# Comparison of municipal and tannery sludge effect on soil Cr mobility and barley bio accumulation

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## Abstract

A pot experiment was set up to investigate the effect of municipal and tannery sewage sludge loads on four soils (acid and calcareous sandy soils as well as acid and calcareous loamy more heavy soils with different basic soil properties) and plants. The examined soil element fractions were: mobilisable:  $0.5 \text{ M NH}_4$ -acetate + 0.02 M EDTA extractable and the mobile:  $1 \text{ M NH}_4\text{NO}_3$ extractable. Applied sewage sludge loads were: 0, 5, 10, 20 g sludge D.M. kg/air-dry soil.Number of treatments was: 4 soil x 2 sludge x 4 load level = 32, in 4 replications. The test plant was barley. Our results showed that the relative amount of soluble Cr content in soil does not increase by the amount of sludge loads. Thus the risk of contamination of food chain and groundwater by Cr after sludge application does not increase linearly by the volume of sludge applied.

Based on the result of this experiment one can state that Cr accumulates more in the barley straw than in the grain. In function of sludge loads the BCF values for Cr lessened.

Key words: sewage sludge, bio-concentration, Cr

#### Introduction

The sewage sludge volume is supposed to be grown with increasing sewage system and capacity of wastewater treatment. In Hungary, the amount of sewage sludge dry matter is 150-160 thousand tons per year at present. This value is supposed to be increasing to 350-400 thousand tons by 2015 (Ötvös, 2006).

The most cost effective treatment of sludge is agricultural utilisation (Csathó, 1994). The benefits of sewage sludge application to the agricultural soils as a source of nutrients and soil ameliorant have been widely acknowledged. The most positive effect of sewage sludge or compost application on field is organic matter increment, which improves also the soil physical and chemical properties (Simon et al., 2000; Izsáki and Debreczeni, 1987; 1989). However, the sewage sludge may contain high concentrations of potentially toxic elements, especially Cr.

The properties of the toxic elements and their chemical forms or types of binding in soil and in sludge may strongly influence their uptake by plants or leaching. Depending on their origin, sewage sludges have different properties that affect the availability of their metal content (Kádár, 2005). The objective of this work was to compare the influence of high Cr sewage sludges on soil mobilisable ( $NH_4$ -acetate +EDTA soluble) and mobile ( $NH_4NO_3$  soluble) fractions and barley uptake by growing on the acidic and calcareous sand and loamy soil.

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#### Materials and methods

A pot experiment was set up in 1999 for examining the effect of sewage sludge loads on soils and plants (Kádár and Morvai, 2007; 2008). Four soils were used from the plough layer (0-20 cm) of the field experimental stations of Research Institute for Soil Science and Agricultural Chemistry. Parameters of the investigated soils are shown in Table 1.

	Site /soil type					
Parameter	Nyírlugos acid sand	Őrbottyán calc. sand	Nagyhörcsök calc. loam	Gyöngyös acid loam		
pH (KCl)	3.9 - 4.8	7.3 - 7.6	7.5 - 7.6	5.8 - 6.3		
CaCO <sub>3</sub> %	-	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		

Table 1. Several properties of soil samples at the establishment of the experiment in 1999 (based on Kádár and Morvai, 2008)

The soils were treated with tannery and municipal sludge. The pre-treatment of the sludges was the following: the sludge was dried then sieved 3 times for homogenisation. The properties of the sludge are shown in Table 2.

Parameter	Unit	Municipal sludge	Tannery sludge
рН		6.1	7.4
ash	%	45	67
organic matter	%	35	11
Ν	%	2.8	3.2
Р	%	2.4	0.3
К	%	0.4	0.1
NH4-N	mg/kg	113	44
NO3-N	mg/kg	374	794
Cr	%	0.18	0.52
Са	%	4.6	21.5

Table 2. Several properties of sludge samples (Kádár and Morvai, 2007; 2008)

The mixture of air-dried soil (<5 mm particle size) and the air-dry sludge was dispensed into 10-liter pots (10 kg soil). To take soil water supply under control the pots were in field situation, but covered by roof. Soils were irrigated by deionised water according to the plants water requirement. Applied sewage sludge loads were the followings: 0, 5, 10, 20 g sludge D.M. / kg air-dry soil. Number of treatments was: 4 soil x 2 sludge x 4 load level = 32, in 4 replications.

The soil and sludge mixing was followed by 1-month incubation then spring barley (30 seeds per pot on 3<sup>th</sup> May) was sown. The barley had 3 months growing period. Soil sampling was taken on 20<sup>th</sup> October. Composite soil samples consisted of 20 cores/pot and all above-ground total plant mass was used for analysis and yield assessment.

Determination of plant, soil pseudo total and sludge element concentrations was carried out with ICP-AES method after microwave teflon bomb digestion with cc.  $HNO_3 + H_2O_2$  (ISO 11466, 1995).

From the soil samples the mobilisable: 0.5 M  $NH_4$ -acetate + 0.02 M EDTA extractable (Lakanen and Erviö, 1971) and the mobile: 1 M  $NH_4NO_3$  extractable (DIN 19730, 1995) element concentrations were measured by ICP-AES method.

Measurement of pH was carried out in 1:2,5 soil 1 M KCl solution 24 hours after mixing. The soil organic matter content was measured by oxidation with  $K_2Cr_2O_7$  according to the method of Tyurin (Hargitai, 1988). The total N content was measured after cc.  $H_2SO_4 + H_2O_2$  digestion according to the modified method of Kjeldahl (ISO 11261, 1995).

#### **Results and discussion**

The investigated soils represent all combinations of basic soil properties: acid and calcareous sand; acid and calcareous loam.

The sludges used for the experiment had different properties (Table 2). The tannery sludge had neutral pH while the municipal sludge was slightly acidic. The organic matter content of municipal sludge was three times higher than the tannery sludge. There was a great difference in P content also: municipal sludge had 8 times more P than the tannery sludge. The total Cr content in the municipal sludge was 0.18 mg/kg and in the tannery sludge 0.52 mg/kg. In tannery sludge the Ca content was also high (21.5%). Due to these values the sludge had significant effect on soil properties. The tannery sludge increased the pH of each type of soil while the municipal sludge had only a positive effect on the pH of sandy soils. Both sludge increased the organic matter of soils and the tannery sludge had a liming effect by its high Ca content.

The mobile and mobilisable Cr fractions increased significantly on each soil after the addition of tannery sludge while the municipal sludge did not change the mobile Cr content of the loamy soils. Table 3 and 4 show the changes in the mobile and mobilisable Cr fractions of soil in the percentage of the added Cr. The original data were published in Kádár and Morvai, 2007; 2008.

Soil	Lo	ad (g sludge D. M. /		Avorago	
	5	10	20	L3D5%	Average
		Cr-load, mg Cr/kg	soil		
	26	52	104		
	Soi	l mobile (NH₄NO₃ so	oluble) Cr content		
acid sand	0.156	0.197	0.131		0.161
calc. sand	0.124	0.088	0.067	0.008	0.093
calc. loam	0.026	0.025	0.024	0.008	0.025
acid loam	0.045	0.022	0.014		0.027
Average	0.088	0.083	0.059		0.077
	Soil mobilisable	(ammonium-acetat	te + EDTA soluble	) Cr content*	
acid sand	2.14	3.19	2.95		2.76
calc. sand	3.36	3.87	2.97	1 22	3.40
calc. loam	2.75	2.99	2.91	1.22	2.88
acid loam	2.34	2.28	2.33		2.32
Average	2.65	3.08	2.79		2.84

Table 3. Change of the mobile and mobilisable fraction in the percentage of the added Cr (in tannery sludge) (%)

\*Based on Kádár and Morvai, 2008

Soil	Lo	Load (g sludge D. M. / kg soil)			Average
	5	10	20	L3D5%	Average
		Cr-load, mg Cr/kg	soil		
	8.8	17.6	35.2		
	Soi	l mobile (NH₄NO₃ so	oluble) Cr content		
acid sand	0.131	0.094	0.051		0.09
calc. sand	0.057	0.045	0.031	0.014	0.04
calc. loam	0.057	0.038	0.018	0.014	0.04
acid loam	0.054	0.027	0.014		0.03
Average	0.075	0.051	0.028		0.05
	Soil mobilisable	(ammonium-aceta	te + EDTA soluble	) Cr content*	
acid sand	1.63	2.66	2.39		2.23
calc. sand	0.19	0.49	0.51	0.56	0.40
calc. loam	0.29	0.12	0.19	0.56	0.20
acid loam	1.07	0.54	0.26		0.62
Average	0.80	0.95	0.84		0.86

Table 4. Change of the mobile and mobilisable fraction in the percentage of the added Cr (in municipal sludge) (%)

\*Based on Kádár and Morvai, 2007

Investigating the solubility of the Cr fractions of the two sludge we found that the Cr from municipal sludge is less mobile than the Cr of tannery sludge. Only 0.05% of the added Cr could be found in the mobile fraction after the addition of municipal sludge in the average of four soils (Table 4). This value for tannery sludge was 0.077% (Table 3). In function of sludge loads less percentage of the added Cr can be found in the mobile fraction. The only exception is the calcareous loamy soil in municipal sludge treatments, where 0.025% of the added Cr was mobile irrespectively of the sludge loads. On the same soil the ratio between the NH<sub>4</sub>NO<sub>3</sub> soluble and added Cr decreased in function of tannery sludge loads.

Soil	L	Load (g sludge D. M. / kg soil)				Average
	0	5	10	20	— LSD <sub>5%</sub>	Average
		Cr trans	fer barley graiı	n		
acid sand	3.53	0.47	0.19	0.09		1.01
calc. sand	3.87	0.27	0.11	0.08	1.20	0.95
calc. loam	3.48	0.44	0.12	0.07		0.89
acid loam	1.34	0.33	0.24	0.10		0.53
Average	3.05	0.38	0.16	0.08		0.85
		Cr trans	fer barley strav	v		
acid sand	16.4	2.3	0.8	0.5	7.5	4.4
calc. sand	10.1	0.9	0.7	0.6		2.7
calc. loam	16.5	2.1	0.5	0.5		4.4
acid loam	8.2	1.0	0.7	0.7		2.6
Average	12.8	1.6	0.7	0.6		3.5

Table 5. Bio concentration factor (BCF) in tannery sludge treatment (Plant element concentration/soil NH<sub>4</sub>- acetate + EDTA extractable fraction) Based on the data of Kádár and Morvai, 2008.

The 2.8% of the Cr added in the tannery sludge could be measured in the mobilisable fraction of soils (Table 3). This ratio was constant in function of load levels. In case of municipal sludge treatments only 0.86% of the added Cr could be found in the mobilisable fraction as average (Table 4). But in this treatment the ratio between the mobilisable Cr increment and added Cr decreased on the acidic loamy soil.

These results show that the relative amount soluble of Cr content in soil does not increase by the amount of sludge loads. Thus the risk of contamination of food chain and groundwater by Cr after sludge application does not increase linearly by the volume of sludge applied.

Soil	L	Load (g sludge D. M. / kg soil)			- LSD <sub>5%</sub>	Average
	0	5	10	20	- LSD5%	Average
		Cr trans	fer barley gra	in		
acid sand	3.53	1.18	0.44	0.25		1.35
calc. sand	3.87	3.53	1.22	1.03	1.10	2.41
calc. loam	3.48	2.26	1.74	1.07		2.14
acid loam	1.34	0.83	0.80	0.91		0.97
Average	3.05	1.95	1.05	0.81		1.72
		Cr transf	fer barley stra	w		
acid sand	16.4	5.7	3.1	0.9		6.5
calc. sand	10.1	5.5	3.6	3.6	4.1	5.2
calc. loam	16.5	8.0	6.5	5.7		9.2
acid loam	8.2	5.5	3.6	3.6		5.2
Average	12.8	6.1	4.2	3.4		6.5

Table 6. Bio concentration factor (BCF) in municipal sludge treatment (plant element concentration/soil NH<sub>4</sub>-acetate + EDTA extractable fraction) Based on the data of Kádár and Morvai, 2007.

The transfer of Cr from soil to plant was also different by the type of applied sludge. The transfer of the elements from soil to plant can be described with bio concentration factor (BCF). Table 5 and 6 show the transfer of Cr to the grain and straw of barley. Definiton is BCF = plant element concentration/soil NH<sub>4</sub>- acetate + EDTA extractable fraction. The BCF of grain Cr is decreasing in function of sludge loads on each soil. This is due to the phenomena that the Cr concentration did not change in the grain while the mobilisable Cr content increased on each soil. The BCF values of Cr in straw decreased with the sludge loads like in case of grain.

Comparing the BCF values of the two sludge it can be seen that on soils treated with municipal sludge the transfer values were higher. This is because the plant Cr concentrations were similar but the soil Cr concentrations were smaller in the soils treated with municipal sludge.

#### Conclusions

The relative amount soluble of Cr content in soil does not increase by the amount of sludge loads. Thus the risk of contamination of food chain and groundwater by Cr after sludge application does not increase linearly by the volume of sludge applied.

Based on the result of this experiment one can state that Cr accumulates more in the barley straw than in the grain. In function of sludge loads the BCF values for Cr lessened.

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#### References

- Ötvös, Z. 2006. Programmed wastewater channelling. (In Hungarian) Gazdasági Tükörkép Magazin. 5: 8-9.
- Csathó P., 1994. Heavy metals and other toxic elements in soil-plant system. (In Hungarian). Agrokémia és Talajtan. 43: 371-399.
- 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.
- Izsáki, Z., and I. Debreczeni. 1987. Study of the effect of tannery sewage-sludge fertilization on sandy soil. (In Hungarian) Növénytermelés. 36: 481-489.
- Izsáki, Z., and I. Debreczeni. 1989. Residual effect of tannery sewage treatment on spiked cereals on low productive sand. (In Hungarian) Növénytermelés. 38: 231-239.
- Kádár I., 2005. Soil properties and soil quality standards mineral elements (in Hungarian). Környezetvédelmi Füzetek. ELGOSCAR-2000 Kft. Budapest.
- ISO 11466:1995. Soil quality Extraction of trace elements soluble in aqua regia
- Lakanen, E., and R. Erviö. 1971. A comparison of eight extractants for the determination of plant available micronutrients in soils. Acta Agr. Fenn. 123: 223-232.
- DIN 19730. 1995. Bodenbeschaffenheit, Extraktion von Spurenelementen mit Ammoniumnitratlösung. Deutsches Institut für Normierung. Beuth Verlag, Berlin.
- Hargitai, L. 1988. Determination of soil organic matter. (In Hungarian) In: Handbook of soil analysis and agrochemical assays, eds. Buzás I., 152-155. Mezőgazdasági Kiadó, Budapest.
- ISO 11261. l995. Soil Quality. Determination of total nitrogen. Modified Kjeldahl method.
- Kádár, I., and B. Morvai. 2008. Analysis of tannery sludge in a pot experiment: Analysis of Ca, Na and Cr. (In Hungarian) Növénytermelés. 57: 35-48.
- Kádár I. and Morvai B., 2007. Effect of industrial-municipal sewage sludge loads in pot experiments. (In Hungarian) Agrokémia és Talajtan. 56. 333-352.

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