ± 2.29^{a}	12 ± 0.66^{a}	10 ± 1.16^{ab}	8.5 ± 3.25^{b}
	Ca (kg ha^{-1})	0.3 ± 0.19^{e}	2.4 ± 0.18^{a}	1.1 ± 0.21^{c}	1.8 ± 0.10^{b}	0.9 ± 0.10^{cd}	0.9 ± 0.32^{d}
	S (kg ha^{-1})	1.0 ± 0.68^{c}	6.1 ± 0.45^{a}	5.6 ± 1.04^{a}	5.9 ± 0.33^{a}	5 ± 0.55^{ab}	4.2 ± 1.63^{b}
	B (g ha^{-1})	3.8 ± 2.48^{d}	30 ± 2.26^{a}	28 ± 5.21^{ab}	30 ± 1.65^{a}	23 ± 2.52^{bc}	21 ± 8.13^{c}
	Zn (g ha^{-1})	52 ± 33.4^{b}	261 ± 19.4^{a}	248 ± 45.8^{a}	240 ± 13.2^{a}	222 ± 24.6^{a}	208 ± 79.7^{a}
	Mn (g ha^{-1})	17 ± 11.1^{e}	97 ± 7.21^{a}	79 ± 14.6^{bc}	84 ± 4.62^{ab}	68 ± 7.55^{c}	51 ± 19.5^{d}
	Fe (g ha^{-1})	32 ± 20.4^{d}	201 ± 14.8^{a}	181 ± 33.3^{ab}	180 ± 9.90^{ab}	154 ± 17.1^{bc}	127 ± 48.8^{c}
	Cu (g ha^{-1})	2.9 ± 1.86^{d}	18 ± 1.35^{a}	17 ± 3.13^{a}	18 ± 0.99^{a}	14 ± 1.51^{b}	8.5 ± 3.25^{c}

[a]Above Above-ground biomass includes stems, leaves, husk, and empty cobs.
Superscript letters indicate significant differences in treatment means at the 5% level.
T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, T6 = Soil + PL + iron sulfate (BC, biochar, PL, Poultry litter).

resulting in no differential response among these treatments. In contrast, the lack of response in T1 was primarily due to N limitation, as no external N source was applied. Potassium uptake in biomass was greatest in T2 and lowest in T5, suggesting that alum reduced K uptake. Similarly, grain K was lowest in T5 and T6, indicating that both alum and iron sulfate decreased K uptake, whereas T2 had the highest values. Micronutrient uptake (B and Mn) in biomass was greatest in T2 and T4, while T3 and T5 showed statistically similar concentrations.

3.7 Nitrogen and phosphorus concentration in the pre-sowing and post-harvest soil samples

A two-way factorial analysis was performed (Table 3) to evaluate N and P status in soil before and after corn harvest across various treatments. The Mehlich-3 extractable P was significantly ($p < 0.05$) reduced from 335 ± 108 mg kg^{-1} at planting to 285 ± 92 mg kg^{-1}, harvest while NH_4-N and NO_3-N were decreased from 26 ± 11 to 3.5 ± 1.6 mg kg^{-1} and 3.73 ± 1.53 to 2.05 ± 0.44 mg kg^{-1}, respectively. The effect of treatments were found significant, as control (T1) soil exhibited lowest P (102 ± 6 mg kg^{-1}), NH_4-N (4.46 ± 2.5 mg kg^{-1}) and NO_3-N (1.49 ± 0.61 mg kg^{-1}), while soils receiving PL application recorded a significant amount of P (324–363 mg kg^{-1}), NH_4-N (14.3–20.7 mg kg^{-1}) and NO_3-N (2.81–3.58 mg kg^{-1}), reflecting the nutrient enrichment associated with manure application. A significant ($p < 0.05$) interaction between pre-sowing and post-harvest soil samples for NH4-N and NO3-N was observed across treatments. At pre-sowing, T5 (alum amended) and T6 (iron sulfate amended) recorded the highest level of NH_4-N (35.7 ± 7.26 and 35.0 ± 3.29 mg kg^{-1}, respectively), which was significantly decreased to 5.66 ± 1.35 and 2.65 ± 0.49 mg kg^{-1}. Similarly, at pre-sowing, BC-amended soils (T4 and T3) showed the highest NO_3-N (4.99 ± 0.49 and 4.79 ± 1.21 mg kg^{-1}), which were significantly reduced to 2.18 ± 0.17 and 1.63 ± 0.21 mg kg^{-1}, respectively. Post-harvest soils showed lower levels of extractable N and P than pre-sowing conditions, largely due

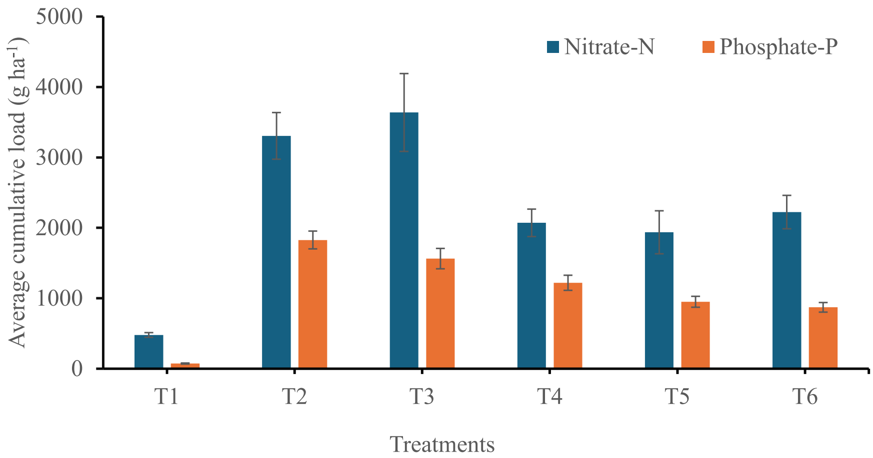

FIGURE 5
Average cumulative load (g ha^{-1}) of nitrate-N (NO_3-N) and phosphate-P (PO_4-P) across treatments following five rainfall events. Each bar indicates the mean ± standard errors. Treatments were: T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, and T6 = Soil + PL + iron sulfate (BC = biochar; PL = poultry litter).

to crop uptake, microbial immobilization-mineralization, and potential leaching during the crop-growing season.

4 Discussion

4.1 Trends of NO_3-N and PO_4-P leaching across different rainfall events

The present study demonstrated distinct NO_3-N and PO_4-P leaching patterns across rainfall events. Phosphate leaching increased markedly during high-rainfall events, whereas NO_3-N leaching was more closely aligned with crop growth dynamics. These findings are consistent with Nguyen et al. (2013), who reported that NO_3-N losses from manure-amended, tile-drained systems were greatest during the early crop growth stages and were driven more by the timing of precipitation than by total rainfall amounts.

Phosphorus leaching patterns observed in our study further reflect the influence of legacy P accumulated from manure applications. As noted by McDowell et al. (2020), elevated soil test P (STP) concentrations indicate long-term buildup of legacy P, which can release dissolved P for years even with little or no new P inputs. The high Mehlich-3 STP values in our soils corroborate this accumulation. Once soil P approaches or exceeds its sorption capacity, the equilibrium shifts from solid-phase P toward greater P release into the soil solution. This mechanism likely contributed to the elevated PO_4-P concentrations observed during high-rainfall events (E1 and E5), where increased water flux facilitated the mobilization of legacy P into the leachate.

4.2 Role of amendments in restricting NO_3-N and PO_4-P leaching loads

The amendments used in this study exhibited variable retention patterns for NO_3-N and PO_4-P, reflecting differences in their chemical properties and interaction mechanisms. Across five rainfall events, the retention of NO_3-N showed the following pattern: alum (T5) > BC-2 (T4) > iron sulfate (T6). However, the ranking represents a descriptive comparison of cumulative values, rather than a statistically supported treatment effect, suggesting that the effect of the amendment on nitrate load was highly variable and influenced by the temporal dynamics of crop growth stages. The BC-1 showed delayed mobilization of NO_3-N that subsequently released more NO_3-N than the unamended soil (T2), consistent with previous findings that reported pristine BC's limited affinity for nitrate and its subsequent release (Hale et al., 2013; Gai et al., 2014). This behavior could be linked with the negative surface charge of BC, causing electrostatic repulsion of anions such as NO_3^-. The retention of PO_4-P was significant between amendments and across five rainfall events; the PO_4-P retention followed the order: iron sulfate (T6) > alum (T5) > BC-2 (T4) > BC-1 (T3). The BC-2 demonstrated greater PO_4-P retention than BC-1, which might be associated with a higher availability of positively charged surface sites within a broader specific surface area. However, the present study did not conduct detailed morphological or surface chemical characterization (e.g., functional group characterization or surface charge determination), causal mechanisms underlying the variable performance of the two BC's cannot be conclusively established. The observed differences in nutrient retention should therefore be interpreted as associated with, rather than directly driven by, differences in specific surface area, metal content, pore structure, and surface chemistry between the BCs.

Phosphate sorption by BC was more effective than NO_3-N retention because PO_4-P interacts through different mechanisms. Rather than relying on electrostatic attraction, PO_4^{-3} can form inner-sphere complexes with Ca, Mg, Al, or Fe on biochar surfaces via ligand exchange (Hale et al., 2013). Previous studies have reported significant reductions in PO_4-P leaching when BC was applied to manured soils, although performance varies widely depending on the feedstock type and pyrolysis temperature, which influence surface chemistry and pore structure. For example, Sun et al. (2011) observed higher PO_4-P sorption by

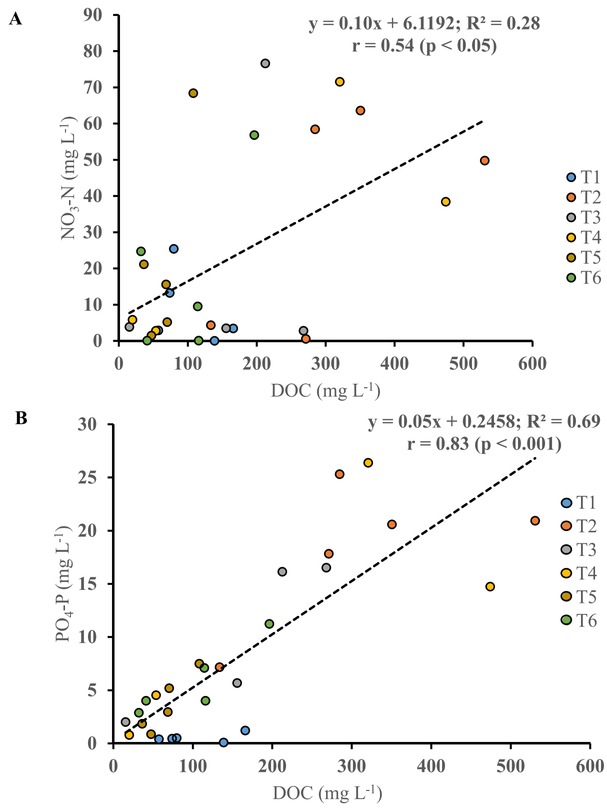

FIGURE 6
Relationships between **(A)** NO_3–N and **(B)** PO_4–P and dissolved organic carbon (DOC) in leachate collected during different rainfall events across treatments. Treatments were: T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, and T6 = Soil + PL + iron sulfate (BC = biochar; PL = poultry litter).

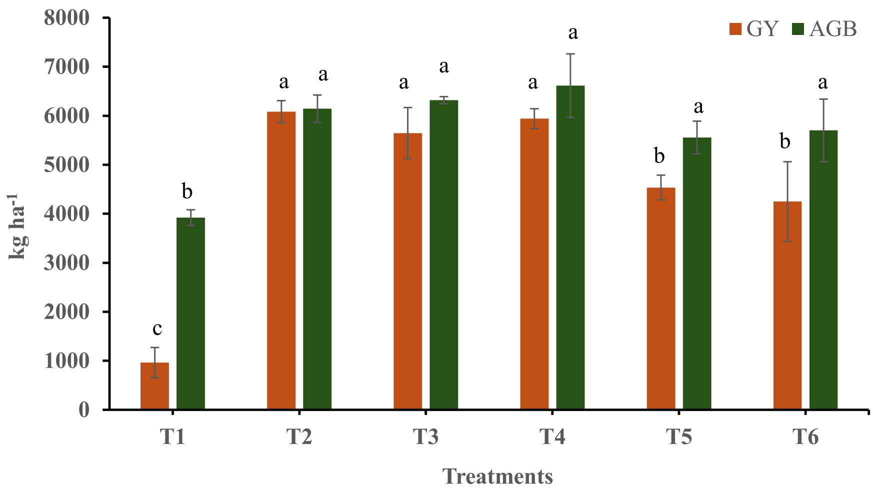

FIGURE 7
Effect of treatments on corn above-ground biomass (AGB) and grain yield (GY). Bars sharing the same letter are not significantly different for AGB or GY at the 5% significance level. T1 = Soil (control), T2 = Soil + poultry litter (PL), T3 = Soil + PL + biochar-1 (BC-1), T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum, T6 = Soil + PL + iron sulfate.

TABLE 3 Nitrogen (NH_4-N, NO_3-N) and phosphorus (P) concentration across various treatments at pre-sowing (PS) and post-harvest (PH) soil samples.

Factors	[a]P (mg kg^{-1})	[b]NH_4-N (mg kg^{-1})	[b]NO_3-N (mg kg^{-1})
Factor A			
PS	335^{a} ± 108	26^{a} ± 11	3.73^{a} ± 1.53
PH	285^{b} ± 92	3.5^{b} ± 1.6	2.05^{b} ± 0.44
Factor B			
T1	102^{c} ± 6	4.46^{d} ± 2.5	1.49^{c} ± 0.61
T2	363^{a} ± 40	15.5^{bc}±13.8	3.05^{ab} ± 0.85
T3	367^{a} ± 54	14.8^{c} ± 12.4	3.21^{ab} ± 1.87
T4	354^{a} ± 48	14.3^{c} ± 11.3	3.58^{a} ± 1.54
T5	352^{ab} ± 34	20.7^{a} ± 16.8	3.21^{ab} ± 1.33
T6	324^{b} ± 44	18.8^{ab} ± 17.4	2.81^{b} ± 1.20
Factor AXB			
PH_T1	99 ± 3.2	2.17^{c} ± 0.50	1.92^{de} ± 0.60
PH_T2	328 ± 18	3.34^{c} ± 1.73	2.32^{d} ± 0.42
PH_T3	343 ± 64	3.48^{c} ± 1.60	1.63^{de} ± 0.21
PH_T4	314 ± 34	3.88^{c} ± 1.81	2.18^{d} ± 0.17
PH_T5	340 ± 31	5.66^{c} ± 1.35	2.45^{d} ± 0.19
PH_T6	286 ± 21	2.65^{c} ± 0.49	1.78^{de} ± 0.36
PS_T1	105 ± 7.5	6.74^{c} ± 0.78	1.06^{e} ± 0.08
PS_T2	398 ± 12	27.7^{b} ± 6.62	3.77^{c} ± 0.29
PS_T3	390 ± 34	26.1^{b} ± 4.00	4.79^{ab} ± 1.21
PS_T4	393 ± 4.3	24.7^{b} ± 2.46	4.99^{a} ± 0.49
PS_T5	364 ± 37	35.7^{a} ± 7.26	3.96^{bc}±1.60
PS_T6	362 ± 9.8	35.0^{a} ± 3.29	3.83^{bc}±0.65

[a]Mehlich 3 extractable.
[b]KCL, extractable.
Factor A = sampling time, Factor B = treatments, Factor AXB, interaction effect.
T1 = Soil (control), T2 = Soil + PL, T3 = Soil + PL + BC-1, T4 = Soil + PL + BC-2, T5 = Soil + PL + Alum T6 = Soil + PL + iron sulfate. (BC, biochar, PL, Poultry litter).
N = 4 observations were used for the standard deviation. Superscript letters denote significant differences between treatment means ($P \leq 0.05$).

PL-BC compared to wheat-straw BC produced at the same temperature (400 ˚C), while Chun et al. (2004) demonstrated that high-temperature BCs (500 ˚C–700 ˚C) exhibit greater sorption capacity due to higher specific surface area (>300 m^2 g^{-1}) compared to low-temperature BCs (<200 m^2 g^{-1}). These findings highlighted the variability of BCs in their adsorption mechanisms, indicating the importance of selecting amendments based on their chemical properties.

4.3 Role of DOC in regulating NO_3-N and PO_4-P leaching

Dissolved organic carbon plays a pivotal role in nutrient mobility by interacting with N and P species in the soil solution. In this study, DOC exhibited a strong positive correlation with both NO_3-N and PO_4-P in leachate, consistent with the previous findings by Corman et al. (2018), who observed strong positive correlations between DOC and nutrient concentrations in Wisconsin lake waters (N: r = 0.68; P: r = 0.54). Dissolved organic carbon can serve as a carbon and energy source for heterotrophic microbes, stimulating denitrification and N immobilization, which under low-N and anaerobic conditions may reduce NO_3-N leaching (Velescu et al., 2016). However, under high N inputs, such as soils receiving excess manure applications, microbial demand becomes saturated. Hence, NO_3-N leaching accelerates due to enhanced mineralization (Tiefenbacher et al., 2020). Some of the N may also leach as dissolved organic nitrogen (DON) together with the DOC and mineralize to NO_3-N deeper in the profile or at the receiving end (Van Kessel et al., 2009).

The positive correlation between DOC and PO_4-P is mechanistically stronger. Organic acids within Dissolved organic carbon (DOC) can chelate Fe and Al oxides that normally bind phosphate (PO_4^{3-}), thereby displacing phosphate and increasing the solubility of PO_4–P (Fetzer et al., 2021). DOC also competes with

PO_4-P for sorption sites and forms soluble metal-DOC complexes that facilitate co-leaching. Furthermore, DOC-driven microbial activity enhances phosphatase enzyme production, promoting mineralization of organic P to inorganic PO_4-P, enhancing the leaching risk (Dong et al., 2022). These interactions explain why soils receiving PL, which are rich in labile organic matter, exhibited elevated DOC and corresponding increases in nutrient losses.

However, in the present study, DOC was not experimentally manipulated to state a direct causal relationship between nutrient leaching and DOC. It acts as a proxy integrator of multiple biogeochemical processes and covaries with multiple factors, i.e., manure loading rate, rainfall intensity, soil nutrient saturation, and rate of microbial activity. Hence, DOC should be interpreted as an associated indicator rather than a sole mechanistic driver of nutrient leaching in this system. However, the strong association observed in this study highlights the importance of DOC dynamics in regulating nutrient mobility, suggesting that the role of DOC must be considered when designing strategies to mitigate nutrient leaching from manured soils.

4.4 Effect of amendments on corn biomass and grain yield

Amendments influenced corn yield and nutrient uptake primarily through their interaction with PL and soil nutrient dynamics. Grain yield was highest in the unamended PL (T2; 6,082 kg ha^{-1}), confirming the critical role of PL in supplying readily available nutrients. BC-amended treatments (T3 and T4) maintained significantly similar yields comparable to T2, suggesting that BC did not hinder nutrient availability and may have improved soil physical properties or nutrient retention. Holatko et al. (2022) enriched PL with 10% and 20% BC and observed a significant increase of 29% and 68% in corn grain yield, along with corresponding increases of 3% and 42% in aboveground biomass yield over unamended PL. While alum (T5) and iron sulfate (T6) effectively reduced nutrient (N and P) losses, these environmental benefits were accompanied by a measurable reduction in grain yield, highlighting a clear trade-off between nutrient loss mitigation and agronomic performance. Both amendments (T5 and T6) maintained total biomass but reduced grain yield, suggesting a possibility of P fixation and subsequent immobilization of P in the acidic soil environment (Chatterjee et al., 2015), reducing grain P uptake in T5 (alum; 28 ± 3.07 kg ha^{-1}) and T6 (iron sulfate; 25 ± 9.59 kg ha^{-1}) compared to T2 (unamended; 34 ± 2.48 kg ha^{-1}), T3 (BC-1; 33 ± 6.04 kg ha^{-1}) and T4 (BC-2; 32 ± 1.75 kg ha^{-1}). Similar to P, Grain K uptake was significantly lower in alum (T5; 29 ± 3.22 kg ha^{-1}) and iron sulfate (T6; 26 ± 10.1 kg ha^{-1}) amended soils compared to unamended (T2; 40 ± 2.93 kg ha^{-1}) and BC-amended (T3; 34 ± 6.35 and T4; 37 ± 2.05 kg ha^{-1}) soils. This revealed that excessive Al and Fe might interfere with K retention and uptake, reflecting antagonistic nutrient interactions that can limit root function and nutrient absorption (Mariano and Keltjens, 2005). Additionally, micronutrient uptake, particularly B and Mn, was significantly lower under alum (B; 23 ± 2.52 g ha^{-1}, Mn; 68 ± 7.55 g ha^{-1}) and iron sulfate (B; 21 ± 8.13 g ha^{-1}, Mn; 51 ± 19.5 g ha^{-1}) treatments compared to unamended PL (B; 30 ± 2.26 g ha^{-1}, Mn; 97 ± 7.21 g ha^{-1}) or BC-amended (BC-2) (B; 30 ± 1.65 g ha^{-1}, Mn; 84 ± 4.62 g ha^{-1}) soils, indicating micronutrient imbalance associated with elevated Al and Fe availability (Baligar and Fageria, 2005). Given corn's known sensitivity to micronutrient availability during reproductive development (Stewart et al., 2021), such imbalances may partially explain the observed grain yield reduction. However, the inclusion of BC may enhance micronutrient availability through improved cation exchange or organic complexation (Xu et al., 2022). The grain N uptake mirrored yield trends, with unamended PL showing the highest uptake (T2; 77 ± 5.68 kg ha^{-1}), followed by BC-amended soils (T3; 69 ± 12.7 kg ha^{-1} and T4; 76 ± 4.19 kg ha^{-1}), while alum (T5; 62 ± 6.89 kg ha^{-1}) and iron sulfate (T6; 58 ± 22.1 kg ha^{-1}) amended soils exhibited lower N uptake, likely due to reduced N mineralization. Overall, these findings indicated that although chemical amendments can minimize nutrient leaching, their application at higher rates may impose agronomic penalties through nutrient antagonism and micronutrient imbalances. Therefore, optimization of amendment rate is critical to balance environmental benefits with crop productivity. Compared to alum and iron sulfate, BC offered a more balanced approach by sustaining grain yield while improving nutrient retention, indicating better suitability for integrated nutrient and environmental management.

5 Conclusion

This study demonstrated that NO_3-N and PO_4-P leaching from manured soils were strongly influenced by crop growth stage and rainfall distribution, respectively. Nitrate losses were greatest during the early crop growth phases when plant nitrogen demand was minimal, whereas PO_4-P losses were driven by high rainfall events that mobilized legacy P through desorption and preferential flow. Among the amendments tested, alum and iron sulfate were most effective in reducing PO_4-P leaching, while BC exhibited variable performance, with BC-2 outperforming BC-1. The limited retention of NO_3-N by the amendments underscores the challenge of implementing effective mitigation strategies for NO_3^- loss in actual soil environments. The effect of BC was contextual and property-dependent, suggesting the critical role of surface chemistry in governing nutrient retention. The strong association between DOC and nutrient leaching suggests that DOC acts as a key indicator in nutrient mobility, especially in heavily manured soil, and should be prioritized during soil management and mitigation strategies. While chemical amendments effectively mitigate P losses, they may reduce crop yield and nutrient uptake, whereas BC offers a more balanced approach to maintaining productivity while partially reducing leaching. It should be noted that the present study employed a relatively high amendment rate (10% w/w relative to PL), representing an upper-bound mitigation scenario rather than a field-optimized recommendation. Therefore, future studies should focus on the amendment rate optimization under field conditions. Long-term studies across diverse cropping systems and rainfall regimes, such as monocropping, mixed cropping, and perennial grass systems under humid temperate and semi-arid climates with subsurface tile drainage systems, can better elucidate the DOC-associated nutrient transport for sustainable manure management and water quality protection.

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 author.

Author contributions

SG: Data curation, Formal Analysis, Methodology, Software, Validation, Writing – original draft, Writing – review and editing. RP: Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Visualization, Writing – original draft, Writing – review and editing. DC: Conceptualization, Investigation, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review and editing. PR: Conceptualization, Formal Analysis, Methodology, Project administration, Writing – original draft, Writing – review and editing.

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Conflict of interest

The 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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