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## Influence of the climate variability and two mineral fertilization programs on nitrogen losses in coffee (Coffea arabica L.)

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Introduction: Global coffee production is increasingly vulnerable to climate change and variability, particularly nitrogen (N) losses via ammonia volatilization (NH<sub>3</sub>) and nitrate (NO<sub>3</sub><sup>-</sup>) leaching. Improved N management could mitigate these losses, yet field-level evidence under ENSO-driven climate variability remains limited. We aimed to quantify N losses via leaching and volatilization under two contrasting fertilization programs in a Colombian coffee plantation and assess their sensitivity to El Niño/La Niña-Southern Oscillation (ENSO) phases.

Methods: A field experiment was conducted from 2022 to 2024 in the Central West coffee region of Colombia. N leaching was monitored using drainage lysimeters, and NH<sub>3</sub> volatilization was measured with semi-open static collectors. This study spanned two ENSO phases La Niña (2022-mid-2023) and El Niño (mid-2023-2024). Two fertilization programs were evaluated: a urea-based NPK blend (UB-NPK), an ammonium-nitrate-based NPK (ANB-NPK), and a no-N control.

Results: Nitrogen losses were significantly influenced by both fertilizer type and climate phase. During La Niña (negative ENSO phase), leaching was dominant loss pathway, with no significant differences between treatments. During El Niño (positive ENSO phase), NH<sub>3</sub> volatilization became the dominant loss mechanism, with significantly higher losses in the UB-NPK treatment. Cumulatively, after 2 years and six fertilizations, mean N losses were 36.7% for UB-NPK and 13.1% for ANB-NPK of the total N applied.

Discussion: ENSO-driven climate variability alters nitrogen loss dynamics in coffee systems. Urea-based fertilizers resulted in greater losses under El Niño conditions, while ammonium-nitrate-based blends showed improved N retention. These findings highlight the potential of fertilizer type selection as a mitigation strategy under variable climate conditions.

leaching, nitrates, ammonium, ammonia, volatilization, climate variability

#### 1 Introduction

Coffee has 103 species (Davis et al., 2006); however, two are the most planted, Coffea arabica L (Arabica coffee) and Coffea canephora Pierre (Robusta coffee). Currently 60% of the global market share is Arabica coffee, and 40% Robusta coffee (Shister, 2024). Coffee is highly susceptible to climate change and variability, which is projected to reduce suitable cultivation areas by 40%-75% across Asia, Africa, and the Americas over the next 30 years (Camargo, 2010; Bunn et al., 2015; Ovalle et al., 2015; Grüter et al., 2022). The Climate Change has the potential to slash Arabica coffee production by a staggering 45.2%, while global Robusta production could suffer a 23.5% decline (Dzebo and Adams, 2022). These reductions are mainly due to increasing climate variability, particularly associated with the El Niño/La Niña-southern Oscillation (ENSO) (Goddard and Gershunov, 2020; Trenberth, 2020; Yang et al., 2018), which causes strong changes in annual temperatures, prolonged dry seasons, and erratic rainfall (Grüter et al., 2022).

The reduction in suitable areas for coffee production warrants the implementation of mitigation strategies to support existing production zones and reduce greenhouse gas (GHG) emissions from the sector. GHG emissions arise from fertilizer production and use, contributing between 2% and 5% of the total emissions (IPCC, 2014; Gao and Serrenho, 2023). The most prevalent GHG emissions are in the form of nitrous oxide-N2O, methane- CH4 and carbon dioxide-CO2, accompanied by high emissions of ammonia-NH<sub>3</sub> (Walling and Veneeckhaute, 2020), At field level, N<sub>2</sub>O being directly produced through nitrification and denitrification of the mineral fertilizers in the field (Pesek et al., 1971). Additionally, N2O is indirectly emitted from nitrate leaching and ammonia volatilization, as both forms of nitrogen loss can be partially converted to N2O by soil microorganisms (Gao and Serrenho, 2023). It is estimated that agriculture is responsible for more than 80% of the anthropogenic emissions of N2O and 70% of anthropogenic NH<sub>3</sub> emissions (Waling and Vaneeckhaute, 2020).

Nitrogen is a critical macronutrient for the growth and development of coffee plants (Coffea spp.), and it's the most demanded followed by potassium and calcium, influencing both vegetative and reproductive phases (Carr et al., 2020; Bruno et al., 2020; Favarin et al., 2021; Sadeghian, 2022). It also plays a key role in enhancing abiotic stress tolerance (Ramirez et al., 2024). Nitrogen from mineral or organic fertilizers, as well as from biological fixation and atmospheric deposition, is not fully absorbed by plants. A large proportion is either incorporated into soil organic matter, adsorbed onto clay particles, volatilized as NH3, emitted as N2O during nitrification and denitrification, or lost through leaching and surface runoff (Di and Cameron, 2002; Harman et al., 2007; Jaramillo, 2003). Low fertilizers-N recovery efficiency (FNRE) values of 6%-29% in coffee have been reported (Salamanca et al., 2017a), Therefore efficient nitrogen use remains a major challenge in sustainable coffee crop production (Salamanca et al., 2017b; DaMatta et al., 2018; Busato et al., 2022; Ramirez et al., 2023).

From the soil perspective, the dominant N form in the soil is  $NO_3^-$  (Tisdale et al., 1985; Harman et al., 2007; Sadeghian, 2022), while all the mineral N applied in ureic and/or  $NH_4$  form need to be transformed trough amonification and nitrification to  $NO_3^-$ . From the physiological and agronomical perspective, coffee plants growth

better when a balance between  $\mathrm{NH_4}$ - $\mathrm{N:NO_3}$ - $\mathrm{N}$  exist in the soil with optimun proportion between 50%  $\mathrm{NH_4}$ - $\mathrm{N:50\%}$   $\mathrm{NO_3}$ - $\mathrm{N}$  to 15%  $\mathrm{NH_4}$ - $\mathrm{N:85\%}$   $\mathrm{NO_3}$ - $\mathrm{N}$  (Carr et al., 2020; Ramirez et al., 2024). Excesive  $\mathrm{NH_4}$  in the soil solution induce excesive protons production by the roots increasing rhizosphere accidification (Tisdale et al., 1985; Marschner, 2012), while under mixed N nutrition, the protons generated by  $\mathrm{NH_4}^+$  assimilation can be used for  $\mathrm{NO_3}^-$  reduction; therefore, it is easier for plants to regulate their intracelullar pH when both form of N are suplied (Hawkesford et al., 2012; Ramirez et al., 2024).

Ammonia (NH<sub>3</sub>) volatilization and NO<sub>3</sub><sup>-</sup> leaching are the most important N losses in coffee production systems (Leal et al., 2007; Cannavo et al., 2013; Gonzalez et al., 2015; Chagas et al., 2019; Sarkis et al., 2023). Among nitrogen sources, urea is the most widely used in coffee cultivation due to its low cost per unit of N and high N concentration (Salamanca et al., 2017a; Chagas et al., 2019). It is the preferred N source in major coffee-growing regions (Ferrão et al., 2012; Matiello et al., 2010; Sadeghian and González, 2012; Sadeghian and Duque, 2019; Wilson, 1999). However, urea is associated with significantly higher ammonia volatilization compared to other N sources such as ammonium sulfate, ammonium nitrate, or nitratebased fertilizers (Chagas et al., 2019; de Souza et al., 2023; Fenilli et al., 2008; Freitas et al., 2022; Gonzalez et al., 2015; Leal et al., 2007; Tiemann et al., 2018).

Nitrate leaching is the second most significant N loss, regardless of the mineral N source. Leaching is influenced by soil type, production system (e.g., monoculture or agroforestry), soil moisture, and climatic conditions (Bortolotto et al., 2012; Harman et al., 2007; Pivotto et al., 2012; Sarkis et al., 2023; Tully et al., 2012). Improving nitrogen use efficiency (NUE) by reducing nitrogen loss is essential to optimize fertilizer application and mitigate environmental impacts (Barłóg, 2023) including direct and indirect GHG (Gao and Serrenho, 2023).

Fluctuations in rainfall, temperature, and soil moisture influence nitrogen dynamics in the soil, altering the rates of mineralization, nitrification, and denitrification (Tisdale et al., 1985; Rawat et al., 2022). In the Central-west Colombian coffee region has been reported changes on the rainfall patterns, solar radiation and soil moistures under El Niño/La Niña-southern Oscillation -ENSO (Guzman and Baldión, 1997; 1999; Peña et al., 2012; Ramirez and Jaramillo, 2009; Garcia et al., 2023), but do not exist scientific evidence of the influence of ENSO fluctuations over nitrogen losses by volatilization and leaching comparing different N sources. We aimed to measure the influence of climatic variability on N losses through leaching and volatilization under two different mineral fertilization programs in coffee under climate variability El Niño/La Niña-southern Oscillation (ENSO) conditions.

#### 2 Materials and methods

#### 2.1 Study site

Between 2022 and 2024, a field trial was conducted on a commercial coffee farm in the central-west coffee region of Chinchiná, Caldas, Colombia (04°56′N, 75°36′W; 1,400 m elevation). The site has a mean air temperature of 20.4 °C, average relative humidity of 79.3%, and annual rainfall of

TABLE 1 Climate conditions obtained from the weather station El Jazmina.

Year	T. max (°C)	T. min (°C)	T. med (°C)	R.H (%)	Rainfall (mm)
2022	25.8	15.6	19.1	81.7	2,439
2023	26.0	16.4	20.4	77.8	2,419
2024	26.2	16.7	20.4	78.5	2,197
Mean	26.0	16.2	20.0	79.3	2,350
2014-2024	26.6	16.0	19.9	77.3	2,290

<sup>\*</sup>El Jazmin weather station (04°55′N-75°38′W), National Coffee Research Center—Meteorological Network. T. max, average maximum air temperature; T min, average minimum air temperature; T. med, average mean air temperature; R.H., average relative humidity; rainfall, cumulative annual precipitation.

2,350 mm (Table 1). According to the USDA Soil Taxonomy, the dominant soil type at the study site is an Andisol, specifically classified as a Typic Melanudand (González, 2013). This soil is characterized by low natural fertility, with a pH of 4.67, 10.56% organic matter, and 8.44 mg kg<sup>-1</sup> of available P. Exchangeable cation levels were 0.24, 0.93, and 0.24 cmol<sub>c</sub> kg<sup>-1</sup> of K, Ca, and Mg, respectively. The soil texture consisted of 54% sand, 29% silt, and 17% clay.

Soil pH was measured in water (1:1), organic matter via the Walkley–Black method, P using Bray-II extraction, and exchangeable K, Mg, and Ca by 1 N ammonium acetate (pH 7.0). Cation concentrations were determined by ICP (Perkin Elmer, Optima 8000, Shelton, CT, USA), and particle size distribution was assessed using the Bouyoucos hydrometer method.

The study area was planted with *Coffea arabica* L. Var Castillo<sup>®</sup>, established in 2012 under full sun at a planting density of 6,666 plants ha<sup>-1</sup>, with 1.0 m between plants and 1.5 m between rows. Prior to the trial, the plantation was stem-pruned to 30 cm in height in January 2021 to rejuvenate the stand and initiate a new production cycle.

#### 2.2 Experimental design

To evaluate the impact of different mineral fertilizer forms on nitrogen losses via leaching and ammonia volatilization, two fertilization programs were evaluated: a) a physical NPK fertilizer blend based on urea—the most used nitrogen source among coffee farmers (UB-NPK), and b) a chemical compound NPK blend based on ammonium nitrate (ANB-NPK), formulated with 20% less N. Mineral fertilization was broadcasting applied, over the canopy projection into the each of the lysimeters.

Additionally, a control treatment without N was included, but phosphorus, potassium, magnesium, and sulfur were applied using single nutrient sources: muriate of potash (60%  $K_2O$ ), calcium phosphate (40  $P_2O_5$ , 26% CaO), and magnesium sulfate (27% MgO, 22% S).

This trial was embedded within a long-term experiment established in 2018 to test the hypothesis that ANB-NPK, with 20% less N and enriched with soluble calcium and micronutrients, would improve NUE and reduce the carbon footprint of coffee production without compromising yield, compared to the urea-based NPK fertilizer commonly used by farmers. Results from the ongoing study (publication in progress) indicate that the AN-NPK program-maintained coffee yields

over 6 years, did not alter soil N stocks, significantly improved NUE, and reduced the CFP.

We aimed to quantify N losses from both fertilization strategies over 2 years with contrasting climate conditions influenced by ENSO variability.

From August 2022 to August 2024, 12 drainage lysimeters were installed in the field to monitor water percolation and N leaching across the two fertilization treatments and the control without N, which received only PK fertilization (Table 2).

#### 2.3 Leaching evaluation

Water percolation and nitrogen leaching were measured using drainage-type lysimeters (Ramirez et al., 2011; Howell, 2005), consisting of round polyethylene containers with a depth of 1.0 m and an exposed soil surface area of 0.22 m². Each lysimeter was equipped with a bottom stopcock to collect percolated water. The drainage system consisted of a 0.2 m layer of coarse gravel at the bottom, followed by a 0.2 m layer of medium gravel, then a 0.2 m layer of fine gravel, all covered with a geotextile drainage mesh. A 0.2 m layer of stockpiled soil was placed above the drainage layers, in reverse order of excavation. In the remaining 0.2 m at the top, a coffee plant was transplanted along with its undisturbed root zone, carefully extracted to preserve root integrity. C. Arabica var. Castillo has 86% of its root system distributed within the top 25 cm of soil and 25 cm around the stem (Rendon and Giraldo, 2019).

Twelve lysimeters (four replicates per treatment across tree treatments) were installed in the middle of the coffee plantation to maintain natural microclimatic conditions. Four lysimeters were equipped with rain gauges placed beneath the coffee canopy to measure net rainfall—precipitation that reaches the fertilized soil surface. An additional lysimeter without a coffee plant was installed to measure external (open-field) rainfall and corresponding percolation.

At installation, soil samples were collected at 0–20 and 20–40 cm depths to estimate baseline nitrogen stocks, with a total N of 641,7 mg.100 g<sup>-1</sup>, 1.85% NO<sub>3</sub>-N and 0.15% NH<sub>4</sub>-N in the 0–20 cm and 350 mg.100 g<sup>-1</sup>, 0.68% NO<sub>3</sub>-N and 0.18% NH<sub>4</sub>-N in the 20–40 cm (Supplementary Material S1) 3) and assess soil physical parameters with a mean bulk density 0.79 g.cm<sup>-3</sup>; porosity 69.5%; volumetric soil moisture at field capacity 0.39 m<sup>3</sup>. m<sup>-3</sup>; and volumetric moisture content at wilting point 0.19 m<sup>3</sup>. m<sup>-3</sup> (Suplemental Material 2). Rainfall was recorded daily, and water

ANB-NPK **UB-NPK** Application no Date NH<sub>4</sub>-N (%) NO<sub>3</sub>-N (%) Rate (kg Rate (kg Sep-2022 100 40 0.0 Jan-2023 100 0.0 0.0 70 0.0 3 Apr-2023 77 23.0 0.0 110 0.0 42 58 4 Sep-2023 50 100 0.0 0.0 30 0.0 52 48 5 Jan-2024 120 100 0.0 0.0 88 0.0 27 73 6 Mar-2024 140 80 20.0 0.0 120 0.0 43 57

0.0

457

TABLE 2 Nitrogen rates and forms for two mineral fertilization programs for 2 years.

percolation through the first 40 cm of soil was measured weekly. The collected leachate samples were analyzed for N concentration in the forms of ammonium (NH $_4$ -N) and nitrate (NO $_3$ -N) using photometry based on colorimetric methods specific to each nitrogen species.

569

93

7.0

Total average

Ammonium was quantified using a mid-range photometer (HI 97715, Hanna Instruments, Italy) using the Nessler method, which forms a yellow-colored complex in the presence of free ammonia (via K<sub>2</sub>HgI<sub>4</sub> in alkaline solution). The device was calibrated for a detection range of 0.00-10.00 mg/L of ammoniacal nitrogen. Nitrate was measured using the HI 97728 photometer (Hanna Instruments, Italy) and the cadmium reduction method. This procedure involves the reduction of nitrate (NO<sub>3</sub><sup>-</sup>) to nitrite (NO<sub>2</sub><sup>-</sup>) using a cadmiumbased reagent, followed by a diazo-coupled reaction in an acidic medium. In the second stage, the resulting nitrite reacts with sulfanilic acid to form a diazonium salt, which is subsequently coupled with an aromatic compound—usually N-(1-naphthyl) ethylenediamine-to form a pink-colored azo complex. The color intensity is proportional to the nitrate concentration in the sample, with a detection range of 0.0-30.0 mg L<sup>-1</sup> of NO<sub>3</sub>-N. For both ammonium and nitrate analyses, 1 mL aliquots of each fieldcollected sample were diluted to a final volume of 10 mL with deionized water in 24.6 mm diameter round cuvettes, ensuring optimal conditions for accurate photometric measurement.

For each lysimeter, the cumulative leaching ( $CL_i$ ) of  $NH_4$ -N and  $NO_3$ -N was calculated as the sum of nitrogen losses over time using Equation 1:

$$CL_{i} = \Sigma C_{N}V \tag{1}$$

where V is the volume of drainage water collected from the lysimeter base for each weekly interval and  $C_N$  is the N concentration in the solution from the leachate (Wang et al., 2012).

#### 2.4 Ammonia volatilization

Ammonia volatilization ( $NH_3$ ) was measured starting from the second fertilizer application using a semi-open static PVC collector with a diameter of 0.150 m and a height of 0.385 m (Marshall and Debell, 1980; Lara et al., 1999; Freitas et al., 2022). The  $NH_3$  absorber consisted of polyethylene-laminated foam discs (15.5 cm diameter,

2 cm thickness, and 0.02 g cm $^{-3}$  density). Two foam discs were used per collector—one positioned 15 cm and the other 30 cm above the soil surface—to reduce environmental contamination. Collectors were mounted on three metal rods and covered by a semi-open cap positioned 10 cm above the PVC tube to facilitate gas movement. Before deployment, foam discs were soaked in approximately 70 mL of 0.5 N sulfuric acid with 3% glycerol (v/v), packed in plastic bags, and stored in a freezer to prevent ambient NH $_3$  contamination.

0.0

41%

59%

Collectors were installed over lysimeters, directly beneath the coffee canopy, coinciding with fertilizer application zones. A total of 12 collectors were used—four replicates per treatment across three treatments.

The amount of fertilizer applied per hectare was divided by the plant density to calculate the N rate per plant. This rate was then adjusted to the lysimeter area and corrected for the surface area of the  $NH_3$  collector base. Foam samples were collected at the following intervals after each fertilization: 1, 2, 3, 5, 9, 14, 20, and 28 days. Sampling was conducted over 2 years, covering five fertilization events.

The foam discs were extracted by rinsing them with approximately 800 mL of deionized water. From the extracts, 10 mL aliquots were analyzed immediately to minimize potential physicochemical alterations that could affect ammonia stability in solution. Ammonia nitrogen concentrations (NH+3) were determined using a mid-range photometer (HI 97715, Hanna Instruments) based on the Nessler method.

The values obtained for each collector were normalized to the area of the collector base and then extrapolated to represent  $\mathrm{NH_{3}}$  losses per  $\mathrm{m^{2}}$ . Cumulative losses were calculated by summing the measured losses at each sampling point over the 28-d period following each fertilizer application.

A daily water balance was estimated using the methodology described by Ramírez et al. (2010) for coffee.

#### 2.5 Statistical analysis

Cumulative leaching and volatilization data between application intervals were analyzed using a completely randomized design with four replicates. All data were subjected to analysis of variance (ANOVA) based on the experimental design. Statistical analyses

Year	DJF	JFM	FMA	MAM	AMJ	MJJ	JJA	JAS	ASO	SON	OND	BDJ
2022	-1.0	-0.9	-1.0	-1.1	-1.1	-0.9	-0.8	-0.9	-1.0	-1.0	-0.9	-0.8
	La Niña											
2023	-0.7	-0.4	-0.1	0.2	0.5	0.5	1.1	1.3	1.6	1.8	1.9	2.0
	La Niña	Neutral			EL Niño							
2024	1.8	1.5	1.1	0.7	0.4	0.2	0.0	-0.1	-0.2	-0.2		
	EL Niño Neutral											

TABLE 3 Ocean Niño Index during 2022-2024 indicates the climate variability conditions.

were conducted using Statgraphics Centurion Version XV (Statgraphics Technologies, Inc., Plains, VA, USA) and InfoStat version 2012 software packages (Di Rienzo et al., 2012). To ensure the validity of the results, data were tested for normality and homogeneity of variance. Mean comparisons were performed using Fisher's LSD test at a 5% significance level.

#### 2.6 Climate variability events

The climate variability events considered in this study were associated with sea surface temperature changes in region 3.4 of the Pacific Ocean, as defined by ENSO, described by Trenberth (1997). These events are monitored by the Climate Prediction Center of the US National Oceanic and Atmospheric Administration through the Oceanic Niño Index (ONI). El Niño conditions are indicated when the ONI is +0.5 °C or higher, reflecting warmer-than-average sea surface temperatures. La Niña conditions are indicated when the ONI is -0.5 °C or lower, reflecting cooler-than-average temperatures. During the study period, both phases were observed: a cooler period (La Niña) occurred from December 2021 to January 2023, and a warmer period (El Niño) occurred between May 2023 and April 2024 (Table 3).

#### 3 Results

## 3.1 Influence of the climate variability on the rainfall distribution and soil moisture in coffee plantations

To analyze the effect of climate variability generated by oceanic-atmospheric El Niño/La Niña-ENSO events during comparable periods, the rainfall, net rainfall, and percolation data obtained from the lysimeters were grouped by quarters. The greatest differences between climate variability events were observed in the January–March quarters. In 2023, under La Niña conditions, rainfall reached 863 mm–2.7 times higher than in 2024 under El Niño conditions (322 mm). This disparity resulted in significant differences in percolation: 171 mm in 2023 versus 0 mm in 2024 (Table 4).

Similarly, during the October–December quarters of 2022 (La Niña) and 2023 (El Niño), although rainfall decreased by 10%, the impact on percolation was more pronounced. Percolation was 2.1 times lower under El Niño, decreasing from 246.3 mm to 116.4 mm.

After each rainfall event, a redistribution of water was observed within the coffee canopy. Of the total 5,518 mm of rainfall recorded over the 2-year study period, 24% was intercepted by the plant canopy, while 76% reached the soil surface beneath the coffee trees as net rainfall (Table 4). A linear relationship was observed between external and net rainfall (Figure 1). Of the 4,207 mm recorded as net rainfall, 778 mm percolated to a soil depth of 40 cm, representing 18.5% of the net rainfall (Table 4).

Changes in Pacific Ocean surface temperature in region 3.4, which determine ENSO phases, directly influenced rainfall quantity and distribution, as well as soil moisture levels in the study area (Figure 2A). Generally, reductions in rainfall and soil moisture were recorded from January to March and from July to August. These reductions were more severe during El Niño conditions than during La Niña or neutral periods.

From September 2022 to March 2023, under La Niña conditions, total water content measured at a 40 cm soil depth average over 90 mm, with only brief reductions during December and March—months historically associated with dry conditions due to the movement of the Intertropical Convergence Zone (ITCZ), which governs the region's wet and dry seasons (Figure 2B). In contrast, from October 2023 to April 2024, under El Niño conditions, volumetric soil moisture at 40 cm depth dropped nearly to zero (Figure 2B). The most severe reductions occurred between December 2023 to March 2024, historically dry months further exacerbated by El Niño conditions.

# 3.2 Influence of climate variability and two mineral fertilization programs on nitrogen leaching

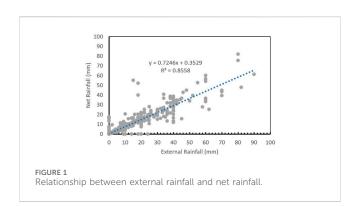
The nitrogen leaching results during the six fertilization events were influenced by climate variability associated with ENSO. The greatest nitrogen leaching occurred after the first and second fertilizations (Figure 3) under La Niña conditions. After May

<sup>+</sup>US, National Oceanic and Atmospheric Administration (NOAA) Climate Prediction Center. Climate Prediction Center - ONI.

<sup>++</sup>Warm (red) and cold (blue) periods based on a threshold of  $\pm$  0.5 °C for the Oceanic Niño Index (ONI) [3-month running mean of ERSST. v5 SST, anomalies in the Niño 3.4 region (5°N-5°S, 120°-170°W)], based on centered 30-year base periods updated every 5 years.

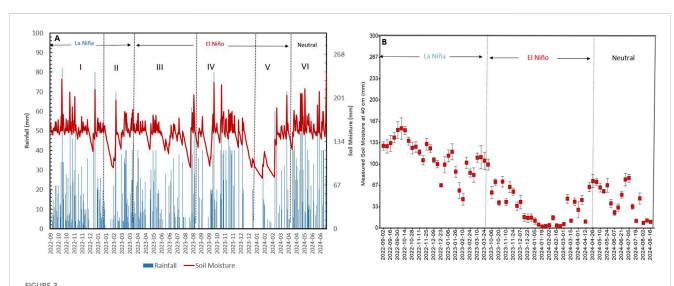
TABLE 4 Rainfall distribution during the 2-year trial period under La Niña and El Niño (ENSO) conditions.

Period	Period Year Condition		External rainfall	Canopy interception	Net rainfall	Percolation				
			Mm							
Oct - Dec	2022	La Niña	987	150	836	246				
Jan - Mar		La Niña	863	205	657	171				
Apr - Jun	2023	El Niño	697	246	450	125				
Jul - Sep		El Niño	548	127	421	22				
Oct - Dec		El Niño	892	71	820	116				
Jan - Mar	2024	El Niño	322	47	274	0.0				
Apr - Jun		Neutral	1,209	461	747	95				
TOTAL			5,518	1,311	4,207	778				
				24%	76%					

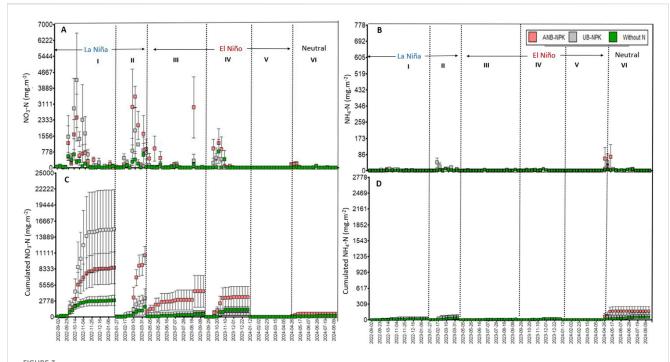


2023, from the third fertilization onwards, nitrogen leaching declined, reaching zero in the period from January to April 2024, when El Niño most strongly influenced hydrometeorological conditions, with reduced rainfall, soil moisture, percolated water, and leached nitrogen.

Significant differences in N leaching between ANB-NPK and UB-NPK were found only during the second fertilizer application period; no differences were observed in later applications (Figure 3). In all samples, fertilized treatments lost significantly more N than the control (Figures 3A,C). Regardless of fertilizer type, 99% of leached N was in the form of nitrate-N (Figures 3A,C), and only 1% as ammonium-N (Figures 3B,D).



Influence of climate variability on: (A) daily rainfall and calculated soil moisture by the water balance method. Numbers indicate mineral fertilization events. (B) measured soil moisture in lysimeters under two different mineral fertilization programs: ammonium-nitrate-based compound NPK (ANB-NPK) and urea-based NPK blend (UB-NPK).



Nitrogen losses by leaching in coffee plantations under two climate variability conditions (La Niña/El Niño-ENSO) from September 2022 to August 2024, interacting with two different mineral fertilization programs: ANB-NPK and UB-NPK. Numbers indicate mineral fertilizer application periods. (A,B) Weekly leaching of NO<sub>3</sub>-N and NH<sub>4</sub>-N after mineral fertilizer application. (C,D) Cumulative nitrogen leaching of NO<sub>3</sub>-N and NH<sub>4</sub>-N during each mineral fertilization period.

After the first fertilization under La Niña, the urea-based NPK fertilizer (UB-NPK) treatment leached 15,273 mg.m<sup>-2</sup> of NO<sub>3</sub>-N, compared to 8570 mg.m<sup>-2</sup> from the ammonium-nitrate-based NPK (ANB-NPK) between September 2022 and January 2023. Following the second fertilization (January–April 2023), ANB-NPK showed greater leaching than UB-NPK, with 10,730 and 3,258 mg.m<sup>-2</sup>, respectively, these being significantly different.

After the third and fourth fertilizations (April–September 2023 and September 2023–January 2024), N leaching remained low due to El Niño conditions beginning in June 2023. No significant differences were observed between fertilizer programs, with mean leaching of 4,441 and 3,414 mg N.m<sup>-2</sup> for ANB-NPK, and 751 and 763 mg N.m<sup>-2</sup> for UB-NPK in the fertilizer periods, respectively (Figure 3C).

No leaching occurred after the fifth fertilization (January–March 2024). During the sixth (March–August 2024), N losses were minimal: 730, 162, and 215 mg.m² for ANB-NPK, UB-NPK, and the control without N, respectively.

A direct relationship was observed between weekly percolation and N leaching under both fertilizer programs (Figure 4). For every 10 mm of percolation in the top 40 cm of soil, 10% of applied N was lost through leaching (Figure 4B).

## 3.3 Influence of climate variability and two mineral fertilization programs on nitrogen volatilization

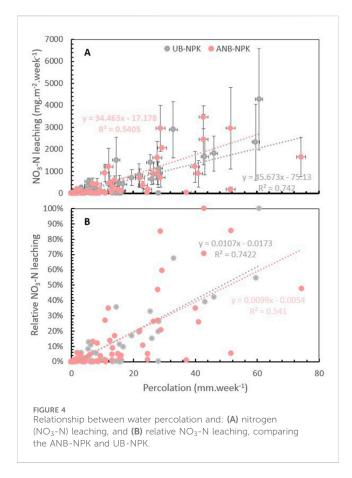
Nitrogen volatilization was also affected by variable climatic conditions, but in the opposite pattern to that observed for leaching.

The lowest N losses due to volatilization occurred during La Niña after the second and third mineral fertilization applications, corresponding to January–February and April–May 2023. Subsequently, N losses by volatilization increased dramatically, especially under El Niño after the fifth application in March 2024, as well as during the transition from El Niño to neutral conditions after the sixth fertilization in August 2024 (Figure 5). In all five fertilization periods, NH<sub>3</sub>-N volatilization was significantly higher in the UB-NPK treatments than in the AN-NPK treatment, which in all cases showed no significant differences in volatilization losses compared to the unfertilized control (Figure 5; Table 5).

Cumulative nitrogen volatilization losses under La Niña conditions for the UB-NPK treatment ranged from 14,545 to 14,595 mg m $^{-2}$  for the second and third applications, reaching a maximum value of 48,219 mg m $^{-2}$  under El Niño after the fifth fertilization, followed by 32,344 mg m $^{-2}$  during the transition from El Niño to neutral conditions after the sixth mineral fertilization (Figure 5).

# 3.4 Influence of two mineral fertilizer programs under climate variability conditions on total nitrogen losses

Cumulative nitrogen losses by leaching for both mineral nutrition programs after six applications over 2 years were not significantly different but were significantly higher compared to the control without N application. The UB-NPK program exhibited significantly lower N loss due to leaching than the ANB-NPK



program during the second fertilization period (January to April 2023). Regarding ammonia volatilization, the UB-NPK treatment showed, during all five evaluation periods, significantly higher cumulative NH<sub>3</sub>-N losses compared to the ANB-NPK and control treatments without N (Table 5). Total N losses for the UB-NPK treatment, calculated as the sum of leaching and volatilization, were highest during La Niña after the first fertilizer application and during El Niño after the fifth application. In the first case, total losses were dominated by leaching, whereas in the second, they were dominated by volatilization. Only after the second fertilizer application during La Niña did the ANB-NPK treatment show higher total losses—primarily from leaching—compared to UB-NPK.

Integrating the cumulative nitrogen losses after six mineral fertilization events during ENSO conditions, the fertilization program based on the UB-NPK showed a 36.7% loss, whereas the program based on ANB-NPK showed a 13.1% total N loss (Table 5).

#### 4 Discussion

## 4.1 Climate variability influenced the rainfall patterns in the study region and N leaching

The fluctuation between rainy and dry periods is the primary expression of climate seasonality in the tropics and is directly linked to the meridional migration of the ITCZ. In Colombia, additional

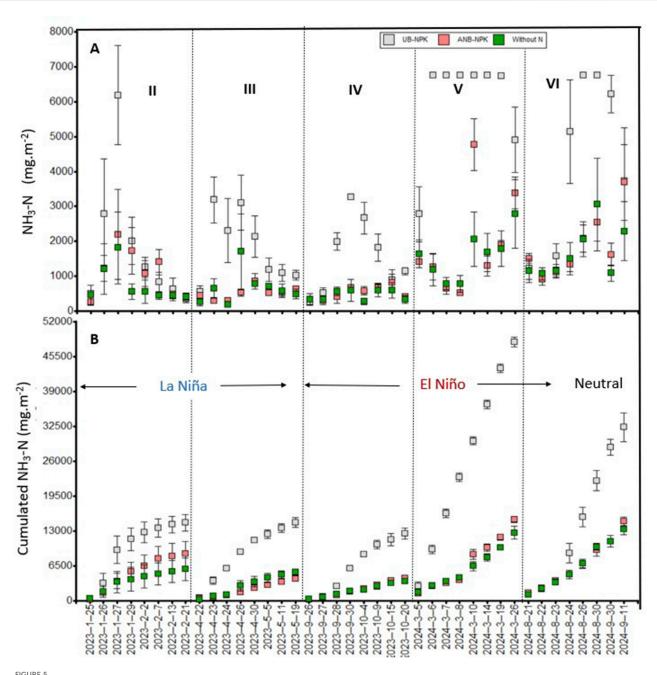
sources of climate variability interact with the ITCZ to define the rainfall distribution patterns, including the Choco low-level jet, the Caribbean jet, atmospheric rivers, the Andes mountain range, advection from the Amazon and Orinoco basins, and ENSO (Urrea et al., 2019). Latin America (LA) is bordered by the Pacific and Atlantic Oceans, and the region's climate is largely influenced by prevailing sea-surface temperatures (SSTs) and associated large-scale ocean-atmosphere interactions such as ENSO. SST conditions in the central and eastern tropical Pacific are crucial for identifying the onset of El Niño and La Niña and their influence on climate extremes. The tropical Pacific and Atlantic are also essential influencers of LA climate variability, particularly in northern Peru and Ecuador, Amazonia, northeastern Brazil, and southeastern South America, and, during the hurricane season, in the tropical North Atlantic, eastern Mexico, and the Caribbean (WMO, 2024).

In Colombia's Andean region, ENSO phases strongly influence hydrometeorological conditions, particularly rainfall distribution. During El Niño (positive ENSO phase), annual rainfall decreases by 10%–35%, whereas during La Niña (negative phase), it increases by 30%–50% (García et al., 2023; Guzmán and Baldión, 1997; 1999; Peña et al., 2012; Poveda et al., 2001; Ramirez and Jaramillo, 2006). Ramirez and Jaramillo (2009) found correlations between ONI and rainfall during the dry seasons (December–February and June–September) in Colombia's central-western coffee region, where this study took place. Typically, El Niño lengthens the dry season, while La Niña shortens it (García et al., 2023; Peña et al., 2012; Ramirez and Jaramillo, 2009).

The multi-year La Niña event began in mid-2020 and ended in early 2023 (Table 3). SSTs in the eastern tropical Pacific subsequently rose, crossing the El Niño threshold by June. However, atmospheric conditions lagged, and El Niño was not fully established until early September. By late 2023, a strong El Niño had developed, with the ONI reaching 2 °C for the November 2023-January 2024—the highest value since the 2015/16 EL Niño event (WMO, 2024). This transition from La Niña to El Niño directly influenced rainfall in the study region: January-March 2023 saw 863 mm of rainfall (2.7 times higher) under La Niña, compared to 322 mm in the same period of 2024 under El Niño. These changes affected percolation, with 171 mm of water percolating between January and March 2023, and 0.0 mm during the same period in 2024 (Table 4). These changes between negative and positive ENSO conditions in the short term were also observed in the soil moisture distribution, with higher volumetric moisture content during La Niña and lower volumetric moisture content during El Niño (Figure 2).

### 4.2 Climate variability influenced the rainfall patterns in the study region and N leaching

Regardless of N source, N losses by leaching were directly correlated with rainfall (Figure 4), which was, in turn, influenced by climate variability, including ITCZ migration and ENSO. Soil  $\mathrm{NH^+_4}$  concentrations in tropical, subtropical, and temperate soils are generally low due to rapid conversion to  $\mathrm{NO_3^-}$  (Di and Cameron, 2002; Harman et al., 2007; Sadeghian, 2022; Ramirez, et al., 2024; Sarkis et al., 2023). Within a month, most soil N is in the soil is in the



Nitrogen losses by NH<sub>3</sub>-N volatilization in coffee plantations during two ENSO phases (El Niño/La Niña) from September 2022 to August 2024, under the two fertilization programs: ANB-NPK and UB-NPK. Numbers indicate mineral fertilizer application periods. (A) Nitrogen volatilization during the 28-d following fertilization. (B) Cumulative nitrogen volatilization over a 28-d period after each fertilization event.

form of  $NO_3^-$ , especially in soils with adequate pH, moisture, and temperature (Cantarella, 2023). Because  $NO_3^-$  is negatively charged and not retained by most soils, it becomes the dominant leached form of N (Di and Cameron, 2002). This pattern was observed in this study's volcanic ash-derived Andosol, where 99% of N leached was as  $NO_3^-$ , and only 1% as  $NH_4^+$ , independent of the treatments evaluated UB-NPK or ANB-NPK—similar to Harman et al. (2007), who found 96% of N leached as  $NO_3^-$ in a Costa Rican Acrisol.

In coffee agroecosystems, nitrogen mineralization varies seasonally, reflecting rainfall. It is lowest during dry months and

highest during wet months, with NO-3-N as the dominant form, independent of shade level or location (Babbar and Zak, 1994; Harman et al., 2007; López et al., 2015). Nitrate leaching occurs when soil NO<sub>3</sub>- accumulation coincides with or is followed by significant water percolation (Di and Cameron, 2002). Sources include fertilizers, effluents, and organic N mineralization (Addiscott, 1996). In our study, N leaching, independent of the N source, was directly correlated with water percolation (Figure 4A) and occurred mainly during the rainy season, as determined by ITCZ positioning. Additionally, water percolation was directly

TABLE 5 Nitrogen losses in coffee plantations comparing two mineral fertilizer programs influenced by El Niño/La Niña (ENSO) climate variability conditions.

Mineral N fertilization	Period	ENSO	N-Source	N-applied	Leaching		Volatilization		Total	Relative losses
				kg ha <sup>-1</sup>						% of N applied
I	Sep 2022 - January 2023	La Niña	UB-NPK	50	34	b	n.a.	n.a.	34	54,6
			ANB-NPK	40	19	a	n.a.	n.a.	19	31,5
			Without N	0	6	a	n.a.	n.a.	6	
II	Jan 2023 - April 2023	La Niña	UB-NPK	90	7	a	32	a	39	25,1
			ANB-NPK	70	24	b	19	b	43	37,5
			Without N	0	4	a	13	b	17	
III	Apr 2023 - September 2023	El Niño	UB-NPK	120	2	a	32	a	34	17,4
			ANB-NPK	110	10	a	9	ь	19	5,4
			Without N	0	1	a	12	b	13	
IV	Sep 2023 - January 2024	El Niño	UB-NPK	50	2	a	28	a	30	37,1
			ANB-NPK	30	7	a	9	ь	16	19,6
			Without N	0	3	a	8	ь	11	
V	Jan 2024-Mar-2024	El Niño	UB-NPK	120	0		106	a	106	65,3
			ANB-NPK	88	0		33	ь	33	6,1
			Without N	0	0		28	b	28	
VI	Mar 2024-August 2024	Neutral	UB-NPK	140	0	a	71	a	71	29,8
			ANB-NPK	120	2	a	33	b	35	3,6
			Without N	0	0	a	29	b	29	
TOTAL	TOTAL	TOTAL	UB-NPK	570	45	A	269	A	314	36,7
			ANB-NPK	458	62	A	103	В	165	13,1
			Without N	0	14	В	90	В	104	

<sup>\*</sup>ANB-NPK, ammonium-nitrate-based NPK.

<sup>++</sup>UB-NPK, Urea blend base NPK.

influenced by La Niña conditions, where rainfall was higher than that during El Niño or neutral conditions. In general, downward water transport below the root zone requires soil moisture to exceed field capacity and rainfall to exceed evapotranspiration (Lehmann and Schroth, 2003). This was reflected in the water balance and soil moisture data during La Niña and El Niño (Figure 2A), which paralleled N leaching behavior (Figure 3A).

In coffee, a perennial crop, cover cropping is uncommon. Thus, N leaching is more influenced by fertilizer inputs and moisture changes between dry and wet seasons, rainfall distribution, irrigation intensity, and climate variability, as shown in this study. Despite the greater availability of N for plant uptake in both shaded and unshaded coffee plantations in Costa Rica, relatively low N losses through leaching have been reported. Babbar and Zak (1994) documented annual leaching losses of only 0.9 and 2.4 g N m<sup>-2</sup> year<sup>-1</sup> in shaded and unshaded systems, respectively. In a separate study, Harman et al. (2007) reported NO<sub>3</sub><sup>-</sup> leaching losses of 26.9 and 15.6 kg ha<sup>-1</sup> yr<sup>-1</sup> in unshaded coffee and coffee intercropped with eucalyptus, respectively, representing 15% and 8.7% of the total mineral N applied in an Acrisol in Costa Rica. In contrast, Cannavo et al. (2013) observed substantially higher N leaching losses, accounting for 54.6% of the total applied N (136.5 kg N ha-1) in a coffee agroforestry system (Coffea arabica-Inga densiflora) during 1 year with 2,678 mm of rainfall, measured in the top 60 cm of the soil profile.

In our study, N leaching losses ranged from 7 to 34 kg ha<sup>-1</sup> per fertilizer application for the UB-NPK treatment and from 24 to 34 kg ha<sup>-1</sup> for the ANB-NPK treatment during La Niña conditions. In contrast, losses were nearly zero under El Niño conditions for both N sources. Over the 2-year study period, encompassing six fertilizer applications, cumulative nitrogen losses by leaching totaled 45 and 61 kg N ha<sup>-1</sup> for UB-NPK and ANB-NPK, respectively, corresponding to 8% and 13% of the total N applied (Table 5).

In Brazil, Pivotto et al. (2012) investigated N leaching in coffee cultivation on Typic Hapludox soil ("Latossolo Vermelho-Amarello") under rainfed and irrigated conditions. They compared two mineral N application rates—400 and 800 kg N ha<sup>-1</sup> yr<sup>-1</sup>—and reported leaching losses of 12 kg N ha<sup>-1</sup> and 88.4 kg N ha<sup>-1</sup> under rainfed conditions, respectively. These losses represented 3.0% and 11.0% of the total N applied. Comparable losses—3.1 and 11.4%—were also observed in treatments that received irrigation during the dry season.

Similarly, under rainfed conditions, Fenilli et al. (2008) studied N leaching in coffee grown on Typic Rhodudalfs soils ("Nitossolo Vermelho Eutroférrico") using ammonium sulfate as the N source. They found total leaching losses at 1 m soil depth equivalent to 2.3% of the applied N in the first year (6.5 kg of 280 kg N ha<sup>-1</sup>) and 1.7% in the second year (10.5 kg of 350 kg N ha<sup>-1</sup>). These relatively low losses were attributed to modest rainfall amounts during the study—1,342 mm and 1,118 mm in the first and second years, respectively.

More recently, Sarkis et al. (2023) evaluated N leaching under varying N rates and sources in Minas Gerais, Brazil, with an average precipitation of 1,493 mm. They reported increasing N leaching with higher application rates, reaching the greatest losses at the optimal rate of 400 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Leaching varied significantly by N source,

with average losses of 1.2% for ammonium nitrate, 11.5% for urea, and 13.0% for urea with a urease inhibitor.

All published field-level studies cited here that measured N leaching losses in coffee agroecosystems used porous ceramic cups. Researchers calculated total  $\mathrm{NO_3}^-$  leaching losses using a water balance approach and/or models simulating water movement in the vadose zone. Lysimeters provide an intermediate-scale method that bridges laboratory and field scales. Their main advantages include the ability to measure total leaching losses from a known sample volume, accommodate a larger soil volume than suction cups, represent the soil pore network more accurately, and expose samples to ambient climate conditions. Lysimeters typically contain undisturbed soil (Wang et al., 2012). In this study, lysimeters enabled the monitoring of leaching across the entire root zone of single coffee trees.

Rainfall interception by the canopy plays a critical role in water movement within coffee agroecosystems by determining the net rainfall reaching the soil. As a key factor in hydrological studies of forests and agroecosystems, interception has been widely studied across different regions (Gash, 1979; Dykes, 1997; Bruijnzeel, 1997; Gash et al., 1995; Jaramillo and Chaves, 1999; Leuning et al., 1994; Lloyd et al., 1998; Niu et al., 2023; Ramirez and Jaramillo, 2006; Rutter, 1975; Tully et al., 2012). In this study, 24% of the total rainfall over 2 years was retained by the coffee canopy, while 76% reached the soil surface. In Costa Rica, Harmand et al. (2007) reported 15% interception by the coffee canopy, and Tully et al. (2012) found 18% in agroforestry systems with C. arabica and Erythrinia poeppigiana. In Colombia, interception rates in different coffee production systems ranged from 10% to 58% (Jaramillo, 2003; Ramirez and Jaramillo, 2006; Velásquez and Jaramillo, 2009). Therefore, in many cases, calculating N leaching losses using vadose zone functions can lead to overestimation, as rainfall retained by the canopy is not accounted for.

#### 4.3 Soil acidity and N leaching

Solutes move not only with soil water, but also within it, in response to concentration gradients (Hillel, 1998). At the same time react among themselves and interact with the solid matrix of the soil in a continuous cycling succession of interrelated physical and chemical process, these interactions involve and are strong influenced by such variable factors as acidity, temperature, oxidation-reduction potential, composition, and concentration of the soil solution (Hillel, 1998). The acid buffering capacity in soils with pH ranging from 4.5 to 7.5 is mostly influenced by CEC, which influence indirectly the nutrients availability and retention. Soils with higher CEC have more cation exchange sites to buffer protons in the soil solution, N deposition in soil reduce buffering capacity of the soil and increasing cation losses to the soil solution (Lieb et at. 2011). The surfaces charge number (SCN) determines the number of ions that can be adsorbed by soil, and the surface charge density plays a key role in the strength of absorption of these ions (Cao et al., 2024), both define the CEC of the soil (Tan, 2011).

The SCN of the permanently/variable charged soils and clay minerals decreases significantly with decreasing pH (Cao et al., 2024), increasing the risk of nutrient leaching. When  $\mathrm{NH_4}^+$  is

applied to soil, it is adsorbed around soil particles through electrostatic attraction. The electric field surrounding soil particles determines the strength of the electrostatic attraction of  $\rm NH_4^+$ , which in turn impacts the nitrification rate. The leaching of  $\rm NO_3^-$  resulting from nitrification is also influenced by the strength of the electrostatic repulsion. The H $^+$  produced during nitrification readily displaces base cations (e.g.,  $\rm Ca^{2^+}$  and  $\rm Mg^{2^+})$  on clay particle surfaces. Consequently, the leaching of  $\rm NO_3^-$  inevitably leads to the coupled migration of base ions due the principle of electrical neutrality, resulting in accumulation of H $^+$  and decrease in base cations on soil particle surface (Cao et al., 2024), and finally increase on soil acidification, reducing the CEC and increasing the N leaching.

Jiang et al. (2011) working in a Pine forest Oxisol, at low pH (pH < 5.3) found high  $\mathrm{NH_4^+}$  activity and low ammonia-oxidizing bacterial (AOB) and archaeal (AOA) indicating nitrification inhibition at low soil pH, in our study the main N leaching was in a  $\mathrm{NO_3^-}$  form, indicating that an a pH of 4.67 the nitrification process in this Andosol was not affected, even though it is considered variable charged soil (Figure 3). Xiong et al. (2010), in a permanent changed soil (pH = 6.7) after ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] application always caused higher  $\mathrm{NO_3^-}$  concentration in terms of both total  $\mathrm{NO_3^-}$  and fertilizers derived  $\mathrm{NO_3^-}$ , in contrasting variable changed (pH = 5.5) soil showed distinctly different, with  $\mathrm{NH_4^+}$  dominating the total N leaching.

### 4.4 Climate variability and nitrogen volatilization

Important N gases emitted by human activities include nitrogen oxides (NOx), nitrous oxide (N2O), and ammonia (NH<sub>3</sub>). Of these gases, NH<sub>3</sub> is emitted from many sources such as volatilization from animal waste and synthetic fertilizers, biomass burning (including forest fires), losses from soils under native vegetation, crops, emissions from human excreta, and fossil fuel combustion (Behera et al., 2013). Approximately 10%-40% of the N (in ammoniacal form as urea or ammonium sulfate) applied to soils (pH 4.1-7.7) is volatilized during the growing season. NH<sub>3</sub> volatilization increases production costs and environmental concerns (He et al., 1999). The estimated global NH<sub>3</sub> emission is between 70 and 92 Tg. a<sup>-1</sup> (Luo et al., 2022). According to the European Environment Agency (Ammonia (NH3) emissions-European Environment Agency), NH3 contributes to acid deposition and eutrophication, which can lead to potential changes in soil and water quality. The subsequent impacts of acid deposition can be significant, including adverse effects on aquatic ecosystems in rivers and lakes, and damage to forests, crops, and other vegetation. Between 11% and 17% of the total estimated global NH<sub>3</sub> emissions are related to the production and use of ammoniacal fertilizers (Behera et al., 2013). Based on the estimation from Luo et al. (2022) and taking an average from Behera et al. (2013) of 14%, these emissions from mineral fertilizers account for 9.8 to 12. 6 million tons of NH3 emitted per year.

Ammonia volatilization depends on the balance between  $\mathrm{NH_4}^+$  ions and  $\mathrm{NH_3}$  gas molecules on the soil surface. The predominance of either chemical form in the soil is a function of pH. In acidic soils (pH < 7),  $\mathrm{NH_4}^+$  prevails and is not transferred to the atmosphere.

Thus, in acid soils, fertilizers containing NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup> are not prone to relevant losses by NH<sub>3</sub> (Cantarella, 2023). However, during urea hydrolysis, H+ are consumed, alkalinizing the soil around the fertilizer and pushing the reaction equilibrium toward NH<sub>3</sub> production. Soil pH increases around urea fertilizer granules, and NH<sub>3</sub> formation occurs even in acidic soils (Cantarella, 2023; Freney et al., 1983). Ammonia volatilization from surface-applied fertilizers consists of a fast reaction that lasts approximately 2-14 days after fertilizer application, followed by a slow emission process during the rest of the incubation period. This fast reaction and peak of NH<sub>3</sub> volatilization have been reported for different soil types and various agroecological conditions (Cantarella et al., 2003; Fenilli et al., 2007; He et al., 1999; Jantalia et al., 2012; Lara et al., 1997; Leal et al., 2007; Sadeghian and González, 2012; Stafanato et al., 2013; Rajkovich et al., 2017; de Souza et al., 2023), similar to the observations in this study during the second, third, and fourth mineral N applications (Figure 5) during the prevailing La Niña conditions with sufficient soil moisture and rain.

A different tendency was observed after the fifth mineral N application, where NH<sub>3</sub> volatilization maintained a linear tendency during the 28 days of evaluation, resulting in NH<sub>3</sub> losses of 65% of total N applied in UB-NPK compared to 6.1% in ANB-NPK (Table 5). This tendency can be explained by the low rainfall and soil moisture levels (Figure 2; Table 2) influenced by the positive phase of El Niño, which was also followed by an increase in the mean air temperature (Table 1). Cantarella et al. (2003) found higher NH<sub>3</sub> volatilization rates in citrus orchards after urea application, followed by a period of 18 days without rainfall. Ammonia emissions were practically stopped by a rainfall event with 41 mm of precipitation. Similar effects are reported by Jantalia et al. (2012) in corn, where irrigation 1 day after N fertilization reduced NH3 losses from urea-based fertilizers to less than 4% of the applied N. Rochette et al. (2013) also observed a temporary reduction in volatilization rates following each water addition, resulting in lower NH<sub>3</sub> losses in barley. In coffee, Freitas et al. (2022) reported NH<sub>3</sub> losses from 40% to 90% due to low rainfall after urea application.

During El Niño conditions, rainfall intensity and frequency reduces, as well as mean air temperature and solar radiation increase (Guzmán and Baldión, 1997; Ramirez and Jaramillo, 2012; Ramirez et al., 2014), with this climatic conditions changes also the micro-climatic conditions into the coffee plantation changes, reducing volumetric soil moisture and increasing soil water deficit (Jaramillo, 2018; Ramirez and Kusters, 2021), with direct effect on the urea transformation. Urea hydrolysis is carried out by enzymes from the urease group, which are ubiquitous in soils, occur at higher concentrations in the presence of straw or crop residues (Cantarella, 2023; Mariano et al., 2012; Sarkis et al., 2023), and show higher activity at elevated temperatures (Cantarella, 2023). Urea dissolution and urea hydrolysis are, apart from soil characteristics as urease concentration and water retention, strongly governed by soil water content and soil temperature (Ni and Pacholski, 2022). When rainfall is low and/or soil moisture is sufficient to dissolve urea granules and activate urease, NH3 volatilization is high because moisture and rainfall are not sufficient to incorporate the fertilizer into the soil

(Cantarella, 2023; de Souza et al., 2023). Independent of the soil moisture, urease activity significantly increases with air temperature increases (Ni and Pacholski, 2022), kinetic volatilization rate coefficient increases with temperature and decrease with soil moisture (Bolado et al., 2005). During El Niño conditions soil moisture reduction reduce the urea dissolution and incorporation and increase the urease activity increasing the NH<sub>3</sub> volatilization.

In Colombia (Leal et al., 2007) measured  $NH_3$  emissions from urea in two contrasting coffee zones and found total losses of 30.4% and 34.8% of total N applied. The differences between the two locations were attributed to environmental conditions such as high organic matter and CEC, higher rainfall, and lower temperature in the zone with reduced volatilization.

Higher rainfall volume and intensity are usually associated with better fertilizer incorporation into the soil, and consequently, lower losses by volatilization. An additional factor in coffee that reduces fertilizer incorporation into the soil is rainfall interception by the canopy, as discussed previously, as well as the fallen leaves in the soil that act as a barrier, creating a favorable environment for NH<sub>3</sub> volatilization from urea due to the high concentration of urease (Mariano et al., 2012; Sarkis et al., 2023). Low soil moisture conditions, rainfall interception by the canopy, and crop residues such as fallen leaves did not increase the risk of N losses by volatilization for ANB-NPK, where the losses were significantly lower (Table 5). This provides greater flexibility in application timing—even under low soil moisture or high temperatures-superficial application, reducing costs as litter removal from the application zone is not necessary.

All these factors contributed to improving NUE in coffee, as presented in this study. The total N losses for ANB-NPK averaged 13.1% over 2 years and two climate variability scenarios (El Niña-La Niña/ENSO), whereas for UB-NPK, losses under similar conditions were 36.7% (Table 5).

In coffee, Freitas et al. (2022) found that conventional urea caused NH<sub>3</sub> losses of 24% of applied N, whereas other N sources, including ammonium nitrate and ammonium sulfate, showed negligible losses, demonstrating their potential as alternatives to mitigate ammonia emissions. Fenilli et al. (2007) compared NH<sub>3</sub> volatilization from urea and ammonium sulfate in coffee and found that losses were much lower for the unfertilized control and ammonium sulfate treatment (only 1.6% of total N applied), whereas urea losses averaged 28%. In Colombia, Sadeghian and González (2012) observed 28% NH<sub>3</sub> losses for urea and less than 0.2% for ammonium sulfate after one fertilizer application at low N rate (18 kg N ha<sup>-1</sup>). Gonzalez et al. (2015) reduced NH<sub>3</sub> losses from urea in a coffee plantation from 26% to 3% by changing from surface application to deep placement at 3–6 cm depth.

The amount of volatilized  $\mathrm{NH_3}$  following urea application depends on soil properties such as texture, organic matter content, cation exchange capacity, pH, and water content (Rochette et al., 2013). In our study, in an acidic soil (pH = 4.67) with high organic matter content (10.56%),  $\mathrm{NH_3}$  volatilization was directly influenced by soil moisture and temperature changes under La Niña and El Niño conditions. During La Niña, soil moisture fluctuated between field capacity and saturation, facilitating urea incorporation. During El Niño, rainfall was low and soil moisture

remained below field capacity, reducing incorporation and increasing NH<sub>3</sub> volatilization.

Mitigation strategies for  $\rm NH_3$  volatilization from mineral N fertilizers in agricultural systems include the use of alternative N sources such as ammonium-nitrate-based mineral fertilizers, subsurface banding or deep placement of urea, split-band applications, adjusted irrigation timing and amount, and the application of amendments such as natural minerals, industrial by-products, or chemicals with high ammonium-binding capacity. Additional strategies include urease inhibitors and slow-release fertilizers (Pan et al., 2016). This study showed that the interaction between N forms and climate variability scenarios—specifically a nutritional plan based on ANB-NPK with 59% of the total N as  $\rm NO_3^-$  and 41% as  $\rm NH_4^+$ —significantly reduced NH<sub>3</sub> losses compared to UB-NPK, from 65% to 6% during El Niño (January 2024), and from 21% to 9% (January 2023) during La Niña phase.

#### 5 Conclusion

In this study, the most significant N loss occurred through volatilization rather than leaching. In the UB-NPK treatment, 31% of the total N applied was lost via volatilization, compared to only 2.8% in the ANB-NPK treatment, with significantly higher losses observed during El Niño. No significant differences between fertilization programs were observed in leaching, with 5.2% and 10% of the total N applied lost through leaching in the UB-NPK and ANB-NPK, respectively; however, leaching losses were significantly higher during La Niña. Regardless of the N source, the risk of NO<sub>3</sub>-N leaching increased during La Niña conditions, highlighting the importance of incorporating climate variability forecasts into the planning of N application time and frequency. Overall, ANB-NPK resulted in lower N losses (13.1%) compared to UB-NPK (36.7%), making it a more sustainable N source for coffee production, particularly under dry and warm conditions that are expected to dominate climate scenarios.

### Data availability statement

The original contributions presented in the study are included in the article/Supplementary material.

#### **Author contributions**

VR-B: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Software, Validation, Writing – original draft, Writing – review and editing. AV: Data curation, Investigation, Project administration, Supervision, Writing – review and editing. MA: Project administration, Writing – review and editing. JS: Project administration, Writing – review and editing. KM: Project administration, Writing – review and editing. PJ: Funding acquisition, Resources, Supervision, Validation, Writing – review and editing.

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#### Conflict of interest

The authors declare that the research 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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#### Generative AI statement

The author(s) declare that no Generative AI was used in the creation of this manuscript.

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### Supplementary material

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