Effect of Long-Term Nitrogen Fertilization on Main Soil Chemical Properties in Cambisol

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Abstract
Nitrogen fertilization is the most influential in terms of increasing crop production. Mineral nitrogen, in addition to increasing the content of nitrate in soil, leads to changes in soil pH and many other soil properties. Long-term mineral nitrogen addition experiments (over 40-years) can give us valuable information about how those changes occur and point out the trends of the changes. The experiment was set up on a Cambisol 40 years ago with 60, 90 and 120 kg of N per ha. The results show significant increases in N content, humus and soil CEC, while the sum of bases and base saturation decreased.

Introduction
The changes in soil quality are closely related to soil physical, chemical and biological fertility (Zhang *et al.* 2007, Brady and Weil 2002). There is general agreement, that of all the nutrient amendments made to soil, N fertilizer application has had and still has by far the most important effects in terms of increasing crop production. Under intensified agricultural production the soil receives ever more nitrogen (Freney, 2005, Erisman *et al.* 2005;). Fertilizer nitrogen, apart from increasing the content of nitrate in soil that leads to its leaching (Porter *et al*. 1996), results in changes in soil pH and many other soil properties (Brady and Weil , 2002,). Long-term field experiments with N fertilization can give a valuable information about how those chnages occur and indicate the trends of the changes.

Materials and Methods
The investigation was conducted on “Mladenovac” experimental station located 55 km from Belgrade in Serbia. This site has received a wide range of different fertilization treatments since 1964. Soil type is *Cambisol*. Mean annual precipitation is about 700 mm and mean annual temperature is 11^{o}C. The mineral N was added as urea and monoammonium phosphate fertilizers in three doses (60-, 90- and 120 kg per ha) for the last 40 years. Soils were sampled from each of three replicates that were designed as 5 x 11 m plots in a randomized complete block experiment, including the control treatment that didn’t receive any fertilizer. Soils were sampled from the 0-30 cm soil interval in spring 1998. Five subsamples were taken from each of the replicates and then mixed to make a composite sample for every replicate. Soil pH, content of humus (Tyurin method), total N (Kjeldahl method), available P and K after extraction by the Egner-Riehm method potassium determined on a flame emission photometer, and phosphorus on a spectrophotometer (Enger and Riehm, 1958). Soil Ca, Mg, Fe and Zn were extracted by ammonium acetate, Cu by HCl followed by determination on atomic absorption analyzer SensAA Dual (Wright and Stuczynski, 1996). Soil microelements were analyzed on a composite sample. Determination of CEC was done by the steam distillation method after treatment of the samples with ammonium acetate (Sumner and Miller, 1996). Statistical analyses were performed by SPSS 16 software program. The effects of treatments on all the variables were tested using an ANOVA method. Statistical differences were determined using t-test for Fishers LSD. The significance of their correlations was analyzed by Pearson correlation matrix (SPSS Inc., 2007).

Results
The studied soil in the control treatment is classified as Eutric Cambisol with medium humus content . The content of available P is medium, and K is high. Nitrogen fertilizer primarily affected the soil pH resulting in an increase in acidity. The clear trend of decreasing soil pH was observed with increasing the rate of applied N-fertilizer where the high statistical significance was observed between the control and the highest rate of N-fertilizer. The content of N also was constantly increasing corresponding to the applied fertilizer rate with statistical significance between all four treatments. Soil organic matter did not show a changing trend, however, there was a significant increase in the content of humus between control and 60 kg and 120 kg N per ha. The content of P increased for 60 and 90 kg N per ha versus control, while in the 120 kg N per ha it somewhat decreased. The content of K also increased compared to the control although the increase was not regular. There was a clear significant increase of soil CEC, while sum of bases decreased parallel with applied N. Magnesium and Ca showed a clear trend of decreasing parallel to the applied N. Changes in the

1 – 6 August 2010, Brisbane, Australia. Published on DVD.

contents of available Fe and Zn were contradictory compared to other microelements showing increases with addition of N-fertilizer.

Table 17. Average contents of main soil properties in long-term N-fertilization experiment in Cambisol, Serbia

kg N per ha	pH	humus	total N	P	K	Ca	Mg	sum of base	CEC	sum of base	Zn	Fe	Cu
		%		mg/100g				Cmol/100g		%	mg/kg		
0	5.79a	2.17a	0.10a	4.83a	19.38a	384	101	12.7a	20.7a	61a	0.55	25.40	8.60
60	5.37b	2.45b	0.13b	11.77b	28.21b	287	71	11.6b	23.4b	50b	1.04	26.00	7.80
90	5.33b	2.27c	0.16c	11.82b	24.79b	304	63	10.7c	23.0b	47c	1.03	26.33	7.43
120	5.00c	2.36d	0.19d	11.48b	26.50b	311	57	9.6d	24.1c	40d	1.04	27.07	7.00
LSD	*	*	*	*	*	ND	ND	*	*	*	ND	ND	ND

*significant at 0.05 level

Discussion

Long-term application of N containing fertilizers (such as MAP) with acidifying effects, results in acidification of soil, thus lowering soil pH (Belay *et al.* 2002). Upon oxidation, NH_4^+ can release H^+ ions – a potential source of soil acidity (Magdoff *et al.* 1997). Soil pH is one of the main factors affecting solubility of trace elements and their phyto-availability (e.g. Kopec and Przetaczk-Kaczmarczyk 2006).

Permanent fertilization with N can lead to its leaching, where firstly the processes of nitrification build up nitrate ions, which are weakly associated to soil adsorptive complex (Mengel and Kirkby, 2001). On the other hand, processes of microorganism metabolism also affect the mineral N and microorganisms are included into the soil humus that is usually reflected in an increased content of SOM. However, in our study the expected increase in soil humus did not show a clear dependence on the amount of applied N. This can be explained partially by the changes in the composition of SOM, where addition of mineral N intensified immobilization of mineral N by microorganisms (Ilyaletdinov, 1988; Karborzova-Saljnikov, 2004), and by adsorption of ammonium by soil CEC and by processes of weak fixation within clay minerals (Mengel and Kirkby, 2001). Such processes can result in gradual accumulation of total N.

Table 18. Pearson Correlation Coefficients of soil main properties as affected by long-term application of N-fertilizer in a Cambisol, Serbia

	pH	humus	TN	P	K	sum of bases	CEC	sum of base
pH	1							
Humus	-.141	1						
Total N	-.703**	.165	1					
P	-.545**	.167	.452**	1				
K	.213	.262	-.324*	-.579**	1			
bases	.749**	-.123	-.663**	-.615**	.402*	1		
CEC	-.552**	.204	.435**	.243	.088	-.003	1	
Sum of bases	.927**	-.216	-.773**	-.672**	.316*	.881**	-.471**	1

** Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Increases in the content of available K and P in the fertilized treatments are expected. However, addition of the highest rates of N resulted in a somewhat decreased content of P, which is probably induced by reduced solubility of P-compounds due to increased soil acidity (Marsh *et al.* 1987). Decreased content of exchangeable Ca compared to the control clearly indicates an imbalance between its input and output. The reason for this is the leaching due to soil acidification and processes of nitrification that particularly apply to soils with a pH <7. This is also confirmed by the decreasing trend in the content of Mg in the studied surface soil, compared to the control (Mengel and Kirkby, 2001).

Decreases in soil pH, followed by leaching of soil bases are also clearly seen in the constant decrease of basic cations on the soil CEC, whilst the increased content of humus resulted in an increased value of soil CEC (Yan *et al.* 2007). The significant decrease of basic cations on the soil CEC resulted in the changes of main soil properties resulting in a change in soil classification: the studied Eutric Cambisol has become aDystric Cambisol. Changes in the content of Zn and Fe are closely connected to the decrease of soil pH, e.g. due to acidification of the medium Zn and Fe are activated and transformed into mobile forms that determine their increased content for the fertilized treatments (Mengel and Kirkby 2001). On the other hand, strong bonds of insoluble Cu with soil particles, and the higher concentration of Cu than of Zn in soil solution resulted in leaching due to soil acidification (Mc Bride 1989; Mengel and Kirkby 2001).

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