

Metal content in soil fertilized with brown coal fly ash

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Abstract. The aim of the studies was evaluation of brown coal ash produced by Power Plant Group Pątnów-Adamów-Konin for agricultural purposes. The subject matter was the estimation of the influence of fly ash applied to light soil on the metal content of soils (aluminium, iron, manganese, copper, nickel and cobalt). The field experiment was conducted on light soil at the area of the Agricultural Experimental Station in Lipnik, Poland. The experiment was set up by means of randomized complete blocks in 4 replications. The study consisted of testing 7 variants (controlburned lime (CaO) dolomite lime $\text{CaCO}_3\cdot\text{MgCO}_3$, ash from 1st electrofilter zone, from 2nd electrofilter zone, from 3rd electrofilter zone and mixture of ashes from three electrofilter zones). Lime fertilizers and ashes were applied in a dose corresponding to 1.0 hydrolytic soil acidity expressed in $\text{cmol H}^+ \text{kg}^{-1}$ of soil. Brown coal fly ash produced by Power Plants ZE PAK S.A., used as soil fertilizer, did not contribute to changes of content of the following metals: iron, zinc, copper, nickel, lead and cobalt in the tested soil. Soil-incorporated brown coal fly ash significantly increased the content of manganese. However, the obtained results did not exceed the allowable standard. In the soil of all fertilizer variants, where brown coal ash was applied, the content of mobile aluminium diminished. When brown coal ash produced by Power Plants ZE PAK S.A. was applied in the experiment, soil reaction changed from acid to neutral and its hydrolytic acidity decreased by ca 50%.

Key words: soil, brown coal ash, aluminium, iron, manganese, zinc, lead, cupper, nickel, cobalt

INTRODUCTION

By-products of coal burning (UPS in short) originate in hard and/or brown coal combustion processes taking place in power plants. During combustion, volatile substances, i.e. burned coal and the majority of its impurities such as clay, schist, quartz and other minerals are subject to melting. Melted particles are carried by off-gases, and after transition to lower temperature are subject to solidification, creating mainly spherical vitreous particles called fly ash, caught by mechanical separators, electrofilters or bag filters. Volatile ash particles are 1–150 μm (Naik & Chun, 2003) in

size. American standard ASTM C618 classifies fly ash from coal combustion as F and C class. C class ashes produced while burning brown coal, are called high-calcium ash containing up to 40% of CaO. In 2000 Polish production of fly ash as a by-product of brown coal burning was 455 000 T (Myszkowska, 2003).

Ash is a specific material; its useful physical and chemical properties should be effectively applied. According to the Ordinance of the Minister of Environment, dated 27 September 2001, stating a list of wastes, combustion by-products (UPS), including brown coal ashes produced by power plants, are non-hazardous wastes (Off. J. No 112, item 1206). One way of using fly ash produced during brown coal combustion is in agriculture. The elements appearing in ash can be divided to matrix elements, main and trace elements. The following matrix elements can be found in fly ash produced by power plants belonging to ZE PAK S.A.: silica, aluminium oxide and ferric oxides (Matusiewicz & Janowicz, 1993). Ashes can contain significant amounts of heavy metals, but washing them out can be difficult because these elements are immobilized in aluminium-silica complex. A significant amount of soluble forms of phosphorus in hydrofluoric acid (HF) indicates that these are the compounds of a structure similar to hydroxyapatite and combinations of phosphates with aluminium and iron (Łączny, 1983). Boron and aluminium contents (overabundant for nutritional requirements of plants) are also a characteristic feature of ash material (Gilewska, 2003). Brown coal ash includes only traces of nickel, cadmium, arsenic and other heavy metals; however, it is rich in calcium and magnesium (Rosik-Dulewska, 2002).

Scientists in many countries are carrying out research on the application of ash in agriculture (Rethman et al., 2001; Kruger, 2003; Yoshiaki & Kazuo, 2003). In Poland, many studies indicate that ash made of brown coal can be used in agriculture (Gilewska & Przybyła, 2001; Siuta, 2001; Gibczyńska et al., 2005); however, these studies relate mainly to the usability of brown coal ash for de-acidification of mineral soils. Reaction changes have significant impact on activation or retrogradation of many nutrients occurring in soil which plants require. Therefore, the study of the effects of fly ash on physical and chemical changes and the chemical composition of mineral soils is justified.

The aim of these studies was evaluation of brown coal ash produced by Power Plant Group Pątnów-Adamów-Konin for agricultural purposes. The subject matter of the study was an estimation of the influence of fly ash applied to light soil on soil metal content (aluminium, iron, manganese, copper, nickel and cobalt).

MATERIALS AND METHODS

The field experiment was carried out on the area of the Agricultural Experimental Station in Lipnik near Stargard Szczeciński, on light soil (good rye complex). The experiment was set up in randomized complete blocks in 4 replications. The area of each plot was 22 m². The study consisted of testing 7 variants (control, burned lime (CaO) – 3.12 kg ha⁻¹, dolomite lime CaCO₃·MgCO₃ – 4.72 kg ha⁻¹, ash from 1st electrofilter zone – 6.74 kg ha⁻¹, from 2nd electrofilter zone – 6.16 kg ha⁻¹, from 3rd

electrofilter zone – 5.84 kg ha⁻¹ and a mixture of ashes from three electrofilter zones – 6.08 kg ha⁻¹) (Table 1). Lime fertilizers and ashes were applied in a dose corresponding to 1.0 hydrolytic soil acidity expressed in cmol H⁺ kg⁻¹ of soil. Doses of each calcium fertilizer included calcium and magnesium oxides. Basic NPK fertilization, was N – 90; P₂O₅ – 40; K₂O – 60; S – 6 kg · ha⁻¹, was applied. The plant tested was spring crop triticale of variety *Gabo*.

The first factor (I) studied was lime and ashes, while the second (II) – depth of soil samples. Combined soil samples were collected from each experimental plot after harvesting triticale, at the depth 0–10 cm and 10–25 cm. The significance of differences between individual determinations was estimated by means of Tukey test at significance level $\alpha = 0.05$. Correlation coefficients were calculated by Statistica 7.1 software.

On average, brown coal ash produced by Power Plants ZE Pątnów-Adamów-Konin S.A. included 22.82% lime, 3.62% magnesium, 0.07% sodium and 0.04% potassium. Reaction of applied fly ashes determined as pH in H₂O varied from 11 to 13.

Table 1. Content of metals in brown coal ash.

Fractions of ash	Calcium	Magnesium	Iron	Manganese	Zinc	Copper	Nickel	Lead	Cobalt
	%		[mg·kg ⁻¹ soil]						
1 st zone ash	20.9	3.38	29730	2986	18.2	11.73	22.32	0.0	11.73
2 nd zone ash	23.0	3.61	26300	3068	26.2	16.78	21.52	0.0	16.78
3 rd zone ash	24.3	3.75	23700	2945	24.8	19.16	19.66	0.0	19.16
Mixture	23.1	3.75	26600	3034	26.4	15.36	20.74	0.0	15.36

The reaction of studied soil samples was determined by potentiometers using extraction solutions: H₂O, KCl and CaCl₂ (PN-ISO 10390/1997). Soil hydrolytic acidity (Hh) was determined using extraction by calcium acetate(II) (Krzywy et al., 1997). General metal content in soil and ash, after wet combustion in a mixture of nitric(V) and chlorine(VII) acids, was determined using atomic absorption spectrometer SOLAAR S (Ostrowska et al., 1991).

Mobile aluminium in soil was determined by the colorimetric method using the Morgan solution for extraction of concentration 0.5 mol dm⁻³ (Nowosielski, 1974). Contents of exchangeable iron in soil were determined by extracting soil with 1-molar concentration of hydrochloric acid by the photo-incandescent method (Krzywy et al., 1997).

RESULTS AND DISCUSSION

Soil reaction and hydrolytic acidity

Soil from the experiment can be considered acid. The reaction of the studied soil after applying calcium fertilizers H₂O-determined varied from 5.75 to 7.68. The results obtained from soil extraction using potassium chloride to determine pH were 4.85 to 7.56. When calcium chloride(II) was used pH values varied from 5.09 to 6.99 (Table 2). Application of both calcium oxide and carbonate as well as individual ash fractions

resulted in an increase of pH in H₂O, in KCl and in CaCl₂. The smallest de-acidifying effect was found after treatment with dolomite lime (CaCO₃·MgCO₃) (Table 2).

Table 2. Soil reaction (pH in H₂O, KCl, CaCl₂) and hydrolytic acidity.

Fertilizers variants	Depth [cm]	pH in H ₂ O	pH in KCl	pH in CaCl ₂	Hydrolytic acidity [cmol(+) kg ⁻¹ of soil]
Check control	0–10	6.29	5.12	5.30	3.56
	10–25	6.25	5.03	5.09	3.69
CaCO ₃ ·MgCO ₃	0–10	6.90	6.24	5.82	2.50
	10–25	6.26	5.13	5.33	3.56
CaO	0–10	7.64	7.36	6.60	2.06
	10–25	6.55	5.59	5.32	3.25
1 st zone ash	0–10	7.68	7.53	6.98	1.94
	10–25	6.28	5.45	5.44	3.62
2 nd zone ash	0–10	7.53	7.44	6.99	2.06
	10–25	5.75	4.85	5.14	3.94
3 rd zone ash	0–10	7.64	7.46	6.76	1.87
	10–25	6.32	5.34	5.78	3.62
Mixture	0–10	7.68	7.56	6.46	2.06
	10–25	5.79	4.91	5.09	3.62
LSD _{0.05} I · II		0.32	0.53	0.57	0.670
II · I		0.80	1.24	1.07	1.322
Fertilizing variants					
Check control		6.27	5.07	5.17	3.64
CaCO ₃ ·MgCO ₃		6.51	5.57	6.40	3.14
CaO		6.99	6.30	5.83	2.77
1 st zone ash		6.84	6.28	6.06	3.08
2 nd zone ash		6.46	5.89	5.87	3.19
3 rd zone ash		6.84	6.19	6.03	2.92
Mixture		6.55	5.97	5.64	3.00
LSD _{0.05} I		0.75	1.13	0.94	0.37
Depth [m]					
0–10		5.34	6.98	6.42	2.29
10–25		6.17	5.19	5.30	3.61
LSD _{0.05} II		0.11	0.12	0.29	0.30

Application of brown coal fly ash changed the reaction at the same level as oxide lime. Changes of soil reaction resulted from the presence of calcium in ash, amounting up to 24% (Table 1). No significant differences in interaction with ash of different zones or ash mixture were observed. However, it should be emphasized that the de-acidifying effect of ash has been found only in the soil surface layer (0 to 10 cm) (Table 2).

At the beginning of the experiment, hydrolytic acidity was 2.98 cmol H⁺ kg⁻¹ of soil in non-fertilized soil. Liming diminished hydrolytic acidity at the humus level, mainly in soil layer 0–10 cm. The lowest value of hydrolytic acidity (1.87 cmol H⁺ kg⁻¹ of soil) was obtained after applying the 3rd ash fraction. Correspondingly, as in the case

of soil reaction changes, the lowest drop in hydrolytic acidity was obtained after applying dolomite lime ($2.50 \text{ cmol H}^+ \text{ kg}^{-1} \text{ soil}$). In general, the use of ash was often more effective than calcium oxide(II) in decreasing the hydrolytic acidity of soil.

Content of mobile aluminium and exchangeable iron in soil

Aluminium is one of the main elements of the earth's crust. However, only its mobile forms exert negative influence on plants and limit root development. The beneficial impact of liming relies mainly on neutralization of exchangeable aluminium, bringing it to a non-toxic limit or to decay in soil. Toxic interaction of aluminium ions with plants has begun when the contents amount to 20 mg Al kg^{-1} of soil (Motowicka-Terelak, 1988).

Table 3. Mobile aluminium and exchangeable iron content in soil.

Fertilizing variants	Depth	Exchangeable aluminum	Exchangeable iron
	[cm]	[mg Al·kg ⁻¹ soil]	[mg Fe kg ⁻¹ soil]
Check control	0–10	34.71	875.99
	10–25	33.13	747.09
CaCO ₃ ·MgCO ₃	0–10	21.02	861.79
	10–25	32.77	722.13
CaO	0–10	19.32	847.96
	10–25	31.56	737.50
1 st zone ash	0–10	26.99	943.07
	10–25	30.10	712.80
2 nd zone ash	0–10	30.89	911.60
	10–25	38.83	723.60
3 rd zone ash	0–10	19.17	921.01
	10–25	31.19	721.94
Mixture	0–10	32.35	915.75
	10–25	37.92	719.86
LSD _{0.05} I · II		11.14	n.s.d.
II · I		24.89	n.s.d.
Fertilizing variants			
Check control		33.76	798.65
CaCO ₃ ·MgCO ₃		28.07	777.99
CaO		26.66	781.68
1 st zone ash		28.87	804.71
2 nd zone ash		35.65	798.82
3 rd zone ash		26.38	801.57
Mixture		35.69	798.22
LSD _{0.05} I		3.39	110.64
Depth [m]			
0–10		26.35	896.74
10–25		33.64	726.42
LSD _{0.05} II		10.06	157.64

n.s.d. – not significant difference.

At the beginning of the experiment, in non-fertilized soil, the content of mobile aluminium was 33.76 mg Al·kg⁻¹ constituting 0.1% of its total content in soil. Application of dolomite lime and oxide lime significantly diminished the mobile aluminium content (Table 3). A similar result was obtained when applying 3rd zone ash and maintaining mobile aluminium content below its toxic level. However, after fertilizing with 1st and 2nd zone ashes and their mixture, the mobile aluminium content of the soil decreased at a slower rate. Changes in mobile aluminium contents corresponded to soil layer 0–10 cm (Table 3). However, from the obtained results no correlation has been found between soil reaction as determined in H₂O, KCl and CaCl₂ and exchangeable aluminium content in the surface soil layer after liming. The correlation coefficient was $r < -0.300$.

Average content of exchangeable iron in soil from the control variant of soil sample was 98.65 mg Fe kg⁻¹ of soil constituting 12% of its total amount (Tables 3, 4). Neither fertilization of soil with ash nor with liming caused any changes in the content of exchangeable iron. Obtained differences did not exceed significance levels. All fertilizing variants from a surface layer of soil contained more exchangeable iron than those from deeper layers.

General soil content of iron, manganese, zinc, lead, copper, nickel and cobalt

Table 4. Total content of iron, manganese, zinc, lead, copper, nickel and cobalt in soil.

Fertilizing variant	Iron	Manganese	Zinc	Lead	Copper	Nickel	Cobalt
[mg kg ⁻¹ of soil]							
Check control	6541	299.7	26.6	14.4	5.25	4.92	2.24
CaCO ₃ ·MgCO ₃	6360	313.1	26.7	15.3	4.94	4.25	2.12
CaO	6100	303.7	26.2	14.2	4.63	4.77	2.05
1 st zone ash	6768	325.5	26.8	14.0	5.12	4.59	2.00
2 nd zone ash	6208	318.0	25.6	15.9	4.78	5.03	2.04
3 rd zone ash	6698	307.5	27.0	14.3	5.12	5.09	1.91
Mixture	6368	320.8	27.2	14.3	4.85	5.33	2.00
LSD _{0.05} I	770.9	16.34	n.s.d.	n.s.d.	n.s.d.	0.91	n.s.d.

n.s.d. – not significant difference.

Because no changes had been found due to ash fertilizing in the deeper layers of soil, only the 0–10 cm layer has been taken into consideration for determining heavy metal content. The total content of iron in soil was ca 0.6%, corresponding to the average range specified for sandy arable soils. Applied calcium fertilizers and fly ashes of iron content up to 3%, similar to exchangeable iron, did not contribute to any significant change of iron value in the tested soil (Tables 1, 3, 4).

The total manganese content in the control soil sample was 299.7 mg Mn kg⁻¹ of soil, which exceeds its average abundance in sandy soil in Poland (Kabata-Pendias & Pendias, 1999). Similarly, in their studies Bowszys et al. (2004) observe that when rye was included in the experiment on liming, the soil revealed a higher value of manganese than values approved as adequate for geochemical background. Both

applied calcium fertilizers and brown coal ashes caused a tenfold increase of the manganese contents in ashes, compared to its abundance in the tested soil (Tables 1, 4). However, manganese content in soil after the fly ash treatment did not exceed the allowable standard (Kabata-Pendias & Pendias, 1999).

Zinc content of soil in the test sample was 26.6 mg Zn; this is a value below the average content of this element in Polish soils and is 4 times smaller than the permissible standard (Off. J. 02/165/1359 dated 4 October 2002). Liming and application of each fractional amount of ash did not change the amount of zinc in the tested soil. It should be emphasized that the amount of zinc in brown coal ash was at the same level as in soil cultivated in the experiment (Tables 1, 4). The amount of total lead in the tested soil was 14.4 mg Pb kg⁻¹ which is exactly the average content of lead in Polish soil (Sękara, 2005). Fertilizing soil with ash could not have changed the lead content in the soil because no traces of lead were found in the applied fertilizers (Table 1).

The average content of copper and nickel in Polish soil is 6 milligrams per 1 kg of soil (Sękara, 2005), whereas in 1 kg of tested soil, the copper and nickel amount was ca 5 milligrams. In this case, fertilizing with ash did not change the amount of copper and zinc in soil (Table 4). Among the studied metals cobalt was the least abundant (ca 2 mg Co kg⁻¹ of soil) in experimental soil and – as in the case of reported earlier metals – neither ash nor dolomite and oxide lime treatment changed these values.

Summarizing, although large amounts of the calcium fertilizers, both traditional and brown coal ash, were applied, they did not contribute to the change of content of studied metals in the tested soil, except for manganese. The soil remained relatively low in metal content; the quantitative changes have been analysed in the experiment.

CONCLUSIONS

1. Brown coal fly ash produced by Power Plants ZE PAK S.A. Pątnów–Adamów-Konin, used as soil fertilizer did not contribute to changes of content of the following metals: iron, zinc, copper, nickel, lead and cobalt in tested soil.
2. The incorporation of brown coal fly ash into the soil significantly increased the content of manganese. However, the obtained results did not exceed the allowable standard.
3. In soil of all fertilizer variants, where brown coal ash was applied, the content of mobile aluminium diminished. Changes in mobile aluminium content were found in soil layer 0–10 cm.
4. When brown coal ash produced by Power Plants ZE PAK S.A. Pątnów–Adamów-Konin was applied, soil reaction changed from acid to neutral and its hydrolytic acidity decreased by ca 50%.

REFERENCES

- Bowszys, T., Ruszkowski, K., Bobrzecka, D. & Wierzbowska, J. 2004. The effect of liming and multicomponent fertilizers on the soil reaction and heavy metals content in soil. *J. Elementol.* **4**, 551–558 (in Polish).

- Gibczyńska, M., Meller, E., Stankowski, S., Wołoszyk, Cz. & Kornaś, B. 2005. The effect of ashes from brown coal on physical properties of light soil. In *Mat. X Międzynarodowej Konferencji „Popioły z energetyki” Sopot 12-14 X 200.*, 185–199 (in Polish).
- Gilewska, M. & Przybyła, Cz.. 2001. Utilization of sewage in recultivation of ash disposal sites. *Zesz. Probl. Post. Nauk Roln.* **477**, 217–222 (in Polish).
- Gilewska, M. 2003. Biological reclamation of grounds of PAK S.A. ash landfills. In *Mat. X Międzynarodowej Konferencji „Popioły z energetyki” W-wa 14-17 XI 2003*, 331–342 (in Polish).
- Kabata-Pendias, A. & Pendias, H. 1999. Biochemistry of trace elements. PWN Warszawa (in Polish).
- Kruger, R.A. 2003. Successful use of coal ash in South Africa. In *Mat. X Międzynarodowej Konferencji „Popioły z energetyki” W-wa 14-17 XI 2003*, 53-70, (in Polish).
- Krzywy, E., Nowak, W. & Wołoszyk, Cz. 1997. Agricultural chemistry. AR Szczecin (in Polish).
- Łączny, M. J. 1983. The equilibrium concentration of phosphates ions in water solution of fly ashes. *Arch. Ochr. Środ.* **3-4**, 83–93 (in Polish).
- Matusiewicz, H. & Janowicz, K. 1993. Physico-chemistry characteristic of brown coal ash produced by Power Plants „Konin” from 3rd electrofilter zone and investigation in leaching. *Arch. Ochr. Środ.* **3-4**, 59–81 (in Polish).
- Motowicka-Terelak, T. 1988. Harmfulness for plants of chemically active form Al. i Mn and ways of neutralization in acid soils. *Materiały Sympozjum: Rola nawożenia w podniesieniu produktywności i żyzności gleb. Cz II. Olsztyn 24-25 czerwca, AR-T Olsztyn 213* (in Polish).
- Myszkowska, A. 2003. “CCPs Production and Utilization in Poland in 2000,” *Eko Technology Sp. z o.o. (Ekotech Poland Inc.), Poland, Personal Communication August 1*, 3.
- Naik, T. R. & Chun, Y. 2003. Use of class C fly ash in cement-based construction materials. In *Mat. X Międzynarodowej Konferencji „Popioły z energetyki” W-wa 14-17 XI 2003*, 121–164 (in Polish).
- Nowosielski, O. 1974. Fertilization of vegetable plants. PWRiL Warszawa (in Polish).
- Ostrowska, A., Gawliński S. & Szczubiałka, M. 1991. Methods of analysis and estimation of characteristics soils and plants. IOŚ Warszawa (in Polish).
- Polish norm - PN-ISO 10390/1997, (in Polish).
- Rethman, N., Kruger, R.A., du Toit, E., Ramagadza, E., Truter, W. & Reynolds K. 2001. The use of fly ash biosolids to ameliorate soils, revegetate disturbed areas and improve plant productivity. In *14ty International Symposium on Management and Use of Coal Combustion Products (CCPs)*, **1**, 1–9.
- Rosik-Dulewska, Cz. 2002. Basis of waste management. PWN Warszawa (in Polish).
- The Ordinance of Minister Environment, 09. 09. 2002. Off. J. 02/165/1359 dated 4 October 2002 (in Polish).
- The Ordinance of Minister Environment, 27.09. 2001, Off. J. No 112, item 1206 (in Polish).
- Sękara, A. 2005. Heavy metals in environment. *Hasło ogrodnicze* **6**, 1–3 (in Polish).
- Siuta, J. 2001. Waste management in environment. *Zesz. Probl. Post. Nauk Roln.* **477**, 275–285 (in Polish).
- Yoshiaki, S. & Kazuo, H. 2003. Current state of effective coal ash utilization in Japan. In *Mat. X Międzynarodowej Konferencji „Popioły z energetyki” W-wa 14-17 XI 2003*, 71–86.