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THE INFLUENCE OF FERTILIZATION WITH BROWN COALS, WASTE ACTIVATED SLUDGES AND THEIR MIXTURES ON THE CONTENT OF CHROMIUM AND NICKEL IN SOIL MATERIALS AND ITALIAN RYEGRASS

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WPŁYW NAWOŻENIA WĘGLAMI BRUNATNYMI, OSADAMI ŚCIEKOWYMI I ICH MIESZANINAMI NA ZAWARTOŚĆ CHROMU I NIKLU W MATERIALE GLEBOWYM I ŻYCICY WIELOKWIATOWEJ

Doświadczenie wazonowe przeprowadzono w latach 1998–2000. Celem badań było określenie wpływu węgli brunatnych, osadów ściekowych oraz ich mieszanin i obornika na zawartość Cr i Ni w podłożu glebowym i życicy wielokwiatowej odmiany Kroto. W doświadczeniu wykorzystano piasek gliniasty lekki (jako podłoże), węgiel brunatny odmiany ziemistej o niskiej wartości energetycznej z KWB w Sieniawie i Koninie, osady ściekowe z oczyszczalni w Siedlcach, Łukowie i z Drosedu oraz obornik mieszany. W każdym roku badań zbierano po cztery pokosy trawy. Całkowitą zawartość Cr i Ni w podłożu glebowym i suchej masie trawy oznaczono metodą ICP-AES na spektrometrze emisyjnym z indukcyjnie wzbudzaną plazmą po uprzedniej mineralizacji „na sucho" badanych prób. Najwyższy poziom chromu i niklu stwierdzono w podłożu glebowym z osadem ściekowym z Siedlec. Średnią zawartość chromu w suchej masie życicy wielokwiatowej oznaczono na poziomie 5,15 mg/kg s.m. a niklu 3,05 mg/kg s.m.

Summary

In years 1998–2000 the pot experiment was carried out. The aim of this investigation was to determine the influence of brown coal, waste activated sludge, their mixtures and farmyard manure on the content of Cr and Ni in soil material and in the dry mass of *Lolium multiflorum* Kroto variety. The pots were filled with loamy sand as soil material, brown coal which had low energetic value from Sieniawa and Konin mines, waste activated sludges were taken from mechanical-biological sewage purification plants located at Siedlce, Łuków and Drosed (poultry processing plant) and mixed farmyard manure. In each year of experiment four cuts were harvested. The total content of Cr and Ni in soil materials and in dry mass of grass after dry combustion of samples was determinate by ICP-AES method on spectrometer Optima 3200 RL manufactured by Perkins-Elmer. The highest content of Cr and Ni was determinate in soil materials from objects fertilized with waste activated sludge from Siedlce. The average content of Cr in dry mass of grass reached 5.15 mg/kg and Ni 3.05 mg/kg.

INTRODUCTION

Brown coals (often called soft) which have low energetic value and waste activated sludge are classified as wastes [17].

For during the last years the decrease in the content of organic matter in Polish soils has been observed what is connected with the decrease of FYM application (5.6 Mg/ha), mineralization of soil organic matter and its moving down in soil profile as the result of deeper plaughing. It this situation a very important aim is utilization of brown coals as the source of organic matter [11] and waste activated sludges [10]. The both materials are rich in organic carbon and contain a lot of biogenic elements macro- and micronutrients [8]. After obtaining the certificate for the environmental management of 14001 by local sewage purification plants the possibilities of utilization of waste activated sludge for the plant fertilization increased greatly under the conditions that waste activated sludge is fully in agreement with the chemical and veterinary regulations [14].

The narrow ratio of C:N in waste activated sludge, the big amount of plant nutrients as well as humus substances and good physical conditions were the reason for researching of organic materials which contain big amount of dry mass and organic carbon compounds [7, 8]. The addition of brown coal which is not useful in energetic plants to waste activated sludges caused the increase in the value of the C:N ratio and also the content of dry mass [7]. The results obtained in the incubation experiment have shown big suitability in the fertilization of the mixtures of brown coal and waste activated sludges (1:5 w/w) after two months of incubation [8]. The possibilities of utilization of the brown coal as the supplement of organic substances in soil confirmed the similarity in the structure and properties of their group compounds mainly humic acids, which have the chelatation possibility of heavy metals [9].

The aim of this investigation was to observe the changes in the content of the following elements chromium (which is necessary for human beings and animals) and nickel (necessary for plants and animals) in the soil materials and Italian ryegrass after application of waste (brown coal with waste activated sludge) and after that comparison of determinated elements obtained in this experiment with the norms (figures) taken as the standard in the feedings of animals was performed.

MATERIALS AND METHODS

The pot experiment was carried out in the completely randomized model with control object in three replications. The pots were filled with 8 kg of soil materials (loamy sandy soil). To each pot the organic materials were added in amount of 7.5% to the dry mass of soil material.

The scheme of experiment contained the following objects:

1. control loamy sandy soil (only soil material);
2. soil material + brown coal from Sieniawa mine;
3. soil material + brown coal from Konin mine;
4. soil material + waste activated sludge from Siedlce sewage purification plants;
5. soil material + waste activated sludge from Drosed poultry meat factory plants;
6. soil material + waste activated sludge from Łuków sewage purification plants;
7. soil material + brown coal from Sieniawa + waste activated sludge from Siedlce;

8. soil material + brown coal from Sieniawa + waste activated sludge from Drosed;
9. soil material + brown coal from Sieniawa + waste activated sludge from Łuków;
10. soil material + brown coal from Konin + waste activated sludge from Siedlce;
11. soil material + brown coal from Konin + waste activated sludge from Drosed;
12. soil material + brown coal from Konin + waste activated sludge from Łuków;
13. soil material + cattle farmyard manure.

The pots were filed with soil materials taken from A_1 horizon which had granulometric composition of light loamy sand.

In this experiment the waste activated sludges from sewage purification plants municipal-industrial sewage at Siedlce, at Łuków (municipal sewage and sewage from meat processing factory) and waste from Drosed factory (sewage from slaughter and processing of poultry meat factory) were used. Mineral fertilization in form of Polifoska 8 and ammonium nitrate were applied in the amount of 1 g of N, P and K per pot. The Polifoska 8 fertilizer was applied at spring before sowing of grass seeds, and additional nitrogen fertilization in the form of ammonium nitrate after 1st and 2nd cut.

Sowing of grass seeds Kroto of variety in the amount of 1 g per pot was done on June 8, each year. Shooting of grass was observed after 7 days of sowing. The moisture of soil materials in pots during the vegetation periods was maintained at the 60% of total water capacity. During vegetation period in each year of experiment four cuts were harvested. After each cut the plant material was air dried and grounded. The soil material was air dried, sieved trough 1 mm sieve and prepared for chemical analysis. The samples of plant material (1 g) and soil material (3 g) were weighed out to porcelain crucible (three replicates) and put into muffle oven for „dry combustion" at 450°C for 12 hours. After cooling the crucible to each, 5 cm^3 of diluted HCl (1:1) was added to decompose carbonate and precipitate silica and after that evaporated to dryness.

The content of crucible was transferred with the addition of 10 cm^3 10% HCl through the hard filter paper to the volumetric flask (100 cm^3 volume) and filled up with deionized water to mark. In this basic solution the total content of Cr and Ni were determinated on the spectrometer (Perkin-Elmer Optima RL 3200) by ICP-AES method [16].

The results obtained in this experiment were statistically evaluated using analysis of variance. The significantly of mean values was tested by FR Analvar 4.1 Fisher-Snedecor test and the value of $LSD_{0.05}$ was calculated by Tukey's test.

RESULTS AND DISCUSSION

The chemical composition of materials used in this experiment is presented in Table 1. The content of chromium and nickel in soil material was significantly correlated with the content of organic carbon, silt and the pH value [6]. The soil material (light loamy sand) used in this experiment contained very low amount of Cr and Ni (12.3 mg/kg and 2.5 mg/kg respectively) what is much below according to Polish norms for light soil for Cr 50 mg/kg and Ni 30 mg/kg of dry mass [4].

Table 1. The content [mg/kg D.M.] of chromium and nickel in soil material, brown coals, waste activated sludges and FYM used in experiment

Component	Content in mg/kg D.M.	
	Chromium	Nickel
Light loamy sand	12.3	2.5
Brown coal from Sieniawa	9.9	24.2
Brown coal from Konin	8.7	21.7
Sludge from Siedlce	30.1	36.0
Sludge from Łuków	12.7	27.5
Sludge from Drosed	25.7	31.3
FYM	10.8	25.0

The brown coal from Sieniawa and Konin contained the lowest amount of chromium. The content of chromium and nickel in used waste activated sludges was also very low [4].

The content of determinated elements in analyzed soil material with organic materials added (Tab. 2) was also very low.

Table 2. The content [mg/kg D.M.] of chromium and nickel in soil material mixed with organic materials determinated before and after experiment

Objects	Content in mg/kg D.M.			
	Cr	Ni	Cr	Ni
	Before the experiment		After the experiment	
1. Soil material (control)	12.31	2.56	10.72	1.94
2. Soil material + brown coal from Sieniawa	14.07	3.48	12.83	2.87
3. Soil material + brown coal from Konin	13.31	3.77	12.44	2.97
4. Soil material + sludge from Siedlce	18.97	4.78	17.85	4.00
5. Soil material + sludge from Drosed	13.94	4.12	13.18	3.44
6. Soil material + sludge from Łuków	17.83	4.31	17.09	3.58
7. Soil material + brown coal from Sieniawa and sludge from Siedlce	17.76	4.00	17.19	3.33
8. Soil material + brown coal from Sieniawa and sludge from Drosed	12.99	3.73	11.95	2.97
9. Soil material + brown coal from Sieniawa and sludge from Łuków	15.03	3.76	14.44	2.91
10. Soil material + brown coal from Konin and sludge from Siedlce	15.37	4.05	14.39	3.34
11. Soil material + brown coal from Konin and sludge from Drosed	14.17	4.41	13.63	3.86
12. Soil material + brown coal from Konin and sludge from Łuków	16.01	4.13	15.45	3.58
13. Soil material +FYM	13.34	3.76	12.64	3.22
Means	15.01	3.91	14.14	3.23

		Cr	Ni
$LSD_{0.05}$ for:	objects (A)	1.60	0.82
	terms (B)	0.35	0.18
	interactions (A x B)	n.s.	n.s.
	(B x A)	n.s.	n.s.

The mean content of chromium in soil material mixed with organic substance analyzed before the experiment reached 15.01 mg/kg of dry mass. Among investigated objects the lowest content of chromium was determinated in material taken from the control object (12.31 mg/kg of dry mass) and the highest (18.97 mg/kg of dry mass) in material taken from objects on which waste activated sludge from Siedlce was applied in the amount of 75% of dry mass of soil per pot. The analysis, done after the end of experiment showed that the mean content of chromium reached 14.4 mg/kg of dry mass. The lowest value 10.72 mg/kg of dry mass was determinated in soil material taken from the control object and the highest (17.85 mg/kg of dry mass) from object with waste activated sludge from Siedlce.

The mean content of nickel in investigated samples taken from different objects before starting the experiment reached 3.91 mg/kg of dry mass but after end of experiment 3.23 mg/kg of dry mass. The lowest content of nickel was determinated in material taken from the control object and the highest in sample from object with waste activated sludge from Siedlce. The determinated content of analyzed elements in this experiment was much lower that in investigation carried out by other authors [2].

The results of others authors [3, 15] have shown that the normal content of chromium in plant is on the level 1–5 mg/kg of dry mass and for nickel 0.1–5 mg/kg of dry mass but the content of above trace elements count as toxic for the growing of plants reached for chromium 10–20 mg/kg of dry mass and for nickel 20–30 mg/kg of dry mass.

The mean content of chromium in the dry mass of *Lolium multiflorum* Lam. reached 5.15 mg/kg (Tab. 3). Statistical analysis has shown significant differences in the content of chromium of *Lolium multiflorum* Lam. in dry mass harvested in the 1st and 2nd year of experiment as well as between the 2nd and 3rd year. In the biomass of *Lolium multiflorum* Lam. harvested in the 2nd year of experiment the content of chromium was about 15.6% higher than in 1st year and reached 6.39 mg/kg of dry mass. The content of chromium determinated in dry mass harvested in own presented results was higher than results of other experiments [1, 2, 12] but not reached critical values. The application of high doses of waste activated sludges from 5 to 90 Mg/ha slightly increased the content of chromium in dry mass of *Lolium multiflorum* Lam. (from 1.1 mg/kg to 1.2 mg/kg of dry mass) [12] but in other investigation [5] the chromium was not detected in the dry mass of *Lolium multiflorum* Lam.

Table 3. The content [mg/kg D.M.] of chromium in Italian ryegrass over the years 1998–2000

Objects	Content chromium in mg/kg D.M.)			Means
	Years			
	1998	1999	2000	
1. Soil material (control)	3.21	5.85	4.20	4.42
2. Soil material + brown coal from Sieniawa	4.18	6.24	4.49	4.97
3. Soil material + brown coal from Konin	4.10	6.56	4.34	5.00
4. Soil material + sludge from Siedlce	5.65	6.36	4.42	5.48
5. Soil material + sludge from Drosed	5.15	6.46	4.44	5.35
6. Soil material + sludge from Łuków	3.34	6.38	4.63	4.78
7. Soil material + brown coal from Sieniawa and sludge from Siedlce	6.04	6.42	4.43	5.63
8. Soil material + brown coal from Sieniawa and sludge from Drosed	3.87	6.60	4.78	5.08
9. Soil material + brown coal from Sieniawa and sludge from Łuków	3.49	6.23	4.46	4.73
10. Soil material + brown coal from Konin and sludge from Siedlce	4.18	6.08	4.63	4.96
11. Soil material + brown coal from Konin and sludge from Drosed	3.71	6.48	4.34	4.84
12. Soil material + brown coal from Konin and sludge from Łuków	6.41	6.87	4.81	6.03
13. Soil material + FYM	5.83	6.54	4.78	5.72
Means	4.75	6.39	4.52	5.15

$LSD_{0.05}$ for: objects (A) n.s.
years (B) 0.58
interactions (A x B) n.s.
(B x A) n.s.

The statistical analysis has shown significant differences in the content of nickel in the dry mass of *Lolium multiflorum* Lam. harvested in following years of experiment (Tab. 4). In biomass of *Lolium multiflorum* Lam. harvested in the 2nd year of experiment the level of nickel in the biomass of grass increased by 18.6% but in the 3rd year of experiment only 7.2% in comparison to the results obtained in the 1st year of experiment.

Table 4. The content [mg/kg D.M.] of nickel in Italian ryegrass over the years 1998–2000

Objects	Content nickel in mg /kg D.M.			Means
	Years			
	1998	1999	2000	
1. Soil material (control)	2.72	2.28	2.70	2.57
2. Soil material + brown coal from Sieniawa	2.35	3.63	3.38	3.12
3. Soil material + brown coal from Konin	2.45	3.27	2.76	2.83
4. Soil material + sludge from Siedlce	4.44	2.86	2.55	2.62
5. Soil material + sludge from Drosed	3.79	3.69	4.32	3.93
6. Soil material + sludge from Łuków	3.27	3.90	4.05	3.74
7. Soil material + brown coal from Sieniawa and sludge from Siedlce	2.16	4.11	3.33	3.20
8. Soil material + brown coal from Sieniawa and sludge from Drosed	2.88	3.20	3.13	3.07
9. Soil material + brown coal from Sieniawa and sludge from Łuków	2.42	2.95	2.68	2.68
10. Soil material + brown coal from Konin and sludge from Siedlce	2.68	2.65	2.86	2.73
11. Soil material + brown coal from Konin and sludge from Drosed	2.42	3.33	3.20	2.98
12. Soil material + brown coal from Konin and sludge from Łuków	2.79	4.17	2.71	3.22
13. Soil material + FYM	2.71	3.89	2.28	2.96
Means	2.85	3.38	3.07	3.05

$LSD_{0.05}$ for: objects (A) n.s.
years (B) 0.52
interactions (A x B) n.s.
(B x A) n.s.

The mean content of nickel in dry mass of *Lolium multiflorum* Lam. was on the low level (3.05 mg/kg). Similar results were obtained in other researches [2, 5, 12] but other authors [13] have reported that the content of nickel in dry mass of *Lolium multiflorum* Lam. decreased under the influence of applied liming.

The presented results obtained for the content of Cr and Ni in our investigation are very far from the critical value taken for the fodder which are for Cr 20–50 mg/kg and for Ni 50–100 mg/kg of dry mass.

CONCLUSIONS

1. The brown coals, waste activated sludge and their mixtures as well as FYM can be used in the fertilization of *Lolium multiflorum* Lam.
2. The content of Cr and Ni in soil material has not overcome the critical value for those elements in soils and soil with organic materials.

3. Determinated content of Cr and Ni in the dry mass of *Lolium multiflorum* Lam. was on the low level much more below the critical values for those elements taken as standard for fodder

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