

## EFFECT OF HARD COAL FLY ASH APPLICATION ON CHEMICAL COMPOSITION OF FORESTED (FORMERLY ARABLE) RUSTY SOIL AND SCOTCH PINE NEEDLES

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**A b s t r a c t.** The effect of hard coal fly ash applied on surface of forested (formerly arable) rusty soil on chemical composition of soil surface horizons was evaluated in field experiments conducted between the years 1992-1995. The application of fly ash at the dose 15, 30, 60 and 120 t ha<sup>-1</sup> on the soil surface caused a decrease of acidity of soil surface layer which was dependent on the fly ash rate. The deacidification of soil lasted only two years. The application of fly ash increased also the content of macro- and microelements in the soil as well as in Scotch pine needles.

**K e y w o r d s:** hard coal fly ash, soil, chemical properties.

### INTRODUCTION

Substantial amounts of combustion by products (mainly fly ash) are generated in coal-fired power plants in Poland and there is a growing need to find a means for their disposal or suitable uses for these waste materials. For example, in the Szczecin Voivodeship, it has been estimated that the annual production of hard coal fly ash in the years 1985-1995 ranged from 26.0 to 2.6 thousand tons.

According to extensive literature review the effects of hard coal fly ash application on forested and arable soils caused changes of soil acidity (decrease of pH and exchangeable and hydrolytic acidity) [1,3,5,6,10,14,16-18]. These changes resulted in a high content of soluble basic cations (Ca, K, Na) in fly ash [19]. Usually after application of small (2.5-150 t ha<sup>-1</sup>) doses of fly ash the positive changes of chemical properties of sandy forests soils lasted a few years [3,6,10]. When higher doses of fly ash (200-2000 t ha<sup>-1</sup>) were applied the positive effects were observed longer (even over a period of 15 years) [1,6].

The main objectives of this work were to evaluate the effects of hard coal fly ash applied at the dose 15, 30, 60 and 120 t ha<sup>-1</sup> on: (1) chemical composition of

soil surface horizons of formerly arable rusty soil, and (2) chemical composition of two-year old pine needles.

#### MATERIAL AND METHODS

The experimental plots were located on the sandy terrace of pravalley of the Odra River in the area of Gryfino Forest Inspectorate in Szczecin district (Fig. 1). The area was forested 13 years ago with Scotch pine (*Pinus sylvestris* L.). To check the homogeneity of soil in the area a number of drillings were done which confirmed the lack of differentiation of soil material. The soil surface was sparsely covered by mosses, grasses and pine needles.

The experiment was conducted in the years 1992-1995 using the complete randomisation method. The fly ash was taken from the electrofilters of the "Dolna Odra" Power Plant and applied at 5 doses: zero or control, 15, 30, 60 and 120 t ha<sup>-1</sup> in three replicates. Every replicate comprised 25 pine trees growing in a row. 375 trees were investigated. Fly ash was applied to the soil surface around the tree trunk in an area of approximately 600 cm<sup>2</sup> and was not mixed with the soil. In subsequent years pine needles systematically covered the layer of fly ash. The composite soil samples (0-20 cm) which comprised A and partly Bv horizons were taken from every replicate before and every year after the application of fly ash (1993-1995) in the first days of September. At the same time the two-year old pine needles were sampled.

In soil samples the content of the organic carbon and selected chemical properties of soils (pH, hydrolytic and exchange acidity, content of mobile aluminum, basic cations content and soil complex saturation with basic cations) were analysed using routine procedures. The total contents of macro- and microelements were determined in the soil and plant material after wet digestion in mixture of concentrated HNO<sub>3</sub> and HClO<sub>4</sub> acids. Moreover, in soil samples the contents of soluble macro- and microelements were analysed after extraction with 2.5% CH<sub>3</sub>COOH and 1 M HCl, respectively. The content of Ca, Mg, Cu, Fe, Mn, Ni, Pb and Zn were analysed using atomic absorption method, K and Na by emission spectroscopy, P colorimetrically and S nephelometrically.

The data presented in Tables 1-4 are given as means of 3 replicates for each combination. The analysis variation and LSD values were calculated.

#### RESULTS AND DISCUSSION

The selected chemical properties and macro- microelements content in the soil are presented in Tables 1-3. According to our expectation fly ash applied at the

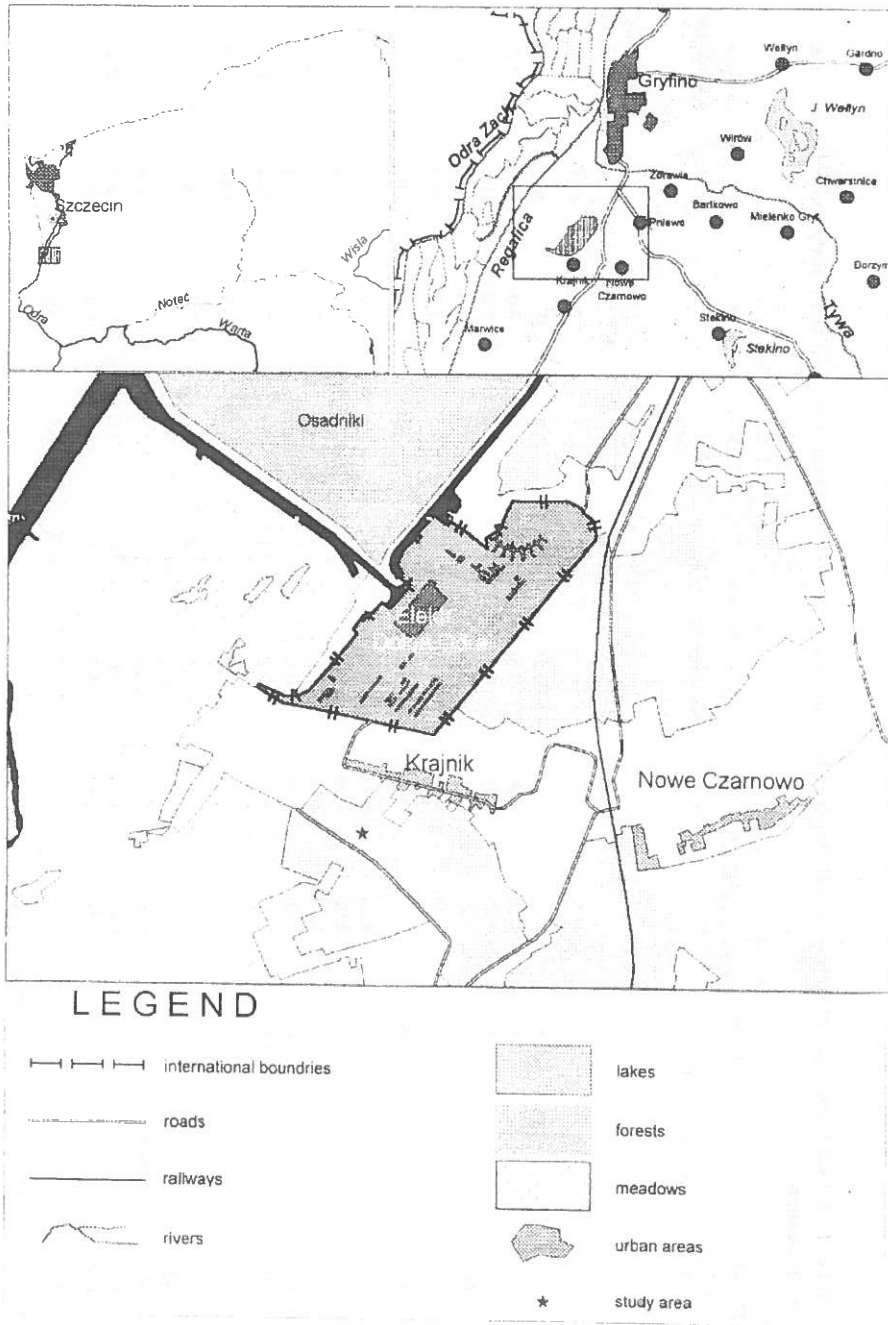


Fig. 1. Localisation of the experimental field.

**Table 1.** Selected properties of composite soil samples (0-20 cm) of formerly arable, forested from 13 years, rusty soil before and after fly ashes application

Fly ashes rate (t ha <sup>-1</sup> )	Years	Organic carbon (% C <sub>org</sub> )	pH in		Acidity		Basic cations content	T	V (%)	Mobile aluminium
			H <sub>2</sub> O	1 M KCl	exchangeable	hydrolytic				
e										
cmol(+) kg <sup>-1</sup> d.m. of soil										
0	1992	0.93	4.1	3.7	0.7	3.7	3.3	7.0	47.1	0.7
0		0.81	4.2a	3.8	0.7	3.8	3.3	7.1	46.5	0.7
15		0.75	4.8b	3.8	0.6	3.4	3.5	6.9	50.7	0.7
30	1993	0.81	4.8b	3.8	0.6	3.4	3.6	7.0	51.4	0.6
60		0.87	5.0b	3.9	0.6	3.3	3.7	7.0	52.9	0.6
120		0.81	5.2b	4.0	0.4	3.0	4.3	7.3	58.9	0.6
LSD <sub>0.05</sub>		NS		NS	NS	NS	0.84	NS	6.01	NS
0		0.81	4.3a	3.8a	0.6	3.6	3.2	6.7	47.8	0.7
15		0.87	5.0b	3.9a	0.5	3.2	3.7	6.9	53.6	0.6
30	1994	0.87	5.1b	4.0b	0.5	3.0	4.3	7.2	59.7	0.4
60		0.87	5.2b	4.3b	0.5	2.7	4.7	7.3	64.4	0.3
120		0.87	6.1b	5.3c	0.2	2.1	5.0	7.1	70.4	0.2
LSD <sub>0.05</sub>					0.25	0.70	0.95	NS	7.44	0.19
0		0.87	4.3a	3.8a	0.7	3.7	3.4	7.0	48.6	0.7
15		0.81	4.9b	3.9a	0.7	3.4	3.6	7.0	51.4	0.6
30	1995	0.87	5.0bc	3.9a	0.6	3.3	3.7	7.0	52.9	0.5
60		0.87	5.2bc	4.0a	0.6	3.0	3.8	6.8	55.9	0.4
120		0.93	5.6c	4.8b	0.4	2.6	3.8	6.4	59.4	0.2
LSD <sub>0.05</sub>		NS			NS	0.37	NS	NS	4.67	0.12

NS - not significant; a, b, c - homogeneity groups.

**Table 2.** Mean content ( $\text{mg kg}^{-1}$  d.m. of soil) of macroelements soluble in the mixture of concentrated acids ( $\text{HNO}_3 + \text{HClO}_4$ ) and in  $2.5\% \text{CH}_3\text{COOH}$  in composite soil samples (0–20 cm) of formerly arable, forested from 13 years, rusty soil before and after fly ashes application

Fly ashes rate ( $\text{t ha}^{-1}$ )	soluble in									
	$\text{HNO}_3 + \text{HClO}_4$					$2.5\% \text{CH}_3\text{COOH}$				
Years	Ca	Mg	K	Na	P	Ca	Mg	K	Na	P
0	381	129	574	80	385	1.95	0.35	0.38	0.39	2.58
0	383	128	571	83	374	2.13	0.36	0.34	0.41	2.91
15	417	133	582	87	389	2.46	1.04	0.38	0.45	2.69
30	500	141	589	94	406	3.04	1.04	0.41	0.45	2.91
60	583	156	600	106	427	3.24	1.23	0.41	0.52	2.85
120	617	163	607	118	483	4.03	1.56	0.50	0.70	3.55
LSD <sub>0.05</sub>	NS	NS	NS	NS	NS	1.159	0.439	0.126	0.261	0.571
0	383	128	574	82	363	1.96	0.38	0.36	0.43	2.85
15	500	141	606	108	391	2.43	0.74	0.38	0.48	2.85
30	750	153	651	114	410	3.49	1.07	0.42	0.51	2.96
60	950	168	684	124	411	3.98	2.06	0.44	0.55	3.01
120	967	246	741	198	512	4.51	2.77	0.45	0.59	3.28
LSD <sub>0.05</sub>	296.1	76.3	NS	105.4	NS	1.715	0.853	0.083	NS	NS
0	400	130	578	81	373	1.81	0.36	0.33	0.39	2.69
15	450	135	583	103	376	1.95	0.58	0.36	0.39	2.58
30	483	149	634	116	383	2.03	0.71	0.37	0.45	2.58
60	517	163	642	119	388	2.88	1.78	0.39	0.48	2.80
120	683	167	660	124	417	3.43	2.39	0.41	0.52	3.12
LSD <sub>0.05</sub>	NS	NS	NS	NS	NS	1.076	0.632	NS	NS	0.548

**Table 3.** Mean content (mg kg<sup>-1</sup> d.m. of soil) of microelements soluble in the mixture of concentrated acids (HNO<sub>3</sub> + HClO<sub>4</sub>) and in 1 M HCl in composite soil samples (0-20 cm) of formerly arable, forested from 13 years, rusty soil before and after fly ashes application

Fly ashes rate (t ha <sup>-1</sup> )	Years	soluble in													
		Co	Cu	Fe	Mn	Ni	Pb	Zn	Co	Cu	Fe	Mn	Ni	Pb	Zn
		HNO <sub>3</sub> + HClO <sub>4</sub>													
		1 M HCl													
0	1992	1.4	2.4	3479	134	1.5	8.5	14	0.26	0.70	741	24.2	0.14	4.83	1.70
0		1.4	2.4	3360	142	1.6	8.5	14	0.23	0.75	741	23.5	0.14	5.33	1.74
15		1.4	2.9	3466	161	2.0	9.8	15	0.24	0.70	740	24.2	0.14	2.29	1.77
30	1993	1.4	3.2	3453	165	2.1	10.1	16	0.25	0.80	780	26.4	0.17	2.80	1.80
60		1.5	3.9	3708	169	2.5	16.4	21	0.29	0.81	810	28.8	0.21	6.41	1.90
120		1.5	4.5	4273	178	3.3	16.6	24	0.33	0.95	860	30.1	0.23	8.09	2.14
LSD <sub>0,05</sub>		NS	1.79	NS	NS	NS	3.82	NS	0.092	0.181	NS	NS	0.052	1.14	NS
0		1.4	2.3	3485	140	1.6	8.2	14	0.25	0.70	759	24.2	0.15	4.99	1.69
15		1.4	3.2	3674	164	1.9	10.3	16	0.25	0.78	768	25.5	0.16	5.70	1.80
30	1994	1.5	3.6	3764	178	2.1	13.4	31	0.29	0.81	795	26.5	0.18	6.44	1.85
60		1.5	4.1	3833	186	2.7	15.8	33	0.33	0.92	854	29.0	0.25	6.58	1.98
120		1.6	4.6	4791	191	3.2	17.6	35	0.35	0.99	889	32.2	0.28	6.84	2.20
LSD <sub>0,05</sub>		NS	1.81	NS	NS	1.58	2.56	13.9	0.098	0.195	NS	NS	0.063	NS	NS
0		1.3	2.5	3400	142	1.5	8.4	15	0.23	0.72	730	23.4	0.15	4.88	1.71
15		1.4	2.9	3607	160	1.9	10.6	17	0.24	0.77	770	25.1	0.15	6.19	1.81
30	1995	1.5	3.4	3663	168	2.0	11.6	17	0.28	0.85	790	26.8	0.22	6.20	1.84
60		1.5	4.2	3829	175	2.2	15.1	17	0.27	0.86	871	29.2	0.25	6.64	2.01
120		1.6	4.3	3985	179	2.6	17.2	17	0.40	1.11	898	30.9	0.29	6.47	2.11
LSD <sub>0,05</sub>		NS	0.84	NS	NS	NS	2.09	7.9	0.096	0.192	NS	NS	0.074	NS	2.11

Table 4. Mean content of elements ( $\text{mg kg}^{-1}$  d.m. of soil) in two-year old pine needles (*Pinus sylvestris* L.) before and after fly ashes application

Fly ashes rate ( $\text{t ha}^{-1}$ )	Years	Elements contents											
		Ca	Mg	K	Na	P	S	Cu	Fe	Mn	Ni	Pb	Zn
0		3233	1399	2272	59.6	1247	1421	2.62	138.9	147.3	2.33	12.6	28.0
15		3617	1399	2292	59.8	1275	1437	2.65	132.8	138.5	2.97	12.2	27.7
30	1993	4033	1428	2305	66.5	1233	1538	2.75	145.4	128.1	2.93	12.4	32.7
60		4283	1676	2359	75.6	1212	1504	2.97	172.8	121.8	3.13	13.3	36.8
120		4517	1692	2405	92.3	1245	1588	3.02	192.5	118.6	3.67	18.5	43.4
LSD <sub>0.05</sub>		455.9	284.2	NS	13.72	NS	NS	NS	27.14	22.08	NS	1.10	10.97
0		3067	1321	2410	59.7	1187	1304	2.47	132.1	144.0	2.60	11.7	27.5
15		3183	1312	2470	64.4	1103	1320	2.52	137.3	139.5	2.38	11.9	30.6
30	1994	3663	1327	2448	68.0	1078	1354	2.87	130.2	131.1	3.03	12.0	30.3
60		3937	1454	2515	72.5	1064	1471	3.02	165.2	124.0	3.54	12.5	38.2
120		4143	1573	2583	87.9	1068	1655	2.85	167.6	119.0	3.40	16.2	40.9
LSD <sub>0.05</sub>		645.8	249.3	NS	16.16	NS	NS	NS	24.61	12.41	NS	NS	9.24
0		2850	1254	2298	59.5	1173	1437	2.50	123.0	147.2	2.35	12.2	27.8
15		3400	1210	2316	66.0	1176	1170	2.68	129.0	141.2	2.53	12.9	30.9
30	1995	3617	1206	2349	67.4	1140	1287	2.97	130.8	134.3	3.40	12.6	31.4
60		3783	1499	2435	71.9	1238	1304	2.89	158.1	126.7	3.43	14.2	38.7
120		4050	1477	2492	93.3	1259	1304	2.87	163.2	121.8	3.58	15.5	42.0
LSD <sub>0.05</sub>		590.2	214.2	NS	19.73	NS	NS	NS	31.21	16.64	NS	NS	6.67

dose 15-120 t ha<sup>-1</sup> decreased the soil acidity which was demonstrated as increase of pH, decrease of hydrolytic as well as exchange acidity and decrease of content of mobile aluminium. Moreover, the increase of basic cations content and soil complex saturation with basic cations were observed after the introduction of fly ash onto the soil surface. These changes of chemical properties of surface horizons of rusty soil were strongly dependent on the dosage of fly ash. The intensity of change was the highest two years from the application of fly ash and was confirmed by the data presented in Table 1. The main reason for such change was the gradual decrease of basic cations (Ca, Na and K) content. These cations were leached from the fly ash layer deposited on the soil surface. Similar results for arable soils were reported by Wojcieszczuk *et al.* [19].

Chemical composition of fly ashes varies a lot and depends on the origin of coal deposition [6,17]. Generally, after the application of fly ash, an enrichment of soil in macroelements and trace elements as well as heavy metals has been observed [1,3,6]. Therefore, it was important to find out if chemical compounds in fly ash from the "Dolna Odra" Power Plant caused a significant increase of their content in soil.

After application of all the doses of fly ash (with 2.1 and 1.3% Ca and Mg content, respectively) the content of calcium and magnesium soluble in the mixture of concentrated acids (HNO<sub>3</sub> and HClO<sub>4</sub>) and in 2.5% CH<sub>3</sub>COOH significantly increased in the soil. The content of total and soluble P, K and Na increased significantly only when higher doses of ash (60-120 t ha<sup>-1</sup>) were applied (Table 2). Similar results were given by Bogacz [1], Furdyna [3], Koter *et al.* [10].

The content of heavy metals in the surface horizons of rusty soil before fly ash application was very low and within the range accepted for unpolluted soils [8,9,15]. Even after the increase of contents of soluble cobalt, copper, iron, lead, nickel, manganese and zinc after fly ash application, their level was still within the range accepted for unpolluted soils (Table 3) [8,9,15].

Table 4 shows the changes of total elements content in two-year old pine needles before and after the fly ash application. The level of macro- microelements content in the needles from control plots were in the range reported for unpolluted forest tree populations [2,7,11,13,16]. The fly ash application increased the macroelements (Ca, Mg, K, Na and P) as well as most heavy metals (Cu, Fe, Pb, Ni and Zn) in pine needles but caused a decrease of Mn content. The significant changes of the above mentioned elements contents were found only after the application of the higher doses (60 and 120 t ha<sup>-1</sup>) of fly ash. The substantial increase of Ca, Fe,



Zn, Cu contents and the decrease of Mn in pine needles after liming the sandy forest soils was pointed out by Ferm *et al.* [2], Gawliński [4] and Sienkiewicz [16].

The results of the experiment confirmed that fly ash from the "Dolna Odra" Power Plant may be used for the improvement of chemical properties of sandy soils. The main limitation of their application arises from the higher transportation costs which increase on account of the distance from the Power Plant. Moreover, there are difficulties with their even distribution on the soil surface because of their dusty form.

### CONCLUSIONS

On the basis of the results of the conducted experiment the following conclusions may be drawn:

1. Fly ash application on the surface of formerly arable rusty soil caused a decrease in exchangeable as well as the hydrolytic acidity of the soil surface layer (0-20 cm) and the increase of saturation of the soil complex with basic cations. The changes of these soil properties depended on the dosage of fly ash.

2. The positive effect of fly ash which was demonstrated as the decrease of acidity of the soil lasted for only a short time. Two years after their application, the acidification process prevailed again.

3. After the application of all the doses of fly ash, there was a significant increase in the content of Ca and Mg soluble in the mixture of concentrated acids ( $\text{HNO}_3$  and  $\text{HClO}_4$ ) and in 2.5%  $\text{CH}_3\text{COOH}$  in the soil but P, K and Na only when higher rates (60-120 t  $\text{ha}^{-1}$ ) of ash were applied.

4. Despite rather low heavy metal content in fly ash from the "Dolna Odra" Power Plant its application to the rusty soil increased the contents of soluble cobalt, copper, iron, lead, nickel, manganese and zinc. The contents of the above listed elements were still within the range accepted for unpolluted soils.

5. The application to the soil surface of fly ash caused the increase of macro elements (Ca, Mg, K, Na and P) and most of heavy metals (Cu, Fe, Pb, Ni and Zn), with exception of Mn in two-year old pine needles. Significant changes of these elements in the plant material were found only after the application of higher doses (60 and 120  $\text{tha}^{-1}$ ) of fly ash.

6. The fly ash from "Dolna Odra" may be used to improve the chemical properties of sandy soils. The limitation of their application arises from higher transportation costs which are increasing on account of the distance from Power Plant and difficulties with their even distribution on the soil surface.

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