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DETERMINING AGROCHEMICAL FACTORS FOR NITRATE EXCESS IN THE SOIL-PLANT SYSTEM

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Abstract

The excessive presence of nitrates in the soil-plant system, their concentration in certain consumer plant products and last, but not least, their increased presence in water resources raises not only research, but also management issues in certain fields involved in providing food safety and the quality of life and the environment. This paper presents approaches relying on a series of experiments and researches related to some agrochemical factors involved in nitrate chemism and transfer in the soil-plant system. The results confirm predictions and previous findings, which lay large N quantities applied as mineral fertilizers at the basis of soil nitrate excess, an application conducted especially when high levels of residual mineral-N already exist having been determined by the mineralization of the organic forms of this element in soils and by previous fertilizations. Soil acidity and acidification, as well as its dephosphatizing favour nitrate excess and its plant translocation. The reorganization of soil nitrate through organic resources, the optimization of the application of mineral N and P forms may limit nitrate leaching along the soil profile and their plant translocation. Due to the intricacy of this issue and the traceability of these ions in the food chain, approaches in this field require multidisciplinary activities.

INTRODUCTION

For the last decades, one can signal a frequent increase of nitrate (NO_3^-) concentrations in soil, water and plant products (especially fresh products), while the phenomenon of nitrate excess was assessed, in most cases, to coincide with an increase in the employment of mineral N fertilizers and liquid and semi-liquid animal residues in agriculture. Thereby, the same context provides that nitrate excess states are harmful for agricultural and horticultural crops (where "nitric phytotoxicity" is triggered), as well as for the consumers of nitrate-contaminated plant products, where the enhanced risk of diseases can be encountered ("the blue-baby syndrome" in children is caused by the inactivity of the hemoglobin function of O_2 transport and the increased incidence of gastric cancer as an effect of nitrosamines) [1, 2, 4].

Nitrate presence in the soil-plant system, from an agrochemical point of view, can be controlled and monitored through a series of physical, chemical and biologic soil traits (NO_3^-; NH_4^+, MoO_4^{2-} in the substrate, pH, humus, biologic activity and others), as well as plant species and genotypes, assessed through nitrogen consumption and metabolizing activity.

Agriculture is considered to be the main determining agent for nitrate excess and pollution and thus, must attempt at a decrease in nitrate soil representation, limit nitrate accessibility and vulnerability towards phreatic and surface waters and at the same time, attempt at a normalization of nitrate translocation in plant products, which are able to transfer these ions in the food chain onto human and animal consumption [1, 3, 4, 5].

This paper presents results related to the nitrate cycle in the soil-plant system and reveals certain alternatives to regulate this cycle towards the productive employment and metabolizing of nitrogen and thus preventing nitric excess.

MATERIAL AND METHOD

The results interpreted in the present paper originate in field experiments with differentiated fertilization systems and analytical laboratory activity.

Soil-plant analyses were conducted according to ICPAPM Bucharest procedures recommended to agrochemical laboratories.

RESULTS AND DISCUSSIONS

a) Sources of origin for soil nitrates:

• Naturally, a permanent nitrate formation source appears and is maintained in the soil through the preponderantly microbiologic process of humus mineralization (oxidative degradation), and implicitly of organic-N resources, as ammonification and nitrification stages release nutritive nitrogen ions (NH_4^+ and NO_3^-).

The process of ammonium nitrate nitrification is conducted in two stages (involving Nitrosomonas sp. and Nitrobacter sp.), following a global reaction:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

$$\Delta G_{298}^o = -65.2 \text{ kcal/N mole-gram}$$

In effect, this process engages potentially mineralizing and nitrifiable nitrogen in the soil (N_{pmin}) and is influenced by certain chemical and physical soil factors (pH, N_{pmin} and humus soil reserve, alkali saturation, aeration-O_2 and compression level, moisture, temperature and others). According to these parameters, this microbiologic source provides an annual active and accessible N intake of 20-50kg/ha.

• Upon conventional agricultural technology, the most important nitrate source resides in crop fertilization under a mineral, as well as an organic form of N nutritive ions (NO_3 and NH_4^+).

In principle, however, soil nitrate enrichment through a preponderantly fertilizing source must be fully and significantly substantiated, from a scientific point of view. Towards the economy and productivity of nitrogen application, there is a requirement for the correct control and evaluation of nitrogen "surplus", most frequently appearing in a nitric form. This form presents a polluting potential for phreatic and surface waters and can appear contaminating for plant products.
In determining potential N excess with subsequent polluting effects, a complex study can be conducted on nitrogen balance in ecosystem components , by establishing N DOE, crop response curves to nitrogen application and evidently an assessment of N excess in the balance: $N_{ex}=N_{nec}+N_{fix}+N_{prec}-N_{cp}$ (N_{nec}= nitrogen necessary for an optimum crop development; N_{fix}= nitrogen fixed by leguminous plants; N_{prec}= nitrogen in the soil from rainfall; N_{cp}= nitrogen quantity obtained from the soil with the agricultural yield produced).

The exceeding amount of nitrogen becomes accessible to plants, with mostly negative effects ("nitric phytotoxicity") and partly vulnerable to leaching ("washing down") along the profile down to the aquiferous phreatic level.

b) Leaching and nitrate transportation in soils:

Leached nitrate quantities are real losses of nitrogen, while the models of the descending transfer of these anions (along the profile) are size-dependent on the N excess from the crop balance (in the ecosystem), on the soil type and the characteristics of water movement along the profile, on fertilizer types and the season of fertilizer application, on the representation of the support of internal microbiologic activity. The soil may "limit" the process of nitrate leaching, as long it is agrochemically, physically and biologically-optimized (regarding the pH, humus content and m.o. as an energy support for microorganisms, phosphatizing and structuring) and crops involve such plants for which nitrogen efficiency is enhanced, while differentiated vegetation is active in maintaining N reserves in root-exploration area.
Models created after determinations conducted in many areas and points show that the highest NO_3^- in shallow soil horizons, as well as on the profile originate in mineral fertilization technologies with N and in the ones containing liquid and semi-liquid animal residues. The highest concentrations towards the basis of the soil profile (through leaching) are encountered after the application of nitrogen before the cold and damp season for crops sown in autumn. These nitrate quantities (mostly originating in a N surplus) follow, until the end of the growing cycle, a vertical route to depths of 1.0-2.0 m and even higher. [4, 5].
Modeling nitrate leaching can be functionally complicated by the biologic side of the processes for nitrate productive elaboration, especially dependent on the soil organic matter regimen and microbial activity.

c) Nitrate accumulation in plant products

Nitrate accumulation in plants involves their subsequent reduction (as in the case of nitrites) to the ammonium form exclusively employed in nitrogen metabolism for amino-acid synthesis:

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_4^+ + OH^- + 2H_2O$$

This process conducted in the cytoplasm and chloroplasts is active in the presence of light (providing electrons necessary for reduction), of molybdenum (as catalyzer) and nitrate and nitrireductase enzymes. For many plant species (wheat, maize, leguminous plants), nitrate and nitrite reduction is conducted in the roots, whereas for many other plants it is conducted in the leaves (tomatoes, cucumbers, potatoes).

It is thus ascertained that intensive agricultural technologies, adapted especially to vegetables (in the field and greenhouses) favour increased nitrate accumulations, especially in the case of some which are freshly consumed. High quantities of nitrates can be accumulated, up to 2000-2500 mg/1 kg for peppers, tomatoes, salad, spinach, red beat, and radish, while under 2000 mg/1 kg in the case of cabbage leaves, cauliflower, celery and carrots. It is assessable that 54-80% of ingested nitrates in the human organism originate in vegetables and only the rest in other food products. As such, in many EC countries, the maximum accepted limits of NO_3 content were established in the case of the main vegetables.

d) Results of researches regarding the effect of certain agrochemical measures for nitrate accumulation in the soil-plant system:

The application of mineral fertilizers and especially of nitrate fertilizers significantly modifies the mineral nitrogen supplies (NO_3^-+NH_4^+) in the soils (tables 1, 2).

The one-sided employment of nitrogen as fertilizer, as well as its imbalanced application compared to phosphorus, determines the highest mineral-N accumulations on the soil profile and a surplus of this element, which potentially becomes vulnerable to toxicity for plants and leacheable. The presence of phosphorus balances and limits a surplus of nitrates in soils and provides plants with a more productive and efficient consumption. The limiting of mineral-N consumption in the presence of phosphorus enhances fertilization efficacy and the efficacy of nitrogen metabolism.

Similarly, favoured by balanced NP fertilizations, agricultural crops within a rotation have differentiated effects in nitrogen economy and balance. In this context, leguminous crops (the case of soybeans) due to a biologic N input (on each symbiotic) provides a constant supply of nitrogen for plants without any sign of exaggerate accumulation o mineral-N on the soil profile.

Table 1

Mineral-N dynamics in two soil types under autumn wheat crops (NP stationary experience for 12 years)

Soils	NP fertilization (kg/ha)	Mineral-N (kg/ha), depth 0-100 cm			
		1. XII.	**8. II.**	**6. III.**	**9. IV.**
Preluvosoil	N_0P_0	61	46	44	70
	$N_{100}P_0$	156	122	120	113
	$N_{200}P_0$	422	205	190	184
	N_0P_{100}	63	36	76	56
	$N_{100}P_{100}$	98	71	90	87
	$N_{200}P_{100}$	160	169	170	191
Aluvisoil	N_0P_0	44	28	76	67
	$N_{100}P_0$	88	118	121	124
	$N_{200}P_0$	367	236	228	165
	N_0P_{100}	61	33	59	64
	$N_{100}P_{100}$	158	103	127	89
	$N_{200}P_{100}$	291	214	165	150

Table 2

Mineral-N dynamics under autumn wheat crop cultivated in different rotations

Soil	Previous plants	Fertilization of previous plants	Mineral-N (kg/ha), depth 0-100 cm			
			1. XII.	**8. II.**	**6. III.**	**9. IV.**
Aluvisoil	Wheat	Unfertilized	59	71	50	72
	Maize	$N_{120}P_{80}$	141	256	191	72
	Soya	$N_{120}P_{80}$	100	184	204	104
	Wheat	$N_{120}P_{80}$	383	191	398	138

Frequent mineral-N excess, especially on acid and dephosphatized soils creates nutrition deficiencies in plants, due to an excessive accumulation of NO_3^- on the background of a decrease in molybdenum (MoO_4^{2-}) mobility and accessibility in the particular agrochemical substrate (table 3).

It can thus be asserted that the activity: acidification, P and Mo deficiency generates an exaggerate accumulation of nitrates in plant tissues, as it diminishes their reduction in plants and finally determines a blockage of the synthesis process of amino-acids and proteins.

Table 3

Nutrition deficiencies in wheat and maize caused by nitrate excess

Crop/ Soil	Mineral-N 0-100 cm	Soil analyses				Growing state *)	$N\text{-}NO_3$ in plants (ppm)
		pH H_2O	Mobile-Al (m.e.)	P-AL (ppm)	Mo (ppm)		
1. Wheat/ Preluvosoil	71	6.2	-	53	0.25	N	275
	260	5.4	0.51	8	0.17	D	2790
2. Maize/ Preluvosoil	58	5.9	0.11	18	0.21	N	840
	111	5.8	0.14	10	0.19	D	2100
	137	5.7	0.14	7	0.18	D	3010
	206	5.6	0.28	6	0.17	D	3185
	312	5.4	0.52	6	0.16	D	3360

*) N= normal; D= nutritionally imbalanced

For a normal nitrate cycle an efficient fertilization practice, it was proven experimentally that the introduction of organic resources as fertilizers (with organic-N and organic-C input) remedies and even limits the effects of nitrogen mineral inputs, on the basis of the revitalization of the soil's microbiologic activity. (table 4).

Table 4

Effect of fertilizing organic resources in the $N\text{-}NO_3$ dynamics in soils (argic phaeozem)

Fertilization	Depth (cm)	$N\text{-}NO_3$ dynamics (ppm)			
		1. XII.	1. II.	1. III.	20. IV
1. $N_{100}P_{80}$	0-20	60	72	44	37
	20-40	40	52	40	38
	40-60	28	37	47	50
2. Stable manure 20 t/ha+ $N_{40}P_{40}$	0-20	50	60	48	42
	20-40	30	40	35	32
	40-60	25	24	23	23
3. Chopped straw+ $N_{60}P_{60}$	0-20	40	46	47	48
	20-40	32	37	37	40
	40-60	16	13	12	12

Organic resources maintain a constant nitrate dynamics, limit their exaggerate vulnerability and mobility, while also reducing the process of their leaching towards the depth of the soil profile. It is thus obvious that organic N and C reserves within these organic resources favourably reorganize nitrogen cycle and the cycle of its components.

CONCLUSIONS

1. Soil nitrate excess and the high accumulations in plant products coincide with the modernization and intensification of agriculture, which triggered an increase of mineral-N inputs.
2. Present research attribute the same causes to soil, water and vegetation nitrate pollution, proving that the process is aggravated by the one-sided application of mineral-N and in opposition with the soil P and Mo content.
3. Soil acidity and acidification are factors which aggravate the phenomenon of nitrate accessibility and vulnerability, as factors for the enhancement of nitric excess and toxicity.
4. NP balance in fertilization, as well as organic N and C input, through fertilizing organic resources limits nitrate accessibility and vulnerability for soils, phreatic waters and agricultural crops.
5. Organic resources (with a different C/N ratio) effectively determine a reorganization of mineral nitrogen forms in soils.
6. Ensuring soil biologic activity (through N-NO_3-consuming microorganisms and high N-consuming plants) effectively protects nitrate cycle and prevents the manifestation of harmful effects in the soil-plant system.

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