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TRANSLOCATION OF HEAVY METALS FROM SEWAGE SLUDGE AMENDED SOIL TO PLANT

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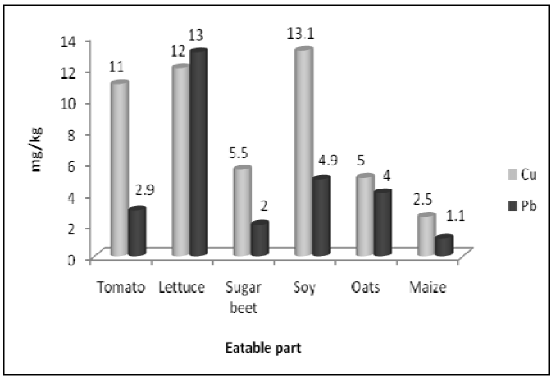
It is crucial to ensure the long-term soil quality by setting limits to the potential pollutants associated with soil amendments. The paper presents the investigations concerning the content and type of heavy metals in the sewage sludge amended soil and their translocation in different plant organs for the rates of 30 t/ha, rates which causes significant statistical changes. The experiments organized in the Greenhouse of R.I.S.S.A. Bucharest were achieved using a soil sampled from an Ao horizon of a Chromic Luvisol and sewage sludge sampled from the Wastewater Treatment Station of Piteşti. More than eight elements (Cu, Zn, Pb, Co, Ni, Mn, Cr, Cd) were determined both in the studied soil and their uptake in plants (tomato, lettuce, sugar beet, soy, oats, maize). The quantitative level of heavy metals from plants for an optimum growth expressed by tolerance index indicated lettuce with 1.70 the most tolerant and sugar beet with 0.94 the least tolerant.



INTRODUCTION

The imbalance between people and the environment, generates serious environmental implications of large and irreversible damage economic implications of paramount importance. Environmental problems have different aspects and the social development needs to be addressed with priority. They are amplified and their growing complexity is due to a direct consequence of the internal process of development of human society. One such problem is the residues from municipal wastewater treatment.[1-3]

Concerns for the elimination of these residues in the environment, without negative implications have multiple functionality. The elimination of residual products, without affecting the environment, constitutes one of major preoccupations for researchers from all fields.[4-8]

The ever higher quantities of sewage sludge coming from wastewater treatment plant need some viable solutions for both neutralization and valorization of its fertilizing elements. Lately, taking out of the agricultural circuit an increasingly surface, by its storage, led to their use on agricultural fields. In order to be used on agricultural fields, when applying the rates of sewage sludge we have to take into account the soil characteristics, the elements possibly polluting from the sewage sludge and the cultivated plant.[9-11]

During the last decades a major change has been noticed in the ways sludge is disposed. Prior to 1998, municipal sludge was primarily disposed at sea waters or was used as a fertilizer on

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agricultural land. An alternative was sludge incineration or simply land filling. Since 1998 onwards, European legislation (UWWTD) prohibits the sea disposal of sewage sludge, in order to protect the marine environment and so in parallel sludge deposits in landfills will be phased out (yet 35-45% of the sludge in Europe is still land filled).

It is true to say, the agricultural use has become the principal disposal method for sewage sludge; 37% of the sludge produced is being utilized in agriculture, 11% is being incinerated, 40% is land filled while 12% is used in some other areas such as forestry, silviculture, land reclamation, etc.

The latest trends in the field of sludge management, *i.e.* combustion, wet oxidation, pyrolysis, gasification and co-combustion of sewage sludge with other materials for further use as energy source, have generated significant scientific interest.[12,13]

In 2003, in Roumania, there were 416 municipal treatment plants. About 9.33% (7901 t/yr) of primary sludge, 28.51% (3922 t/yr) of secondary sludge and 8.59% (9845 t/yr) mixed sludge are applied for agricultural purposes.

To be applied on agricultural lands, sewage sludge meets the following criteria:

- not to be a source of pathogenic organism (in Roumania sludge is decontaminated by mesophilic anaerobic digestion and the lime stabilization of liquid sludge); in other countries, many other methods are used: pasteurization, incineration, composting, irradiation, aerobic digestion, lime treatment to high pH;
- not to contain heavy metals or synthetic organic compounds (polychlorinated biphenyls, etc.) over maximum allowable limits;
- to be applied according to prescribed technologies: suitable land, rates, time and means of application, adequate crop structure and rotation, intervals etc.;
- a system to monitor environmental quality is necessary.

In Roumania, sewage sludge is considered mainly as a phosphorus source and as an organic matter source, taking into account the low content of available phosphorus for 6330 thousand ha and the low supply of humus for 7485 thousand ha of agricultural land. More than 1.5 million ha arable land show Zn deficiency, while sewage sludge contains this microelement in a high enough quantity.

In this study we aimed to identify the effect of sewage sludge upon main chemical soil properties, heavy metals content in soil and their translocation in different plants organs.

EXPERIMENTAL

Experimental part

In order to emphasize the influence of sewage sludge upon the Chromic Luvisol physical-chemical characteristics but also upon its productivity and quality, experiments have been organized in vegetation pots, the experiments being materialized in the administration of sewage sludge increasing rates from 0 to 240 t/ha. When fertilizing with sewage sludge, we have to choose the plants which will assure the highest degree of valorisation of the sludge fertilizing potential, having to gather smaller quantities of heavy metals in order to diminish the risk for the trophic chain.

In order to follow the heavy metals accumulation from the sludge in the soil and their translocation in different plant organs, there have been used: maize, barley, soy, lettuce, beet, tomatoes.

Characterization of sewage sludge and soil

The dry sewage sludge used in the experiments had the following concentrations of heavy metals (Table 1).

By comparing the heavy metal contents of sewage sludge with the maximum allowable limits for agricultural use of sewage sludge in Roumania or with those of the EC Directive nr. 86/278/EEC, generally, the used sewage sludge surpassed the maximum admitted charge of heavy metals (Table 2).

Table 1

Heavy metals content of sewage sludge used in the experiments

No.	Parameter	M.U.	Value
1	Cu	mg/kg	558
2	Zn	mg/kg	3240
4	Mn	mg/kg	630
5	Pb	mg/kg	375
6	Cd	mg/kg	48
7	Co	mg/kg	28
8	Ni	mg/kg	21
9	Cr	mg/kg	760

Table 2

The maximum allowable limits for agricultural use of sewage sludge

No.	Parameter	M.U.	Roumania	EC Directive no. 86/278/EEC
1	Cd	mg/kg	10	20-40
2	Hg	mg/kg	**50**	16-25
3	Cr	mg/kg	**500**	-
4	Cu	mg/kg	500	1000-1750
5	Mn	mg/kg	1200	1200
6	Ni	mg/kg	100	300-400
7	Pb	mg/kg	300	750-1200
8	Zn	mg/kg	2000	2500-4000

Table 3

Chemical characteristics of Chromic Luvisol used in the experiments

No.	Parameter	M.U.	Value
1	pH	-	5.46
2	Organic carbon	%	1.19
3	Total nitrogen	%	0.140
4	Mobil phosphorus	mg/kg	19.0
5	Mobil potassium	mg/kg	40.0
6	Cadmium	mg/kg	0.11
7	Lead	mg/kg	13.0
8	Zinc	mg/kg	48.0

The allowable limits for heavy metals contents of sewage sludge for agricultural use in Roumania could be considered more severe as compared to those established by EPA in the USA or to the European Union recommendations, or too lenient as compared to those of Denmark, Finland, Norway or Sweden.

Experiments organized in pots were made using a soil material collected from an Ao horizon of a Chromic Luvisol, its chemical characteristics being presented in Table 3. The soil has a medium fertility.

Parameters of wastewater treatment plant

Sewage sludge was collected from the Wastewater Treatment Plant of Piteşti. Some data in connection with the wastewater treatment plant are given below (Table 4): population served over 150,000; main industrial activity of Piteşti town: tannery, furniture industry, tyre manufacture, textiles; daily amount of wastewater treated: 14,800 m^3; primary and secondary treatment, suspended solids and activated sludge removal; sludge treatment: anaerobic digestion and drying on platforms; current sewage sludge disposal practice: landfill and sometimes land spreading.

Chemical analyses

The following soil parameters were measured: pH in water suspension (1:2.5) by potentiometric method (pH-meter Hanna Instruments, USA); organic C, by dichromate oxidation (Walkley-Black method); total N, by the Kjeldahl method (Gerhardt Vapodest automatic analyzer); mobile P and K extraction with 0.1 M ammonium lactate - 0.4 M acetic acid solution at pH 3.7 (Egner Riehm Domingo method) followed by spectrophotometric (Cecil 2041 UV/VIS spectrophotometer) determination of P as a phosphomolybdenum blue and flame-photometric (Sherwood Scientific 410 flame photometer) determination of K; total forms of Cd, Co, Cu, Pb, Mn, Ni, Cr and Zn by microwave digestion (Milestone Ethos Pro Labstation) with aqua regia (3:1 HCl:HNO_3) and soluble forms of Cd, Co, Cu, Pb, Mn, Cr, Ni and Zn extraction with NH_4NO_3 (1M) followed by determination using atomic absorption spectrometry (Thermo Scientific AA Spectrometer, Flame/Furnace).

Plant samples were analysed for: heavy metals content by digestion with a mixture of acid: HNO_3-$HClO_4$ followed by determination using atomic absorption spectrometry.

All solutions were prepared with analytical grade reagents and deionised water purified through the Direct Q Smart UV system (Millipore). For the calibration curve was used stock solution provided by Merck.

Table 4

Some parameters of wastewater treatment plant

No.	Parameter	Entry	Exit
		mg/L	mg/L
1	Total solids	130	24-25
2	BOD_5^{*}	100	22
3	COD^{**}	20	6
4	Total P	-	0.6

* biochemical oxygen demand at 20°C over 5 days
** chemical oxygen demand

RESULTS AND DISCUSSION

Chemical composition of the sewage sludge used in the experiments (presented in Table 1) showed that this material is an important source of organic matter and nutrients for agricultural soils (which recommends its use as fertilizer, Fig. 1).

The application of sewage sludge in soil has positive effects on soil organic matter and on soil reaction. But high doses of sewage sludge incorporated in soil may determine high accumulations of extractable forms of Copper, Zinc, Lead, Nickel, and Cadmium.[14-16]

In order to avoid high accumulation of heavy metals in soil[17, 18, 2, 19] it is recommended to apply annually sewage sludge in soil in amounts which should not increase the heavy metal concentrations with more than the values presented in the Table 5.

Additionally, by annually applying of sewage sludge in soil it should be avoided accumulation of maximum permissible rates in soil (Table 6).

Application of sewage sludge as fertilizer has increased the organic carbon content and soil nutrient content (nitrogen, phosphorus and potassium), the increase being statistically significant (Figs. 2, 3, 4 and 5).

From these figures is evident that the changes in soil fertility confirm the fertilizer potential of the sludge and support its agricultural use as an organic fertilizer.[14, 0-22]

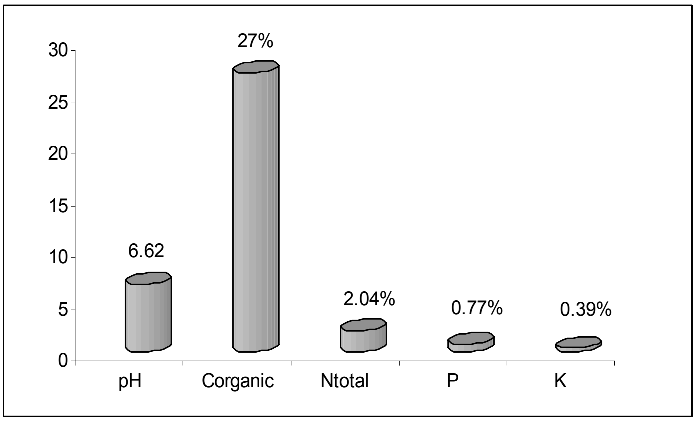

Fig. 1 – Main chemical characteristics of sewage sludge.

Table 5

The heavy metals concentration of soil

No.	Parameter	M.U.	Value
1	Cu	kg/ha	10
2	Zn	kg/ha	25
3	As	kg/ha	0.35
4	Se	kg/ha	0.2
5	Pb	kg/ha	10
6	Cd	kg/ha	0.1
7	Hg	kg/ha	0.4
8	Ni	kg/ha	2
9	Cr	kg/ha	10

Table 6

Maximum permissible amounts of heavy metals in soil

No.	Parameter	M.U.	Value
1	Cu	mg/kg	50-100
2	Zn	mg/kg	150-300
3	As	mg/kg	20
4	Se	mg/kg	5
5	Pb	mg/kg	50-100
6	Cd	mg/kg	1-3
7	Hg	mg/kg	2
8	Ni	mg/kg	30-50
9	Cr	mg/kg	100

Research has shown that the plants cultivated on the same types of soil behave in a different way when applying the same treatment, they give different productions, they gather quantities of different polluting substances and they have different sprouting sensitivities.[23]

The sludge fertilization resulted in a significant increase in humus, nitrogen and phosphorus of the chromic luvisol.

At the same time with the significant increase of the macroelement contents in soil, it was observed a significant increase in heavy metals when high rates of sewage sludge were applied (Table 7).

In general, by applying the sewage sludge on agricultural fields the crop production increases due to high content in fertilizing elements of the sludge. In addition, the research showed that there is a trend of production increase as a consequence of fertilization with sewage sludge for most of the crop plants, but, on the other hand, by increasing the rates of sludge, the crop production decreases (Fig. 6).

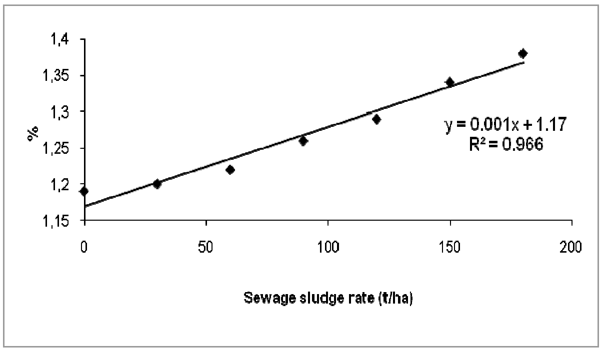

Fig. 2 – Effects of sewage sludge and mixed fertilization on the organic carbon content of Chromic Luvisol.

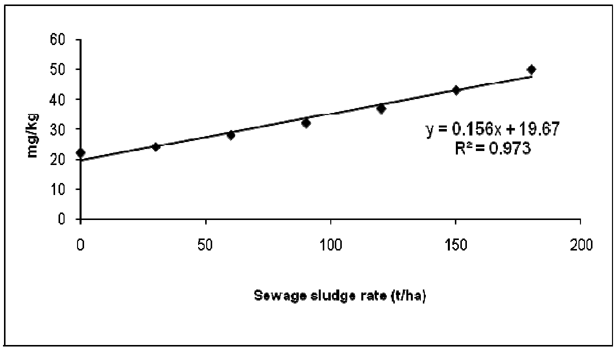

Fig. 3 – Effects of sewage sludge and mixed fertilization on the mobile phosphorus content of Chromic Luvisol.

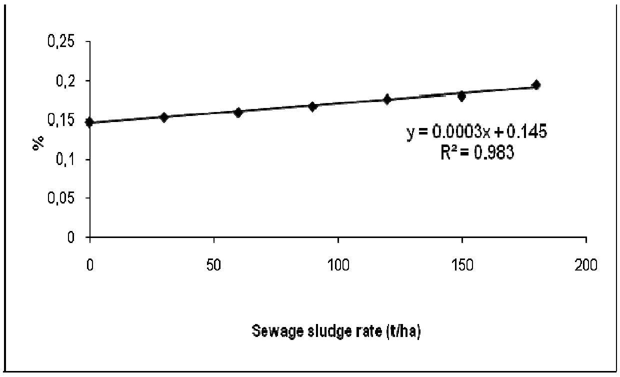

Fig. 4 – Effects of sewage sludge and mixed fertilization on the total nitrogen content of Chromic Luvisol.

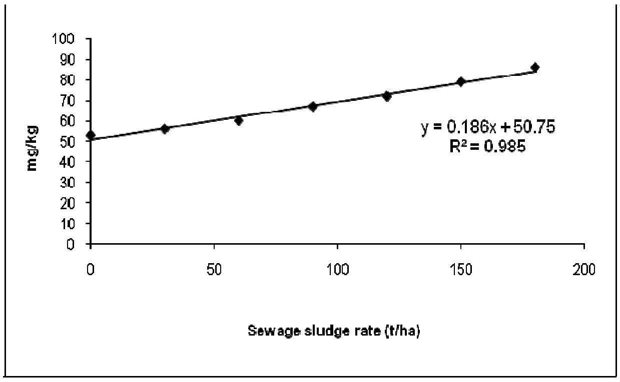

Fig. 5 – Effects of sewage sludge and mixed fertilization on the mobile potassium content of Chromic Luvisol.

Table 7

Accumulation of heavy metals in Chromic Luvisol fertilization with sewage sludge

Treatment	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Co (mg/kg)	Ni (mg/kg)	Mn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)
Control	18.9	68.1	18.9	10.4	22.2	268	43	0.7
30 t/ha	21.9	69.3	20.9	10.8	24.2	257	49	0.9
60 t/ha	26.7	72.1*	21.3	11.6**	24.8	256	58	1.3
90 t/ha	28.0	75.3**	21.5	11.5**	25.5	242**	75***	1.6*
120 t/ha	32.9*	74.9*	22.9	11.8***	26.8*	241***	92***	1.5
150 t/ha	34.0*	79.1***	22.2	11.8***	27.2**	236***	83***	2.1**
180 t/ha	37.4*	83.5***	23.0	11.8***	30.2***	298***	105***	2.2**
210 t/ha	49.3***	85.2***	26.9*	12.0***	32.5***	309***	122***	2.3**
240 t/ha	51.4***	87.1***	27.2*	12.1***	33.0***	302***	157***	2.3**
DL 5%	*14*	*5*	*6*	*0.7*	*4*	*14*	*17*	*0.9*
DL 1%	*19*	*7*	*9*	*1.0*	*5*	*19*	*23*	*1.3*
DL 0.1%	*26*	*10*	*12*	*1.4*	*7*	*27*	*32*	*1.7*

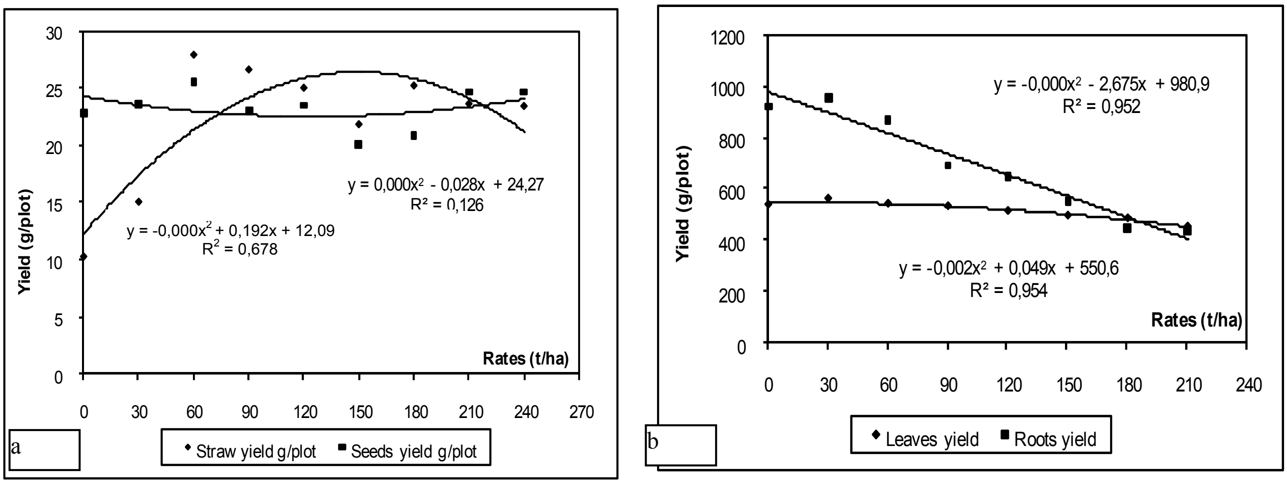

Fig. 6 – Influence of sewage sludge upon production a) oats; b) sugar beet.

A special issue is represented by the heavy metals translocation in soil and in different plant tissues. Most research has shown that inside the grains the metals concentration is seldom significant in order to prohibit its use for animal feeding.[24-27]

The research has shown that the first crop which follows after the sludge application has a higher content of metals in tissues.

If the sludge application doesn't repeat any longer, the heavy metals content of the subsequent crops will decrease until a stable level will be attained, which will be however still higher than the untreated control pot.

Even for the soils where the sludge application ceased a long time ago, the plants tissues continue to have high contents in heavy metals.

For the sewage sludge used in experiments, significant statistical changes appeared for some crops when applying some bigger rates of 30 t/ha.

Taking into account the heavy metals concentrations, the sewage sludge rates applied in the soil should be adapted in order to avoid the risk of excessive heavy metals accumulations in soil and its translocation in plant. For estimating the effect of sewage sludge on plant quality the tolerance index and the concentration index were calculated in case of 30 t/ha rate applied. This rate incorporated in soil determined significant changes. The tolerance index expresses the quantitative level of heavy metals from plants for an optimum growth. The tolerance index, calculated as a ratio between the production obtained in the treated variants and that of non-treated variants, for the investigated crops had the following values from the most tolerant to the less tolerant: lettuce (1.70), maize (1.47), soy (1.39), oats (1.09), tomatoes (1.07) and sugar beet (0.94). High concentrations of heavy metals can inhibit the growth of certain plants causing decrease the crop yields. Phytotoxicity and growth reduction are very different from one level to another. The copper is phytotoxical in relatively small quantities, while the lead has very high phytotoxicity for the plants. Perrenial grasses are relatively resistant to zinc, while the sugar beet is more sensitive. The results clearly emphasize the trend of heavy metals accumulation in the soil (total and acccessible forms) and their tendency of translocation in plant. But there is a high variability of heavy metals concentrations in plants (Fig. 7).

Other studies noted that the heavy metals extracted by DTPA(diethylenetriaminepentaacetic acid) showed increases of its concentrations with the sludge rates and elevated bioavailability for the crops.[28]

According to regulations concerning the environmental pollution evaluation, the Roumanian guideline values for heavy metal in agricultural soils are as follows (Table 8).

In comparison with these limits, it can be observed that significant changes occurred for almost all analyzed elements.

Variation of the elements concentration in plant tissues due to sewage sludge application in soil represents a qualitative effect which may be expressed by calculating the concentration index (which is the ratio between the concentration in treated plants and the concentration in untreated plants). The values of the concentration index for the analyzed heavy metals from plant leaves and seeds used in this experiment are presented in Table 9.

Calculating the concentration index for all the analyzed metals has led to the crops distribution depending on this index. The obtained results emphasize the possible presence of a bigger concentration of metals in the lettuce, beet and tomatoes leaves than in the leaves of oats, maize and soy and bigger concentrations in the eatable part of soy, beet and tomatoes plants.

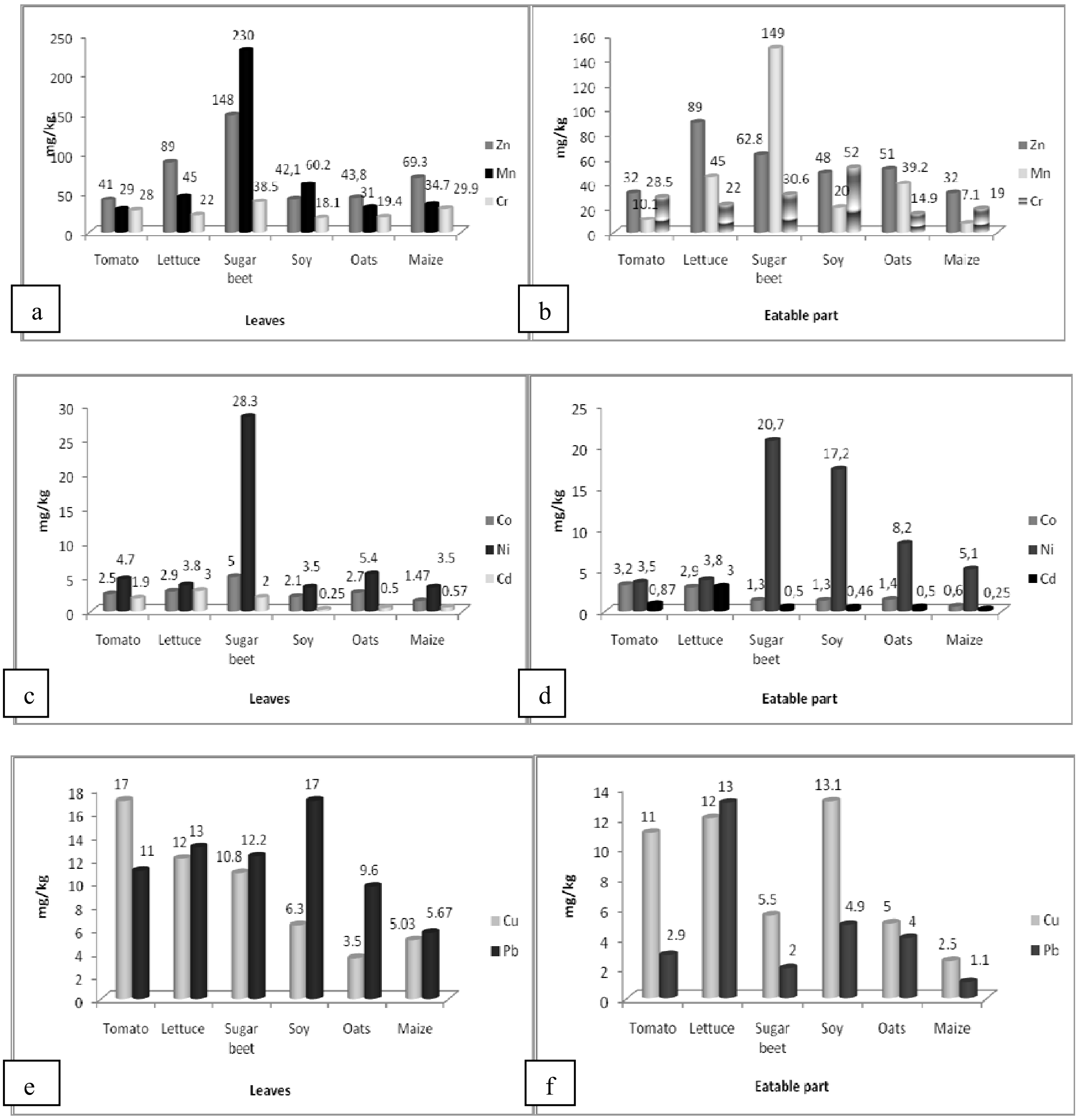

Fig. 7 – Concentration of heavy metals in different plant organs under application of a 30 t/ha rates of sewage sludge: a) Zn, Mn, Cr in leaves; b) Zn, Mn, Cr in eatable part; c) Co, Ni, Cd in leaves; d) Co, Ni, Cd in eatable part; e) Cu, Pb in leaves; f) Cu, Pb in eatable part.

Table 8

Values for heavy metal in agricultural soils

No.	Parameters	Alert values (mg/kg)	Action trigger values (mg/kg)	The maximum allowable levels of heavy metals in soil (with pH>6.5) treated with sewage sludge (mg/kg)	Limits recommended by the EU (mg/kg)
1	Cd	3	5	3	1-3
2	Cr	100	300	100	100-150
3	Co	50	50	-	-
4	Cu	100	200	100	50-140
5	Pb	50	100	50	50-300
6	Mn	1500	2500	-	-
7	Ni	75	150	50	30-75
8	Zn	300	600	300	150-300

Table 9

Concentration index for the analysed metals in the plants leaves and seeds used in the experiments (for 30 t/ha rates)

Cu (mg /kg)		Zn (mg/ kg)		Pb (mg/ kg)		Co (mg/ kg)		Ni (mg /kg)		Mn (mg/ kg)		Cr (mg/ kg)		Cd (mg/ kg)	
Leaves	*Eatable part*	Leaves	*Eatable part*	Leaves	*Eatable part*	Leaves	*Eatable part*	Leaves	*Eatable part*	Leaves	*Eatable part*	Leaves	*Eatable part*	Leaves	*Eatable part*
Tomato 1.29	*Soy 1.39*	Sugar beet 1.48	*Maize 1.33*	Tomato 1.57	*Oats 1.14*	Soy 2.1	*Tomato 1.28*	Lettuce 1.52	*Oats 1.21*	Sugar beet 1.40	*Tomato 1.33*	Soy 1.19	*Tomato 1.32*	Lettuce 2.09	*Tomato 1.85*
Lettuce 1.20	*Tomato 1.10*	Maize 1.43	*Soy 1.20*	Lettuce 1.16	*Tomato 1.12*	Tomato 1.36	*Soy 1.26*	Maize 1.09	*Sugar beet 1.19*	Tomato 1.34	*Sugar beet 1.06*	Tomato 1.17	*Soy 1.13*	Oats 1.67	*Soy 1.39*
Sugar beet 1.16	*Sugar beet 1.09*	Soy 1.29	*Sugar beet 1.10*	Oats 1.14	*Soy 1.04*	Oats 1.17	*Maize 1.10*	Soy 1.06	*Tomato 1.17*	Oats 1.21	*Soy 1.00*	Lettuce 1.16	*Oats 1.11*	Sugar beet 1.42	*Sugar beet 1.0*
Maize 1.10	*Maize 1.04*	Tomato 1.28	*Tomato 1.10*	Maize 1.01	*Sugar beet 0.95*	Lettuce 1.16	*Oats 1.08*	Oats 1.04	*Soy 1.11*	Maize 0.99	*Oats 0.89*	Oats 1.03	*Sugar beet 1.03*	Maize 1.07	*Oats 1.0*
Oats 1.0	*Oats 0.94*	Lettuce 1.22	*Oats 1.06*	Soy 1.04	*Maize 0.8*	Sugar beet 1.1	*Sugar beet 1.0*	Sugar beet 1.04	*Maize 1.02*	Soy 0.88	*Maize 0.84*	Maize 1.02	*Maize 0.79*	Soy 1.0	*Maize 1.0*
Soy 0.91		Oats 1.19		Sugar beet 1.05		Maize 0.91		Tomato 0.96		Lettuce 0.74		Sugar beet 0.99		Tomato 0.88	

The results regarding the concentration of heavy metals after application of a rate of 30 t/ha of sewage sludge in soil show an important variability of the heavy metals concentration in different plant organs.

Data reported in the literature states as normal level in plants the values that are less than 0.5 mg/kg Cd, 8 mg/kg Cu, 3 mg/kg Pb, 40 mg/kg Zn, although it is agreed that plant genotype is an important factor, which could induce other contents, different from those considered normal.

CONCLUSIONS

Fertilization with sewage sludge resulted in yield increases, but the production decreased with increasing the rate of sewage sludge applied (120 t/ha for oats and 90 t/ha for sugar beet).

Sewage sludge applications determine significant increase of soil content in organic carbon (of 1.19% to 1.38%), total nitrogen (of 0.174% to 0.194%), mobile phosphorus (of 22 mg/kg to 50 mg/kg) and mobile potassium (of 53 mg/kg to 86 mg/kg). Highest rates (240 t/ha) have the highest effect.

Total content of Cu, Zn, Pb, Ni, Mn, Co, Cr and Cd is significantly changed with the increase of the sewage sludge rates.

The 30 t/ha sewage sludge rate did not cause significant statistical changes of the chemical composition of the studied plants.

Crops distribution depending on the concentration index show the following order: lettuce (1.70), maize (1.47), soy (1.39), oats (1.09), tomatoes (1.07) and sugar beet (0.94).

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