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Effect of sewage sludge treatment on mobility and soil-plant transfer of Cu, Mn, Ni and Zn

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Abstract
A pot experiment was set up for examining the effect of sewage sludge loads on soils and barley plants (Ni, Mn, Cu and Zn status). Four soils were tested as follows: acid and calcareous sandy soils as well as heavier acid and calcareous loamy soils with different basic soil properties. The examined soil nutrient fractions were: ammonium-acetate + EDTA extractable and pseudo total (cc. HNO_3 + H_2O_2 digestion). The applied sewage sludge loads were: 0, 2.5, 5, 10 and 20 g sludge dry matter / kg air-dry soil. Number of treatments was 80 (4 soil types x 5 sludge load levels x 4 replicates). The transfer values (BCF: ratio of plant /soil element content) for both barley straw and grain were the highest on acidic sand for all investigated elements. The BCF values were decreasing in function of sludge loads in most cases. The transfer of Mn to the straw was 12 times higher than to the grain. This value for Ni and Zn was 1.5 and 1.3 respectively. The Cu transfer to the straw was only 0.78 % of the transfer to the grain. The most mobile (mobility: ratio of soil pseudo total concentration/soil NH_4-acetate + EDTA extractable fraction) element among the investigated elements was Cu. Ni was the most fixed in the soils. The investigated elements were the most mobile on acidic sand.

Key words: barley, heavy metal, sewage sludge, soil type

Introduction
The most cost effective treatment of sludge is the agricultural utilisation (Wittchen and Püschel, 1995). The benefits of sewage sludge application to agricultural soils as a source of nutrients and soil conditioner have been widely acknowledged. Next to the positive effects there are harmful consequences as well. The sewage sludge may contain high concentrations of potentially toxic elements. The contamination of soils with these elements continues to be a matter of great concern because of their persistence in soils and increased uptake by crop plants, even many years after sludge applications (Kádár, 1999; Simon et al., 2000; Kelly et al., 1999). The properties of the elements and their chemical forms in soil and sludge may strongly influence their uptake by plants or their leaching (Pichtel and Anderson, 1997; Ortiz and Alcañiz, 2006). Sewage sludges have different properties depending on their origin (Moser and Pálmai, 1999). The objective of this work was to study communal-industrial sewage sludge application in barley crops growing in acidic sand and loam as well as calcareous sand and loam. Transfer of potentialy toxic elements from soil to plant and the mobility of these elements are discussed.

Material and methods
A pot experiment was set up in 1999 (Kádár and Morvai, 2007). Four soils were used from the plough layer (0-20 cm) of the field experimental stations of RISSAC (Table 1).

Table 1. Some properties of soil samples at the establishment of the experiment in 1999 (based on Kádár and Morvai, 2007)

Parameter	Nyírlugos	Őrbottyán	Nagyhörcsök	Gyöngyös
	acid sand	calc. sand	calc. loam	acid loam
pH (KCl)	3.9 – 4.8	7.3 – 7.6	7.5 – 7.6	5.8 – 6.3
$CaCO_3$ %	–	10 – 13	8 – 10	–
Clay (<0.002 mm) %	3 – 4	4 – 5	20 – 24	40 – 45
Organic matter %	0.5 – 0.8	0.6 – 0.8	2.6 – 3.0	3.0 – 3.5

The soils were treated with communal-industrial sludge. The mixture of air-dried soil (<5 mm particle size) and the air-dry sludge was placed into 10-liter pots (10 kg soil). In order to have soil water supply under control, the pots were kept in open-air conditions, but protected by the roof. Soils were irrigated with deionised water according to the plant water requirements. The applied sewage sludge loads were as follows: 0, 2.5, 5, 10 and 20 g sludge D.M. / kg air-dry soil. Number of treatments were: 4 soil x 5 load level = 20, with 4 replications.

The soil and sludge mixing was followed by 1-month incubation, then spring barley and after its harvest and removal of the roots peas was sown. The barley had 3 months growing period. Soil sampling was taken after peas harvest on 20th October. Composite soil samples consisted of 20 cores/pot and total above-ground plant mass was used for analysis and yield assessment. Before soil sampling, the soil was sieved in order to remove plant residues. In this paper only the results with barley are discussed.

Determination of plant, soil pseudo total and compost element concentrations was carried out with ICP-AES method, after microwave teflon bomb digestion with cc. HNO_3 + H_2O_2 (MSZ 21470-50:2006). In the soil samples, the pseudo total and the mobile element concentrations were estimated, using 0.5 M NH_4-acetate + 0.02 M EDTA extraction (Lakanen and Erviö, 1971), followed by ICP-AES measurement.

Results and discussion

Amongst the harmful elements that were in high concentrations in sludge, Cu, Mn, Ni and Zn are discussed in this paper. The content of Zn soluble in cc. HNO_3 + H_2O_2 was 6157, Cu reached 1885, Ni 159 and Mo 7 mg/kg in the sludge. Table 2 and 3 show the transfer of the examined elements to the barley grain and straw. The transfer of the elements from soil to plant can be described by bioconcentration factor (BCF), what is equal to the ratio between plant element concentration and its concentration in soil NH_4-acetate + EDTA extractable fraction.

Considering grain, the BCF values for each element decreased significantly except for Mn and Ni on acidic loam and Ni on calcareous loam. The highest value (10.3) can be seen on acidic sand in the case of Zn. The average BCF values were the highest on acidic sand for all elements. The sequence of elements by their transfer to the grain was the following: Zn, Cu, Ni and Mn.

The BCF for straw decreased in most cases but there were exceptions. On acid sand the transfer of Zn as well as the transfer of Mn on calcareous sand did not change in function of sludge loads.

Table 2. Bioconcentration factor for barley grain (BCF = Ratio of plant element concentration/soil NH_4-acetate + EDTA extractable fraction)

Element	Soil	Load (g sludge D. M. / kg soil)					LSD 5%	Average
		0	2.5	5	10	20		
Cu BCF	acid sand	7.08	4.27	3.64	1.46	1.07	1.72	3.50
	calc. sand	2.72	2.16	2.21	1.02	0.64	0.65	1.75
	calc. loam	2.32	1.47	1.32	0.86	0.50	0.32	1.29
	acid loam	0.88	0.67	0.51	0.45	0.50	0.15	0.60
	Average	3.25	2.14	1.92	0.95	0.68		1.79
Mn BCF	acid sand	0.92	0.88	0.90	0.90	0.67	0.22	0.85
	calc. sand	0.17	0.18	0.17	0.16	0.15	0.02	0.17
	calc. loam	2.32	1.47	1.32	0.86	0.50	0.01	0.08
	acid loam	0.05	0.05	0.05	0.05	0.05	0.01	0.05
	Average	0.87	0.64	0.61	0.49	0.34		0.29
Ni BCF	acid sand	1.96	1.47	1.12	0.55	0.45	0.43	1.11
	calc. sand	0.73	0.30	0.18	0.16	0.10	0.34	0.29
	calc. loam	0.11	0.09	0.14	0.07	0.09	0.08	0.10
	acid loam	0.03	0.04	0.03	0.03	0.03	0.02	0.03
	Average	0.71	0.47	0.37	0.20	0.17		0.38
Zn BCF	acid sand	10.3	10.0	7.1	3.5	2.5	4.2	6.7
	calc. sand	4.5	3.8	4.2	1.6	1.0	1.3	3.0
	calc. loam	3.3	2.7	2.6	1.5	0.9	1.2	2.2
	acid loam	2.7	1.8	1.3	1.1	1.3	0.5	1.6
	Average	5.2	4.6	3.8	1.9	1.4		3.4

On calcareous loam only the BCF value of Zn changed whereas the transfer of the other elements remained the same in every treatment. This means that on this soil type the uptake of Cu, Mn and Ni increased as much as the concentration of these elements changed in the soil mobile fraction. On acid loam, the Ni had the same BCF value in every treatment. The highest BCF values for straw can be found on acidic sand in the case of Mn (12.4) and Zn (11.7). The highest BCF values for straw were on acidic sand in all elements. The sequence of elements regarding their transfer to the straw was: Zn, Mn, Cu and Ni.
The BCF values for straw and grain were evaluated by linear regression. The slope of the regression line showed that the transfer of Mn to the straw was 12 times higher than to the grain. The transfer of Ni and Zn to the straw was 1.5 and 1.3 times more than to the grain respectively. In the case of Cu the BCF value for the straw was lower than that for the grain. The Cu transfer to the straw was only 0.78 % of the transfer to the grain.

The BCF can be interpreted as an indicator of the element mobility in the soil-plant system. The other aspect of the mobility of an element can be its solubility in the soil solution. This mobility can be defined as the ratio of different mobile fractions of the element. The mobility of elements in our experiment was defined as a ratio of pseudo total element content to NH_4-acetate + EDTA extractable element content. The higher this value the lower the mobility of the given element (Table 4). The most mobile among the investigated elements was Cu. Ni was the most fixed in the soils: the pseudo total concentration was 14 times higher than the extractable. The mobility of the elements decreases in function of sludge loads as did the BCF. But the mobility of Cu on calcareous sand as well as Mn on loamy soils and acidic sand did not change significantly.

Table 3. Bioconcentration factor (BCF = Ratio of plant element concentration/soil NH_4-acetate + EDTA extractable fraction) for barley straw

Element	Soil	Load (g sludge D. M. / kg soil)					LSD 5%	Average
		0	2.5	5	10	20		
Cu BCF	acid sand	6.16	2.84	3.10	2.07	1.65	1.47	3.16
	calc. sand	3.17	1.75	1.64	0.93	0.79	1.40	1.66
	calc. loam	2.43	1.38	1.87	2.67	0.41	2.38	1.75
	acid loam	0.89	0.56	0.54	0.41	0.47	0.24	0.58
	Average	3.16	1.63	1.79	1.52	0.83		1.79
Mn BCF	acid sand	12.38	10.35	10.64	9.59	4.56	2.84	9.51
	calc. sand	0.46	0.44	0.49	0.45	0.45	0.11	0.46
	calc. loam	0.38	0.40	0.30	0.37	0.36	0.08	0.36
	acid loam	0.17	0.15	0.17	0.13	0.11	0.04	0.15
	Average	3.35	2.83	2.90	2.64	1.37		2.62
Ni BCF	acid sand	3.28	2.28	1.68	1.02	0.48	1.41	1.75
	calc. sand	0.92	0.53	0.71	0.41	0.42	0.30	0.60
	calc. loam	0.29	0.18	0.32	0.20	0.19	0.21	0.23
	acid loam	0.09	0.11	0.07	0.08	0.11	0.07	0.09
	Average	1.14	0.77	0.70	0.43	0.30		0.67
Zn BCF	acid sand	11.7	12.7	11.9	7.5	5.4	7.7	9.8
	calc. sand	3.6	2.9	4.0	1.8	1.6	1.4	2.8
	calc. loam	2.9	2.3	2.6	1.8	1.2	1.7	2.2
	acid loam	2.8	1.8	1.4	1.1	1.4	0.4	1.7
	Average	5.2	4.9	5.0	3.0	2.4		4.1

Table 4. Mobility of Cu, Mn, Ni and Zn (Ratio of soil pseudo total concentration/soil NH_4-acetate + EDTA extractable fraction)

Element	Soil	Load (g sludge D. M. / kg soil)					LSD 5%	Average
		0	2.5	5	10	20		
Cu mobility	acid sand	5.57	3.75	3.36	1.99	1.99	1.93	3.33
	calc. sand	3.14	2.98	3.29	2.23	2.50	1.75	2.83
	calc. loam	7.12	5.30	5.05	3.19	2.68	1.06	4.67
	acid loam	5.02	3.44	3.00	2.75	3.67	1.20	3.57
	Average	5.21	3.87	3.68	2.54	2.71		3.60
Mn mobility	acid sand	5.00	5.96	6.68	6.49	5.86	1.01	6.00
	calc. sand	3.72	3.41	3.28	3.32	3.31	0.22	3.41
	calc. loam	3.55	3.36	3.30	3.73	3.50	0.37	3.49
	acid loam	3.17	2.99	3.08	3.13	3.13	0.27	3.10
	Average	3.86	3.93	4.09	4.17	3.95		4.00
Ni mobility	acid sand	45	28	21	11	8	8	23
	calc. sand	22	18	17	11	8	3	15
	calc. loam	15	13	13	13	11	1	13
	acid loam	5.2	4.9	4.9	4.8	4.8	0.4	4.9
	Average	22	16	14	10	8		14
Zn mobility	acid sand	4.80	4.34	3.32	3.46	2.03	2.30	3.59
	calc. sand	3.67	2.87	3.47	2.15	2.01	1.61	2.83
	calc. loam	8.45	7.52	7.04	3.58	2.73	3.11	5.86
	acid loam	7.01	4.82	4.18	3.54	4.67	1.35	4.84
	Average	5.98	4.89	4.50	3.18	2.86		4.28

The investigated elements were the most mobile on acidic sand: the ratio between the pseudo total and NH_4-acetate + EDTA extractable fraction was 9 in the average of all elements. On the two calcareous soils this value was about 6 and on acidic loam it was 4.

Conclusions

Based on the results of this experiment it can be concluded that the transfer values for either straw and grain (BCF: ratio of plant element concentration/soil NH_4-acetate + EDTA extractable fraction) were the highest on acidic sand in all investigated elements (Cu, Mn, Ni and Zn). The BCF values were decreasing in function of sludge loads in most cases. The transfer of Mn to the straw was 12 times higher than to the grain. This value for Ni and Zn was 1.5 and 1.3 respectively. The Cu transfer to the straw was only 0.78% of the transfer to the grain. The most mobile (Mobility: ratio of soil pseudo total concentration/soil NH_4-acetate + EDTA extractable fraction) element among the investigated elements was Cu. Ni was the most fixed in the soils. The investigated elements were the most mobile on acidic sand soil.

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References

Kádár I. (1999). Contamination of the food chain with heavy metals. (In Hungarian) Agrokémia és Talajtan. 48: 561-581.

Kádár I., and Morvai B. (2007). Effect of industrial-municipal sewage sludge loads in pot experiments. (In Hungarian) Agrokémia és Talajtan. 56: 333-352.

Kelly J. J., Häggblom M., Tate R. L. (1999). Effects of the land application of sewage sludge on soil heavy metal concentrations and soil microbial communities. Soil Biology and Biochemistry. 31: 1467-1470.

Lakanen E., and Erviö R. (1971). A comparison of eight extractants for the determination of plant available micronutrients in soils. Acta Agr. Fenn. 123: 223-232.

Moser M., and Pálmai Gy. (1999). The basics of environmental protection. (In Hungarian) Budapest. Nemzeti Tankönyvkiadó.

MSZ (2006). Environmental testing of soils. Determination of total and soluble toxic element, heavy metal and chromium (VI) content. (In Hungarian) [MSZ21470-50:2006] Hungarian Standard Association, Budapest.

Ortiz O., and Alcañiz J. M. (2006). Bioaccumulation of heavy metals in Dactylis glomerata L. growing in a calcareous soil amended with sewage sludge. Bioresource Technology. 97: 545-552.

Pichtel J., and Anderson M. (1997). Trace metal bioavailability in municipal solid waste and sewage sludge composts. Bioresource Technology. 60: 223-229.

Simon L., Prokisch J., Győri Z. (2000). Effect of municipal sewage sludge compost on heavy metal accumulation of maize (Zea mays L.) (In Hungarian). Agrokémia és Talajtan. 49: 247-255.

Wittchen F., and Püschel M. (1995). Ausgangssituation und Zielstellung der Klärschlammbehandlung und -entsorgung. Das Gas- und Wasserfach, Wasser, Abwasser. 136: 23-31.