«M.M. Gryshko» National
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SILICEOUS MINERALS AS NATURAL NITRIFICATION INHIBITORS

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IN THE NEXT 20-30 YEARS

a significant increase in the world's population is expected. Accordingly, it is necessary to produce food in sufficient quantities.

BY 2050

To achieve this, the use of nitrogen fertilizers will have to double.

PROBLEM

For environmental reasons, this is not possible as nitrate levels in drinking water, eutrophication of surface waters and greenhouse gas emissions have already reached critical levels in many countries of the world.

SOLUTION

The use of nitrification inhibitors can reduce the use of fertilizers and significantly increase their efficiency. Therefore, there is a need for environmentally friendly nitrification inhibitors, as well as methods for their study.

- preservation and restoration of plant diversity, rational use of plant resources;
- preservation of soil fertility;
- reduction of greenhouse gas emissions;
- stopping the processes involved in raising the temperature.

8 COMPOUNDS COMMERCIALLY RECOGNIZED AS NITRIFICATION INHIBITORS, ALTHOUGH THE MOST COMMONLY USED AND MOST STUDIED ARE:

- 2-chloro-6-(trichloromethyl)-pyridine (nitrapyrine),
- dicycanediamide (DCD) and 3,4-dimethylpyrazole phosphate (DMPP).

These compounds inhibit microbial activity for several days to weeks depending on soil moisture and soil type, although there are differences in the way they are used.
In general, nitrification inhibitors are more effective on sandy soils or soils with low organic matter content and low temperature effects.

The objectives of the given study was to compare the effectiveness of nitrapyrin and the mixture of natural siliceous minerals (analcite and tripoli) on the balance soil nitrogen, the dynamics of the different functional groups of microorganisms in the soil, metabolism and productivity in economically important C3 and C4 crops (viz. wheat and corn) grown under high nitrogen fertilization conditions.

The mentioned siliceous minearals are readily available in Ukraine (Vinnytsia and Rivne regions) and present unexpensive and environmentaly safe source of fertilizers for agricultural needs.

In addition, unlike nitripapyrin, these minerals neither are hazardous for human health nor explosive.

The effectiveness of nitrapyrin and a mixture of siliceous minerals (analcite and tripoli) as nitification inhibitors was compared using different types of substrates (sand and soil mix) and crop species in the laboratory pot experimernts.

The latter were conducted in the plant growth chamber at the department of Allelopathy of the M.M.Gryshko National Botanical Garden of the National Academy of Sciences of Ukraine (Kyiv, Ukraine).

FIELD EXPERIMENTS

5-YEARS FIELD STUDIES

were conducted on the experimental plots (plot area - 2 ha) situated at the Agricultural Research Station of the Institute of Bioenergy Crops and Sugar Beet of the National Agrarian Academy of Sciences of Ukraine (Kyiv region, Ksaverovka Village, Kagarlytsky District during 2015-2019).

APPLICATION

The nitrification inhibitors were applied to winter wheat (Triticum aestivum L.) cv. «Samuray» and corn Zea mays L. hybrid «Adevei 4014»). The rate of the applied nitrapyrin was 1.7 liters per 1 ha (2,69 kg per 1 ha), and the amount of siliceous minerals was 10 kg per 1 ha for winter wheat and 6 kg per 1 ha for corn. For winter wheat, the rate of urea application was 100 kg/ha, and for corn - 60 kg/ha.

Nitrification ingibitors were applied simultainiously with fertilizers (N20 P60K60): for winter wheat at the stage of spring tillering (on frozen thawed ground), for corn - in the phase of 3-5 leaves under harrowing.

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Treatment	Type of substrate	pH of soil solution	Humus %	The content of nitrate nitrogen, mg / kg Duration of plant exposure, days		
				15	30	45
		Wheat				
Control	Sand	7,2	0,03	115,7	193,6	298,1
	Soil mix	6,2	7,5	146,9	235,8	334,2
Nitrapyrin	Sand	7,2	0,03	97,5	83,9	92,4
	Soil mix	6,2	7,5	101,7	88,3	95,6
Analcite+Tripoli	Sand	7,2	0,03	71,3	64,9	61,7
	Soil mix	6,2	7,5	73,8	66,1	64,3
LSD (P=0,05)		*0,01*	*0,01*	*1,23*	*1,88*	*1,74*
		Corn				
Control	Sand	7,2	0,03	99,3	168,4	255,8
	Soil mix	6,2	7,5	125,7	191,0	287,1
Nitrapyrin	Sand	7,2	0,03	81,2	73,7	77,6
	Soil mix	6,2	7,5	87,9	76,4	82,3
Analcite+Tripoli	Sand	7,2	0,03	52,4	43,9	42,5
	Soil mix	6,2	7,5	54,3	45,1	43,2
LSD (P=0,05)		*0,01*	*0,01*	*1,74*	*1,45*	*1,58*

TABLE 1. THE EFFECT OF EXOGENOUS NITRAPYRIN AND A MIXTURE OF SILICEOUS MINERALS (ANALCITE AND TRIPOLI) ON THE CONTENT OF NITRATE NITROGEN IN THE SOIL

FIELD EXPERIMENTS

Application of analcite-tripoli mixture with urea demonstrated more pronounced effect on the quantity of these two groups of microorganisms for the whole period of experimentation with the minimum values registered on the 45-th day, which indicated a more prolonged effect of silicon compounds on the inhibition of nitrification processes in the soil compared to nitrapyrin.

Both nitrification inhibitors studied had a positive effect on the content of ammonifiers in the soil. However, the siliceous mixture again had a more prolonged effect on this group of microorganisms compared to nitrapyrin.

Treatment	Microorganisms	Period of whinter wheat cultivation, days		
		15	30	45
Control	Total number, million /g	20,6	16,2	11,9
Nitrapyrin		21,4	24,7	14,3
Analcite+Tripoli		23,8	24,3	25,1
LSD (P=0,05)		*0,62*	*0,89*	*097*
Control	Ammonifying, million /g	4,6	10,4	3,2
Nitrapyrin		9,7	17,5	12,0
Analcite+Tripoli		11,5	17,4	16,9
LSD (P=0,05)		*0,71*	*0,35*	*037*
Control	Denitrifying, million /g	3,1	4,3	3,8
Nitrapyrin		1,8	1,3	1,5
Tripoli+Analcite		0,7	0,6	0,4
LSD (P=0,05)		*0,48*	*069*	*077*
Control	Nitrifying, million /g	3,9	4,1	3,3
Nitrapyrin		3,0	2,1	2,3
Analcite+Tripoli		2,4	1,8	1,5
LSD (P=0,05)		*0,43*	*0,31*	*0,44*

TABLE 2 .THE DYNAMICS OF THE DIFFERENT FUNCTIONAL GROUPS OF MICROORGANISMS IN THE SOIL FROM POTS WHERE WINTER WHEAT WAS CULTIVATED WITH DIFFERENT NITRIFICATION INHIBITORS

Field experiments

The results of agrochemical analysis of the rhyzosphere soil of field experiments were in good agreement with the tendencies observed in the laboratory tests (Table 3).

In the absence of nitrification inhibitors, the nitrate nitrogen content in the soil gradually decreased during the growing season, reaching to the end of the growing season (the phase of physiological maturity of crops) the level of 20% of the initial (tillering phase).

Combined application of urea (100 kg / ha) and analcite+tripoli mixture (10 kg / ha) to winter wheat had a positive effect on the nitrogen supply to plants compared with nitrapyrin treatment (2.69 kg per 1 ha).

Table 3. The effect of nitrification inhibitors on the content of nitrate nitrogen in the soil under winter wheat, mg /L

Treatment	Phenological phase			
	tillering	first node	flowering	physiological maturity
Control	78,3	51,8	28,3	15,9
Analcite+Tripoli	63,7	58,4	50,9	42,1
Nitrapyrin	71,3	50,9	37,4	28,2
LSD (P=0,05)	*2,12*	*1,87*	*124*	*1,77*

Field experiments

Microbiological analysis of the root layer of the soil (depth -0-20 cm) showed a significant long-term positive effect of the analcite+tripoli mixture on the microorganisms producing phytotoxic allelochemicals (Table 4).

The positive effect of nitrapyrin was significantly lower. Data from microbiological analysis were in good agreement with the results of the assessment of the soil allelopathic activity using radish seeds as a bioassay.

Table 4. Allelopathic activity of soil and the number of microorganisms that produce phytotoxic allelochemicals 60 days after application of nitrification inhibitirs

Treatment	Wheat				Corn			
	Germination of radish seeds,%	The number of phytotoxic microorganisms, million /g			Germination of radish seeds,%	The number of phytotoxic microorganisms, million /g		
		Bacteria	Micro-mycetes	Actino mycetes		Bacteria	Micro-mycetes	Actino mycetes
Control	72,1	13,6	10,1	2,8	70,7	14,5	10,8	3,1
Analcite+Tripoli	92,2	3,3	4,5	1,7	91,0	3,8	5,1	1,9
Nitrapyrin	75,8	11,9	9,4	3,0	77,5	12,4	9,8	3,4
LSD (P=0,05)	*2,33*	*0,67*	*1,11*	*0,25*	*1,76*	*0,78*	*0,99*	*0,76*

Table 5. The effect of nitrification inhibitors on the content of phenolic allelochemicals in the soil

Treatment	Phenolic allelochemicals, mg/kg of dry soil			
	70% acetone extract		Ethanol extract	
	Corn	Wheat	Corn	Wheat
Control	39,3	33,8	151,3	147,2
Analcite+Tripoli	22,7	19,4	112,7	104,9
Nitrapyrin	31,5	28,7	144,3	138,7
LSD (P=0,05)	*1,13*	*1,65*	*2,05*	*1,25*

The decrease in soil phytotoxicity is evidenced by a 1.2-1.9-fold decrease in the concentration of phenolic compounds.

Field experiments

The content of photosynthetic pigments in the leaves of winter wheat and corn plants 30 days after application of urea with nitrification inhibitors differed significantly between treatmnets.

Application of siliceous mixture contributed to a marked increase in the content of chlorophyll a and b, as well as carotenoids in the leaves of the studied crops. While nitrapyrin caused a decrease in the biosynthesis of chlorophyll b and carotenoids and a slight increase in the content of chlorophyll a in the leaves of the test-plants (Table 7).

A significant increase in the concentration of chlorophyll b in the leaves of wheat and corn plants treated with analcite+tripoli mixture should be noted.

Table 6. The effect of nitrification inhibitors on the yield of winter wheat

Treatment	Wheat			Corn		
	Chlorophyll		Carotenoids	Chlorophyll		Carotenoids
	a	b		a	b	
Control	74,2	22,7	92,5	80,9	37,6	105,7
Nitrapyrin	76,9	21,8	91,7	96,3	34,2	88,2
Analcite+Tripoli	82,5	40,3	112,6	95,1	58,9	121,3
LSD (P=0,05)	*1,12*	*0,84*	*0,95*	*0,98*	*0,86*	*0,92*

The data in Table 8 clearly show that the highest yield of winter wheat was observed on plots where mixture of tripoli and analcite was applied. Grain was characterized by the highest content of protein and fiber. Nitrapyrin showed significantly less efficacy compared to the siliceous mixture.

Table 8. The effect of nitrification inhibitors on the yield of winter wheat

Treatment	Yield, quintal/ha	Protein content, %	Fiber, %
Control	68,4	12,6	24,3
Analcite+Tripoli	82,5	13,5	25,1
Nitrapyrin	75,3	12,9	24,7
LSD (P=0,05)	*0,97*	*0,54*	*0,48*

Results

The results of our laboratory and field experiments confirmed good potential of the mixture of the natural siliceous minerals (analcite and tripoli) to reduce nitrification process and NO3-leaching from different types of agricultural soils under sowings of whinter wheat and corn.

In our study application of mixture of the natural siliceous minerals (analcite and tripoli) was noticeably more effective in altering soil inorganic N content, composition of microbial community and nitrogen metabolism in crops as compared to nitrapyrin.

The duration of the observed effects for siliceous mixture was more lasting as compared to nitrapiryn.

Results

In particular, the mixture of tripoli and analcite more effeciently preserved nitrogen in the soil in comparison with the synthetic nitrification inhibitor (nitrapine).

In addition, the use of the mixture of tripoli and analcite provided a longer preservation of nitrogen in the soil.

At the same time it is found out that decrease in pH and quantitative parameters of humus of soil substrates stimulated processes of nitrification in treatments with nitrapyrin more essentially in comparison with treatments with siliceous minerals.

Conclusions

The comparative study on the effects of nitrapyrin and the mixture of natural siliceous minerals (analcite+tripoli) on nitrification processes in different types of agricultural soils under wheat and corn sowings under high nitrogen fertilization conditions clearely indicated higher effectiveness of the siliceous mixture as compared to nitrapyrin.

In particular, analcite+tripoli mix had more profound effect in slowing down nitrification processes for prolong period of time, strongly inhibited the number of nitrifiers, denitrifiers and micromicetes producing phytotoxic allelochemicals compared with nitrapyrin.

Crops treated with siliceous minerals had higher photosynthetic pigment content and higher glutamic acid concentration, which indicated the intensification photosynthetic processes.

Conclusions

Nitrapyrin reduced the concentration of chlorophyll b and carotenoids, but slightly increased the content of chlorophyll a in the leaves of wheat and corn. The content of aspartate and some aromatic amino acids decreased, while arginine and lysine increased.

Such metabolic changes suggested disintegration of nitrogen and phosphate metabolism in the studied crops. Thus, the use of siliceous minerals is more advantageous than nitrapyrin in terms of their effectiveness, persistence in various types of soils and beneficial effect on soil microbiota and crop`s functional state and productivity.

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