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EFFECTS OF FERTILIZATION WITH SEWAGE SLUDGE AND SEWAGE SLUDGE-BASED MIXTURES OF HEAVY METALS MOBILITY

The presented work aimed at evaluating a fertilizing mixture of sewage sludge, brown coal and brown coal ash enriched with potassium mineral fertilizer on mobility of heavy metals. The effects of fertilization were compared with the effects obtained from fertilization with: sewage sludge, mixture of sewage sludge and mineral fertilizer, mixture of brown coal and mineral fertilizers and mineral fertilizers. Soil was slightly contaminated with zinc and cadmium (II°) and showed elevated concentration of lead (I°). The uptake of heavy metals by plants depended on the concentration of bioavailable metal forms determined with 0.01 M $CaCl_2$ and 1 M HCl. Fertilization with the mixture of sewage sludge, brown coal, brown coal ash enriched with potassium mineral fertilizer resulted in the reduction in the concentrations of zinc by 30–38%, cadmium by 28–34% and lead by 11–50% in plant biomass compared to soil with no fertilization.

1. INTRODUCTION

The results from a number of research studies show that mobility and availability of heavy metals to plants can be limited by maintaining an adequate pH of soil and applying fertilizers which increase sorption capacity of soil [1–3]. These fertilizers include traditional fertilizers such as manure, various types of composts or unconventional fertilizers produced from sewage sludge or brown coal. The presented work aimed at evaluating the effects of a fertilizing mixture of sewage sludge, brown coal and brown coal ash enriched with potassium mineral fertilizer on solubility of Cd, Zn and Pb in soil and *Spartina pectinata* plant biomass. The composition of the investigated fertilizing mixture and its dose was tested and developed. The composition and doses were adjusted to the plant requirements, soil quality and current legal regulations. Brown coal ash was introduced to increase pH of the fertilizing mixture, and

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potassium salt enriched the mixture with potassium due to low concentration of this element in the final mixture.

2. MATERIALS AND METHODS

Description of pot experiment. The experiment included analysis of soil samples and plant biomass conducted in a pot system in the field from April 2008 to October 2010. The PVC open-bottom pipes with the diameter of 30 cm and height of 80 cm were used as pots. These pots were filled with 40 kg of soil, placed in the ground and subjected to fertilization treatments specified in Table 1. The soil used in pot experiments was sampled from 30 spots evenly distributed along the diagonal of the 1500 m^2 area located about 1 km North-West of the Częstochowa Steel Mill, Poland. The depth of soil sampling ranged from 0 to 25 cm.

Table 1

Investigated fertilization combinations in the pots experiment

Fertilization combination	Fertilization type and dose
C	control – 40 kg of soil
SS	40 kg of soil + 2892 g of sewage sludge (36 t d.m/ha)
SS + BC + BCA	40 kg of soil + 1736 g of sewage sludge + 308 g of brown coal + 80 g of brown coal ash (about 36 t d.m /ha) + 2.0 g potassium salt (100 kg/ha)
SS + NPK	40 kg of soil + 1448 g of sewage sludge (18 t d.m/ha) + 3.0 g Polifoska 8 fertilizer + 2.0 g calcium ammonium nitrate + 1.0 g ammonium nitrate (300 kg/ha)
BC + NPK	40 kg of soil + 1024 g of brown coal (36 t d.m/ha) + 3.0 g Polifoska 8 fertilizer + 2.0 g calcium ammonium nitrate + 1.0 g ammonium nitrate (300 kg/ha)
NPK	40 kg of soil + 6.0 g Polifoska 8 fertilizer + 4.0 g calcium ammonium nitrate + 2.0 g ammonium nitrate (600 kg/ha)

Two seedlings of *Spartina pectinata* were planted in each pot. In the first year of the pot experiment – before planting the seedlings – single doses of the following treatments were applied: sewage sludge, brown coal, brown coal fly ash and mineral fertilizers. During the next two years of the pot experiment, fertilization with mineral fertilizers (the doses of fertilizers are provided in Table 1) was applied each spring before the start of plant vegetation. Samples of soil and plant biomass were taken during and after completion of the pot experiment. Collection and preparation of soil samples for further analysis were performed according to the BN-78/9180-02 standard.

Characteristics of soil and fertilizing substrates. With reference to the structure of soil profile and the analysis of soil maps the soil used for the experiments showed characteristics of lessive top gelic soil and belonged to the granulometric group of slightly loamy sand with acidic reaction. The soil was classified as the IV bonitation class with agricultural suitability complex of 6. The total content of phosphorous in the soil was 0.67 mg/g, potassium – 0.74 mg/g, nitrogen – 1.00 mg/g, magnesium – 0.60 mg/g, calcium – 0.66 mg/g and organic carbon – 11.3 mg/g. Based on the total content of heavy metals in the soil used for the pot experiments, the soil showed insignificant contamination with cadmium and zinc (II°) and elevated content of lead (I°). Fertilizing mixtures were prepared from sewage sludge collected from a mechanical and biological municipal wastewater treatment plant. Sewage sludge (SS) was stabilized, dewatered, and showed slightly acidic reaction, high content of organic matter and relatively low content of heavy metals. Physical, chemical and microbiological properties of sewage sludge allowed fertilization of plants not intended for human consumption and production of forage [4]. Brown coal (BC) – the primary substrate for the applied fertilizing mixtures – was collected from the Brown Coal Mine in Bełchatów. Brown coal showed the characteristics of soft brown coal, i.e. earthy coal. The particle size of the coal used for the experiments was lower than 3 mm, water content was 29.8% and the reaction was acidic. Due to physical and chemical properties, brown coal could be applied for plant fertilization. Brown coal ash (BCA) was obtained from the third dust collector for exhaust gases generated in the process of brown coal combustion in the power plant in Bełchatów. Brown coal ash was added to organic and mineral mixture to increase pH, and thus to deacidify the soil. Brown coal ash was a significant source of Ca and Mg as well. Due to physical and chemical properties, it could be applied for plant fertilization. Commercially available fertilizer Polifoska 8 was used for the preparation of fertilizing mixtures.

Methods. Collection and preparation of samples prior to further analysis was performed according to the BN-78/9180-02 standard. The soil and plant biomass samples were tested for [5]:

- pH in 1 M KCl by the potentiometric method with CyberScan pH meter 10 according to the PH-ISO-10390:1997 standard,
- hydrolytic acidity by the Kappen modified method according to the PN-R-04027,
- the total sum of alkaline cations in soil determined by the Kappen modified method according to the procedure presented by Karczewska and Kabała ([5],
- the content of organic matter based on the loss on ignition [5],
- the total content of heavy metals in soil and plant biomass determined with a plasma spectrophotometer ICP-AES (Thermo) according to the PN-ISO 11047:2001 standard after mineralization of the investigated samples in the mixture of concentrated HCl and HNO_3 in the ratio of 3:1 + 30% H_2O_2,
- bioavailable forms of metals determined by the atomic absorption spectrometry after extraction with 0.01 M $CaCl_2$ solution was performed (readily available forms). The contents of heavy metal forms potentially available were determined after the extraction with 1 M HCl solution according to the procedure developed by Karczewska and Kabała [5].

3. RESULTS

3.1. EFFECTS OF FERTILIZATION ON pH AND SORPTION PROPERTIES OF SOIL

The soil used in the experiment showed acidic reaction (pH in 1 M KCl – 5.5). Although the effect of fertilization on the soil pH was insignificant it has to be emphasized that after reaching the geochemical equilibrium, the soil fertilized with SS + BC + BCA, SS and SS + NPK reached pH close to 6.0 being sufficient for light soils.

The applied fertilization improved sorption properties of the soil used in the experiment as the increase in the sum of exchange cations and significant increase in sorption capacity of soil and degree of sorption complex saturation with bases was observed. Fertilization with the mixture of sewage sludge, brown coal and brown coal ash had the most significant effect on the increase in the sorption capacity of the soil in comparison to the remaining fertilization combinations. Soil fertilized with SS + BC + BCA showed the sorption capacity above 8.0 cmol(+)/kg which proved that the sorption conditions were sufficient. The remaining types of fertilization resulted in less significant increase in the sorption capacity (Table 2).

Table 2

The effects of the applied fertilization on pH and sorption capacity of soil

Fertilization combinations	pH (H_2O)	pH (1 M KCl)	H_h Hydrolytic acidity	S Sum of basic exchange cations	T Sorption capacity	V Degree of sorption complex saturation with bases
			cmol(+)/kg soil			%
C	5.90	5.50	2.80	3.00	5.80	51.7
SS	6.20	5.80	2.50	5.70	8.30	69.9
SS + BC + BCA	6.30	6.00	2.38	6.34	8.72	72.7
SS + NPK	6.30	5.90	2.42	5.10	7.52	67.8
BC + NPK	5.90	5.60	2.78	4.60	7.38	62.3
NPK	6.00	5.60	2.84	3.66	6.50	56.3

3.2. TOTAL CONTENT AND SOLUBLE FORMS OF HEAVY METALS IN SOIL

The total content of zinc, cadmium and lead and bioavailable forms of these metals were determined before, during and after completion of the experiment.

Content of zinc in soil. The total content of zinc in the soil used in the experiment (the control) was 122.3 mg/kg. According to this result, the soil used in the experiment was classified as soil slightly contaminated with zinc II°. Adding the substrates to the fertilizing mixtures resulted in the increased content of zinc in comparison to the control (fertilization with BC + NPK was an exception due to very low content of Zn in brown coal). It has to be pointed out that the substrates used in the fertilizing mixtures did not significantly change the content of zinc in the soil and the classification of soil contaminated with this metal remained the same. The highest increase in the content of zinc was observed in the soil fertilized with sewage sludge, i.e. 8–9 mg/kg (depending of the experiment) in comparison to the control. Only in this particular case the content of zinc in the soil was statistically significant.

The content of zinc soluble in 1 M HCl in the soils after reaching the geochemical equilibrium and depending on the type of fertilization ranged from 77.1% (the control) to 60.4% (SS + BC + BCA). The least significant decrease in the concentration of this form of zinc in the soil was observed for mineral fertilization. After the last harvesting of plants, the fraction soluble in 1 M HCl (depending on the type of fertilization) ranged from 68.8 to 78.5% of the total content of zinc for the soil used for cultivation of *Spartina pectinata* (Table 3). The content of zinc soluble in 0.01 M $CaCl_2$ in the soils after reaching the geochemical equilibrium (depending on the experiment and the type of fertilization) ranged from 4.8% (the control) to 2.6% (SS + BC + BCA) of the total content of zinc in the pot experiment. The least significant decrease in the concentration of this form of zinc in the soil was observed for fertilization with sewage sludge. After the last harvesting of plants, the fraction soluble in 0.01 M $CaCl_2$ (depending on the type of fertilization) ranged from 3.5% to 4.4% of the total content of zinc.

Table 3

The effect of fertilization on the content of zinc in soil in the pot experiment

Fertilization combination	The total content [mg/kg]	Content of forms soluble in 1 M HCl		Content of forms soluble in 0.01 M $CaCl_2$	
		[mg/kg]	[%] of the total content	[mg/kg]	[%] of the total content
Zinc in soil after reaching the geochemical equilibrium					
C	122.3±4.00	95.5 ±2.45	77.1	5.92 ±0.31	4.8
SS	130.5*±3.8	89.2 ±5.02	68.4	4.03* ±0.50	3.1
SS + BC + BCA	125.9±9.90	76.0* ±2.57	60.4	3.22* ±0.18	2.6
SS + NPK	126.0±8.90	90.5 ±3.90	71.8	4.71* ±0.37	3.7
BC + NPK	122.0±3.80	77.4* ±8.60	63.4	3.60* ±0.24	2.9
NPK	123.9±4.90	90.7 ±1.35	73.2	4.94* ±0.39	3.9
After the 3rd harvesting of *Spartina pectinata* (after completion of the experiment)					
C	121.1±5.02	95.0 ±3.92	78.5	5.30 ±0.12	4.4
SS	128.8±9.70	92.2 ±5.02	71.6	5.20 ±0.61	4.0
SS + BC + BCA	125.7±8.85	85.1* ±5.51	67.7	4.80 ±0.50	3.8
SS + NPK	124.6±6.90	87.6 ±6.37	70.3	4.85 ±0.37	3.9
BC + NPK	121.0±3.80	83.2* ±3.06	68.8	4.20* ±0.50	3.5
NPK	122.2±1.22	94.2 ±1.47	77.1	5.27 ±0.40	4. 3

$^*p = 0.05$

Content of cadmium in soil. The total content of cadmium in the soil used in the experiment (the control) was 1.22 mg/kg and it fell in the classification of soil slightly contaminated with cadmium II°. Fertilization with sewage sludge and mineral fertilizers resulted in an insignificant increase in the content of cadmium in the soil by about 0.01–0.02 mg/kg in comparison to the control. This did not change the classification of soil contamination with this metal (Table 4). The content of cadmium soluble in 1 M HCl in the soil after reaching the geochemical equilibrium (depending on the type of fertilization) ranged from 60.3% (SS + BC + BCA) to 77.8% (control) of the total content of cadmium. Fertilization with SS + BC + BCA, BC + NPK and SS + NPK facilitated the limitation of the content of Cd forms soluble in 0.01 M HCl in comparison to other fertilization combinations. The content of cadmium soluble in 0.01 M CaCl$_2$ in the soils after reaching the geochemical equilibrium (depending on the experiment and the type of fertilization) ranged from 4.1% (SS + BC + BCA and BC + NPK) to 7.4 % (control) of the total content of cadmium. The least significant decrease in the content of Cd forms soluble in 0.01 M CaCl$_2$ in the soil was observed for fertilization with mineral fertilizers and sewage sludge. After the last harvesting of plants the fraction soluble in 0.01 M CaCl$_2$ ranged from 2.6% to 5.2% of the total content of cadmium. Solubility of Cd in 0.01 M CaCl$_2$ was the most limited by fertilization with SS + BC + BCA and BC + NPK.

Table 4

The effect of fertilization on the content of cadmium in soil

Fertilization combination	The total content [mg/kg]	Forms soluble in 1 M HCl		Forms soluble in 0.01 M CaCl$_2$	
		[mg/kg]	[%] of the total content	[mg/kg]	[%] of the total content
Cadmium after reaching the geochemical equilibrium					
C	1.21±0.01	0.95±0.04	77.8	0.09±0.01	7.4
SS	1.23±0.02	0.84±0.05	68.3	0.07*±0.00	5.7
SS + BC + BCA	1.21±0.04	0.80*±0.03	66.3	0.05*±0.02	4.1
SS + NPK	1.23±0.11	0.84*±0.02	68.3	0.06*±0.01	4.9
BC + NPK	1.21±0.06	0.79*±0.06	65.3	0.05*±0.02	4.1
NPK	1.23±0.12	0.90±0.04	73.8	0.08±0.01	6.6
After the 3rd harvesting *Spartina pectinata* (after completion of the experiment)					
C	1.16±0.01	0.97±0.02	83.6	0.06±0.01	5.2
SS	1.14*±0.00	0.96±0.05	84.2	0.05±0.02	4.4
SS + BC + BCA	1.16±0.01	0.91*±0.01	79.1	0.03*±0.01	2.6
SS + NPK	1.16±0.04	0.88*±0.04	76.5	0.04*±0.00	3.5
BC + NPK	1.17±0.02	0.75*±0.05	64.1	0.03*±0.01	2.6
NPK	1.16*±0.01	0.85±0.10	75.2	0.05±0.01	4.4

*$p = 0.05$.

Content of lead in soil. The total content of lead in the soil not subjected to fertilization (the control) was 39.00 mg/kg, and thus the soil fell into the category of soil contaminated with the elevated content of lead I°. Fertilization with sewage sludge resulted in a slight increase in the content of lead by about 0.02–0.03 mg/kg (except from the fertilization with brown coal and mineral fertilizers where the content of lead decreased insignificantly) in comparison to the control. This did not change the category of soil contaminated with lead. The changes in the content of lead had no statistical significance (Table 5).

Table 5

The effect of fertilization on the content of lead in soil

Fertilization combination	The total content [mg/kg]	Forms soluble in 1 M HCl		Forms soluble in 0.01 M $CaCl_2$	
		[mg/kg]	[%] of the total content	[mg/kg]	[%] of the total content
Lead in soil after reaching the geochemical equilibrium					
C	39.00±0.20	19.89±0.05	51.0	0.57±0.02	1.5
SS	39.03±0.08	18.14*±0.02	46.5	0.37*±0.00	0.9
SS + BC + BCA	39.01±0.75	17.92*±1.10	46.0	0.30*±0.15	0.8
SS + NPK	39.02±0.02	17.67*±1.12	45.2	0.39*±0.10	1.0
BC + NPK	38.90±0.90	15.95*±0.55	41.0	0.34*±0.04	0.9
NPK	39.01±0.05	18.81*±0.01	48.2	0.53±0.02	1.4
After the 3rd harvesting *Spartina pectinata* (after completion of the experiment)					
C	38.72±0.12	24.00±0.50	61.8	0.52±0.02	1.3
SS	38.78±0.28	19.85*±1.15	50.9	0.50±0.03	1.3
SS + BC + BCA	38.80±1.15	17.00*±1.60	43.8	0.40*±0.02	1.0
SS + NPK	38.80±1.08	19.80*±0.73	50.9	0.51±0.01	1.4
BC + NPK	38.78*±0.10	18.85*±1.10	48.6	0.35*±0.05	0.9
NPK	38.82±0.12	21.55±1.35	55.3	0.51±0.03	1.4

*$p = 0.05$.

The content of lead soluble in 1 M HCl in the soils after reaching the geochemical equilibrium (depending on the experiment and the type of fertilization) ranged from 41.0% (BC + NPK) to 51.0% (the control) of the total content of lead. After the last harvesting of plants, the fraction soluble in 1 M HCl was from 43.8% to 61.8% of the total content. Fertilization with SS + BC + BCA and BC + NPK facilitated the limitation of the content of Pb forms soluble in 1 M HCl in comparison to the remaining fertilization combinations.

The content of lead soluble in 0.01 M $CaCl_2$ in soils after reaching the geochemical equilibrium (depending on the type of fertilization) ranged from 0.8% (SS + BC + BCA) to 1.5% (the control) of the total content of lead. Elevated contents of Pb forms soluble in 0.01 M $CaCl_2$ were observed in the soil not subjected to any fertilization (the control), soil fertilized with mineral fertilizers and sewage sludge in comparison to the remaining fertilization combinations. After the last harvesting of plants the fraction soluble in 0.01 M $CaCl_2$ (depending on the type of fertilization) ranged from 0.9% to 1.4% of the total content of lead (Table 5). Solubility of Pb in 0.01 M $CaCl_2$ in most cases was the most limited by fertilization with BC + NPK.

3.3. CONTENT OF HEAVY METALS IN PLANT BIOMASS

With the reference to the results presented in Table 6, a significant effect of fertilization on the availability and the content of Zn and Cd in above-ground part of plants was observed. This relationship was determined for all harvested plants. The results of the experiments showed that plant biomass from the first year of the experiment had far lower contents of the investigated metals in comparison to the second one, and in particular, third year of the experiment.

Table 6

Content of heavy metals in the above-ground parts
of the plants in the pot experiment [mg/kg d.m.]

Fertilization combination	Zn	Cd	Pb
Spartina pectinata – 1st harvesting			
C	27.5 ±2.45	0.25 ±0.01	1.61 ±0.10
SS	21.0*±1.35	0.23*±0.00	1.40 ±0.13
SS + BC + BCA	18.6*±1.10	0.18*±0.03	1.42 ±0.89
SS + NPK	20.5*±0.98	0.20*±0.02	1.45 ±0.05
BC + NPK	17.4*±1.71	0.16*±0.03	1.38*±0.04
NPK	22.3 ±3.60	0.23 ±0.02	1.45 ±0.02
Spartina pectinata – 2nd harvesting			
C	50.8 ±2.69	1.65 ±0.05	4.05 ±0.24
SS	50.0 ±1.02	1.55*±0.01	3.60 ±0.18
SS + BC + BCA	31.6*±2.33	1.20*±0.10	2.05*±0.17
SS + NPK	44.5*± 1.00	1.60 ±0.08	3.68 ±0.01
BC + NPK	38.7*±2.45	1.15*±0.50	2.20*±0.04
NPK	52.2 ±1.90	1.58 ±0.13	3.70 ±0.12
Spartina pectinata – 3rd harvesting			
C	66.3 ±2.82	2.58 ±0.06	4.98 ±0.12
SS	60.5 ±4.00	2.50 ±0.12	4.05 ±0.80
SS + BC + BCA	40.0*±3.40	1.70*±0.10	4.00*±0.16
SS + NPK	59.0 ±3.18	2.00*±0.11	4.22*±0.09
BC + NPK	45.6*±1.10	1.85*±0.13	4.15*±0.04
NPK	63.8 ±2.45	2.65*±0.00	4.58 ±0.02

*$p = 0.05$.

4. DISCUSSION

The soil reaction and its sorption properties such as the content of alkaline exchange cations, sorption capacity and the degree of sorption complex saturation with bases show critical effect on solubility and migration of heavy metals in soil environment. In order to improve the sorption conditions of soil it is necessary to introduce selected fertilizing substrates to soil humus [6, 7]. Many investigations showed that sewage sludge due to its organic matter content improved the structure and sorption complex especially of light soils [6, 8–14] Fertilizing properties of brown coal are due to permanent enrichment of soil with organic substance [15]. It has to be pointed out that the exchange capacity of humus exceeds the exchange capacity of soil mineral constituents by 4 to 12 times. The humus content of 1% in soil for moderate climate corresponds to more or less 2 cmol (+) of sorption capacity per 1 kg of soil whereas the sorption capacity of the same amount of clay minerals ranges from 0.1 to 1.0 cmol(+) per 1 kg of soil. Significant improvement of the sorption conditions due to the applied fertilization was confirmed by the increase in the degree of sorption complex saturation of the soils from all the experiments with alkaline cations. The most favorable effects were obtained from fertilization with sewage sludge. In this case, the increase in the degree of sorption complex saturation (depending on the experiment) ranged from several up to twenty percent. The results indicated a direct relationship between the reaction of soil and its sorption properties. Upon increasing in soil pH, the decrease in hydrolytic acidity and the increase in the sum of bases – in particular the sorption complex saturation with bases – were observed. The results of the investigations pointed to a beneficial effect of sewage sludge, brown coal and the fertilizing mixtures prepared based on sewage sludge and brown coal on the improvement of sorption properties of the investigated soils.

The content of metal forms soluble in 1 M HCl in the control was close to the content of Cd and Zn and amounted to 77% whereas for Pb it was 51%. The results obtained by Mercik [6] showed that about 70% of Cd and up to 90% of the total content of Zn and Pb went into the 1 M HCl solution. Solubility of zinc and cadmium in 0.01 M $CaCl_2$ was significantly lower than in 1 M HCl and amounted to few percent of the total content. It has to be pointed out that 1 M HCl is far stronger extraction solution than 0.01 M $CaCl_2$. 1 M HCl solution dissolves metals bound to various fractions such as exchange, carbonate, oxides and organic matter, and thus such significant differences in the solubility of metals in used solutions were observed. The concentrations of bioavailable forms of metals determined in 0.01 M $CaCl_2$ were very diversified. Pogrzeba [16] determined 16% of bioavailable forms of cadmium and 3.6% of bioavailable forms of zinc in soil heavily contaminated with zinc, cadmium and lead. McGowen [17] determined only 0.84% of bioavailable forms of zinc and the concentration of bioavailable cadmium did not exceed 1% of the total content of this metal in the soil. Significantly higher concentrations of bioavailable forms of Zn, Pb and Cd were determined by Ruttens [18] and amounted to 38%, 2.6% and 46.5%, respectively.

The majority of results analyzed by the author indicated that the content of heavy metal forms recognized as bioavailable forms did not depend on the total content of these elements in the soil but on soil pH and the content of organic matter. The applied additions had a significant effect on limiting the solubility of metals in both extraction solutions. This resulted mostly from considerable enrichment of soils with organic matter, increased soil pH (from 0.1 to 0.5 depending on the fertilization combinations) and in consequence led to changes in mobility and bioavailability of heavy metals. The decrease in solubility differed for selected metals, types of fertilization and applied extraction solutions. Solubility of Zn, Cd and Pb in the applied extraction solutions changed in each phase of the experiment. It has to be emphasized that fertilization with SS + BC + BCA and BC + NPK had the most favorable effect on limiting the content of soluble forms of the investigated metals in 0.01 M $CaCl_2$ and 1 M HCl. Solubility of the investigated metals in 0.01 M $CaCl_2$ decreased in the case of fertilization with SS + BC + BCA and BC + NPK and was about 50% in comparison to the control. The decrease in solubility of metals in 1 M HCl for fertilization with SS + BC + BCA and BC + NPK was similar to the investigated metals up to 20% in comparison to the control. Significant limitation of solubility of Cd in 1 M HCl was observed also in the case of fertilization with SS + NPK. The obtained results proved that solubility of metals is affected by the content of organic matter and the reaction of soil. However, it needs to be emphasized that significant decrease in solubility of metals (depending on the type of fertilization) was observed primarily for the forms determined with 0.01 M $CaCl_2$ solution. The amount of metals extracted with 1 M HCl was far lower dependent on the type of fertilization.

Opinions on the effect of soil conditions on solubility of metals in 1 M HCl are diverse. Kabata-Peniadas [19] pointed out a direct correlation between these properties whereas Gębski's [20] research did not confirm this correlation. The increase in solubility of zinc, cadmium and lead in the soil after fertilization with sewage sludge, brown coal and brown coal ash was beneficial in case of the limitation of bioavailability of these metals to plants. Literature provides a great number of contradictory opinions on the relationships between the total content of metals in soil and their bioavailability to plants. Some studies indicated a direct correlation between these properties whereas others do not confirm the relationships between the total content of trace elements in soil and the amount taken up by plants [1, 7, 21–23]. The uptake of Zn, Cd and Pb by *Spartina pectinata* depended primarily on the concentration of forms of these metals in the soils determined with 0.01 M $CaCl_2$ and 1 M HCl. Generally, the highest contents of metals were determined in plant biomass in the control and in the soil fertilized with NPK – this did not have any relation to the highest contents of metals in soil for these fertilization combinations. Only in the case of Cd, positive correlation between the total content of this metal in soil and in plants was observed. The concentration of Zn, Cd and Pb in the above-ground parts of *Spartina pectinata* was high in comparison to most grasses and crops but lower than in case of hyperaccumulators.

5. CONCLUSIONS

1. Significant differences between the total content of metals and metal forms in the soil determined with 1 M HCl and 0.01 M $CaCl_2$ were observed.

2. The applied types of fertilization had no considerable effect on the change in the total content of Zn and Cd. However, the addition of fertilizing substrates to the soil significantly changed the content of bioavailable forms of these metals.

3. Fertilization combinations with brown coal resulted in the decrease in the concentration of bioavailable forms of metals. This was shown by significant limitation of metals soluble in 0.01 M $CaCl_2$.

4. The uptake of Zn and Cd by plants depended strongly on the concentration of forms of these metals in the soil determined with 0.01 M $CaCl_2$ and 1 M HCl.

5. Fertilization with sewage sludge despite the fact that it resulted in the highest concentration of heavy metals in the soil did not facilitate higher uptake of these elements by plants. The reasons for that were improved sorption conditions and increased soil pH.

6. The highest concentrations of Zn and Cd in plant biomass were determined in the third year of the experiment in the control and the soil fertilized with mineral fertilizers. The lowest concentrations were determined in plant biomass from soils fertilized with BC + NPK and SS + BC + BCA. In the case of these fertilization combinations, the contents of zinc in plant biomass was lower by 45–50%, cadmium by 35–67% and lead by 11–50% (depending on the harvesting year) in comparison to the soil not subjected to any fertilization.

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