Original scientific paper
DOI: /10.5513/JCEA01/27.3.4952
Journal of Central European Agriculture, 2026, 27(3), p.839-855

Critical nitrogen loads of arable Fluvisols determined by the simple mass balance (SMB) method in southern Bulgaria

Определяне на критични натоварвания за азот на обработваема Алувиално-ливадна почва чрез метода на Мас баланса (SMB) в Южна България

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Received: July 24, 2025; accepted: April 30, 2026

ABSTRACT

This study aimed to estimate the maximum nitrogen input, referred to as the critical load, that maintains soil acidification within stable limits while ensuring that plant growth is not constrained. The critical load was determined using a mass balance approach based on major nitrogen and base cation input–output fluxes. The assessment was based on data collected during a four-year field experiment (2020–2023), which evaluated changes in the principal nitrogen and base cation pools under different nitrogen inputs, including mineral fertilization, atmospheric deposition, and irrigation. The experiment was conducted on a Fluvisol near Plovdiv, southern Bulgaria, under a maize–wheat crop rotation. The experimental design comprised a control treatment (T_0) and three nitrogen application rates: for wheat, T_1 (100 kg N/ ha), T_2 (140 kg N/ha), and T_3 (180 kg N/ha); and for maize, T_1 (120 kg N/ha), T_2 (160 kg/N ha), and T_3 (200 kg/ N/ ha). The results showed that annual nitrogen inputs from atmospheric deposition ranged from 10 to 23 kg N/ha during the study period (2020–2023). Nitrogen inputs through irrigation were of a comparable magnitude, ranging from 19.8 to 24.1 kg N/ha. Atmospheric deposition of Ca^{2+} and Mg^{2+} exhibited a declining trend over the study period, with annual average inputs of 42 kg Ca/ha and 15.9 kg Mg/ha, respectively. In contrast, the input of base cations through irrigation was three to four times greater than that supplied by precipitation. The average annual nitrogen leaching loss from the control treatment was 4.5 kg N/ha, which was four to five times lower than the losses recorded in the fertilized treatments (T_2 and T_3). Annual Ca^{2+} leaching losses ranged from 10 to 52 kg/ha, depending on the nitrogen application rate. Soil pH declined by approximately one unit after maize cultivation under the highest mineral nitrogen application rate (200 kg N/ha) compared with the control treatment. The estimated critical load for acidifying nitrogen was relatively high for this Fluvisol under irrigated maize, ranging from 170 to 227 kg N/ha/yr. These high values are likely attributable to the substantial input of base cations through irrigation, which enhanced the soil's buffering capacity. In contrast, following wheat cultivation, when irrigation was not applied, the critical load for acidifying nitrogen decreased markedly to 31–82 kg N/ha/yr.

Keywords: critical load, nitrogen, base cations, input-output, acidification

РЕЗЮМЕ

Настоящата разработка има за цел да оцени максималното количество вложен азот наречено критично натоварване, което поддържа равновесието на системата в границите на стабилност по отношение на вкиселяването на почвата, без същевременно да ограничава растежа на растенията, чрез изчисляване на мас-баланса на елементите. Използвани са данни, получени при извеждане на 4-годишен полски експеримент (2020–2023 г.), за промените в основните входно-изходни пера на азот и основни катиони в резултат на различни натоварвания с азот (торови норми, атмосферни отлагания, напояване). Изследването е проведено върху Алувиално-ливавна почва (Fluvisol) близо до Пловдив, Южна България, при сеитбообръщение царевица–пшеница. Методиката на експеримента включва три норми на азотно торене и контролен вариант: (T_0–контрола, T_1 N_{100}, T_2 N_{140}, T_3 N_{180}) за пшеница и (T_1 N_{120}, T_2 N_{160}, T_3 N_{200}) kg/ha, съответно за царевица. Резултатите показват, че средното количество азот, внесено чрез валежите за периода 2020–2023 г., варира от 10 до 23 kg/ha. Подобни стойности са установени и за прихода на азот чрез напояване (19.8–24.1 kg/ha). Приходът на Ca^{2+} и Mg^{2+} чрез валежите показва тенденция за намаляване през последните години. Измереното средногодишно количество внесен Ca^{2+} достига 42 kg/ha и 15.9 kg/ha Mg^{2+}. Приходът на основни катиони чрез напояване е три до четири пъти по-висок в сравнение с този от валежите. Средното количество азот, изнесен с дренажните води при контролния вариант е 4.5 kg/ha, което е четири до пет пъти по-ниско в сравнение с торените варианти T_2 и T_3. Загубите на Ca^{2+} варират от 10 до 52 kg/ha годишно в зависимост от нивата на торене. Установено е понижение на pH на почвата с около единица при варианта N200, спрямо контролната след отглеждане на царевица. Установено е, че критичното натоварване за азот за този почвен тип е сравнително високо (170–227 kg/ha годишно) при царевица. Това може да се обясни с високото количество основни катиони, внесени чрез напояване. Значително намаляване на критичното натоварване за азот е установено след отглеждане на пшеница, когато не се прилага напояване (31–82 kg/ha годишно).

Ключови думи: критично натоварване, азот, основни катиони, входно-изходен баланс, вкиселяване

INTRODUCTION

Significant transformations of nutrients occur in soils under the influence of both natural processes and anthropogenic factors, including climate change. Understanding the fate and behavior of nutrients deposited in ecosystems is essential for assessing their environmental impacts (Ludanai et al., 2007). Agroecosystems frequently receive substantial inputs of chemical elements from industrial and agricultural sources (Oenema and Roest, 1998; Grieve, 2001), resulting in adverse environmental effects, including soil acidification. In recent decades, atmospheric deposition of sulfur (S) and nitrogen (N) has been identified as a major driver of acidification and eutrophication in forest soils across Europe and North America, leading to nutrient imbalances, cation leaching, and forest ecosystem degradation (De Vries, 1991, 1993; Waldner et al., 2015; Hao et al., 2020). Růžek et al. (2019) demonstrated that sulfate and nitrate anions are neutralized by soil cations, thereby depleting the soil cation exchange complex. Although emission reduction policies implemented across Europe have significantly decreased atmospheric deposition over recent decades, southeastern Europe and the Balkan Peninsula continue to be identified as hotspots for sulfur dioxide emissions and sulfur wet deposition in several modelling studies (Georgieva et al., 2022). The critical nitrogen (N) load approach is primarily used to assess the vulnerability of natural ecosystems, or specific ecosystem components, to atmospheric nitrogen deposition (De Vries et al., 2007, 2015). This concept has been widely adopted in forest ecosystem research and has undergone substantial refinement since its introduction (Hettelingh et al., 2007). A critical load is defined as “the maximum deposition that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function” (Nilsson and Grennfelt, 1988). Ecosystems receiving atmospheric deposition above their critical load

are considered to be in exceedance and are therefore at risk of adverse ecological impacts. Several approaches have been developed to estimate critical loads for atmospheric nitrogen deposition. According to Posch et al. (2011) and Waldner et al. (2015), one approach is based on empirical observations of ecosystem responses to nitrogen inputs. A second approach derives critical loads from ecosystem models by applying predefined criteria to nutrient fluxes or concentrations. This method is generally based on the steady-state mass balance (SSMB) approach, which accounts for nitrogen input sources and output sinks within the ecosystem (Sverdrup and De Vries, 1994). Within the SSMB framework, a fundamental criterion is that the nitrogen leaching flux below the root zone should not exceed an acceptable threshold (Spranger et al., 2004), typically defined by critical limits for mineral nitrogen (Nmin). Critical nitrogen loads are ecosystem-specific and are generally estimated using a combination of field observations and dose–response relationships (Delon et al., 2022). However, extending the critical load concept to agricultural soils requires the establishment of appropriate criteria defining what constitutes a "harmful effect." These criteria form the basis for the qualitative assessment of critical nitrogen loads in agricultural systems. Establishing such criteria is particularly challenging because the primary objective of sustainable agriculture is to maintain, and where possible enhance, soil fertility while ensuring stable crop production. Unlike natural ecosystems, agricultural systems are actively managed through crop rotation, fertilization, irrigation, and other agronomic practices, all of which strongly influence nutrient cycling. Consequently, evaluating or applying the critical load concept in agricultural systems requires long-term field experiments involving contrasting nitrogen application rates, consistent crop management practices, and comprehensive monitoring of nitrogen and base cation inputs and outputs. Nutrient budgeting and mass balance approaches have been widely applied at various spatial scales to assess nutrient dynamics and identify long-term trends in nutrient sources and sinks within ecosystems (Dechert et al., 2005; Schlecht and Hiernaux, 2004). Nevertheless, most studies have focused on individual nutrient cycles, whereas relatively few investigations have examined the long-term dynamics of both major cations and anions in agricultural soils (Stoichev, 1989; Erisman et al., 2003, 2010). Furthermore, calculations of critical loads should account for temporal and spatial variations in the atmospheric deposition of base cations, as these play a crucial role in buffering soil acidity and mitigating acidification processes (Zhao et al., 2007; Watmough, 2024; Xu et al., 2024).

This study analyzes four-year trends in the major input and output pools of nitrogen (N) and the principal macronutrients (the base cations K, Ca, and Mg) under different cropping systems and nitrogen input regimes, including fertilizer application, atmospheric deposition, and irrigation. The objective was to estimate the maximum sustainable nitrogen input, defined here as the critical nitrogen load for agricultural soils.

MATERIALS AND METHODS

The field experiment was conducted at the experimental station of the N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection, located in the village of Tsalapitsa, southern Bulgaria (24°35′ E, 42°14′ N). The study area lies within the transitional zone between the temperate continental and Mediterranean climates, resulting in climatic conditions influenced by both climate regimes. Annual precipitation during the experimental period was 447 mm in 2020, 601 mm in 2021, 410 mm in 2022, and 200 mm in 2023, with a mean annual precipitation of 415 mm for the study period. By comparison, the long-term climatic normal (1961–1990) for the region is 492 mm. The long-term mean annual air temperature ranges from 12.5 to 12.8 °C. The warmest month is July, with a mean temperature of 23.4 °C, while the coldest month is January, with a mean temperature close to 0 °C. During the study period (2020–2023), annual mean air temperatures exceeded the long-term average by approximately 2–3 °C (Figure 1). A detailed description of the climatic conditions at the experimental site during the study period (2020–2023) is provided by Gerasimova et al. (2024).

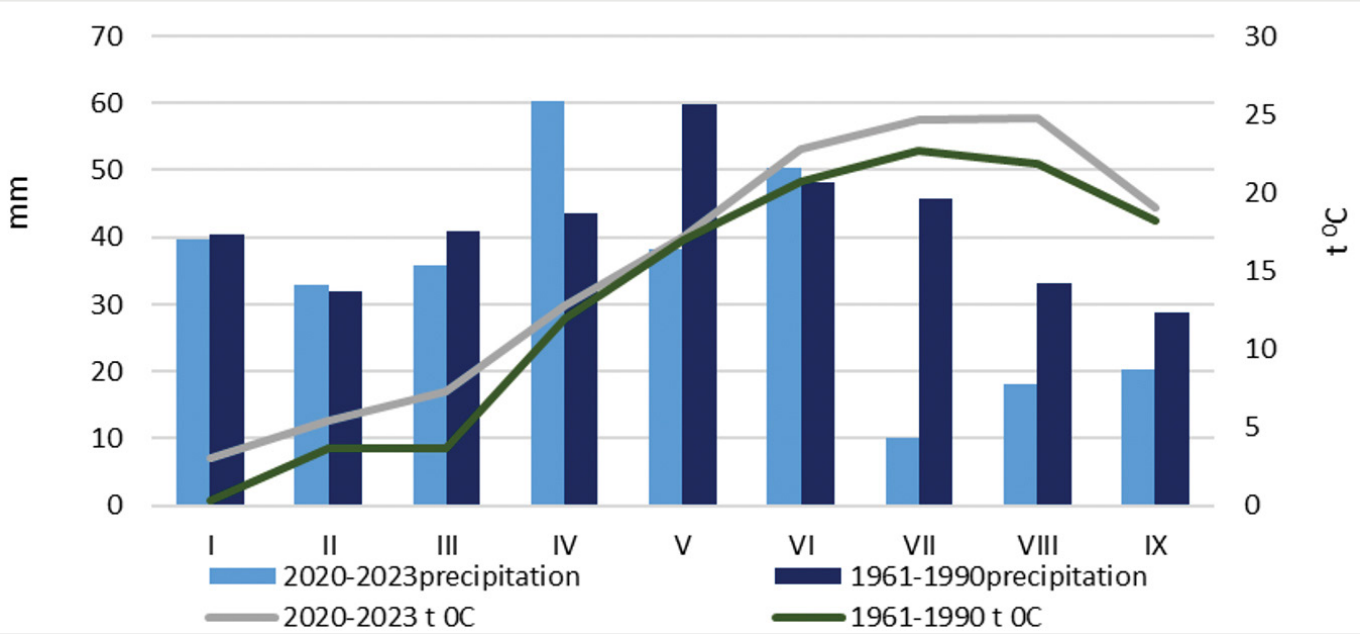


Figure 1. Climatic characteristics of the experimental field area during the study period (2020-2023)

The studied soil is an alluvial-meadow soil, classified as a Eutric Fluvisol according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015).

Fluvisols are widely distributed along river floodplains and are characterized by highly variable fertility. Owing to their high agricultural potential, they are extensively cultivated, making them well suited for this study. The soil profile has a coarse texture, low water-holding capacity, and relatively high permeability, creating favorable conditions for the active downward migration of chemical elements. The Fluvisols in the study area are classified as sandy clay loam and have developed on non-calcareous sandy-clay alluvial deposits. The soil profile is of the AC type, consisting of a humus-rich A horizon that gradually transitions into the parent material (C horizon). The arable horizon is characterized by a coarse texture, low clay content (18.6%), bulk density ranging from 1.54 to 1.66 g/cm^3, a slightly acidic reaction (pH 6.0), total nitrogen content of (0.052%), humus content of (1.23%), and a cation exchange capacity ranging from 7.92 to 22.7 cmol/kg (Table 1) (Stoichev, 1997). The average field capacity in the 0–100 cm soil layer is 19.6%, the permanent wilting point is 11.1%, and base saturation varies with soil depth, ranging from 79.4% to 84.4%.

This study was conducted as part of a long-term field experiment established in 1995, initially with vegetable crops. The determination of nitrogen and base cation input–output budgets, as well as the calculation of critical loads, was based on data collected during the 2020–2023 experimental period under a cereal crop rotation. The rotation consisted of maize (*Zea mays* L.) grown in 2020 and 2022, and winter wheat (*Triticum aestivum* L.) grown in 2021 and 2023. The experiment was arranged in four treatments differing in fertilizer application rates, as summarized in Table 2.

An experiment was arranged in a randomized complete block design. Each experimental plot covered 0.2 ha, with a harvest area of 100.8 m^2. Nitrogen fertilizer was applied as ammonium nitrate. For winter wheat, nitrogen was applied in two split applications: two-thirds at sowing and the remaining one-third as a top dressing in spring. For maize, two-thirds of the nitrogen was incorporated before sowing, while the remaining one-third was surface-applied 40 days after planting. Phosphorus fertilizer, in the form of superphosphate, was applied once before sowing at the rates specified in Table 2. No potassium fertilizer was applied. Maize was irrigated using a drip irrigation system to maintain soil water content close to field capacity, based on regular soil moisture

Table 1. Physico-chemical characteristics of the studied soil

Horizons	Depth, cm	pH_{H_2O}	Organic C %	Total N %	C:N	$CaCO_3$ %	CEC cmol/kg	Particle size, %		
								0.05–0.001 mm	<0.001 mm	<0.01 mm
Alluvial-meadow soil – Eutric Fluvisol (WRBSR)										
A_{arable}	0–35	6.0	0.70	0.052	7.8	0.0	7.92	33	18.6	32
A_2	35–60	6.4	0.55	0.050	6.4	0.0	18.18	32	33	35
A_3C_1	60–87	6.5	0.42	0.042	5.8	0.0	22.77	37	36	40
C_2	87–118	6.5	0.38	0.030	7.5	0.0	23.11	47	27	-

Table 2. Cereal crop rotation and fertilizer application rates

Grown crops	Variants kg/ha			
	T_0	T_1	T_2	T_3
Maize 2020	N_0P_0	$N_{120}P_{80}$	$N_{160}P_{120}$	$N_{200}P_{160}$
Wheat 2020/2021	N_0P_0	$N_{100}P_{60}$	$N_{140}P_{100}$	$N_{180}P_{140}$
Maize 2022	N_0P_0	$N_{120}P_{80}$	$N_{160}P_{120}$	$N_{200}P_{160}$
Wheat 2022/2023	N_0P_0	$N_{100}P_{60}$	$N_{140}P_{100}$	$N_{180}P_{140}$

measurements, thereby ensuring non-limiting soil water conditions throughout the growing season. The annual irrigation amount ranged from 250 to 300 mm. All experimental plots were managed under a conventional tillage system, and all agronomic practices were carried out in accordance with standard recommendations for the respective crops.

Measurement and monitoring of nutrient inputs

Input of elements via atmospheric deposition and irrigation water

Nutrient inputs included nitrogen and base cations supplied through atmospheric deposition (wet and dry deposition) and irrigation water. Annual input values were calculated for each year of the study period. Atmospheric inputs were estimated from the total annual precipitation, calculated by summing all individual rainfall events, and the corresponding chemical concentrations measured in the collected precipitation samples. Wet and dry atmospheric deposition were collected according to the standard methodology using Vild-type open-field collectors installed in an open area adjacent to the experimental site (Vekilska et al., 1992). During the study period, irrigation water was supplied from groundwater extracted at a depth of 4–8 m. The input of nitrogen and base cations through irrigation was calculated from the volume of irrigation water applied and the measured concentrations of these elements in the irrigation water.

Soil minerals weathering

Mineral weathering is an important component of the nutrient budget, but it is also one of the most difficult terms to quantify. Numerous methodological approaches have been proposed for estimating the release of base cations through mineral weathering, and these are comprehensively reviewed by UBA (1996). Most of these methods have been developed for forest and other nat-

ural mineral soils. In contrast, the present study focuses on arable land, where agricultural management practices such as tillage, fertilization, and irrigation may influence both the rate of mineral weathering and the release of ions into the soil solution. In addition, long-term cultivation may alter the intensity and direction of weathering processes through anthropogenic impacts. To evaluate these effects, the chemical composition of the soil solution can be interpreted using the geochemical mass-balance approach proposed by Garrels and Mackenzie (1971), which is based on the stoichiometric relationships among dissolved ions. The analysis indicated that the equivalent release of base cations into the soil solution under the applied agricultural practices did not exceed the rates expected under natural conditions. Therefore, for the calculation of critical nitrogen loads, the default weathering rate recommended by UBA (1996) for Fluvisols was adopted, namely 1250 eq/ha/yr.

Measurement and monitoring of nutrient uptake

Net nutrient uptake and removal in harvested biomass

Plant uptake represents one of the major pathways of nitrogen and base cation removal from the agroecosystem. During the study period, plant samples were collected at harvest to determine aboveground dry matter production and nutrient uptake. From each treatment and replicate, five representative plants reflecting the average crop condition were sampled. The plant samples were oven-dried to a constant weight, and dry matter yield was determined. The concentrations of chemical elements in the harvested biomass were analysed according to the method described by Peterburgskii (1986). Calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) concentrations were determined by atomic absorption spectrometry (AAS). Nitrogen (N) concentration in each plant organ was determined following wet digestion using the Ginsburg method, followed by Kjeldahl distillation (Peterburgskii, 1986).

Losses associated with drainage below the rooting zone

The vertical migration of chemical elements was assessed by analysing the chemical composition of soil leachate collected with lysimeters. Modified Ebermayer–Shilova lysimeters (collection area: 0.11 m^2) (Stoichev, 1974) were installed at a depth of 1.0 m beneath treatments T_0, T_1, T_2, and T_3, with three replicates per treatment, to collect drainage water. The lysimeter collection plates were carefully inserted into the soil profile without disturbing the overlying soil layers. Each collection plate was made of plastic and filled with polyethylene granules to ensure efficient infiltration and unrestricted water flow into the lysimeter. Leachate samples were collected at monthly intervals, depending on the volume of drainage, in 5.0 L plastic containers connected to the outlet of each lysimeter.

Soil and water sample analysis

Soil samples were collected from the 0–30 cm layer before sowing and after harvest using a hand auger. Soil pH (H_2O) was measured potentiometrically in a soil-to-water suspension at a ratio of 1:2.5. The main soil physicochemical properties were determined according to the methods described by Arinushkina (1970). All water samples, including precipitation, irrigation water, and soil leachate collected by lysimeters, were analysed for pH and major ions. However, the present study focuses only on K^+, Na^+, Ca^{2+}, Mg^{2+}, and nitrate nitrogen (NO_3^-–N). Nitrate nitrogen was determined spectrophotometrically using a Pharo 100 spectrophotometer. Potassium and sodium concentrations were measured by flame photometry, whereas calcium and magnesium were determined by atomic absorption spectrometry (AAS) (Page et al., 1982). All input and output fluxes used for the calculation of critical loads are expressed as eq/ ha/yr.

Calculation of the Steady-State Mass Balance (SSMB)

The Simple Steady-State Mass Balance (SSMB) method was used to determine the critical load of acidity ($CL_{(A)}$). This approach estimates the maximum long-term acid input that an ecosystem can tolerate without exceeding critical chemical thresholds for the selected re-

ceptor. The method is based on identifying the long-term average fluxes of acidity and alkalinity within the system and determining the maximum acid input that can be balanced under steady-state conditions. The critical load of acidity induced by sulphur and nitrogen deposition, $CL_{(S+N)}$, is derived from the steady-state charge balance of major ions expressed as annual input and output fluxes (eq/ha/yr) (Reinds et al., 2008). The SSMB model assumes a time-independent equilibrium between the production and consumption of acidic compounds (Sverdrup et al., 1993) and is therefore widely used for assessing the critical load of acidification. Although the SSMB approach has been applied primarily to forest ecosystems (De Vries, 1993; Ignatova et al., 1998), its conceptual framework can also be adapted to agricultural systems. In forest ecosystems, where nitrogen fertilization is absent, soil acidification is driven mainly by atmospheric sulphur deposition and the depletion of exchangeable base cations, resulting in a reduced soil acid-neutralizing capacity (Freer-Smith and Kennedy, 2003). In contrast, in agroecosystems, the dominant source of acidification is nitrogen fertilization (Guo et al., 2010; Stoichev et al., 1996). Under these conditions, the critical nitrogen load may be defined as the maximum nitrogen input that does not result in soil acidification beyond the established critical limits for soil pH and aluminium, while also preventing nitrogen accumulation and excessive nitrogen losses from the system (Koleva, 2003). Because agroecosystems are highly dynamic systems in which nutrient transformations are strongly influenced by management practices, several input and output fluxes cannot be measured directly. Consequently, the application of the SSMB approach requires a number of assumptions and simplifications (Koleva, 2003). Under the conditions of the present experiment, sulphur deposition had a negligible effect on soil acidification (Stoichev, 1997). Therefore, nitrogen inputs from atmospheric deposition and fertilizer application were considered the primary drivers of acidification. The critical load of acidity resulting from sulphur and nitrogen inputs was calculated using the following equation:

$$CL(S_{dep}+N_{dep}) = BC_{dep} - Cl_{dep} + BC_w - BC_u + N_i + N_u + N_{de} - ANC_{le} \quad (1)$$

where S_{dep}, N_{dep} and BC_{dep} represent the total deposition flux (including atmospheric depositions and inputs via irrigation water) of S, N and base cations, respectively. The term Cl_{dep} denotes chloride input via atmospheric deposition. In this equation, it is assumed that chloride behaves conservatively in the system, with no net sources or sinks (i.e., chloride leaching is equal to deposition). BC_w represents the release of base cations through mineral weatheringare; while BC_u and N_u denote the net uptake and removal of base cations and nitrogen by aboveground biomass, respectively. N_i is a critical long-term N immobilisation, N_{de} represents denitrification losses, and ANC_{le} refers to alkalinity leaching at the critical load level (Reinds et al., 2008).

BC_{dep}, was determined from direct measurements of the chemical composition of atmospheric deposition and irrigation water, followed by calculation of total deposition fluxes. The fluxes BC_u and N_u were derived from analyses of base cation and nitrogen concentrations in plant biomass and subsequent calculation of total biomass uptake. For BC_w, the net weathering rate recommended in the Mapping Manual (UBA, 2004) for the calculation and mapping of critical loads for Fluvisols was applied. Denitrification rates (N_{de}) were calculated according to the following equation:

$$N_{de} = f_{de.}(N_{dep} - N_i - N_u - N_{le}) \quad (2)$$

where f_{de} is the denitrification fraction, which depends on soil type and organic matter content; for the present soil type, f_{de} is assumed to be 0.1 (UBA, 2004); N_{dep} represents total nitrogen deposition, including atmospheric deposition, irrigation water, and nitrogen applied via fertilizers; The estimated value of N_i from this soil is 140 eq /ha /yr (Dinchev, 1983); N_u – denotes N uptake by plant biomass and N_{le} represents the amount of nitrogen leached from the 0–1 m soil layer.

ANC_{le} represents the critical leaching of Acid Neutralising Capacity (ANC), which is derived for a selected critical threshold above which harmful effects on sensitive environmental receptors may occur (UBA, 2004).

$ANC_{le,crit}$ is calculated based on a critical aluminium concentration (critical limit: Al^{3+} = 0.4 eq/m³). Aluminium concentration is modelled assuming equilibrium with gibbsite, and the critical hydrogen ion concentration is derived as follows:

$$[Al] = K_{gibb.}[H]^3 \text{ or } [H] = ([Al] / K_{gibb})^{1/3} \quad (3)$$

where K_{gibb} is the solubility constant of gibbsite, with a default value of 300 m⁶ eq² for soils with very low organic matter content (UBA, 2004), which was applied in this study. The aluminium concentration at the critical level (Al_{crit} = 0.4 eq/m³) is derived from the exchangeable aluminium content of the soil at the critical pH. Consequently, ANC is derived as follows:

$$ANC_{le(crit)} = - Al_{le(crit)} - H_{le(crit)} = - Q.[Al]_{crit} + [H]_{crit} \quad (4)$$

where Q is the water flux at the bottom of the rooting zone; $[H]_{crit}$ and $[Al]_{crit}$ represent the hydrogen and aluminium concentrations at the critical level, expressed as [eq/ha/yr].

RESULTS AND DISCUSSION

Input-output parameters of the SSMB model for the agroecosystem

Input of N and base cations via atmospheric deposition

The data show that the annual nitrogen input during the study period varied between 10.1 kg/ha (2023) and 23 kg/ha (2020). The lowest N input was recorded in 2023, which can be attributed to the very low precipitation in that year (200 mm/year). In the other years of the study period, an increase in atmospheric nitrogen deposition was observed. The highest nitrogen input occurred in 2020, which may be explained by the presence of local atmospheric nitrogen sources. The nitrogen input in 2021 was similar; however, it did not deviate from the long-term average value of 22.4 kg/ha typical for the region (Table 3). The pH of precipitation remained within a slightly acidic range (6.5–6.8). In a study by Simeonova and Nenova (2023) covering the same period at the experimental field, significant seasonal and interannual variability in precipitation chemistry was reported, with a higher coefficient of variation for nitrogen (61%) and cations (68%). The observed significant correlation between Ca^{2+} and Mg^{2+}, as well as the weak correlations between NH_4^+ and NO_3^-N and between NH_4^+ and SO_4^{2-}, suggests a buffering effect against precipitation acidity. According to Małecki et al. (2022) and Georgieva et al. (2022), despite the presence of certain hotspots, an overall improvement in air quality has been observed in recent years. This trend is also reflected in the measured ion concentrations and the reduced wet deposition loads of acid-forming compounds, particularly nitrogen species. Atmospheric deposition is also considered a contributing source of neutralising compounds in the mass balance equation. The average annual atmospheric input of Ca^{2+} over the experimental period ranged between 20.7 and 42.6 kg/ha (Table 3). Magnesium concentrations in precipitation followed a similar pattern of correlation with Ca^{2+}, showing a decreasing trend, albeit within a lower range. Potassium input via precipitation was comparable to that of magnesium, ranging between 2.6 and 15.4 kg/ha.

Inputs of N and base cations via irrigation

Irrigation, alongside precipitation, is considered a key factor governing the water balance and, consequently, crop productivity. Depending on the water source, as well as the associated input of chemical elements, irrigation can significantly influence soil loading and buffering capacity. The obtained results indicate that the irrigation water exhibits a weakly alkaline reaction (pH 7.75–8.20) and a calcium–hydrocarbonate composition. Irrigation was applied only during two years of the experimental period, 2020 and 2022, when maize was cultivated. It should be noted that the irrigation water was derived from groundwater pumped from aquifers at a depth of 4–8 m in the vicinity of the experimental site. The data show that nitrogen input via irrigation is comparable to that from atmospheric deposition (17–22.2 kg/ha). In contrast, the input of base cations is substantially higher, being approximately three to four times greater than that delivered by precipitation (Table 3). This represents a precondition for an increase in the acid-neutralizing capacity of the weakly buffered, non-calcareous Fluvisols.

DOI: /10.5513/JCEA01/27.3.4952

Table 3. Average annual input-output balances for N, K, Ca and Mg (kg/ha)

Treatments-	Elements kg/ha															
	N				K				Ca				Mg			
Input	T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3
Maize 2020																
Atmosph.depositions	23	23	23	23	10.5	10.5	10.5	10.5	39	39	39	39	7	7	7	7
Irrigation	17	17	17	17	8	8	8	8	167	167	167	167	51	51	51	51
Fertilizer application	0	120	160	200	0	0	0	0	0	0	0	0	0	0	0	0
Total	40	160	200	240	18.5	18.5	18.5	18.5	206	206	206	206	58	58	58	58
Output- (AGB)	69	172	179	191	83	209	236	241	16	22	24	38	14	18	20	23
Leaching	4.5	8.5	10	14	1	0,9	1	1	20	12	21	31	6	3	3	7
Total	73.5	180.5	189	205	84	210	237	242	36	34	45	69	20	21	23	30
Difference	-34	-21	11	35	-66	-192	-219	-224	170	172	161	137	38	37	35	28
Wheat 2021																
Atmosph.depositions	19	19	19	19	15.40	15.40	15.4	15.4	42.6	42.6	42.60	42.60	15.9	15.9	15.9	15.9
Irrigation	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fertilizer application	0	100	140	180	0	0	0	0	0	0	0	0	0	0	0	0
Total	19	119	159	199	15.4	15,4	15.4	15,4	4.6	42.6	42.6	42.6	15,9	15,9	15,9	15.9
Output- (AGB)	32	67	94	143	33.3	97.90	133.1	142.7	6.9	16.9	17.7	23,6	2.4	11.3	11.2	13.2
Leaching	1	9	15	16	0.4	0.7	0,8	1.7	7.1	32.2	50.7	37.1	2,4	8.3	13,7	11.3
Total	33	76	109	159	33.7	98.6	133.9	144.4	14	49.1	68.4	60.7	4,8	19.6	24.9	24.5
Difference	-14	43	50	40	-18.3	-83.2	-118.5	-129	28.6	-6.5	-25.8	-18.1	11.1	-3.7	-9	-8.6

Continued Table 3

Treatments-	Elements kg/ha															
	N				K				Ca				Mg			
Input	T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3
Maize 2022																
Atmosph.depositions	14	14	14	14	7	7	7	7	31	31	31	31	9,90	9,90	9,90	9,90
Irrigation	22	22	22	22	3	3	3	3	213	213	213	213	57	57	57	57
Fertilizer application	0	120	160	200	0	0	0	0	0	0	0	0	0	0	0	0
Total	36	156	196	236	10	10	10	10	216	216	216	216	67	67	67	67
Output -(AGB)	50	119	212	275	62	133	164	185	15	18	19	28	12	14	15	22
Leaching	4	12	13	20	0,5	1,0	0,7	1,5	20	10	25	52	6	4	9	16
Total	54	131	225	295	62,5	134	164,7	187	35	28	44	80	18	18	24	38
Difference	-18	25	-29	-59	-54	-124	-155	-177	181	188	173	136	49	49	43	29
Wheat 2022																
Atmosph.depositions	10.1	10.1	10.1	10.1	2.6	2.6	2.6	2.6	21	21	21	21	3.9	3.9	3.9	3.9
Irrigation	16.1	16.1	16.1	16.1	0	0	0	0	0	0	0	0	0	0	0	0
Fertilizer application	0	100	140	180	0	0	0	0	0	0	0	0	0	0	0	0
Total	26	126	166	206	2.6	2.6	2.6	2.6	21	21	21	21	3.9	3.9	3.9	3.9
Output -(AGB)	21.7	45.8	87.9	115.3	15.4	29.9	61.9	115.9	8.9	13.5	18.7	19.7	1.7	7.3	9.2	15.2
Leaching	1.9	4.8	7.5	17.9	0.3	0.4	0.7	0.9	5.9	12.7	15.4	34.5	1.3	4.3	4.6	8.4
Total	23.7	59.6	95.4	133.2	15.7	30.3	62.6	116.8	14.8	26.2	34.1	54.2	3.0	11.6	13.8	23.6
Difference	2.3	66	71	73	-13	-27	-60	-114	6.2	-5.2	-13	-33	0.9	-7.7	-9.9	-19

Net nitrogen and base cations removal by plant production

Nitrogen and base cation removal through crop production represents the major upward flux of nutrients from the soil and is a key process determining the impact of anthropogenic inputs on the most sensitive ecosystem components used as assessment criteria. Evaluating critical soil loading thresholds and the extent to which nitrogen fertilization compensates for acid inputs requires quantifying the amount of base cations removed with the harvested above-ground biomass, as these elements are essential for maintaining the soil's acid-neutralizing capacity. Annual crop uptake and net removal of nitrogen and base cations from the agroecosystem were calculated based on the net above-ground biomass production and the concentrations of these elements in the harvested plant organs. According to Xu et al. (2024), natural soil acidification is driven not only by bicarbonate (HCO_3^-) leaching and the removal of base cations (BCs) through crop harvesting but also moderated by the return of HCO_3^- and BCs through fertilizer and manure applications. As shown in Table 3, the highest nitrogen removal occurred during the maize-growing seasons of 2020 and 2022, ranging from 69 to 191 kg/ha/yr and from 50 to 275 kg/ha/yr, respectively. In contrast, nitrogen removal during the wheat-growing seasons was considerably lower, varying from 32.3 to 143.3 kg/ha/yr in 2021 and from 21.7 to 115.3 kg/ha/yr in 2023. This difference can be attributed to the lower nutrient demand of wheat compared with maize, the rainfed cultivation conditions, and the severe drought recorded in 2023. The average annual potassium removal ranged from 62.3 to 241 kg/ha/yr under maize and from 15.4 to 142.7 kg/ha/yr under wheat (Table 3). In contrast, sodium uptake was negligible compared with that of the other macronutrients. Among the base cations, calcium and magnesium make the greatest contribution to the soil's acid-neutralizing capacity. Their inputs are derived primarily from the weathering of primary minerals and from wet and dry atmospheric deposition, while only minor amounts are supplied as secondary constituents of compound nitrogen and phosphorus fertilizers (Koleva, unpublished data). Total calcium uptake by maize during the 2020–2022 growing seasons ranged from 14.7 to 37.9 kg/ha/yr, whereas wheat removed between 6.9 and 23.9 kg/ha/yr. As shown in Table 3, magnesium uptake followed a pattern similar to that of calcium, increasing with higher nitrogen application rates but remaining lower in absolute terms. A reduction in base cation inputs to the soil, together with increased removal through crop uptake, may progressively diminish the soil's acid-neutralizing capacity and increase its susceptibility to acidification.

Leaching of elements in lysimeter drainage water

Leaching of chemical elements below the root zone via drainage water represents one of the major pathways of nutrient loss from the soil and is an important component of the overall mass balance. The amounts of chemical elements leached below the 1 m soil profile were calculated from the measured drainage volumes and the corresponding concentrations of the elements in the lysimeter water. Drainage volumes were strongly influenced by precipitation, irrigation, evapotranspiration, and other site-specific hydrological factors. The results obtained during the 2020–2023 study period showed that the pH of the lysimeter water ranged from 7.30 to 7.80 in the fertilized treatments (T_2 and T_3), whereas slightly higher values (7.90–8.30) were recorded in the control treatment (T_0). These results indicate that the drainage water percolating below the 1 m soil layer was slightly alkaline under all experimental treatments. The lowest drainage volumes were recorded in 2023, ranging from 11.5 to 26.9 l/m², whereas the highest values occurred in 2020, varying between 53.2 and 76.0 l/m². On average, the amount of water leached below the 1 m soil profile accounted for approximately 1–15% of the total incoming water, depending on the treatment and year (Table 4).

Table 4. Lysimeter drainage volumes during the study period (2020–2023)

Year	Water amounts		Sum P + I	Lysimetric water, out of 1m soil layer, l/m²				% from the total water income			
	Precipitation, mm	Irrigation mm		T_0	T_1	T_2	T_3	T_0	T_1	T_2	T_3
2020	447	250	697	53.2	75	59.6	75.9	7.6	10.7	8.1	11
2021	601	-	601	13.5	25.0	32.7	41.4	2.3	4.1	5.5	7.0
2022	410	300	710	5.77	13.3	29.0	48.1	1.0	1.9	4.1	6.8
2023	200	-	200	11.5	30.7	26.9	22.8	5.7	15.3	13.5	11.4

Accurate estimation of the mass balance of chemical elements for critical load assessment requires quantification of the amounts of macronutrients leached below the 1 m soil profile (Table 4). It should be noted that nearly all nitrogen leached through the soil profile was present in the form of nitrate (NO_3^-). The data show that the average nitrogen loss from the unfertilized treatment ranged from 1.4 to 1.9 kg/ha under wheat and from 4.3 to 4.5 kg/ha under maize. Nitrogen fertilization consistently increased nitrate leaching in all fertilized treatments. Comparisons among the fertilized treatments indicate that nitrate losses varied considerably with nitrogen application rate and were strongly influenced by precipitation and irrigation, which determined the volume of drainage water (Table 4). Simeonova et al. (2024) reported that nitrogen losses through lysimeter drainage under cereal crops are approximately four to five times lower than those observed under row crops. Calcium (Ca^{2+}) was identified as the most mobile base cation, accounting for the largest proportion of cation losses below the 1 m soil layer. Average calcium losses ranged from 20 to 52 kg/ha under maize and from 5.9 to 23.6 kg/ha under wheat, depending on the nitrogen application rate (Table 3). Calcium leaching increased with increasing nitrogen inputs, indicating enhanced cation mobility under higher fertilization rates. Magnesium (Mg^{2+}) exhibited a similar response to nitrogen fertilization, although the absolute leaching losses were considerably lower and showed relatively little variation among treatments. In contrast, the leaching of potassium (K^+) and sodium (Na^+) was only marginally affected by fertilizer application, and the losses of these cations remained negligible throughout the study period.

Changes in soil pH

Accelerated soil acidification induced by nitrogen fertilization is primarily attributed to proton (H^+) production during the nitrification of ammonium-based nitrogen fertilizers. In addition, under conditions of high rainfall or irrigation, nitrate (NO_3^-) is leached from the soil together with substantial amounts of base cations, resulting in a net accumulation of H^+ and further soil acidification (Liu et al., 2023). Soil pH is widely recognized as a key indicator regulating nutrient availability, plant productivity, and numerous soil processes, including microbial community composition and activity (Koleva et al., 2003; Kemmitt et al., 2006). Therefore, changes in soil pH were considered an appropriate criterion for evaluating the adverse effects of additional nitrogen inputs on agricultural soils. According to Waldner et al. (2015), progressive soil acidification depletes soil base cations (BCs) and promotes the mobilization of aluminium (Al^{3+}) into the soil solution. However, the potential toxicity of dissolved aluminium may be partially alleviated by the presence of dissolved base cations. The results of the present study demonstrate that long-term nitrogen fertilization affected both soil pH and base saturation in the upper 0–30 cm soil layer across all fertilized treatments. Following maize cultivation in 2020 and 2022, soil pH decreased in all treatments, with the greatest reductions observed in the highest nitrogen application rates (T_2 and T_3). The mean soil pH was 6.10 ± 0.41 in 2020 and 6.00 ± 0.26 in 2022.

In contrast, after wheat cultivation, the average pH of the plough layer was slightly higher, reaching 6.35 ± 0.31 in 2021 and 6.40 ± 0.09 in 2023.

Throughout the crop rotation, soil pH in the fertilized treatments declined by approximately 0.5–0.8 units relative to the unfertilized control, with the greatest acidification occurring after maize cultivation (Figure 2). Although wheat cultivation partially moderated the decline in soil pH, this effect was insufficient to restore soil reaction to values approaching those observed under the control treatment.

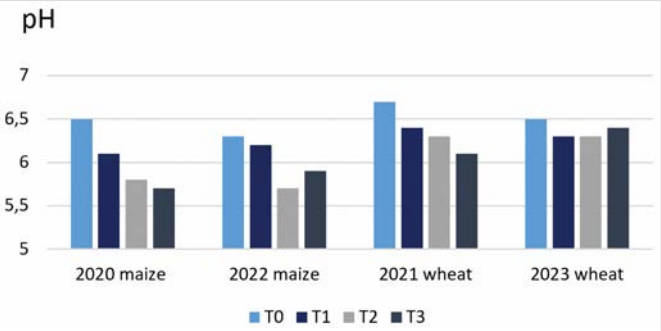


Figure 2. Soil pH during the study period at the Tsalapitsa experimental field

Calculation of the critical load of acidifying nitrogen $CL(A)_N$

As discussed above, soil acidification in arable systems is primarily driven by nitrogen inputs. Accordingly, the assessment of critical loads in the present study is expressed in terms of nitrogen. In this context, the critical nitrogen load is defined as the maximum nitrogen input that results in a soil acidification status in which the established critical limits for soil pH and aluminium (Al^{3+}) are not exceeded, and conditions promoting nitrogen accumulation or nitrogen losses do not occur. Agroecosystems are highly dynamic systems in which chemical elements undergo continuous transformation and redistribution. Because many input and output fluxes cannot be measured directly, the application of critical load models inevitably requires certain assumptions and simplifications. To approximate steady-state conditions, several assumptions were adopted to facilitate model application without substantially compromising the accuracy of the calculations. These assumptions are as follows: weathering rates and element export are assumed to be uniformly distributed throughout the soil profile; water movement and solute transport occur exclusively in the vertical direction; the physicochemical constants used to calculate the critical concentrations of hydrogen (H^+) and aluminium (Al^{3+}) are assumed to remain constant throughout the soil profile; sodium (Na^+) is excluded from the equivalent sum of base cations because of its negligible contribution to the neutralization of soil acidity; denitrification losses are assumed to be negligible; cation exchange within the soil exchange complex is assumed to be at steady state, with no changes in base saturation; all variables are expressed as long-term annual mean values. The calculated critical loads characterize the sensitivity of the agroecosystem to the combined effects of nitrogen inputs from atmospheric deposition, irrigation water, and nitrogen fertilization. Consequently, they provide a quantitative basis for regulating nitrogen fertilizer application in order to minimize the risk of soil acidification. Potential exceedance of the critical load was assessed by comparing the total annual nitrogen input with the calculated critical load values. Based on the assumptions outlined above, and considering nitrogen as the principal acidifying agent in the studied agroecosystem, the frequency of critical load exceedance was evaluated for the different nitrogen fertilization treatments (Koleva, 2002).

Table 5 presents the equivalent values of the parameters used to calculate critical loads based on the pH criterion, together with the corresponding critical load values. The results indicate that this criterion produced relatively high critical nitrogen loads during maize cultivation, particularly in 2022, with values of 227 kg N/ha for treatment T_2 and 261 kg N/ha for treatment T_3. This can most likely be attributed to the higher inputs of base cations supplied by precipitation and irrigation water, which increased the acid-neutralizing capacity of the Fluvisol despite its inherently low buffering capacity. Treatment T_2 (160 kg N/ha) may be regarded as the optimal fertilization rate because it achieved an almost complete balance between nitrogen inputs and outputs

while remaining below the maximum nitrogen application rate permitted by the Nitrates Directive (Council Directive 91/676/EEC). Similarly, Simeonova et al. (2015) reported that a balance between nitrogen inputs and outputs was achieved at nitrogen application rates of 80 and 160 kg N/ha. Comparison of the nitrogen loads for all treatments in 2022 with the calculated critical loads showed that only treatment T_3 (200 kg N/ha), which received the highest nitrogen application rate, exceeded the critical load.

Table 5. Calculation of the critical load for acidifying nitrogen (CL(A)N) and its individual components

	Atmosph. deposit. + irrigat. water BC_{dep}	Chlorine input Cl^-	Weather. rates BC_w	Total biomass uptake BC_{up}	N Input by precipit, irrig, fertigation $N_{pr} + N_{ir} + N_{fer}$	Immobil.nitrogen N_{im}	Total biomass uptake N_{up}	Leaching N_{le}	**Critical load** $CL(A)_N$	**Critical load** $CL(A)_N$ *kg/ha*
	eq/ha per year									
	Maize, 2020									
T_0	8362	2270.8	1250	3097.8	2850.1	140	4968.2	779.7	876.8	122.7
T_1	8362	2270.8	1250	6666.7	11420.0	140	12320.7	444.3	12882.9	180.4
T_2	8362	2270.8	1250	7481.9	14271.3	140	12798.8	682.3	12299.8	172.3
T_3	8362	2270.8	1250	8038.6	17126.6	140	13619.8	1084.8	12169.6	170.5
	Wheat, 2021									
T_0	1472.6	1190	1250	1122.5	1372.5	140	2305.7	99.9	2934	41.1
T_1	1472.6	1190	1250	3390.1	8510.8	140	4789.8	663.9	2274.1	31.8
T_2	1472.6	1190	1250	4306.2	11366.2	140	9272.6	1099.2	5298.9	74.2
T_3	1472.6	1190	1250	4781.2	14221.4	140	10229.1	1149.3	6062	84.9
	Maize, 2022									
T_0	8924.6	2699	1250	2453.5	2541.9	140	3562	306.9	770.1	107.9
T_1	8924.6	2699	1250	4453.6	11111.8	140	8523.1	849.5	11005.3	154.1
T_2	8924.6	2699	1250	5305	13963.1	140	15147.4	942.3	16210.1	227.1
T_3	8924.6	2699	1250	6317.7	16818.4	140	19607.4	1456.2	18628,5	26.0
	Wheat, 2023									
T_0	586.8	908,3	1250	685.8	707.2	140	1549	142.1	1805.8	25.2
T_1	586.8	908.3	1250	1401.7	7845.5	140	3911.8	343.6	3157.1	44.2
T_2	586.8	908.3	1250	2428	10700.8	140	6274.5	532.4	4406.1	61.7
T_3	586.8	908.3	1250	4080.7	13556.1	140	823.,4	127.8	4071.4	57.0

The exceedance amounted to 18628.5 eq/ha/yr and resulted in a decline in soil pH of approximately 0.6–0.8 units. In contrast, considerably lower critical load values were obtained for wheat cultivation in 2021 and 2023 across all treatments. Since the wheat crop was grown under non-irrigation, no additional base cations were supplied through irrigation, thereby reducing the input of acid-neutralizing cations. Although lower amounts of nitrogen fertilizer were applied, the removal of base cations through harvested biomass was also reduced, resulting in only minor changes in soil pH. Koleva (2002) have found that critical load estimates are strongly influenced by crop-specific characteristics, particularly the amounts of nitrogen and base cations accumulated in the aboveground biomass. As shown in Table 5, the higher critical nitrogen load recorded in 2021 may also be attributed to the relatively high precipitation during that year, which increased the input of base cations. Overall, the critical load values obtained throughout the experimental period indicate that the mass balance approach provides a robust and informative assessment of the effects of individual anthropogenic factors on nitrogen critical loads. The results further demonstrate that the principal factors controlling critical nitrogen load thresholds are land-use practices, crop characteristics, and the intrinsic physicochemical properties of the soil.

CONCLUSIONS

In this study, we presented nitrogen and base cation budgets following a four-year maize–wheat rotation and applied the critical load concept to agricultural soils using a Simple Mass Balance (SMB) model for soil acidification. The soil's capacity to neutralize acidifying effects depends primarily on the input of base cations via atmospheric deposition and irrigation water. A marked decline in base cation inputs from atmospheric deposition has been observed in recent years, while, concurrently, higher amounts of these elements are supplied through irrigation water. Changes in base cation deposition may therefore contribute to a reduction in critical loads for acidity. The key finding of this study is that the calculated critical load of acidifying nitrogen ($CL(A)_N$), estimated using the SMB approach, was high across all fertilization treatments following maize cultivation, particularly in 2022, indicating conditions conducive to soil acidification. In contrast, after wheat cultivation in both 2021 and 2023, a pronounced decrease in the critical nitrogen load for acidity was observed, accompanied by very low inputs of base (alkaline) cations. From a nitrogen management perspective, it is essential to quantify nitrogen inputs and $CL(A)_N$ values, as this can support optimization of fertilizer application rates, minimize soil acidification, and reduce liming costs, thereby contributing to more sustainable agricultural production.

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