

Assessment of Metal Contents in Soil after Sewage Sludge Treatments Associated or not with Mineral Fertilization

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Considering the scientific evidence that application of sewage sludge provides a lot of agronomic benefits but presents environmental inconvenient as well, we developed a bifactorial experimental model to study the effects of sewage sludge application on soil. There were applied different doses of sewage sludge (corresponding to 100, 200, 300, 400, 500, 600 kg N/ha) collected from Wastewater Treatment Plant from Pitesti that were associated ($N_{100}P_{100}K_{100}$) or not ($N_0P_0K_0$) with mineral fertilization. Results indicated that organic carbon, total nitrogen, mobile phosphorus and potassium from soil show statistic significant increases under conditions of sewage sludge treatments in different doses, meanwhile the levels of metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) in the soil did not exceed the limits described in both Romanian and European Union regulations.

Keywords: sewage sludge, heavy metals, fertilizer, soil

Recently, a lot of attention has been accorded to sewage sludge application and to its effects on soil and environment, generally. It is used in agriculture as fertilizer [1] because it is characterized by nitrogen and phosphorus plant availability and high content of organic matter [2]. Nitrogen availability from sewage sludge depends on inorganic N content, C/N ratio, soil type and application method and timing [3]. Also, the use of sewage sludge after composting as a nutrients source became an economical option [4].

The interest emerged from the yearly increasing amounts of sewage sludge and also because of its advantageous effects on the physical and chemical properties of soil. It is known that sewage sludge application can improve soil structure, increase soil fertility and also plant growth. Beside beneficial effects, application of sewage sludge may present environmental risk due to heavy metals [1], organic pollutants [5-7] and pathogenic organisms [7,8] that can be found in its composition.

Literature studies highlights that the heavy metals content in sewage sludge amended soils are higher than in the case of typical soils [9].

In China the heavy metal ecological risk and environmental quality standard for soil was evaluated in an experimental research with 0, 15, 30, 60, 120 and 150 t/ha applied quantities of sewage sludge. Heavy metal concentrations in soil increased content of Zn, Pb, Cu did not exceed the maximum limit specified for farmland, vegetable land, tea land, fruit land and grazing land, only Cd concentration has exceeded and the suggestion was

that the sewage sludge produced from the wastewater treatment plant should be applied to forestry land and the land with higher absorption capacity [10].

Because recently heavy metal pollution is increasing, it is irreversible and has long lasting character, application of sewage sludge must be monitored strictly and environmental risk produced by metals is necessary to be estimated.

The increasing tendency of sewage sludge application for beneficial effects (nutritive species, improvement of soil characteristics and of fertility) despite the fact these wastes may present undesirable properties (pollution with heavy metals, organic compounds, pathogens) allowed us to develop an experiment to analyze the effect of sewage sludge application (associated or not with mineral fertilization) on soil.

The main objectives of this experimental study were to: **(i)** investigate the effects of application in different doses of sewage sludge collected from Wastewater Treatment Plant (WWTP) from Pitesti associated ($N_{100}P_{100}K_{100}$) or not ($N_0P_0K_0$) with mineral fertilization on agrochemical characteristics of soil, and **(ii)** to assess the potential environmental impact of metal accumulation in the soil as outcome to the sewage sludge application according to limits described in both Romanian and European Union regulations.

Experimental part

Experimental model

It was developed a bifactorial experimental model that is described in table 1.

a factor =sewage sludge doses	b factor = fertilizer type applied
a ₁ - unfertilized with sewage sludge	b ₁ - sewage sludge ($N_0P_0K_0$ - without mineral fertilization)
a ₂ - fertilization with sewage sludge corresponding to 100 kg N/ha	b ₂ - sewage sludge and mineral fertilizer
a ₃ - fertilization with sewage sludge corresponding to 200 kg N/ha	$N_{100}P_{100}K_{100}$ - fertilization 100 kg N/ha + 100 kg P/ha + 100 kg K/ha
a ₄ - fertilization with sewage sludge corresponding to 300 kg N/ha	.
a ₅ - fertilization with sewage sludge corresponding to 400 kg N/ha	.
a ₆ - fertilization with sewage sludge corresponding to 500 kg N/ha	.
a ₇ - fertilization with sewage sludge corresponding to 600 kg N/ha	.

Table 1
DESCRIPTION OF BIFACTORIAL
EXPERIMENTAL MODEL

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Analyses Analyzed material	pH	Organic carbon (C _{org})	Mobile phosphorus (P _{AL})	Mobile potassium (K _{AL})	Total nitrogen (N _{total})	Total phosphorus (P _{total})	Total potassium (K _{total})	Metals total forms
Soil	✓	✓	✓	✓	-	-	-	✓
Sewage sludge	✓	✓	-	-	✓	✓	✓	✓
Soil (after treatments)	✓	✓	✓	✓	✓	-	-	✓

Table 2
CHEMICAL ANALYSES
PERFORMED ON SOIL AND
SEWAGE SLUDGE

Basic parameters				Metals (total forms), mg/kg							
pH	C _{org} , %	P _{AL} , mg/kg	K _{AL} , mg/kg	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
5.20	1.19	19	40	0.11	6.6	19	12	500	15	13	48

Table 3
AGROCHEMICAL CHARACTERISTICS
OF SOIL

Chemical parameter	Found value (min-max)	Av.± SD	CV, %	Maximum admitted levels	
				Romania MO 344/2004	Directive 86/278/EEC
pH	6.53-6.70	6.62±0.09	1.4	-	-
C _{organic} , %	26.00-28.00	27.00±1.00	3.7	-	-
N _{total} , %	1.97-2.09	2.04±0.06	2.9	-	-
P _{total} , %	0.75-0.78	0.77±0.02	5.1	-	-
K _{total} , %	0.38-0.41	0.39±0.02	5.1	-	-
Cd, mg/kg	3.04-3.40	3.21±0.18	5.6	10	20-40
Co, mg/kg	5.70-7.50	6.10±0.40	6.6	50	-
Cr, mg/kg	115-131	124±8	6.5	500	-
Cu, mg/kg	114-122	117±4	3.4	500	1000-1750
Mn, mg/kg	320-350	338±16	4.7	-	-
Ni, mg/kg	32-36	34±2	5.9	100	300-400
Pb, mg/kg	91-105	97±7	7.2	300	750-1200
Zn, mg/kg	1211-1252	1237±22	1.8	2000	2500-4000

Table 4
CHEMICAL CHARACTERISTICS
OF SEWAGE SLUDGE

Av.- average of determinations
SD-standard deviation
CV-coefficient of variation

Chemical characterization of soil (before and after treatments) and sewage sludge

For experimental model there were used 56 vegetation pots (20 L capacity), each of 14 treatments in four repetitions. For experiments was used soil collected from A₀ horizon of luvisol meanwhile sewage sludge that was used in experiment was collected from the Wastewater Treatment Plant (WWTP) from Pitești.

In order to study the influence of sewage sludge application on crop quality and yield, in experimental pots were used as test sunflower plants. The results concerning these aspects will be discussed in detail in a future paper.

Soil, sewage sludge and soil after treatments were fully characterized. The performed analyses are presented in table 2.

The reaction of soil and sewage sludge (pH) was carried out through potentiometric method, in an aqueous suspension, 1:2.5 (w/v). Organic carbon was determined using Walkley-Black-Gogoasa method. Organic matter content was calculated on the basis of organic carbon by multiplying its value with factor 1.724. Mobile phosphorus content was evaluated by spectrophotometric molybdenum blue method, using ammonium acetate-lactate (AL) as extractive solution, at pH 3.7 (Egner-Riehm-Domingo method). The mobile form of potassium was quantified in the same extract (AL) by flame photometry technique. Total form of nitrogen was determined using Kjeldahl method, meanwhile total phosphorus was assessed spectrophotometrically (as molybdenum blue) and potassium using flame photometry method.

Total forms of metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) were assessed using atomic absorption spectrometry, after aqua regia digestion [9,10].

Results and discussions

Chemical analyses performed in order to characterize the soil led to the results presented in table 3. Metal contents from soil are below thresholds set by Order of the Minister of Agriculture, Forests, Waters and Environment no.344/2004 [13] and there are no environmental problems from this point of view.

Sewage sludge collected from wastewater treatment plant from Pitești was characterized and the results are presented in table 4. According to chemical analyses, the composition of sewage sludge indicates an important source of organic matter and nutritive elements for agricultural soils [14,15] even if, according to literature may present some inconveniences as presence of pesticides [16], poorly biodegradable organic compounds and pathogenic organisms (bacteria, viruses) that are present in waste waters [8, 17].

Sewage sludge has a slightly acidic reaction (6.62 as average) and there are no restrictions for using it on agricultural soils. Organic carbon content is high (27% as average) and it could be used as fertilizer and a source of organic matter.

The potassium content in sewage sludge is known to be low [18]. In our study, potassium level was of 0.39% (as average). According to different studies, the content of nitrogen in sewage sludge is subject of a wide variation [15]; in our study found concentration was 2.04% as average.

The main factor limiting the application of sewage sludge to agricultural soils is represented by heavy metals that may be toxic for plants, animals and human at certain concentrations. Metal contents in sewage sludge are regulated by Directive 86/278/CEE [20] and this one it has been transposed through the Order of the Minister of Agriculture, Forests, Waters and Environment no.344/2004

Analyses		pH			C _{org} , %		
		b ₁	b ₂	Av.(b)	b ₁	b ₂	Av.(b)
Sewage sludge							
a ₁	0 kgN/ha	5.22	5.13	5.18a*	1.21	1.20	1.21a
a ₂	100 kgN/ha	5.23	5.13	5.18a	1.21	1.23	1.22a
a ₃	200 kgN/ha	5.21	5.14	5.18a	1.23	1.26	1.25ab
a ₄	300 kgN/ha	5.21	5.12	5.17a	1.29	1.30	1.30abc
a ₅	400 kgN/ha	5.20	5.12	5.16a	1.31	1.33	1.32bcd
a ₆	500 kgN/ha	5.22	5.11	5.17a	1.36	1.37	1.37cd
a ₇	600 kgN/ha	5.20	5.11	5.16a	1.40	1.42	1.41d
Av.(a)		5.21a	5.12b	-	1.29a	1.30a	-

b₁ corresponds to N₀P₀K₀ (without mineral fertilization)

b₂ corresponds to N₁₀₀P₁₀₀K₁₀₀ (mineral fertilization)

Av. - average

*Mean values accompanied by same letter (a or b) does not present significant differences (Tukey multiple comparison test - significance level 0.05)

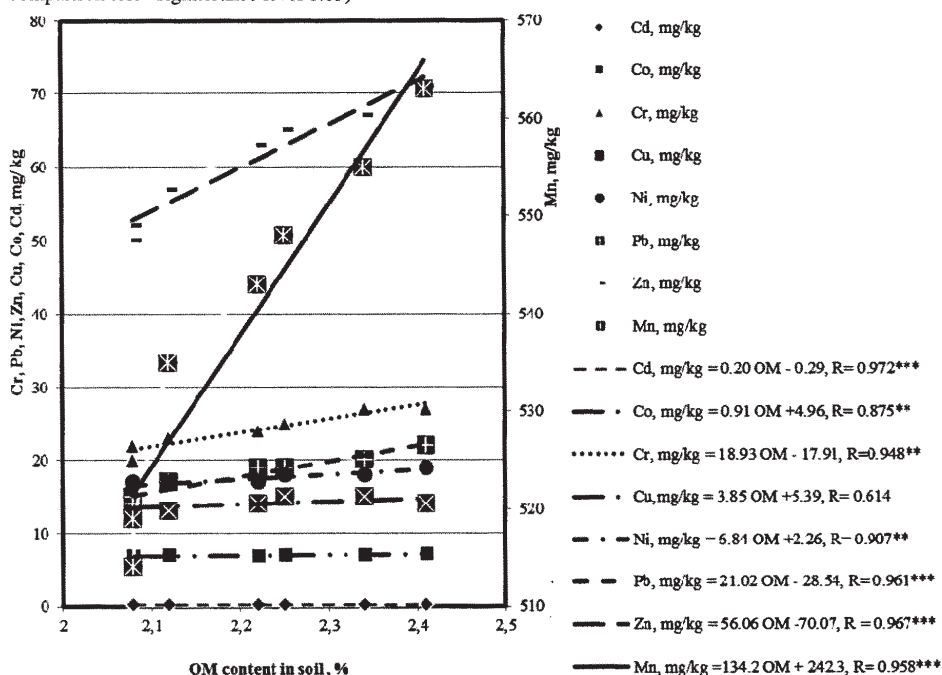


Fig.1. Correlation between organic matter content and metal accumulation in soil at variants with sewage sludge applied without mineral fertilization

[13]. It was observed that limits set by many countries are more restrictive than those set by European Directive.

Metal contents (as total form) in sewage sludge from our study reveal that there are no restrictions concerning application of sewage sludge on agricultural soils and meets the requirements imposed by legislation [13, 20].

Use of sewage sludge in doses equivalent with 100, 200, 300, 400, 500, 600 kg N/ha on a soil with moderate acidic reaction did not lead to significant statistical differences of soil reaction that remained in the same interval. Mineral fertilization with N₁₀₀P₁₀₀K₁₀₀ led to significant differences of pH values from 5.21 (N₀P₀K₀) to 5.12 (N₁₀₀P₁₀₀K₁₀₀). The acidification effect of mineral fertilizers is evidenced by comparison between values obtained for experiments fertilized with sewage sludge associated with mineral fertilization and those obtained for experiments with sewage sludge fertilization but without mineral fertilization.

Results concerning organic carbon presented in table 5 allowed us to obtain the following conclusions:

- application of increasing doses of sewage sludge equivalent with 100, 200, 300, 400, 500, 600 kg N/ha led to statistic significant increase of organic carbon from soil from 1.21% (control variant) up to 1.41%;

- mineral fertilization has no effect on organic carbon content from soil. Application of sewage sludge with total nitrogen of 2.04% (as average) produced an increase of total nitrogen from soil that is statistically significant (from 0.148% up to 0.193%) (table 6). Total nitrogen content from

soil increased under mineral fertilization (N₁₀₀P₁₀₀K₁₀₀) conditions.

Soil organic matter plays a key role in retaining metals. Organic matter (OM) forms complexes with metal by exchange and chemisorption reactions [21] and retains heavy metals in an exchangeable form [22]. Increasing the amount of organic matter in the soil helps to minimize the absorption of heavy metals by plants [23].

In the case of experiments where it was applied only sewage sludge, the correlation coefficients in metal accumulation of Cd, Pb, Zn and Mn depending on organic matter content indicate very significant differences. In the case of Co, Cr and Ni differences are significantly distinct. Copper presents insignificant differences in correlation with organic matter content (fig. 1). The equations that describe correlation between organic matter and metal content in soil are presented in the right side of figure 1.

Mineral fertilization variants influenced the soil metal accumulation process depending on organic matter content. Correlation coefficients indicate very significant differences in metal accumulation of Cd, Co, Cr, Pb, Zn and Mn, significant differences in retaining of Ni and insignificant differences in the case of Cu (fig. 2). The equations that describe correlation between organic matter and metal content in soil are presented in the right side of figure 2.

Mobile phosphorus content from soil recorded a statistically significant modification starting with sewage sludge dose equivalent with 400 kg N/ha. The highest value (49 mg/kg) was recorded for variant that was fertilized with maximum dose of sewage sludge (600 kg N/ha).

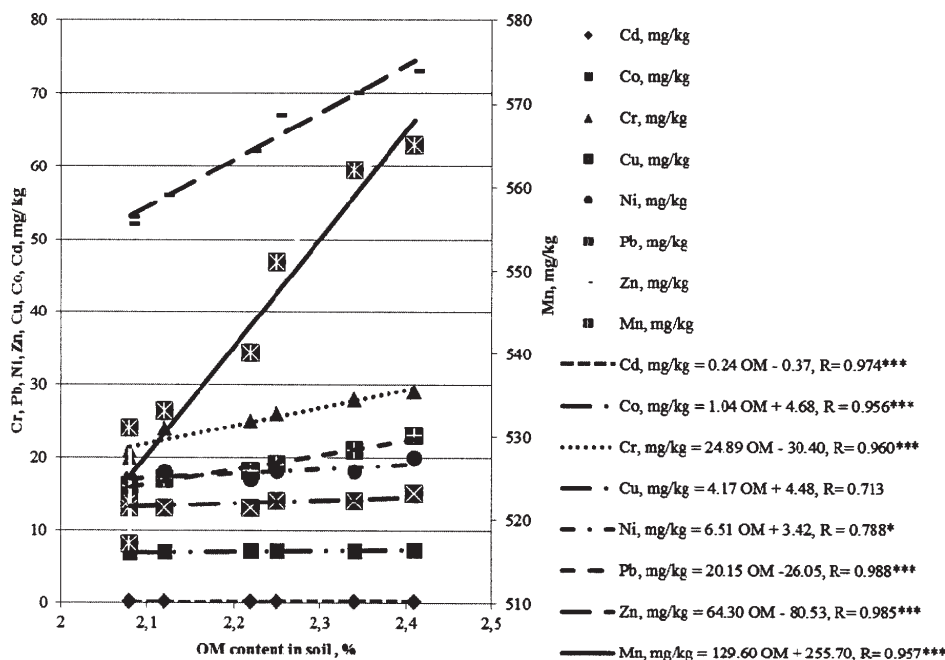


Fig.2. Correlation between organic matter content and metal accumulation in soil at variants with sewage sludge applied with mineral fertilization

Analyses	N _t , %			P _{AL} , mg/kg			K _{AL} , mg/kg		
	b ₁	b ₂	Av.(b)	b ₁	b ₂	M _b	b ₁	b ₂	Av.(b)
a ₁ 0 kgN/ha	0.145	0.151	0.148a*	24	28	26a	43	68	56a
a ₂ 100 kgN/ha	0.151	0.159	0.155ab	26	29	28a	47	73	60a
a ₃ 200 kgN/ha	0.154	0.165	0.160ab	28	32	30a	51	76	64ab
a ₄ 300 kgN/ha	0.156	0.171	0.164abc	28	33	31a	58	82	70bc
a ₅ 400 kgN/ha	0.156	0.182	0.174bcd	30	38	34ab	60	93	77cd
a ₆ 500 kgN/ha	0.174	0.187	0.181cd	36	48	42bc	68	100	84de
a ₇ 600 kgN/ha	0.184	0.201	0.193d	46	53	49c	74	102	88e
Av.(a)	0.161a	0.174b	-	31a	37b	-	57a	85b	-

Table 6
MACRONUTRIENTS CONTENT FROM SOIL AFTER SEWAGE SLUDGE APPLICATION (WITHOUT/WITH MINERAL FERTILIZATION)

b₁ corresponds to N₀P₀K₀ (without mineral fertilization)

b₂ corresponds to N₁₀₀P₁₀₀K₁₀₀ (mineral fertilization)

Av - average

*Mean values accompanied by same letter (a or b) does not present significant differences (Tukey multiple comparison test - significance level 0.05)

Analyses	Cd, mg/kg			Co, mg/kg			Cr, mg/kg			Cu, mg/kg		
	b ₁	b ₂	Av.(b)	b ₁	b ₂	M _b	b ₁	b ₂	M _b	b ₁	b ₂	Av.(b)
a ₁ 0 kgN/ha	0.14	0.13	0.14a*	6.8	6.9	6.9a	20	20	20a	14	13	14a
a ₂ 100 kgN/ha	0.14	0.14	0.14a	6.9	6.8	6.9a	22	21	22a	13	14	14a
a ₃ 200 kgN/ha	0.16	0.15	0.16a	7.0	6.9	7.0a	23	24	24a	13	13	13a
a ₄ 300 kgN/ha	0.16	0.17	0.17a	6.9	7.0	7.0a	24	25	25a	14	13	14a
a ₅ 400 kgN/ha	0.18	0.19	0.19a	7.0	7.1	7.1a	25	26	26a	15	14	15a
a ₆ 500 kgN/ha	0.20	0.21	0.21a	7.1	7.1	7.1a	27	28	28a	15	14	15a
a ₇ 600 kgN/ha	0.21	0.21	0.21a	7.2	7.2	7.2a	27	29	28a	14	15	15a
Av.(a)	0.17a	0.17a	-	7.0a	7.0a	-	24a	25a	-	14a	14a	-

Table 7
METAL CONTENTS FROM SOIL AFTER SEWAGE SLUDGE APPLICATION (WITHOUT/WITH MINERAL FERTILIZATION)

b₁ corresponds to N₀P₀K₀ (without mineral fertilization)

b₂ corresponds to N₁₀₀P₁₀₀K₁₀₀ (mineral fertilization)

Av - average

*Mean values accompanied by same letter (a or b) does not present significant differences (Tukey multiple comparison test - significance level 0.05)

Mineral fertilization produced an increase from 31 mg/kg to 37 mg/kg (average values).

Sewage sludge treatments determined significant statistical differences of mobile potassium from soil. The highest level (88 mg/kg) was associated with variant that was treated with maximum quantity of sewage sludge (table 6). Mineral fertilization produced statistic significant increases of mobile potassium, average values, from 57 mg/kg (control) to 85 mg/kg (mineral fertilization, N₁₀₀P₁₀₀K₁₀₀).

The application of sewage sludge did not influence statistically the cadmium content from soil (table 7). Even if the highest concentration of cadmium (0.21 mg/kg) was found in the case of variant with sewage sludge maximum dose applied (600 kg N/ha), there is no concerns regarding accumulation of this metal in soil. Treatments with sewage

sludge indicate insignificant statistical differences of cobalt content from soil. The same trends were observed in the case of copper (table 7). In the case of chromium, it was observed that application of growing doses of sewage sludge led to slightly increases of chromium levels in soil, but with insignificant statistical differences.

Application of sewage sludge in growing doses produced accumulation of manganese in soil (table 8). The manganese concentration obtained for highest dose of sewage sludge was with 48 mg/kg higher than the concentration recorded for control variant but the concentration is below threshold set by legislation.

Nickel and lead concentrations from soil did not presented any statistic significant changes under sewage sludge treatments (table 6). In the case of zinc content from soil it has been found an increase that is statistic

Analyses	Mn, mg/kg			Ni, mg/kg			Pb, mg/kg			Zn, mg/kg			
	b ₁	b ₂	Av.(b)	b ₁	b ₂	Av.(b)	b ₁	b ₂	Av.(b)	b ₁	b ₂	Av.(b)	
Sewage sludge													
a ₁	0 kgN/ha	514	517	516a*	17	17	17a	14	16	15a	50	52	51a
a ₂	100 kgN/ha	519	531	525a	16	17	17a	15	16	16a	52	53	53ab
a ₃	200 kgN/ha	535	533	534a	17	18	18a	17	17	17a	57	56	57abc
a ₄	300 kgN/ha	543	540	542a	17	17	17a	19	18	19a	63	62	63abc
a ₅	400 kgN/ha	548	551	550a	18	18	18a	19	19	19a	65	67	66bc
a ₆	500 kgN/ha	555	562	559a	18	18	18a	20	21	21a	67	70	69bc
a ₇	600 kgN/ha	563	565	564a	19	20	20a	22	23	23a	71	73	72c
Av.(a)		540a	543a	-	17a	18a	-	18a	19a	-	61a	62a	-

b₁ corresponds to N₀P₀K₀ (without mineral fertilization)

b₂ corresponds to N₁₀₀P₁₀₀K₁₀₀ (mineral fertilization)

Av - average

*Mean values accompanied by same letter (a or b) does not present significant differences (Tukey multiple comparison test - significance level 0.05)

Table 8
METAL CONTENTS FROM SOIL AFTER
SEWAGE SLUDGE APPLICATION (WITHOUT/
WITH MINERAL FERTILIZATION)

significant from 51 mg/kg (control) up to 72 mg/kg (highest dose of sewage sludge) (table 8). There is no reason for concern regarding phytotoxicity effects of zinc.

Conclusions

Sewage sludge application and its effects on soil and environment are studied intensively because of effects on the physical and chemical properties of soil. Beside beneficial effects, there are some concerns regarding environmental risk due to heavy metals, organic pollutants and pathogenic organisms.

Our study was developed with the purpose to analyze the effect of sewage sludge application in various doses (associated or not with mineral fertilizers) on agrochemical characteristics of soil and to evaluate the potential environmental impact of metal accumulation in the soil. The analytical measurements allowed us to conclude:

- use of sewage sludge in doses equivalent with 100, 200, 300, 400, 500, 600 kg N/ha on a soil with moderate acidic reaction did not lead to significant statistically changes of soil reaction that remained in the same interval; in contrast, mineral fertilization with N₁₀₀P₁₀₀K₁₀₀ led to significant declines of pH values from 5.21 (N₀P₀K₀) to 5.12 (N₁₀₀P₁₀₀K₁₀₀);
- application of increasing doses of sewage sludge led to statistic significant increase of organic carbon from soil from 1.21% (control variant) up to 1.41%, meanwhile mineral fertilization produced no modifications;
- use of sewage sludge with total nitrogen of 2.04% (as average) produced an increase of total nitrogen from soil that is statistically significant ;
- mobile phosphorus content from soil recorded a significant statistical differences starting with sewage sludge dose equivalent with 400 kg N/ha;
- sewage sludge treatments associated or not with mineral fertilization determined statistic significant increases of mobile potassium from soil;
- the application of sewage sludge did not influenced statistically the cadmium content from soil, but in the case of chromium it was observed that application of growing doses of sewage sludge led to slightly increase of this metal in soil, but with insignificant statistical differences;
- application of sewage sludge in growing doses produced accumulation of manganese in soil but the concentration is below threshold set by legislation;
- nickel and lead concentrations from soil treated with sewage sludge did not presented significant statistical differences;
- in the case of zinc content from soil it has been found an increase that is statistic significant but without any environmental concerns;
- the levels of metals in the soil did not exceed the limits described in both Romanian and European Union regulations.

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