Asian Journal of Agriculture and Food Sciences (ISSN: 2321 – 1571)
Volume 03 – Issue 05, October 2015

Changes in Fertility of Vertisol and in the Content of Available Forms of Fe, Mn, Cu and Zn after Thirty Years of using Phosphate Fertilizers

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ABSTRACT— ***A long-term application of mineral fertilizers affects many soil properties, including the content of essential microelements. This study has been conducted to determine the effect of thirty years of using two doses of phosphorus (80 and 160 kg ha^{-1}) on major agrochemical properties of Vertisol in leaching (pH, Y1, the content of organic matter, total N, total P, total K, available P, and available K), as well as the content of available forms of certain microelements (Fe, Mn, Cu, and Zn). The research has been carried out on a stationary model farm in Kragujevac in central Serbia. A long-term, continuous application of phosphate fertilizers in the surface layer has had a less effect on the acidification of Vertisol than nitrogen and potassium fertilizers, at the same time, it has significantly contributed to the increase in total and available phosphorus. Thirty years of fertilization, both by type of fertilizer and the amount of phosphorus used, has had a different effect on the content of available forms of microelements. Fertilization with nitrogen and potassium has had the greatest effect on the contents of Fe and Zn. A long-term use of phosphate fertilizers has led to a reduction in available forms of Mn and Cu in the surface layer.***

Keywords— long-term fertilization, Vertisol, phosphate fertilizer, microelements

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1. INTRODUCTION

Getting high and stable crop yields today is unthinkable without the use of fertilizers. It is known that their continued implementation, in various forms and amounts, affects numerous soil properties. However, the effect of mineral fertilizers on soil properties is much smaller compared to the changes that occur when various organic fertilizers are used. Regardless of the smaller effect, it has been noted that a continuous and multiyear use of nitrogen, phosphorus, and potassium in the mineral form is reflected on the physical (Pernes-Debuyser and Tessier, 2004, Herencia *et al.*, 2011), much more on chemical and biological soil properties (Belay *et al.*, 2002; Liu *et al.*, 2010; Zhong *et al.*, 2010; Liang *et al.*, 2011), and may also affect its enzymatic activity (Koper and Piotrowska, 2003; Piotrowska and Wilczewski, 2012).

A long-term continuous use of phosphoric fertilizers (MAP, superphosphate, triple superphosphate) can significantly affect numerous soil properties. Their effect can be observed from several aspects, of which two are most prominent. The first is a small utilization of phosphorus by plants, which, in conditions of constant implementation, leads to an inevitable accumulation of this element in the soil, especially its available forms (Berti and Cunningham, 1997; Pizzeghello *et al.*, 2011). The second refers to the fact that phosphoric fertilizers are produced from raw materials containing microelements (Ricchards *et al.*, 2011), as well as some potentially hazardous trace elements, and they remain as impurities in the fertilizer after fabrication (Kabata-Pendias and Pendias, 2001), and in the system of multiyear use, cadmium (Brennan and Bolland, 2004; Grant and Sheppard. 2008.), arsenic and lead (Jiao *et al.*, 2012) have the potential to be accumulated in the soil and transmitted through the food chain.

Long-term experiments with the application of fertilizers are an important source of information for understanding the factors that affect the soil fertility (Zhao *et al.*, 2010) and sustainable production on them (Camara *et al.*, 2003). The advantage of long-term research compared to short-term is primarily reflected in the fact that these experiments provide information about the viability of fertilization treatments over several seasons. Over time, crop yields, as well as the direction and intensity of changes in soil properties, reflect on the justification of both the use of certain types of fertilizers, and the quantities in which they are applied, as gives an economic and ecological significance to the research. Therefore, the aim of the study is to, in a long-term field experiment, in sour conditions, determine the effect of phosphate fertilizers on the accumulation of available forms of iron, manganese, copper, and zinc, but also on other properties of Vertisol in the process of leaching.

2. MATERIALS AND METHODS

2.1. Experimental sites

The research has been carried out on a stationary model farm of Small Grains Research Center in Kragujevac, 44°00′51″ and 20°54′42″. Since 1984, the examination of the effect of long-term application of phosphorous mineral fertilizers on the properties of Vertisol soil has been performed.

2.2. Agrochemical soil characteristics

The soil on which the research has been carried out was characterized by leaching processes. The main characteristics of Vertisol before the beginning of the experiment are shown in Table 1.

Table 1. Agrochemical characteristics of Vertisol before the beginning of the experiment

pH		Y1	OM	Total	Total		Available		Available microelements			
		cm^3		N	P	K	P	K	Fe	Mn	Cu	Zn
H_2O	KCl		----- % -----		------------ mg kg^{-1} ------------				---------- mg kg^{-1} ----------			
5.90	4.60	13.29	2.69	0.170	977.4	15000	26.0	180	71	118	2.4	1.7

The basic properties of Vertisol in the surface layer, before the beginning of the experiment, are an expressed sour reaction, a low content of available phosphorus, a mean content of organic matter and available potassium.

2.3. Experimental design

During the experiment, two doses of phosphorus were continuously applied, a lower one, where phosphorus was entered every year in the amount of 80 kg P ha^{-1} (P1 variant) and higher of 160 kg P ha^{-1} (P2 variant). Both doses of phosphorus were combined with a constant amount of nitrogen (120 kg N ha^{-1}) in NP1 and NP2 variants and a constant amount of nitrogen (120 kg N ha^{-1}) and potassium (80 kg K ha^{-1}) in NP1K and NP2K variants. Nitrogen and potassium were applied independently in a special variant (NK variant). Fertilization treatments were compared with the control variant, i.e. with the variant where fertilizers were not applied (O).

The total amounts of phosphorus and an appropriate part of nitrogen were entered by the application of MAP fertilizers ($NH_4H_2PO_4$). The remainder of the provided amount of nitrogen was supplemented by applying Urea fertilizers ($CO(NH_2)_2$). An appropriate amount of potassium chloride (KCl) was used for potassium intake.

The experiment was performed as a random complete block design (RCBD) in four replications. The average (composite) soil samples were collected in the layer from 0 – 20 cm, and they were formed of five sub-samples for each treatment. By mixing the sub-samples, so-called average or composite sample was singled out, which was chemically analyzed after a proper preparation. Soil samples were taken in the fall of 2013 (after the corn harvest).

2.4. Soil laboratory analysis

The soil pH was determined by the pH meter with a glass electrode in a 1:2.5 suspension with water and 1 M KCl. The hydrolytic acidity, i.e. Y1, was determined by Kappen’s method by treating a soil sample with $(CH_3COO)_2Ca$, and then a neutralization of excess acid with 0.1 M NaOH was carried out. Accessible phosphorus and potassium were determined by Al method, where ammonium lactate (pH = 3.7) was used as the extractant. After the extraction, potassium was determined by flame emission spectrometry, and phosphorus by spectrophotometry after developing color with NH_4MoO_4 and $SnCl_2$). Total phosphorus was determined spectrophotometrically at the wavelength of 400-490 nm after a digestion with $HClO_4$ and a treatment with ammonium paramolybdate-vanadate reagent, and total potassium was determined photometrically after the destruction of the sample with a mixture of HF and H_2SO_4. The content of available forms of soil microelements (Fe, Mn, Cu and Zn) was determined by atomic absorption spectrophotometry with Carl Zeiss Jena apparatus – AAS-1, Analityk Jena, Jena, Germany. The content of available Fe was determined after the extraction in a solution of 1M CH_3COONH_4 (pH=7). For determining the content of available Mn, 0.1M H_2SO_4 was used as an extraction agent, and Zn 0.1 M HCl was used for available Cu.

2.5. Statistical analyses

Statistical analyses were performed on SPSS software, variant 16. The effects of the treatment on all variants were tested by ANOVA. Statistical differences between the treatments were determined by using the t-test (95 and 99%) by Pearson for Fisher's LSD. The significance of correlations between them was analyzed through Pearson correlation matrices (SPSS, 2007).

3. RESULTS AND DISCUSSION

The long-term continuous application of mineral fertilizers has contributed to an additional acidification of Vertisol (Table 2), and the reason should be sought in the fact that it is the fertilizer application zone, thereby the zone of their direct effect. On that occasion, it was established that, in the layer from 0 – 20 cm, the differences between active, substitution, and hydrolytic acidity between the control and fertilization variants were highly significant ($p > 0.01$).

Table 2. Agrochemical properties of Vertisol after 30 years of fertilizing with phosphorus

Variants	pH		Y1	OM	total N	total P	total K	avail P	avail K
	H_2O	KCl	cm^3	----- % -----		--------------- mg kg^{-1} ---------------			
O	5.58	4.18	14.10	2.70	0.157	924	13200	18.9	188.0
NK	5.30	4.02	17.80	2.15	0.125	967	16500	20.2	258.3
NP1	5.36	4.10	16.98	2.38	0.138	1202	14100	104.4	168.9
NP2	5.40	4.12	16.37	2.40	0.140	1381	14000	115.5	154.8
NP1K	5.42	4.10	16.43	2.36	0.137	1283	15000	125.5	288.3
NP2K	5.52	4.13	16.18	2.48	0.144	1605	16000	168.2	255.5
Lsd 0.05	0.066	0.069	0.174	0.135	0.008	86.6	530.3	4.37	4.08
Lsd 0.01	0.091	0.094	0.238	0.184	0.011	118.6	726.5	5.99	5.58

The contribution to acidification of used fertilizers was not the same. The highest acidification was caused by nitrogen and potassium fertilizers, i.e. NK variant. This implies that a long-term use of only nitrogen and potassium fertilizers significantly increases the acidity of soil, rather than when the same fertilizers are used with phosphorous ones. This trend has been expected because soil acidification by long-term application of nitrogen fertilizers is well-known and confirmed by numerous experiments (Barak *et al.,* 1997; Bolan *et al.,* 1991; Khonje *et al.,* 1989; Zhao *et al.,* 2010). However, multiyear, continuous use of fertilizers that, in addition to N, contain phosphorus, such as MAP, frequently result in an increased acidification (Magdoff *et al.,* 1997; Belay *et al.,* 2002; Saleque *et al.,* 2004).

In all variants of fertilization, the content of organic matter and total nitrogen in the surface layer was significantly reduced compared to the control variant ($p < 0.01$). Although the importance of long-term fertilization with nitrogen to maintain or increase the organic matter content (Bundy *et al.,* 2011), total (Tong *et al.,* 2009) or nitrate nitrogen (Zhang, 2012) is often emphasized, in this research, the nitrogen from fertilizers has not had a positive effect on their contents.

As for the contents of phosphorus and potassium in Vertisol, it has been found that the fertilizers containing this element directly affect their concentration in relation to the initial level from 1984. Thus, after 30 years, in all the variants where P fertilizers were applied, the contents of total and available phosphorus increased. The differences in relation to the control and NK variants were statistically highly significant ($p < 0.01$) and in proportion with the rates of applied fertilizers, and the long-term application of fertilizers has strongly contributed to the accumulation of available forms in the area of intake (Maroko *et al.,* 1999; Otto and Kilian, 2001; Cakmak *et al.,* 2010; Selles *et al.,* 2011). It has also been noted that, in this layer, the same rates of phosphorus from NPK variants had a significantly greater contribution to the accumulation of this element in relation to the NP variant.

Thirty years of fertilization, both by type of fertilizer and the amount of phosphorus used, has had a different effect on the content of available forms of microelements in Vertisol (Table 3).

Table 3. The content of available microelements in Vertisol after 30 years of fertilization

Variants	Fe	Mn	Cu	Zn
	----------------------------------mg kg^{-1}		----------------------------------	
O	88 ± 20	134 ± 18	2.9 ± 0.7	1.4 ± 0.5
NK	94 ± 15	125 ± 20	2.5 ± 0.5	0.8 ± 0.4
NP1	81 ± 15	105 ± 18	2.6 ± 0.9	1.3 ± 0.3
NP2	88 ± 24	110 ± 25	2.0 ± 0.4	1.2 ± 0.3
NP1K	93 ± 32	121 ± 19	2.8 ± 1.1	1.6 ± 0.2
NP2K	84 ± 19	118 ± 30	2.4 ± 0.5	1.5 ± 0.7
Lsd 0,05	14.77	14.90	0.496	0.300
Lsd 0,01	20.23	20.41	0.678	0.412

Fertilization with nitrogen and potassium has had the greatest effect on the contents of Fe and Zn (NK variant). Namely, in this variant, the highest content of Fe and the lowest content of Zn have been found. At the same time, the effect of phosphate fertilizers on Fe content in Vertisol is not entirely clear. The effect of this fertilizer on the contents of Mn and Cu is much clearer. Namely, a long-term intake of phosphate fertilizers has led to a reduction in available forms of both elements in the surface layer compared to the control variant. Thus, it can be noted clearly that the lowest content of Mn has been found in the variants where only nitric and phosphoric fertilizers (NP1 and NP2) were applied, with no clear effect of the quantity of phosphorus.

On the other hand, the amounts of applied phosphorus influenced the reduction of Cu, so the lowest content of this element was noted in the variants where the largest amount of phosphorus had continuously been applied for thirty years – 160 kg P ha^{-1} (NP2 and NP2K variants). Concentrations of any of microelements did not show any significant dependence on agrochemical properties of Vertisol (Table 4).

Table 4. Pearson coefficients

	pH KCl	Y1	OM	P tot	P avail	K avail	Fe	Mn	Cu
pH KCl	1								
Y1	-.702	1							
OM	.654	-.858	1						
P tot	.158	.152	.035	1					
P avail	.129	.274	.013	.948	1				
K avail	-.334	.466	-.319	.114	.146	1			
Fe	.452	.173	-.418	-.406	-.433	.567	1		
Mn	-.336	.369	-.377	-.467	-.517	.557	-.566	1	
Cu	214	.459	-.451	-.643	-.598	.050	.184	.550	1
Zn	.528	-.546	.130	.535	.429	-.377	.324	.014	.009

Experiences regarding the impact of fertilizers on the content of available forms of microelements, among others Fe, Mn, Cu and Zn, in soil are different. Mainly, they come down to the denial of a greater role of mineral fertilizers in the change of their concentration (Rutkowska *et al.*, 2009) with an emphasis on a greater importance of long-term application of organic fertilizers compared to mineral ones (Li *et al.*, 2010; Richards *et al.*, 2011). On the other hand, there are opinions that the content of microelements can be affected, in addition to organic fertilizers, also by mineral fertilizers (Thakur *et al.,* 2011), especially phosphoric ones (Molina *et al.*, 2009), and that they contain heavy metals (As, Cd, Cr), as well as numerous micronutrients, especially Zn, so the intake of P fertilizers can result in an increase in its concentration, which has exactly happened to NP1K and NP2K variants.

4. CONCLUSION

The thirty-year use of mineral fertilizers has caused an additional acidification of Vertisol, and then a reduction of the content of organic matter and total nitrogen. Phosphoric fertilizers, regardless of the amount entered, have had a smaller effect on acidification. The concentrations of total and available phosphorus and potassium have increased in all cases where fertilizers containing these two elements were used, and they have been proportional to the doses applied.

The content of available forms of Fe, Mn, Cu, and Zn, after thirty years, depended on the fertilizer type and the amount of phosphorus entered. NK fertilizers have significantly influenced the contents of Fe and Zn, and phosphoric fertilizers have significantly influenced the contents of Mn and Cu. At the same time, Cu has reacted the most to the amount of phosphorus entered, in such a way that the content of its available forms has been decreasing with a dose increase of phosphorus applied, which should be taken into account, so that, over time, its low concentrations would not become a limiting factor of a high and stable production.

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