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Calculation of the critical loads for acidity and nitrogen levels on arable Fluvisol

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Abstract

This paper aims to estimate the maximum nutrient nitrogen input, called critical load that will balance the system in the stability limits regarding soil acidification while also not limiting plant growth as a result of mass balance calculation. The assessment was made on the basis of data obtained during a 4-years (2020-2023) field experiment and changes in the major input-output pools of nitrogen and base cations as a result of changing N loads. The study was carried out on Fluvisol, near Plovdiv in Southern Bulgaria under a cereal crop rotation. The experiment design included four N rates (T_0-control, T_1 N_{100}, $T_2 N_{140}$, T_3 N_{180}) for wheat (*Triticum aestivum* L.) and (T_1 N_{120}, T_2 N_{160}, T_3 N_{200}) kg/ha for maize (*Zea mays* L.) respectively. Results show that average amount of N added by atmospheric deposition and irrigation water for the period 2020-2023 ranged from 10 to 24 kg.ha^{-1}. Depositions of Ca^{2+} and Mg^{2+} via rainfall was reaching to 42 kg.ha^{-1} Ca^{2+} and 15.9 kg.ha^{-1} Mg. The average amount of N leached out of the control treatment (reaching 4.5 kg.ha^{-1} N) was four to five times lower in comparison with fertilized treatments T_2 and T_3. It was established that when using criteria - pH of the soil the critical load for acidifying N for this soil type was considerably high (170-227 kg.ha^{-1} per year) in case of maize. A significant reduction in the critical load for acidifying N was registered after wheat when irrigation was not applied (31-82 kg.ha^{-1} per year).

Key words: critical load, nitrogen, base cations, input-output

Introduction

Significant transformations of nutrients take place in soils under the influence of both natural processes and those caused by human activity and climate change. It happens very often introducing of a significant amount of chemical elements into agroecosystems from industrial or agricultural sources (Oenema and Roest, 1998; Grieve, 2001), which lead to negative changes in the environment as well as to soil acidification. Last years, it has been observed that atmospheric deposition of sulfur (S) and nitrogen (N) has caused acidification and eutrophication of forest soils in Europe and North America, leading to imbalances, leaching and degradation of forest stands. (De Vries, 1991, 1993; Waldner et al., 2015; Hao et al., 2020). In their study, Růžek et al. (2019) found that sulfate and nitrate anions are neutralized by cations in the soil and deplete its cation exchange complex. In Europe, emission reduction measures implemented in recent decades led to a significant decrease also in deposition fluxes. On the other hand, South-East Europe and the Balkans were indicated as hot-spots for sulfur dioxide and sulfur wet depositions in several modeling studies (Georgieva et al., 2022). The critical N loading approach is primarily used to describe the vulnerability of natural ecosystems or part of an ecosystem to atmospheric N deposition (De Vries et al., 2007, 2015). This concept is widely used today in forest ecosystems. The critical load concept, is defined as “the maximum deposition that will not cause chemical changes leading to longterm harmful effects on ecosystem structure and function” (Nilsson and Grenfelt, 1988). Ecosystems that receive deposition above their critical load are said to be in exceedance, i.e., they are at risk of undergoing biological damage. Studies by Posch et al. (2011), Waldner et al., (2015) reported that different approaches are used to estimate critical loads for atmospheric deposition of nitrogen, such as making the empirical observations. The second approach derives critical loads for N deposition from a criterion applied to nutrient fluxes or levels in an ecosystem model and is generally implemented with a steady-state mass balance (SSMB) of input sources and output sinks (Sverdrup and de Vries, 1994). A general criterion for calculating critical N deposition loads using SSMB is that the N extraction flux below the root zone should not exceed a certain acceptable level (Spranger et al., 2004), which is often based on critical limits for Nmin. Nitrogen critical loads are usually system-dependent and are estimated or calculated using a combination of field observations and dose-response parameterizations (Delon et al., 2022). However, in order to apply critical load definition to nitrogen in agricultural soils, it is necessary to decide upon the “harmful effect” criteria, which should make the basis for the “qualitative estimate” of critical load for nitrogen Determination of the estimation criteria in case of agricultural soils is a very difficult task, because maintaining, and if possible increasing, soil fertility is the major goal of sustainable agriculture. So in order to implement or test the critical load model in agricultural systems, we need long term-crop experiment that compare different levels of nitrogen applications, consistent crop management practices and accurate data collection on nitrogen and base cation fluxes in and out of the systems. Nutrients budgeting and balances approaches have been widely applied in variety of scales (Dechert et al., 2005; Schlecht and Hiernaux, 2004), in order to assess and understand the status and dynamics of nutrients and to indicate trends in sources and sinks at ecosystem level. However, the focus of element cycling has mainly been on single compounds but very few studies on agricultural soils address major sources and sinks of cations and anions in a long-term perspective (Stoichev, 1989, Erisman et al., 2003; 2010). In the calculations of the critical load, it is necessary to take into account the influence of the variation in the deposition of basic cations, which plays an important role in mitigating acidification (Zhao et al., 2007, Watmough, 2024, Xu et al., 2024).

This paper provides an analysis of the four years trends and changes in the major input-output pools of N and major macro nutrients (base cations K, Ca, Mg) as a result of changing crops and N inputs (fertilizer rates, atmospheric depositions, inputs with irrigation) for to estimate the maximum nutrient nitrogen input, defined as critical load.

Materials and methods

The field experiment was set up at the experimental station of the N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection in the village of Tsalapitsa, Southern Bulgaria ($24^0$35'E; $42^0$14 N). The region is a transitional region of the European moderate-continental climate zone influenced by the Mediterranean type of climate. The average annual precipitation during the experimental period was as follows: 2020 – 447 mm, 2021 - 601 mm, 2022 - 410 mm, 2023 - 200 mm, average for the study period 415 mm. The period accepted as a norm 1961-1990 has an amount of precipitation of 492 mm. The average annual air temperature is 12.5-12.80º C in July – 23.4º C in January - it is around zero degrees. For the studied period deviation from temperature norms (by about 2-3^0 C) was established. The climatic characteristics during the studied period (2020-2023) of the experimental field area are presented in detail in a publication by Gerassimova et al. (2024).

The studied soil is Alluvial-Meadow, which corresponds to Eutric Fluvisol (IUSS Working Group WRB, 2015). This type of soil is used for intensive agriculture and is therefore it is suitable for the purposes of the study. The soil profile has a coarse texture, low water holding capacity and fairly high water permeability, which creates conditions for active migration of chemical elements along the profile. Flivisols of this region are sandy clay loam and have been formed on non-calcareous sandy-clay alluvial depositions. Soil profile is AC type - humus layer, with graduality passes over parent matrix. The arable horizon has the following mean characteristics: coarse texture, low clay content (18.6%), bulk density between 1.54 and 1.66 $g.cm^{-1}$, slightly acidic reaction pH_{H2O} (6.0), total nitrogen (0.052%), humus content - 1.23%, and cation exchange capacity varies between 7.92 - 22.7 $cmol.kg^{-1}$ (Table 1) (Stoichev, 1997). The average value of the field capacity in the 0-100 cm layer is 19.6%, the wilting point is 11.1%. Base saturation depends on the soil depth and ranges between 79.4 and 84.4%.

Determination of input-output budgets of nitrogen and base cations and calculation of critical loads was based on data from experiment with cereal crop rotation grown in the period 2020-2023. Cereal crops were grown in the following rotation: maize (*Zea mays* L.), during 2020 and 2022, wheat (*Triticum aestivum* L.), during 2021 and 2023. The experiment design includes four treatments with the following fertilization rates: (T_0-control, T_1 N_{100}, T_2 N_{140}, T_3 N_{180}) for wheat and (T_0, T_1 N_{120}, T_2 N_{160}, T_3 N_{200}) $kg.ha^{-1}$ for maize respectively.

Input of elements by atmospheric deposition and irrigation water. This includes input of nitrogen and base cations by rainfall and irrigation water. Input data is presented as total annual input for each year from the study period. Atmospheric inputs are obtained by simple calculation from average precipitation totals received from all individual rainfall events and chemical concentration of these samples. During the period of research for irrigation was used groundwater from a depth of 4-8 meters. For the study period plant samples for determination of absolutely dry matter and elements uptake were taken after harvesting. Elements composition of harvested biomass was determined according to Peterburgskii (1986). Ca, Mg, and K are determined with AAS. N content in each plant organ was determined by wet digestion by Ginsburg method and Kjeldahl distillation (Peterburgskii, 1986). Vertical migration of chemical elements was detected studying the chemical composition of the collected of drainage flux with lysimeters. Modified Ebermaier-Shilova type of lysimeters (Stoichev, 1974) were installed under treatments (T_0, T_1, T_2 and T_3) at 1m soil depth in three replications to collect the leachate volumes.

Soil samples were taken by hand auger before sowing and after harvesting from 0-30 cm depth, $pH_{(H2O)}$ values were determined potentiometrically in a soil: water ratio 1:2.5. Soil characteristics were determined according to Arinushkina (1970). All water samples (rainfall, irrigation and soil lysimetric water) were analyzed for pH and macroelements, but in the article only discussed K^+, Ca^{2+}, Mg^{2+}

Table 1. Physico-chemical characteristics of the studied soil

Hori-zons	Depth, cm	pH_{H2O}	Organic C, %	Total N, %	C:N	$CaCO_3$, %	CEC, cmol. kg^{-1}	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	-

and NO_3-N. Nitrogen was analyzed carried out by spectrophotometer "Pharo 100". Potassium were determined by flame photometer, calcium and magnesium – by AAS (Page et al., 1982), Input and output budgets for critical loads calculations are presents in eq/ha per year.

Calculation of Steady-state mass balance - The basic principle of the SSMB method is to identify the long-term average fluxes of acidity and alkalinity in the system and to determine the maximum tolerable acid input that will balance the system at safe limits for the selected receptor. Simple mass balance (SMB) method was used to determine the critical load of acidity $CL_{(A)}$. The $CL_{(A)}$ is induced by deposition of N and S, $CL_{(S+N)}$, which can be derived from steady-state charge balance for the ions (in eq ha^{-1} $year^{-1}$) from input and output into a system (Reinds et al., 2008). This model assumes a time-independent equilibrium between production and consumption of acidic compounds (Sverdrup and Warfvinge, 1993) and is used for assessment of the critical acidification level. The method is widely used for forest ecosystems (De Vries, 1993; Ignatova et al., 1998). Since forest ecosystems are not fertilized with N, the main source of acidity is associated with S deposition as well as soil cation depletion, which leads to low soil acid neutralizing capacity (Freer-Smith and Kennedy, 2003) whereas in agricultural systems, the main source of acidification is N fertilization (Guo et al., 2010). A critical nitrogen load in this case can be seen as the nitrogen input, which produce a final acidification stage of the soil, in which the critical limits set for pH and aluminum are not exceeded and no conditions for N accumulation and losses occur. (Koleva, 2003). Agroecosystems are quite dynamic environment for the chemical elements transformations and many of the input-output budgets cannot be easily measured and making some assumptions and simplifications is inevitable (Koleva, 2002). The sulphur deposition has negligible acidification effect under the conditions of this experiment (Stoichev, 1997). Hence the main factor, which cause acidification is N deposition via various input sources (atmospheric or fertilizers). Critical loads for acidity were calculated using the following equation:

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

In which, S_{dep}, N_{dep} and BC_{dep} are the total deposition flux (atmospheric depositions and irrigation water) of S, N and base cations, respectively. The Cl_{dep} term represents Cl^- obtained from atmospheric deposition. In this equation, it is assumed that there are no sources or sinks of chloride (leaching=deposition). BC_w are the base cations released by the weathering processes; BC_u and N_u are the net uptake flux and removal of base cation and N by aboveground biomass, N_i is a critical long-term N immobilisation, N_{de} is denitrification rate and ANC_{le} is a alkalinity leaching flux at critical level (Reinds et al., 2008).

BC_{dep}, was obtained from direct measurements of chemical content of the atmospheric depositions and irrigation water and calculating the depositions. BC_u and N_u were obtained by analysing base cation and nitrogen content in the plant biomass and then calculated the total biomass uptake. For BC_w, we used the net weathering rate pointed in the Mapping Manual (UBA, 1996) for calculation and mapping of critical loads for Fluvisols. 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 a denitricification fraction, which depends on the soil type and organic matter content and f_{de}= 0.1 for this type of soil (UBA, 1996); Ndep equals the total N_{dep} (N atmospheric depositions and irrigation water + N deposited as fertilizer); The estimated N_i from this soil is 140 eq.ha^{-1} per year; N_u – N uptake by plant biomass and N_{le} is the nitrogen leached out from 1 m soil layer.

ANC_{le} is the critical leaching of ANC (Acid Neutralising Capacity), which can be derived for a selected critical limit, above which harmful effects on sensitive elements of the environment can occur (UBA, 1996). $ANC_{le,crit}$ in this paper is calculated based on critical Al concentration (critical limit, Al = 0.4 eq.m^{-3}). The concentration of Al is modelled by gibbsite equilibrium and critical [H], derived from:

$$[Al] = K_{gibb}.[H]^3$$

or

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

Where K_{gibb} is solubility constant of gibbsite and K_{gibb}= 300 m6eq^{-2} is a default value for soil with very low organic matter (UBA, 1996), which has been used here. Al at critical limit ($Alcrit$=0.4 eq.m^{-3}) calculated by the exchangeable Al content of this soil at critical pH. Hence ANC is derived as follows:

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

Where Q is water flux at the bottom of rooting zone; $[H]_{crit}$ and $[Al]_{crit}$ are the hydrogen and aluminium leaching at critical level [eq.ha^{-1} per year]. Critical acidification (N) loads were calculated.

Results and discussion

Input of N and based cations with atmospheric deposition

Data shows that the annual input of nitrogen for the period of research vary between 10.1 (2023) and 23 kg.ha^{-1} (2020). The lowest N input was registered in 2023 and it is caused by the very less precipitation amounts within this year (200 mm.y^{-1}). For the other years of the research period an increase in N air deposition has been observed. Especially high N input was achieved in 2020, this could explain by appearance of some local N sources in the air. The amount of imported nitrogen is similar in 2021, but nevertheless it does not differ from the long-term average values of 22.4 kg.ha^{-1} typical for this area (Table 2). The pH values of the precipitation are in the slightly acidic range (6.5-6.8). In a study by Simeonova and Nenova (2023) for the same period in the experimental field, they found a significant seasonal and annual variation of the elements in precipitation with a higher coefficient of variation reported for nitrogen (61%) and cations (68%). The established significant correlation between Ca^{2+} and Mg^{2+} and the weak one between NH_4^+ and NO_3-N as well as between NH_4^+ and SO_4^{2-} suggest a buffer factor against precipitation acidity. According to Małecki et al., (2022); Georgieva et al., (2022), despite some hotspots there has been an increasing trend of air quality improvement in recent years. This trend is also observed in the measured ion concentrations and reduced wet deposition loads of the containing acid-forming compounds, especially the nitrogen compounds. Atmospheric deposition in the mass balance equation are assumed also a source of neutralizing compounds. Deposition of Ca^{2+}, which is the basic compensation agent adds significantly to the Ca^{2+} turnover within the agroecosystem. The average annual input by atmosphere for the experimental period vary between 20.7 and 42.6 $kg.ha^{-1}$ (Table 2). The content of magnesium cations in rain water follow the pattern correlation with Ca^{2+} and the same tendency of decreasing but in lower range. It has been found that the potassium input with precipitation is similar to that of magnesium, between 2.6 and 15.4 $kg.ha^{-1}$.

Inputs of N and base cations with irrigation

Irrigation, as well the precipitation is considered as a factor for control of water balance and crop potential respectively. Depending on the source of water supply irrigation and the input of chemical elements it could have a significant influence on soil loading or soil buffering capacity. The obtained results show that the waters used for irrigation have a weak alkaline reaction (pH 7.75 - 8.20) and a calcium-hydrocarbonate composition. Irrigation within the experimental period was applied only for two years – 2020 and 2022, when maize was grown. It is important to say that irrigation was used groundwater pumped up from the depth 4-8 m aquifers in the vicinity of the watershed area near the experimental site. As it could be seen from the data input of nitrogen from irrigation is very similar to the amounts added by atmosphere depositions (17-22.2 $kg.ha^{-1}$), while base cations input is noticeable and seems to be three even four times higher than the input precipitation (Table 2). This fact is a precondition for increasing of the acid-neutralizing capacity of the low-buffered non-calcareous Fluvisols.

Net nitrogen and base cations removal by plant production

Nitrogen and base cation removal by plant productions are considered as the most important upward flux, which determine the impact of anthropogenic loading on the most sensitive elements of the ecosystem, selected as criterion for evaluation. For evaluation of soil loading thresholds and compensation of acid charge from N fertilizer treatment in the soil, it is necessary to determine the amount of base cations, which are removed by above-ground biomass and regulate the neutralizing capacity of the soil. On the basis of the net above-ground biomass formed, nitrogen and base cations concentrations in plant organs was derived the annual plant uptake of these elements and the net removal from the agroecosystem. According to Xu et al., 2024, natural soil acidification due to bicarbonate (HCO_3^-) leaching and base cation (BC) removal by crop harvest also affect soil acidity whereas the input of HCO_3^- and BC via fertilizers and manure counteract soil acidification. As indicated in (Table 2) the highest removal level of N was reached in 2020 and 2022 when maize was grown and it ranges from 69 to 191 $kg.ha^{-1}$ per year and from 50 to 275 $kg.ha^{-1}$ per year. It could be seen from the (Table 2) that less nitrogen amount was removed by the wheat in 2021 (from 32.3 to 143.3 $kg.ha^{-1}$ per year) and 2023 (from 21.7 to 115.3 $kg.ha^{-1}$ per year) which is due to the specific characteristics of the crop and due to the fact that the wheat was grown under non-irrigated conditions and in 2023 a drought was reported. The total average annual removal of K ranges from 62.3 to 241 $kg.ha^{-1}$ per year when maize was grown and between 15.4 to 142.7 $kg.ha^{-1}$ per year, when wheat was grown (Table 2). The quantity of sodium uptake is negligible in comparison with the other macro elements. Calcium and magnesium are the elements with the greatest role, regarding acid neutralizing capacity of the soil. Input of these elements is controlled mainlt by weathering of primary minerals and wet and dry atmospheric depositions and a small part is introduced through combined nitrogen and phosphorus fertilizers as a side elements (Koleva, unpublished data). Total amount of calcium uptake by maize production for the period 2020-2022 varies between 14.7-37.9 $kg.ha^{-1}$ per year and between 6.9-23.9 $kg.ha^{-1}$ per year when wheat was grown. Table 2, shows that variation in magnesium uptake follows the same tendency as a calcium, of increasing with N rates but with lower absolute values. It should be noted that decline in base cation input in the soil and higher uptake could lead to increasing of soil sensitivity towards acidification.

Leaching of elements with the lysimetric wa-

Table 2. Average net annual input-output budgets for N, K,Ca and Mg(kg.ha^{-1})

Treat-ments-Input-	Maize 2020- N				Wheat 2021-N				Maize 2022-N				Wheat 2021-N			
	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
Input-Atm. deposit.	23	23	23	23	19	19	19	19	14	14	14	14	10.1	10.1	10.1	10.1
Irrigation	17	17	17	17	0	0	0	0	22	22	22	22	16.1	16.1	16.1	16.1
Fertilizer	0	120	160	200	0	100	140	180	0	120	160	200	0	100	140	180
Total	10	160	200	240	19	119	159	199	36	156	196	236	26	126	166	206
Output-Biomass	69	172	179	191	32	67	94	143	50	119	212	275	21.7	45.8	87.9	115.3
Leaching	4.5	8.5	10	14	1	9	15	16	4	12	13	20	1.9	4.8	7.5	17.9
Total	73.5	180.5	189	205	33	76	109	159	54	131	225	295	23.7	59.6	95.4	133.2
Difference	-34	-21	11	35	-14	43	50	40	-18	25	-29	-59	2.3	66	71	73
	Maize 2020- K$^+$				**Wheat 2021-K$^+$**				**Wheat 2021-K$^+$**				**Wheat 2021-K$^+$**			
Input-Atm. deposit.	10.5	10.5	10.5	10.5	15.4	15.4	15.4	15.4	7	7	7	7	2.6	2.6	2.6	2.6
Irrigation	8	8	8	8	0	0	0	0	3	3	3	3	0	0	0	0
Fertilizer	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	18.5	18.5	18.5	18.5	15.4	15.4	15.4	15.4	10	10	10	10	2.6	2.6	2.6	2.6
Output-Biomass	83	209	236	241	33.3	97.9	133.1	142.7	62	133	164	185	15.4	29.9	61.9	115.9
Leaching	1	0.9	1	1	0.4	0.7	0.8	1.7	0.5	1.0	0.7	1.5	0.3	0.4	0.7	0.9
Total	84	210	237	242	33.7	98.6	133.9	144.4	62.5	134	164.7	187	15.7	30.3	62.6	116.8
Difference	-66	-192	-219	-224	-18.3	-83.2	-118	-129	-54	-124	-155	-177	-13	-26	-60	-114
	Maize 2020- Ca^{2+}				**Wheat 2021-Ca^{2+}**				**Wheat 2021-Ca^{2+}**				**Wheat 2021-Ca^{2+}**			
Input-Atm. deposit.	39	39	39	39	42.6	42.6	42.6	42.6	31	31	31	31	21	21	21	21
Irrigation	167	167	167	167	0	0	0	0	213	213	213	213	0	0	0	0
Fertilizer	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	206	206	206	206	4.6	4.6	4.6	4.6	216	216	216	216	21	21	21	21
Output-Biomass	16	22	24	38	6.9	16.9	17.7	23.6	15	18	19	28	8.9	13.5	18.7	19.7
Leaching	20	12	21	31	7.1	32.2	50.7	37.1	20	10	25	52	5.9	12.7	15.4	34.5
Total	36	34	45	69	14	49.1	68.4	60.7	35	28	44	80	14.8	26.2	34.1	54.2
Difference	170	172	161	137	28.6	-6.5	-25.8	-18.1	181	188	173	136	6.2	-5.2	-13	-33
	Maize 2020- Mg^{2+}				**Wheat 2021-Mg^{2+}**				**Wheat 2021-Mg^{2+}**				**Wheat 2021-Mg^{2+}**			
Input-Atm. deposit.	7	7	7	7	25.9	15.9	15.9	15.9	9.90	9.90	9.90	9.90	3.9	3.9	3.9	3.9
Irrigation	51	51	51	51	0	0	0	0	57	57	57	57	0	0	0	0
Fertilizer	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	58	58	58	58	15.9	15.9	15.9	15.9	67	67	67	67	3.9	3.9	3.9	3.9
Output-Biomass	14	18	20	23	2.4	11.3	11.2	13.2	12	14	15	22	1.7	7.3	9.2	15.2
Leaching	6	3	3	7	2.4	8.3	13.7	11.3	6	4	9	16	1.3	4.3	4.6	8.4
Total	20	21	23	30	4.8	19.6	24.9	24.5	18	18	24	38	3.0	11.6	13.8	23.6
Difference	38	37	35	28	11.1	-3.7	-9	-8.6	49	49	43	29	0.9	-7.7	-9.9	-19

Table 3. Volumes of lysimeters for the investigated period

Year	Water amounts		Sum P+I	Lysimetric water, out of 1m soil layer, $l.m^{-2}$				% 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	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

Table 4. Critical load for acidifying N ($CL(A)_N$) calculation with individual components

	Atmosph. deposit.+ irrigat. water BC_{dep}	Chlorine input Cl^-	Weather. rates BC_w	Total biomass uptake BC_{up}	N Input by prepit, 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 $(A)_N$ $kg.ha^{-1}$
					$eq.ha^{-1}$ 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

ter

The removal of chemical elements with lysimeter waters outside the root soil layer is one of the most important sources of loss in the balance of substances. The amount of chemical elements drained out of one meter soil was obtained taking into account the basis data for the volume and concentration of lysimetric water. Drainage flow volume highly depends on precipitation, irrigation, evapotranspiration and etc. The results obtained for 2020-2023 show that the pH values of the waters range from 7.30 - 7.80 in the fertilizer variants (T_2 and T_3) to 7.90-8.30 from the drainage obtained under the control variant T0. As a result of the conducted research, it was established that slightly alkaline lysimeter waters circulate outside the one-meter soil layer. The lowest drainage obtained in 2023 was between 11.5 $l.m^{-2}$ and 26.9 $l.m^{-2}$, while the highest was in 2020 with values between 53.2 $l.m^{-2}$ and 76 $l.m^{-2}$. The average amount of water leached out below 1 m ranged between 1-15 % from the incoming water (Table 3).

With respect to calculation of mass balance of elements for determination of critical loads it is important to calculate the amount of macroelements leached out of one meter soil layer. This data is presented in Table 2. It should be pointed that almost the whole amount of nitrogen leached through soil profile is in nitrate form. Data analysis show that average amount of nitrogen leached out of non-fertilized variants is 1.4-1.9 $kg.ha^{-1}$ under wheat and from 4.3-4.5 $kg.ha^{-1}$ under maize. In all cases fertilization has led to increasing of N loses. The comparison between the treated variants of investigation shows that nitrate leaching variation regarding different rates very in large range depending on fertilization, precipitation and irrigation volume (Table 2). Simeonova et al., (2023) found that nitrogen losses with lysimeter waters under grain crops are about 4-5 times lower compared to growing trench crops. It has established that Ca^{2+} is the cation with high mobility which determine to a great extent its losses from one meter soil layer. The results show that average losses of this element ranges between 20-52 $kg.ha^{-1}$ under maize and between 5.9-23.6 $kg.ha^{-1}$, depending on fertilizer rates (Table 2). It was observed that calcium leaching increases with increasing of N rates. The same trend could be seen in Mg^{2+} migration but the absolute values in different fertilizer rates vary in short limits with low fluctuation. K^+ and Na^+ leaching is insignificantly affected by fertilizer rated and the losses of this element are negligible.

Changes in soil pH values

Accelerated soil acidification due to nitrogen fertilization is believed to be directly caused by the production of protons through nitrification following the application of ammonium nitrogen. In addition, during heavy rainfall, nitrate ions (NO_3^-) are leached from the soil along with a large number of base ions, leaving more H+, which is the indirect cause of soil acidification (Liu et al., 2023). Soil pH is widely accepted as a dominant factor that regulates soil nutrients bioavailability, plant primary productivity and a range of soil processes including microbial community structure and activity. (Koleva et al., 2003, Kemmitt et al., 2006). Therefore, we assumed that changes in pH values could be appropriate criteria to define negative impacts of additional N loads on agricultural soils. According to Waldner et al., (2015), soil acidification can lead to BC depletion in the soil and mobilization of aluminum (Al^{3+}) into the soil solution, however, on the other hand, the toxic effects of dissolved Al are reduced by the presence of dissolved basic cations. The results from this research show that long-term N fertilizer application has influenced soil pH values and base saturation in all treatments in the upper (0-30 cm) soil layer It was found that after maize harvesting in 2020. And 2022, the pH values were lower in all studied variants, especially in the fertilizer variants T_2 and T_3. (Fig. 1).

The average pH values reported were 6.10± 0.41 in 2020 and 6.0± 0.26 in 2022. While under wheat in 2021, it was found that the average value of the soil reaction of the arable layer was slightly higher 6.35 ± 0.31, in 2023 6.4±0.09. A change of about 0.5-0.8 units in the pH values compared to the control variant was found in the crop rotation, which is more pronounced after maize growing.

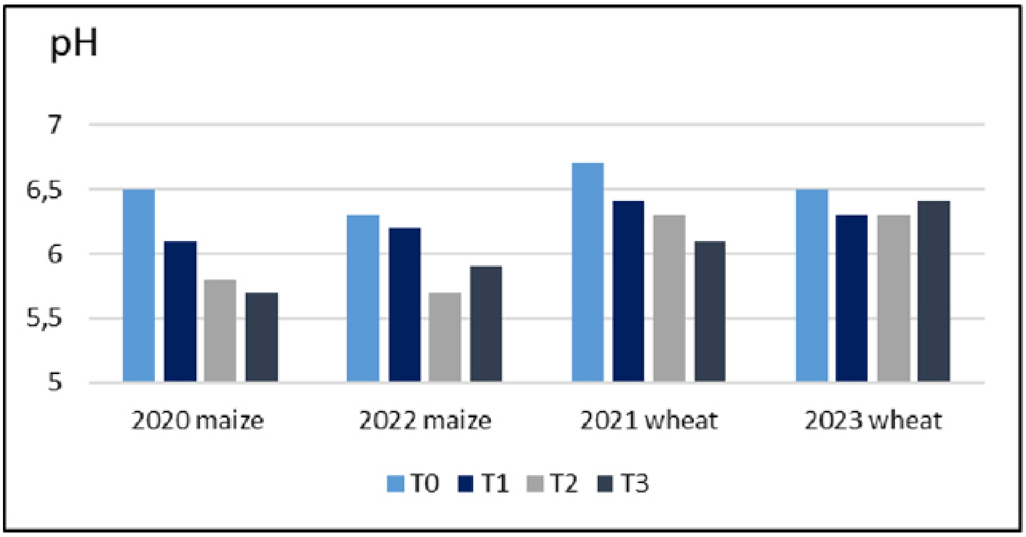

Fig. 1. pH values during the research period at the experimental field Tsalapitsa

The cultivation of grain crops has led to some leveling of the soil reaction, but it is not enough to restore the soil to a state close to natural

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

It has been mentioned that in the arable soils, acidity results mainly from nitrogen deposition and therefore in the paper the calculation of acidity critical loads is described in terms of nitrogen. A critical nitrogen load in this case can be seen as the nitrogen input, which produce a final acidification state of the soil, in which the critical limits set for pH and aluminum are not exceeded and no conditions for N accumulation and losses occur. Agroecosystems are quite dynamic environment for the chemical elements transformations and many of the input-output budgets cannot be easily measured and making some assumptions and simplifications is inevitable. In order to identify conditions maximum close to steady state situation. The application of the model in agroecosystem conditions requires certain restrictions that simplify the calculation procedure without significantly affecting the accuracy. These include: weathering and export are considered as unevenly distributed throughout the soil profile; water movement and migration of chemical elements along the soil profile occur only in the vertical direction; the physicochemical constant used in calculating the critical values of hydrogen and aluminum ions is assumed to be the same throughout the soil profile; sodium is not included in the equivalent sum of alkalizing cations due to its small role in counteracting acidification processes; no denitrification processes occur; the exchange of alkalizing cations in the soil-absorbing complex occurs in a steady state - there is no change in base saturation; all indicators are presented with average annual values. The resulting critical loads reflect the sensitivity of the agroecosystem to the combined impact of nitrogen input through the atmosphere, irrigation and applied nitrogen rates in quantitative terms, therefore they could be used as a mechanism for regulating the amount of nitrogen input in the form of fertilizers. The comparison of the amount of nitrogen input and critical loads is made to determine whether there is an excess of the critical load. (Koleva, 2002).

Table 4, presents data on the equivalent values of the indicators involved in the calculation of critical loads under the pH criterion and the determined critical loads. The analysis of the results shows that this criterion resulted in a high critical level of nitrogen loading when growing maize, especially in 2022 (N= 227 $kg.ha^{-1}$ for variant T_2

and N= 261 kg.ha^{-1} for variant T_3), which is most likely due to the larger amounts of alkaline cations introduced with precipitation and irrigation water, which increase the acid neutralization potential of the Fluvisol, despite its weak buffer properties. The variant T_2 (N_{160} kg.ha^{-1}) is considered optimal due to the fact that almost equalization of incoming and outgoing nitrogen is observed, as well as the nitrogen norm does not exceed the norm according to the Nitrates Directive. Simeonova et al. (2015) was observed that compensation between the amounts of N input and output was achieved in two variants N_{80} and N_{160}. From the comparison made between the nitrogen load obtained from all variants for 2022 with the determined critical load, it was found that in the variant with the maximum nitrogen rate T_3 (N_{200} kg.ha^{-1}), an excess of the critical load was observed, reaching 18628.5 eq.ha^{-1} per year, which led to a decrease in pH by about 0.6-0.8 pH units. It has been reported that in 2021 and 2023, when growing wheat, significantly lower absolute values of critical loads are obtained for the studied options. The cultivated cereals are not irrigated, which contributes to the reduction of the import of alkaline neutralizing cations. In addition to the smaller quantities of nitrogen fertilizers imported, a smaller quantity of basic cations is also exported with the plant production, and the soil reaction does not change significantly. In a study by Koleva, (2002) was found that the greatest influence on critical loads is exerted by the specific characteristics of the crop and the amount of accumulated nitrogen and basic cations in the formed aboveground biomass. As can be seen from the Table 4, in 2021 a higher critical nitrogen fertilization was observed, which can also be associated with the significant amounts of precipitation during this period and the larger amounts of imported basic cations. The analysis of the obtained values of the critical load during the experimental period gives grounds to conclude that the use of the mass balance method gives quite indicative results regarding the degree of impact of the individual factors of anthropogenic influence. The greatest influence on the determination of the critical load limits for nitrogen is exerted by the methods of land use, the peculiarities of the grown crop and some basic characteristics of the soil.

Conclusions

In this paper, we presented budgets of nitrogen and base cations after growing a 4-year maize-wheat rotation and applied critical load concepts for agricultural soils using simple mass balance (SMB) model for soil acidification. Soil capacity to neutralize the acidifying effect mainly depends on the amount of base cations input through depositions or irrigation. A profound depletion of base cation input through deposition was observed over the last years, and at the same time a higher amount of these elements is added with the irrigation water. Changes in base cation depositions can lead to decrease in the critical loads of acidity. The key finding of this study was that the calculated $CL(A)_N$ using SMB method was high in all fertilization variants after maize cultivation, especially in 2022 and hence soil acidification was observed. After growing wheat during both periods 2021 and 2023, a significant decrease in the critical nitrogen level for acidity was found, as well as a very low input of alkaline cations. In terms of nitrogen management, it is essential to identify the N inputs, $CL(A)_N$, which could reduce N fertilizer application rates, minimize the acidification and reduces the cost of liming for sustainable agricultural production.

Conflict of interest: The authors declare there are no conflicts of interest

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