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Research Article

CHANGES IN THE CONTENTS OF SELECTED HEAVY METALS IN TEST PLANTS FERTILISED WITH SEWAGE SLUDGE AND HARD COAL ASH

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ABSTRACT
The study aimed at determining changes in the contents of selected metals in the biomass of test plants due to fertilisation with fresh and composted sewage sludge, hard coal ash, and sludge-ash mixture, as well as liming at a background of mineral nutrition. The experimental design was a completely randomised arrangement with three replicates. The following factors were examined: fertilisation with organic and mineral materials (fresh sewage sludge; composted sewage sludge; hard coal ash; calcium carbonate) and mineral fertilisation (no fertilisation; NPK fertilisation). An application of sewage sludge, hard coal ash, and sludge-ash mixture significantly increased maize content of barium. Addition of hard coal ash into sewage sludge contributed to an increase in lead content determined in cocksfoot biomass harvested from the first and second cut, and barium in maize biomass. Soil liming significantly affected barium content the biomass of plants harvested from the first and second cut, as well as in maize biomass. NPK nutrition significantly increased barium concentrations in the biomass of test plants and maize.

Keywords: sewage sludge, ash of hard coal, liming, heavy metal, cocksfoot , maize

INTRODUCTION

Sewage sludge, which is a by-product of wastewater treatment plants, constitutes a considerable group of organic waste which is generally rich in organic matter as well as nutrients for plants [Castaldi et al. 2006, Farasat and Namli 2016]. Due to the presence of biogenic elements, the waste is thought to be a valuable fertiliser and a contributor to soil formation [Czekała 2002].

However, depending on the origin, they can contain significant quantities of heavy metals and toxic organic substances, e.g. PAHs or PCBs. Moreover, they do not meet the sanitary standards set for materials used for agricultural or natural purposes, which can affect crop yield quality and lead to soil contamination and a decline in crop yields [Soriano et al. 2008, Yürük and Bozkurt 2006]. Sewage sludge is produced during a biological-mechanical process of municipal and industrial wastewater purification. The sludge which meets the standards, can be used directly for plant fertilization or subjected to further biological or chemical processing by adding waste mineral materials, e.g. brown coal ash, hard coal ash, hard coal dust or calcium oxide. These substances make sludge pH higher, thus decreasing the solubility and phyto-availability of most metals [Maksimovic et al. 2008, Kalembasa et al. 2008]. One has to remember that, in addition to components which are favourable from the standpoint of agriculture, combustion wastes contain heavy metals as well.

The study aimed at determining changes in the contents of selected metals in the biomass of test plants due to fertilisation with fresh and composted sewage sludge, hard coal ash, and sludge-ash mixture, as well as liming at a background of mineral nutrition.

MATERIALS AND METHODS

A pot experiment was established in a glasshouse located at the experimental unit of Siedlce

University of Natural Sciences and Humanities. The experimental design was a completely randomised arrangement with three replicates. The following factors were examined:

I. fertilisation with organic and mineral materials:
   a) fresh sewage sludge;
   b) sludge obtained from the wastewater treatment plant in Siedlce and composted for three months (industrial and municipal wastewater);
   c) hard coal ash obtained from an electricity distribution company in Siedlce;
   d) calcium carbonate.

   Sewage sludge was applied once, adding 5% relative to soil weight. Sewage sludge and coal ash were mixed at the ratio of 2:1 when converted to dry matter.

II. mineral fertilisation:
   a) no fertilisation;
   b) NPK fertilisation.

Mineral fertilisers: urea, triple superphosphate and potassium sulphate, were applied preplant. The soil used in the experiment was very loamy sand obtained from the 0–20 cm layer of grey brown podzolic soil. Before the experiment was set up, soil contents of nitrogen, carbon, available phosphorus and potassium were determined (respectively: 1.10, 8.20, 0.052 and 0.071 g kg^{-1}). Pots were filled with 10 kg of soil and kept during the growing season at the moisture level of 60% maximum water holding capacity of the soil.

Cocksfoot (*Dactylis glomerata*) was the test plant in the first study year; it was sown at the amount of 1.0 g $\cdot$ pot^{-1}, and three cuts per growing season were harvested. In the second study year, maize was grown at the density of 3 plants per pot, and harvested at the flowering stage. In the dried and powdered plant biomass, the total quantities of Pb, Cd, Ba were determined by means of the ICP–AES technique after 'dry' mineralisation. Plant material was digested in a muffle furnace at 450°C with gradually increased temperature; then digested samples were dissolved in water solution of hydrochloric acid ($HCl:H_2O$, 1:1) and evaporated until dry to decompose carbonates and separate silicates. The ash obtained was transferred to measure flasks containing 10% HCl solution through a hard filter paper. Total lead, cadmium and barium contents in sewage sludge and hard coal ash were also determined by the ICP-AES method following 'dry' mineralisation.

STATISTICA (data analysis software system), version 12 (www.statsoft.com) was used to statistically analyse the results. Significance of differences between means for the experimental factors were checked using Tukey's test at the significance level of $\alpha \leq 0.01$.

RESULTS AND DISCUSSION

Hard coal ash and sewage sludge are non-uniform materials, and their chemical composition and properties depend on many factors [Kalembasa et al. 2008, Antonkiewicz 2007b]. Sewage sludge applied in the present study (Table 1) contained five times as much cadmium as hard coal ash. Lead content in the ash was twice as high as in the sludge. The quantities of Cd and Pb in the materials studied were at low levels and, in addition, heavy metals contained in ashes are poorly available for plants [Antonkiewicz 2009]. The waste materials discussed here had different barium contents. Hard coal ash contained seven times as much barium as sewage sludge.

The test grass contained an average cadmium amount (Table 2) (from 0.342 to 0.461 $mg \cdot kg^{-1}$ DM), the content being quite uniform in individual combinations but declining in subsequent cuts. An application of fresh and composted sewage sludge, hard coal ash, and sludge-ash mixture insignificantly influenced the cadmium concentration in cocksfoot biomass. It could be attributed to a low Cd level in the materials incorporated into the soil. Moreover, fresh sludge combined with combustion ash can lead to a decline in the forms of metals which are bio-available for plants [Jackowska 2002]. In soils enriched with organic matter, the share of heavy metal forms available for plants decreases, which is accompanied by an increased toxicity of the metals [Mercik and Kubik 1995]. Results reported by other authors examining an application of sewage sludge on cadmium content in plants differ. Experiments performed by Antonkiewicz [2007a] revealed that sewage sludge, ash, and their mixture clearly

Table 1. The content of Cd, Pb and Ba in D.M. in sewage sludges and ash hard coal

Element	Sewage sludge	Ash hard coal
	$mg \cdot kg^{-1}$	
Cd	3.69	0.736
Pb	35.6	65.1
Ba	131	972

Table 2. The content of Cd (in mg · kg^{-1} DM) in cocksfoot

NPK fertilization	0				NPK			
Organic Cuts and mineral materials	I	II	III	Means	I	II	III	Means
control object	0.433	0.362	0.393	0.396	0.352	0.383	0.367	0.367
sewage sludge	0.295	0.384	0.301	0.327	0.414	0.361	0.361	0.379
fermented sewage sludge	0.484	0.379	0.261	0.375	0.383	0.366	0.311	0.353
ash hard coal	0.584	0.360	0.432	0.459	0.466	0.400	0.301	0.389
sewage sludge + ash	0.479	0.429	0.303	0.404	0.358	0.403	0.346	0.369
ferment. sewage sludge +ash	0.618	0.404	0.374	0.465	0.266	0.362	0.354	0.327
liming	0.357	0.300	0.270	0.309	0.325	0.318	0.347	0.330
liming + sewage sludge + ash	0.435	0.379	0.389	0.401	0.461	0.376	0.274	0.370
liming + ferment. sewage sludge + ash	0.466	0.414	0.353	0.411	0.375	0.330	0.384	0.363
Means	0.461	0.379	0.342	0.394	0.378	0.367	0.338	0.361

Cuts I, II, III means:
$LSD_{(o.o5)}$ for: organic and mineral materials n.s. 0.063 n.s. n.s.
fertilization NPK 0.063 n.s. n.s. 0.03
organic and mineral materials x fertilization NPK n.s. n.s. n.s. n.s.

decreased the cadmium uptake by the grass-bird's foot trefoil mixture. According to Jasiewicz et al. [2006], an application of municipal sludge increased the heavy metal content in the first cut of tall oat-grass. Wong and Selvam [2009] found that fertilisation with composted sewage sludge contributed to a more intensive cadmium uptake by plants.

A significantly lower cadmium content was found in the biomass of the second cut of cocksfoot grown on limed soil compared with the remaining experimental units. Cadmium amount in the biomass of the first and third cut was also the lowest in the limed units compared with the remaining plots, but the differences were insignificant. Gębski [1998] has reported that Cd and Zn are heavy metals that are the most vulnerable towards pH value change. NPK nutrition decreased the cadmium content in the plants of all the cuts. It also significantly affected the cadmium level in cocksfoot biomass harvested from the first cut and the mean value across the three cuts.

The cadmium content in maize biomass (Table 3) was affected by the experimental factors and ranged from 0.707 to 0.997 mg·kg^{-1} DM, the mean value being 0.813. The lowest Cd level was recorded in the biomass harvested from ash-treated units. Significantly the highest cadmium concentration was found in the maize biomass harvested from limed units treated with fresh sewage sludge mixed with ash, compared with the control. An application of hard coal ash contributed to a significant decline in maize biomass content of cadmium, which was consistent with results reported by Su and Wong [16]. Fertilisation with fresh sludge contributed to an increase in the maize content of cadmium compared with control plants, although the differences were insignificant. Gondek [2004] applied tanning sediments as a manure and observed a slight increase in the maize content of cadmium

Table 3. The content of Cd (in mg · kg^{-1} DM) in maize

NPK fertilization Organic and mineral materials	0	NPK	Means
control object	0.752	0.685	0.718
sewage sludge	0.772	1.05	0.911
fermented sewage sludge	0.615	0.798	0.706
ash hard coal	0.629	0.685	0.657
sewage sludge + ash	0.758	0.864	0.811
ferment. sewage sludge +ash	0.643	1.03	0.836
liming	0.714	0.800	0.757
liming + sewage sludge + ash	0.900	1.10	1.000
liming + ferment. sewage sludge + ash	0.904	0.945	0.925
Means	0.743	0.884	0.813

$LSD_{(o.o5)}$ for: organic and mineral materials 0.259
fertilization NPK 0.073
organic and mineral materials x fertilization NPK 0.219

compared with untreated plants. NPK nutrition significantly increased cadmium concentration in maize biomass. Moreover, when examining the cadmium accumulation in the test plant, significant interactions between the experimental factors were found.

Lead content in cocksfoot biomass (Table 4) varied for individual fertilisation combinations and ranged from 1.09 to 1.62 mg·kg^{-1} DM. The lead accumulation in the grass was the lowest for the control plants and the highest for the hard coal ash-treated plants. Manuring with sewage sludge slightly increased lead concentration in the test grass compared with the control plants. Also Kumar and Chopra [2015] reported increased lead contents in sewage sludge-treated plants, whereas Tlustos et al. [2003] and Varavipour et al. [2009] found that plants grown in soils treated with sewage sludge accumulated less lead compared with non-treated soils. A significantly higher lead content was recorded in the cocksfoot biomass harvested in the first cut and fertilised with fresh sewage sludge mixed with hard coal ash, compared with control plants and plants treated with fresh and composted sludge. In the second and third cut, ash mixed with sludge increased lead quantity in the test grass, although the differences were insignificant. However, Antoniewicz [2007a] demonstrated that ash-sludge mixture significantly decreased the lead content in the plants he cultivated. Liming of units treated with sludge-ash mixtures contributed to a decline in lead uptake by plants. Mineral nutrition had no significant effect on lead concentration in plants; however, higher accumulation of the element was observed in the biomass of NPK-fertilised cocksfoot. Significant interactions of the experimental factors were found when lead uptake by the test plant was analysed.

Lead content in maize plants (Table 5) amounted to 13.8 mg · kg^{-1} DM, on average, and was significantly affected by treatment with

Table 4. The content of Pb (in mg · kg^{-1} DM) in cocksfoot

NPK fertilization	0				NPK			
Organic Cuts and mineral materials	I	II	III	Means	I	II	III	Means
control object	0.907	0.869	1.38	1.05	1.15	1.02	1.37	1.18
sewage sludge	1.03	1.07	1.31	1.14	0.907	1.25	1.81	1.32
fermented sewage sludge	0.827	0.929	1.02	0.925	1.18	1.53	1.45	1.39
ash hard coal	0.883	2.39	2.48	1.92	1.39	1.36	1.55	1.43
sewage sludge + ash	1.42	1.28	1.35	1.35	1.65	1.47	1.59	1.52
ferment. sewage sludge +ash	0.888	1.87	2.38	1.72	1.44	1.18	0.863	1.16
liming	0.925	0.805	0.723	0.818	1.03	1.94	3.06	2.01
liming + sewage sludge + ash	1.32	1.22	0.761	1.10	0.828	1.30	0.932	1.02
liming + ferment. sewage sludge + ash	1.66	1.44	1.35	1.48	1.17	1.14	1.89	1.38
Means	1.09	1.32	1.43	1.27	1.19	1.35	1.62	1.39

Cuts I, II, III means:
$LSD_{(0.05)}$ for: organic and mineral materials 0.483 n.s. n.s. n.s.
fertilization NPK n.s. n.s. n.s. n.s.
organic and mineral materials x fertilization NPK 0.409 0.723 1.13 n.s.

Table 5. The content of Pb (in mg · kg^{-1} DM) in maize

NPK fertilization Organic and mineral materials	0	NPK	Means
control object	13.2	11.0	12.1
sewage sludge	13.9	13.4	13.6
fermented sewage sludge	12.6	11.4	12.0
ash hard coal	14.2	14.2	14.2
sewage sludge + ash	12.8	12.5	12.6
ferment. sewage sludge +ash	12.4	16.5	14.5
liming	12.3	13.2	12.7
liming + sewage sludge + ash	17.5	15.5	16.5
liming + ferment. sewage sludge + ash	16.1	15.3	15.7
Means	13.9	13.7	13.8

$LSD_{(0.05)}$ for: organic and mineral materials 4.42
fertilization NPK n.s.
organic and mineral materials x fertilization NPK n.s.

waste materials. A significantly higher lead quantity was recorded only in the biomass of maize grown in limed units and plots treated with fresh sludge mixed with ash, compared with the control plants.

The average barium content in cocksfoot biomass (Table 6) averaged 14.2 mg·kg^{-1} DM and it decreased in subsequent grass cuts. An application of fresh sewage sludge significantly increased the barium content in the first and second cuts of cocksfoot, compared with plants treated with waste materials or their mixture. In the third grass cut, manuring with fresh sludge also significantly increased the barium content, but only compared with plants grown in composted sludge-treated units. Hard coal ash, sludge-ash mixture, as well as composted sludge significantly decreased barium content in the second cocksfoot cut compared with the control. Ash combined with composted sewage sludge significantly increased the cocksfoot biomass concentration of barium. Sludge-ash mixture incorporated into limed soil significantly decreased the average barium content in the biomass of test grass. According to Kabata-Pendias and Pendias [1999], barium is readily taken up from acidic soils and probably bound on the surface of cell membranes. Mineral nutrition contributed to a significant decline in barium content in the first cut grass and an increase in the subsequent cuts.

Barium content in maize (Table 7) amounted to 5.33 mg·kg^{-1} DM, on average, and depended on the experimental factors. Similarly to cocksfoot, soil liming considerably increased maize concentration of barium. Fresh sewage sludge mixed with hard coal ash enhanced barium levels in maize as compared to control plants. Barium quantities were higher in maize harvested from the remaining units compared with the control, but the differences were statistically insignificant. NPK nutrition significantly increased the maize biomass content of barium.

Table 6. The content of Ba (in mg · kg^{-1} DM) in cocksfoot

NPK fertilization	0				NPK			
Organic Cuts and mineral materials	I	II	III	Means	I	II	III	Means
control object	13.6	13.0	13.0	13.2	19.4	19.0	15.1	17.8
sewage sludge	28.2	18.4	14.8	20.5	15.1	12.4	16.0	14.5
fermented sewage sludge	13.2	8.40	8.29	9.96	17.1	10.8	11.5	13.1
ash hard coal	16.9	11.4	8.79	12.4	16.5	14.3	12.2	14.3
sewage sludge + ash	17.2	12.4	11.0	13.5	16.3	13.0	14.2	14.5
ferment. sewage sludge +ash	14.2	12.0	7.98	11.4	14.3	12.5	11.7	12.8
liming	31.2	20.1	10.4	20.6	21.9	19.1	19.5	20.2
liming + sewage sludge + ash	15.1	7.84	9.32	10.8	16.1	11.7	6.55	11.5
liming + ferment. sewage sludge + ash	16.5	9.48	7.72	11.2	14.6	11.4	13.4	13.1
Means	18.5	12.6	10.1	13.7	16.8	13.8	13.4	14.6

Cuts I II III Means
$LSD_{(o.o5)}$ for: organic and mineral materials 3.46 1.66 4.22 7.72
fertilization NPK 0.977 0.469 1.19 n.s.
organic and mineral materials x fertilization NPK 4.89 2.35 5.97 n.s.

Table 7. The content of Ba (in mg · kg^{-1} DM) in maize

NPK fertilization Organic and mineral materials	0	NPK	Means
control object	4.12	3.35	3.74
sewage sludge	3.67	7.45	5.56
fermented sewage sludge	4.52	4.74	4.63
ash hard coal	6.97	3.88	5.43
sewage sludge + ash	5.03	6.86	5.95
ferment. sewage sludge +ash	4.29	7.71	6.00
liming	6.38	8.55	7.47
liming + sewage sludge + ash	4.02	4.58	4.30
liming + ferment. sewage sludge + ash	4.85	4.87	4.86
Means	4.87	5.78	5.32

$LSD_{(o.o5)}$ for: organic and mineral materials 2.05
fertilization NPK 0.578
organic and mineral materials x fertilization NPK 2.89

CONCLUSIONS

1. An application of sewage sludge, hard coal ash, and sludge-ash mixture significantly increased maize content of barium.
2. Addition of hard coal ash into sewage sludge contributed to an increase in lead content determined in cocksfoot biomass harvested from the first and second cut, and barium in maize biomass.
3. Soil liming significantly affected barium content the biomass of plants harvested from the first and second cut, as well as in maize biomass.
4. NPK nutrition significantly increased barium concentrations in the biomass of test plants and maize.

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