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Soil fertility changes trends and available Fe, Mn and Zn in a long-term system user nitrogen fertilizers

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Abstract

Among other things, the status of soil fertility can be affected by long-term fertilization and intensive cultivation of crops. Application of inorganic fertilizers can maintain or improve crop yields, but it can also cause changes in the chemical, physical and biological properties of the soil, both directly and indirectly. This study was conducted to determine the effects of the long-term application (33 years) of two rate N (80 and 120 kg ha^{-1}), individually and in combination with P and K, on soil fertility (pH, organic matter, total N, available P and K) and content available Fe, Mn and Zn, at the Vertisol soil tipe in the Central Serbia, Kragujevac. Vertisol at the beginning of the study was characterized by acidic pH, low content of available phosphorus, medium content organic matter, and high content of available potassium. Continuous application of nitrogen fertilizers has contributed to changes in some parameters of Vertisols fertility. Acidity, organic matter and total N in all variants of fertilization compared to the control was very significantly increased ($p > 0.01$). The content of an available Fe, Mn and Zn in all variants in which fertilizers have been applied, have expressed a tendency of increase.

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It is known that inorganic fertilizers besides of improving crop yields, directly or indirectly cause changes in chemical, physical and biological properties of soil. Some studies suggest that perennial use of mineral fertilizers, is resulting in deterioration of soil quality. Thus, the long use of nitrogen fertilizers often leads to a reduction of soil pH (Bolan *et al.,* 1991; Khonje *et al.,* 1989). There are many more representatives of the opinion that the rational application of fertilizers contributes to increase crop yields and improve product quality, but also improves the fertility of soil. (Belay *et al.,* 2002; Hirzel *et al.,* 2011).

Perennial experiments with the application of fertilizers are important sources of information for understanding the factors that affect fertility of soil (Zhao *et al.,* 2010), and its sustainable production (Regmi *et al.,* 2002; Camara *et al.,* 2003). The advantage of long-term research compared to short-term, are primarily being reflected in the fact that by these experiments are being gained information about the sustainability of fertilization treatments throughout several seasons. Over time, crop yields as well as the direction and intensity of change in soil properties, are being reflected on the rationality of the use of certain types of fertilizers, and the applied quantities, which provides economic and environmental importance of such experiments.

Awareness about the possible changes caused by long-term usage of fertilizers is of particular importance in acid soils. Namely, these soils more or less are the unfavorable environment for the successful cultivation of crops, and any inappropriate usage of fertilizers leads to a long-term further degradation. Therefore, the aim of the study has been that the perennial field experiment in acid conditions, determine the effect of nitrogen fertilizers on the accumulation of available iron, manganese and zinc, but also other characteristics of degraded vertisol.

Material and methods

Experimental sites

Investigations were carried out on two-field stationary field trial at the Center for Small Grains in Kragujeva, 44°00′51′′ N, 20°54′42′′ E. Since 1978 it have began trials of the effect of perennial application of inorganic fertilizers on the Vertisol soil type properties. The main properties of vertisol in the study were acidic pH and very low phosphorus content.

Experimental design

Nitrogenic fertilizers have been applied in two quantities, at the levels of 80 and 120 kg N ha^{-1} individualy (variants: N80– T-2 and N120– T-3), then in combination with 60 kg ha^{-1} phosphorus and60 kg ha^{-1} potasium (variants: N80P60– T-4, N120P60– T-5, N80K60– T-6, N120K60– T-7, N80P60K60– T-8 and N120P60K60– T-9. Treatments in which fertilizers which have been applied have been compared with the control, or with a variant which has not been fertilized (T-1). In total there have been 9 combinations which have been repeated 4 times, and the design of the trial was a random block design (RCBD).

Soil sampling and analysis

Average soil samples for analysis have been taken from the surface up to of 20 cm depth in the autumn of 2010. Formation of average samples has been done at level of basic plot and the samples have been represented by a combination of the given plots.

Soil pH has been measured with pH-meter with a glass electrode in 1:2.5 suspensions with distilled water (active acidity) and 1N KCl (substitution acidity). Available P and K were determined by the Al-method of Egner-Riehm, were 0.1 M ammonium lactate (pH=3.7) was used as an extract. After the extraction, K was determined by flame emission photometry and P by spectrophotometry after color development withammonium molybdate and $SnCl_2$ (Egner and Riehm, 1958). Humus has been determined by the Kotzmann’s method and total N using the Kjeldahl method. Available iron, manganese and zinc have been determined by atomic absorption spectrophotometry (AAS) after extraction of Mn in 0.05 M H_2SO_4, Fe and Zn in 1 M CH_3COONH_4 (pH =

4.8).

Statistical analyses

Statistical analyses were performed with SPSS version 16 softwere. The effects treatments on all the variables were tested by ANOVA. Statistical differences between the treatments were determined using the t test (95 and 99%) by a Pearson for Fisher's LSD. The significance of their correlations was analyzed via Pearson corelatiom matrix (SPSS, 2007).

Results and discussion

Application of N fertilizers in the period of 33 years has contributed to significant changes in some parameters of Vertisols fertility. The measured pH values indicate that significant changes of occurred after years of applications of all types of fertilizers (table 1). Acidity in all variants of fertilization compared to the control was increased, an exception was noted only in the substitution acidity on the variant T-8 (N80P60K60). It should be pointed out that the average pH of the active acidity when entering fertilizer reduced compared to the control, and set differences were generally statistically very significant. The biggest changes were in the treatment where there has beenapplied 120 kg N ha^{-1} (T-3, T-7, T-9).

Table 1. Soil pH characteristics of Vertisol in long-term nitrogen fertilization experiment.

Treatments	pH H_2O				pH KCl			
	x	±	SD	SV	x	±	SD	SV
T-1	5.54	0.14	0.065	1.16	4.28	0.07	0.033	0.77
T-2	5.32	0.24	0.102	1.92	4.03	0.09	0.039	0.97
T-3	5.08	0.33	0.143	2,12	4.05	0.31	0.132	3.26
T-4	5.20	0.22	0.101	1,94	4.18	0.07	0.032	0.77
T-5	5.19	0.14	0.066	1,27	4.20	0.19	0.083	1.98
T-6	5.13	0.21	0.093	1,81	4.11	0.22	0.092	2.22
T-7	5.05	0.39	0.177	5,50	4.12	0.24	0.100	2.43
T-8	5.30	0.24	0.103	1,94	4.34	0.17	0.031	0.71
T-9	5.05	0.17	0.081	1,60	4.21	0.14	0.062	1.47
LSD 0.05	0.158				0.109			
LSD 0.01	0.214				0.147			

It have been changes with substitutional acidity.This direction in change and intensity of acidity justifies the idea that the perennial application of N fertilizers, particularly where the applied combination was 120 kg N ha^{-1}, had the highest influence on the reduction of vertisol'spH.The influence of nitrogen fertilizers on soil acidification and its further destruction is well known and confirmed by many perennial experiments (Barak *et al.,* 1997; Bolan *et al.,* 1991; Khonje *et al.,* 1989; Zhao *et al.,* 2010). Particularily in vertisol, which is characterized by primary acidity, the use of N fertilizers led to a obvious increase of acidity, which can be considered as its further degradation.

Other elements of fertility have been improved and in accordance with the type of applied fertilizer (table 2). The content of humus and total N in all variants of fertilization increased compared to unfertilized. Although the importance of perennial nitrogen fertilization is often being emphasized on maintaining or increasing the content of organic matter (Bundy *et al.,* 2011) these studies have shown a better effect of NP and NK, NPK fertilizers and it can be said that it has largely contribution to an increase of organic carbon and total N content (Tong *et al.,* 2009) and nitrate nitrogen (Zhang *et al.,* 2012).

Considering an available phosphorus and potassium in Vertisol it has been determined that the fertilizers containing these elements, NP, NK and NPK, had direct impact on their concentration in the soil. After 33 years in the most physiologically active P_2O_5 content has been recorded in NPK variants (T-8 and T-9), followed by NP variant (T-4 and T-5). Thus, perennial application of fertilizers with phosphorus (NP and NPK) has been strongly influenced on its content in the soil, contributing to the accumulation of available forms in the area of application (Richards *et al.,* 1998; Maroko *et al.,* 1999, Otto and Kilian, 2001, Cakmak *et al.,* 2010; Selles *et al.,* 2011), and on this balance of available phosphorus certainly influenced his incomplete use. A similar trend was recorded for the effect of fertilizers on the content of available K_2O. The only difference is that there is less visible effect of NPK (T-8 and T-9) fertilizer on potassium content increased, compared to the variants where it have been applied NK fertilizers (T-6 and T-7).

Table 2. Soil chemical characteristics of Vertisol in long-term nitrogen fertilization experiment.

Treatments	Organic matter	N total	avail. P	avail. K
	--------------- % ---------------		---------- mg 100 g^{-1} ----------	
T-1	2.42 ± 0.89	0.165 ± 0.01	4.25 ± 1.5	22.13 ± 5.5
T-2	2.84 ± 0.26	0.178 ± 0.03	3.88 ± 3.0	21.33 ± 1.2
T-3	3.00 ± 0.21	0.173 ± 0.01	5.33 ± 8.8	24.65 ± 3.2
T-4	3.43 ± 0.21	0.168 ± 0.02	12.63 ± 6.5	23.80 ± 9.0
T-5	3.36 ± 0.21	0.178 ± 0.03	11.38 ± 5.5	24.50 ± 7.0
T-6	3.11 ± 0.40	0.163 ± 0.02	4.63 ± 1.5	31.38 ± 5.0
T-7	3.08 ± 0.41	0.175 ± 0.02	3.38 ± 2.0	33.75 ± 2.5
T-8	3.24 ± 0.60	0.185 ± 0.03	15.13 ± 8.5	31.63 ± 4.5
T-9	3.17 ± 0.14	0.180 ± 0.03	14.08 ± 5.0	33.45 ± 3.1
LSD 0.05	0.284	0.016	3.58	3.31
LSD 0.01	0.382	0.022	4.83	4.47

The content of an available iron in all variants in which fertilizers have been applied, have expressed a tendency of increase compared to the control. A review of the results shown in Table 3, it can be noted that after 33 years, the combination in which were applied120 kg N ha^{-1} (T3), then 60 kg N ha^{-1} and 60 kg P ha^{-1} (T-4), as 80 kg N kg ha^{-1} and 60 kg P ha^{-1} (T-5) have mostly affected the change in the content of available forms of Fe. Thus, the content of available Fe in variants has been significantly ($p < 0.01$) higher than in the other variants, regardless of whether they were fertilized or not.

Table 3. Content of available Fe, Mn and Zn in Vertisol in long-term nitrogen fertilization experiment.

Treatments	avail. Fe	avail. Mn	avail. Zn
	------------------------------------ mg 1000 g^{-1} ----------------------------------		
T-1	97.25 ± 6	80.3 ± 13	2.25 ± 0.7
T-2	96.25 ± 9	88.0 ± 25	2.05 ± 0.1
T-3	123.00 ± 11	107.0 ± 24	3.55 ± 1.0
T-4	122.50 ± 15	88.3 ± 6	3.13 ± 0.2
T-5	124.75 ± 19	88.0 ± 2	4.48 ± 0.5
T-6	110.75 ± 5	104.3 ± 17	2.88 ± 0.5
T-7	110.75 ± 6	106.5 ± 24	3.78 ± 0.9
T-8	109.50 ± 9	88.3 ± 11	2.93 ± 0.4
T-9	106.75 ± 23	98.3 ± 5	4.50 ± 0.5
LSD 0.05	8.193	10.688	0.390
LSD 0.01	11.048	14.412	0.526

The content of available Mn in the vertisol have been within the medium content and in all the variants of fertilization it has been significantly increased compared to the control (Table 3). The biggest contents have been concluded in variants in which is N applied in quantity of 120 kg ha^{-1}. However, higher values of Mn at variant with applied higher doses N compared to the control were highly significant (p <0.01). The trend of higher available manganese content with increasing amounts of fertilizer it has been observed at a concentration of available Zn in vertisol. Differences were very significant ($p < 0.01$) compared to the control and in relation to a combination fertilizer with a lower intake of active ingredient.

Table 4. Pearsson correlation coefficients of the studied soil chemical parameters and micro elements.

	pH H_2O	pH KCl	Org. matt.	N-total	P	K	Fe	Mn	Zn
pH H_2O	1								
pH KCl	.440*	1							
Org. mat.	- .634**	.046*	1						
N-tot	- .180	.225	.340	1					
P	- .124	.632**	.663**	.536*	1				
K	- .601**	.021	.361	.245	.253	1			
Fe	- .556*	- .087	.732**	.001	.351*	.031	1		
Mn	- .853***	- .559*	.234	- .071	-.295	.586*	.323	1	
Zn	- .722**	.069	.603**	.354*	.454*	.472*	.617**	.407*	1

Experiences with impact of fertilizers on the content of available forms of trace elements, including Mn and Zn in the soil are different. Mainly they deny an important role of fertilizers on change of concentration (Rutkowska *et al.,* 2009) by highlighting the growing importance of perennial application of organic fertilizers versus to mineral (Li *et al.,* 2010; Richards *et al.,* 2011). On the other hand there is the view that the content of trace elements, in addition to organic, can be affected by mineral fertilizers (Thakur *et al.,* 2011), especially phosphorus (Molina *et al.,* 2009) which contain heavy metals (As, Cd, Cr), and numerous micronutrients, especially Zn and P fertilizer application may result in the increase of their concentration in the soil, which should be taken into account.

Concentrations of available Fe were highly correlated (Table 4) with content organic matter (r = 0.603), available Mn with pH in H_2O (r = 0.853) and available Zn were pH in H_2O (r = 0.722) and organic matter (r = 0.603).

Conclusion

Long-term application of fertilizers has affected the change of Vertisols fertility parameters. Nitrogen fertilizers increase the acidity and contributed to the acid destruction and further degradation of the soil type. Phosphorus and potassium were significantly increased only in the variant with the application of these two elements, and organic matter and total nitrogen for all the fertilization variants. Fertilization, especially the application of larger amounts of nitrogen fertilizers, with increase of acidity, was contribute solubility Mn from soil reserves, because (consequently) an increase of the concentration of available Mn. For the same reasons, higher doses of fertilizers significantly influenced the increase of Zn content. After 33 years of fertilization, the achieved level of available Fe, Mn and Zn, make the caution, because over the time concentration of these elements can increase to the undesirable economic and environmental level.

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