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THE LONG-TERM IMPACT OF AMELIORATING DOSES OF HARD COAL FLY ASH ON SHAPING THE CONTENT OF SELECTED MICROELEMENTS IN AGRICULTURAL SOIL

Abstract. The effect of ameliorating doses of hard coal fly ash (HCFA) on chemical properties of soil and on yields and chemical composition of crops was examined based on an experiment established in 1984. At first, typical agricultural crops were grown in the experiment, but in 1992 the field was turned into permanent grassland. The current study took place twenty-nine years after hard coal fly ash had been applied. Soil samples were collected from the 0–20 cm soil layer, corresponding to the compared treatments. The residual effect of HCFA doses increasing from 100 to 800 $Mg \cdot ha^{-1}$ caused a regular increase in the total content of Cd, Cr, Cu, Mn, Fe, Zn and Pb, as well as the forms of Zn, Cu, Mn, Fe and B soluble in 0.1 M HCl. The total content of the analyzed microelements increased by a maximum of 30% for cadmium up to 176% for zinc. The highest increase in the content of soluble forms ranged from 25% for Fe to 760% for boron. The share of Zn_{bd}, i.e. permanently bound to soil, to Zn_{tot}, i.e. the total zinc form, was positively correlated with pH in KCl, the C:N ratio and the content of Cu permanently bound with soil. Regarding the share of Fe_{bd} in Fe_{tot}, correlations with pH in H_2O and in KCl, content of organic matter (SOM) and the C:N ratio were demonstrated. No such correlations were proven with respect to the other elements.

Hard coal ash is usually seen as a waste product, originating mainly from the power generation industry, where it is termed a combustion by-product. The

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limitation of dust emission imposed by the legal regulations introduced to the Polish law after the country's accession to the European Union [14–16] led to the reduction of the annual fly ash emission from power generating plants, industrial power plants, industrial technologies, local boilers, household furnaces, trade workshops, agriculture, etc. from 115,000 Mg in 2000 to 76,000 Mg in 2011 [20]. However, the volume of fly ash still remains very large and this stimulates the search for its possible applications in economy. In Europe and in the USA, 70% of fly ash on average is used by the construction industry. Hard coal fly ash contains several biogenic macro – and microelements, compounds with deacidifying properties and highly sorptive substances, which often gives rise to concepts of using it in agriculture [4, 5, 8, 10, 12, 22, 29, 30, 32, 41, 42, 44]. Possible applications of fly ash in farming attract much attention in Asian countries, such as India and China, where just 38 to 45% of the fly ash produced is used by civil engineering [34, 38].

Despite quite convincing evidence in favor of hard coal fly ash (HCFA), this by-product was not included in the list of the waste with possible agricultural applications, published in the attachment to the regulation of the Ministry of the Environment of 5 April 2011, on the R10 recovery process [17]. One of the reasons is the highly diverse chemical composition of coal burnt for power generation. The agricultural use of HCFA raises many controversies due to its content of toxic trace elements, such as Cu, Sr, Ni, Cr, Zn, Cd, Mo, Se, Pb, As, V, Hg, Ba, U, Ra, Th and B, which can be a potential hazard for the natural environment [4, 9, 27, 28, 37, 38, 41].

A possible solution to control the toxic effect of metals introduced to soil together with HCFA recycled as an environmental resource is the concurrent application of other substances, e.g. straw, tree bark, composts and brown coal, which can bind insoluble metal-mineral or metal-organic forms. Under favorable conditions, such compounds can remain in the soil for a long time as harmless substances [7, 10, 36, 46, 47]. This is also a way to improve the soil's balance in terms of nitrogen compounds, of which hard coal fly ash is practically void [12, 19], and carbon compounds, whose concentrations range from 2.3% to 25.3% by weight [39].

The objective of the research was to demonstrate the residual effect of ameliorating doses of hard coal fly ash on the content of selected microelements in the arable horizon of soil. The studies comprised the total content of Cd, Pb, Cr, Zn, Cu and Mn as well as the concentration of the forms of Zn, Cu, Mn, Fe and B soluble in 0.1 M HCl.

MATERIAL AND METHODS

The research was based on a field experiment started in 1984 by Grzegorz Nowak and Zdzisław Ciećko, both from the University of Agriculture and Technology (today's University of Warmia and Mazury in Olsztyn). The experiment was situated in the commune of Lelis, in the village called Łęg Starościński (53°11'30,81"N 21°57'20,20"E), in the Province of Masovia (Poland). It was set up on fluvisol with the textural composition of sandy loam: 63% sand, 30% silt, and 7% clay according to the World Reference Base [21]. In the Polish soil valuation system, it belongs to the poor rye complex, class V.

Initially, the soil was moderately rich in available phosphorus (55 mg P kg^{-1}), but rich in available potassium (152 mg K kg^{-1}) and magnesium (55 mg Mg kg^{-1}). The soil reaction measured in water and in 1 mol KCl dm^{-3} was 6.5 and 5.6, respectively. The complex sorptive capacity was 12,5 cmol (+) kg^{-1}.

When being established, the experiment consisted of two factors. The first one comprised incremental doses of HCFA, obtained from electrofilters at the Ostrołęka Power Plant, which equalled 0, 100, 200, 400, 600 and 800 Mg ha^{-1}. The fly ash used in the experiment contained (per 1 kg of dry matter): 491 g SiO_2, 1.7 g P, 2.9 g K, 15.0 g Ca and 7.1 g Mg, and its pH in 1 M KCl was 9.2. The second factor was the use of organic substances, introduced to soil together with fly ash. The following were incorporated into the soil in the amount of 10 Mg of dry matter per 1 ha: manure, straw and tree bark. The experiment was set up according to the random block method with four replicates. The surface area of each plot was 54 m^2. HCFA and the organic substances were applied once, in the autumn of 1984, under winter ploughing. During the first six years, typical agricultural crops were grown on the experimental field, but in 1992 it was all sown with a mixture of grasses and transformed from a ploughed field into permanent grassland.

The residual effect of fly ash and the simultaneously applied organic substances on the physicochemical soil properties was tested in 1985, 1986, 1987, 1988, 2003 and in 2013. The soil analyses made in 2003 showed that the organic supplement introduced to soil 19 years earlier no longer had any significant effect on the soil's content of macro – and microelements [44]. Hence, since 2003, the experiment has been treated as a single-factor one, in which the only experimental factor is the application of various doses of HCFA.

The study discussed herein was based on representative aggregated soil samples taken on 10 August, 2013 from individual plots. The samples were collected from the 0–20 cm soil layer at four repetitions across a plot, using an Egner sampler. The soil samples were air dried, passed through a sieve with the 1.0 mm mesh size and stored in plastic containers.

The total content of microelements (Me_{tot}), i.e. Cd, Pb, Cr, Zn, Cu, Mn and Fe, was determined in air-dry soil. Samples were mineralized in a mixture of HNO_3 and $HClO_4$ (1:1) under infrared, in a Turbotherm TT 125 Rapid Digestion System (Gerhardt Fabrik und Lager Chemischer Apparate GmbH & Co. KG Germany).

The content of soluble forms of microelements (Me_{av}), i.e. Zn, Cu, Mn, Fe and B, was determined after soil extraction in 0.1 M HCl (at the 1:10 soil to solution ratio)

Both forms of elements were analyzed with flame atomic absorption spectroscopy (FAAS) on an AAS 1 apparatus (Carl Zeiss Jena, Germany). Merck standard solutions of the elements were taken for reference.

Percentage shares of the forms of elements fixed in soil (Me_{bd}) were presented as the difference between the total form and the soluble form of elements, expressed relative to the total form, according to the formula:

$$Me_{bd}(\%) = \frac{Me_{tot} - Me_{av}}{Me_{tot}} \cdot 100 \qquad (1)$$

where: Me_{tot} – total content of element (mg kg^{-1} of soil),
Me_{av} – available form of element (mg kg^{-1} of soil).

The results underwent statistical processing with a one-way analysis of variance at the significance level of p=0.05, aided by the statistical calculation module of Statistica v. 10.0 [40]. Least significant differences (LSD) and homogenous groups were distinguished with the significance test by Newman-Keulus. Starndard error (±SE) and correlation power between the analyzed characteristics were expressed by the Pearson's simple correlation coefficient (*r*), calculated with the help of MS Excel 2010 [31]. Statistical significance of the correlation coefficients at n-2 degrees of freedom was computed based on critical value tables [6] at the level of significance of α=0.05 (*) and α=0.01(**), assigning symbols of significant and highly significant correlation, accordingly. Frequency of pairs of observations (n) of the determinations performed is given in the keys under the tables and diagrams.

RESULTS AND DISCUSSION

Despite the 29 years elapsing from the application of hard coal fly ash (HCFA), their impact on the content of the analyzed microelements in the arable layer of soil is still evident (Table 1). The analysis of variance showed that in principle the content of all the microelements corresponded positively with a dose of HCFA, regarding both their total and soluble forms. The maximum increase in the total content of the microelements in the extreme treatments, i.e. treated with the doses of 100 and 800 Mg ha^{-1} of fly ash, versus the control soil (CS), without addition of HCFA, was as follows: Mn – from 2 to 52%, Pb – from 15 to 55%, Fe – from 1 to 77%, Cu – from 5 to 90%, Cr – from 17 to 95% and Zn – from 38 to 176%. It needs to be underlined that 29 years after the application of fly ash, the content of the most toxic element, which is cadmium, did not differ significantly among the 0–100–200 Mg HCFA ha^{-1} treatments. However, it was significantly elevated versus CS after the application of 400 Mg of HCFA ha^{-1}. The treatments which had received the doses of 400 and 800 Mg of HCFA ha^{-1} composed a homogenous group, with no statistically significant differences observed between the two variants. The dose of 100 Mg HCFA ha^{-1} significantly modified the concentrations of Cr_{tot}, Zn_{tot} and Pb_{tot}, whereas with respect to Cu_{tot}, Mn_{tot} and Fe_{tot} their content remained on a significantly higher level than in control soil (CS) in the plots treated with 200 Mg of HCFA ha^{-1}. Each of the HCFA doses applied 29 years before resulted in an increase in the soil content of Zn_{tot}. A comparison of the content of the analyzed elements with the recommendations proposed by the IUNG in Puławy [23] suggests that none of the elements (Cd, Cu, Zn and Pb) exceeded significantly the content corresponding to the zero contamination degree of soils, i.e. the natural content. Analogously, fly ash introduced to soil in the doses of 100–800 Mg ha^{-1} did not demonstrate any significant impact on contamination of the soil environment in the previous studies. The concentrations of the analyzed elements were only slightly above the standards set for types of land classified as group B, i.e. farmlands, and in some cases were almost within the ranges of concentrations assigned to lands of group A, i.e. protected areas [18].

TABLE 1. LONG-TERM IMPACT OF AMELIORATING DOSES OF HCFA ON SHAPING THE CONTENT OF THE TOTAL FORMS OF SELECTED ELEMENTS IN AGRICULTURAL SOIL

HCFA dose [Mgv ha^{-1}]	Total forms of elements [mg kg^{-1} of soil]						
	Cd_{tot}	Cr_{tot}	Cu_{tot}	Mn_{tot}	Fe_{tot}	Zn_{tot}	Pb_{tot}
0	0.249^{a} ±0.033	5.87^{a} ±0.17	5.87^{a} ±0.05	124^{a} ±2.4	6500^{a} ±14	16.03^{a} ±1.27	12.29^{a} ±0.13
100	0.257^{a} ±0.007	6.86^{b} ±0.04	6.15^{a} ±0.11	127^{a} ±0.8	6550^{a} ±53	22.19^{b} ±1.08	14.09^{b} ±0.20
200	0.275^{ab} ±0.004	7.88^{c} ±0.33	7.60^{b} ±0.21	138^{b} ±5.4	7850^{b} ±99	27.96^{c} ±0.13	15.28^{c} ±0.29
400	0.296^{bc} ±0.011	9.37^{d} ±0.13	9.87^{c} ±0.29	163^{c} ±2.6	9450^{c} ±12	32.37^{d} ±1.72	16.68^{d} ±0.22
600	0.318^{c} ±0.002	9.87^{e} ±0.10	10.58^{d} ±0.20	174^{d} ±1.4	9960^{d} ±100	36.88^{e} ±0.97	17.89^{e} ±0.32
800	0.324^{c} ±0.003	11.48^{f} ±0.30	11.18^{e} ±0.12	189^{e} ±4.1	11510^{e} ±134	44.29^{f} ±2.59	19.09^{f} ±0.56
Average	0.287 ±0.032	8.55 ±1.90	8.54 ±2.11	153 ±24.6	8637 ±1837	22.95 ±9.40	15.89 ±2.31
$LSD_{(0.05)}$	0.03	0.45	0.39	6.96	180.45	3.25	0.69
r	0.88**	0.98**	0.96**	0.98**	0.98**	0.97**	0.97**

Values given are means of four replicates ± standard errors, different letters near value indicate significant differences between the treatments at P=0.05. Simple Pearson's correlation coefficient (r) between HCFA dose and elements content: * r – significant for α=0.05, ** – significant for α=0.01, ns – not significant; n=24

Me_{tot} – total form of metal in soil.

A significant increase in the content of soluble forms of microelements versus CS depended on both the specific element and the dose of HCFA (Table 2). With respect to Cu_{av} and Fe_{av}, a significant rise was caused by the dose of 100 Mg of HCFA ha^{-1}, while Zn_{av} and B_{av} were increased significantly by the dose of 200 Mg of HCFA ha^{-1}. The application of HCFA resulted in an increase in the available forms of the elements in the soil, although a significant effect of the whole range of doses, i.e. 100 do 800 Mg HCFA ha^{-1}, was observed only with respect to Zn_{av}, Cu_{av} and B_{av}. Regarding Mn_{av} and Fe_{av}, it was shown that the threshold dose at which the content of these forms of the elements began to rise was 400 Mg HCFA ha^{-1}.

TABLE 2. LONG-TERM IMPACT OF AMELIORATING DOSES OF HCFA ON SHAPING THE CONTENT OF THE AVAILABLE FORMS OF SELECTED ELEMENTS IN AGRICULTURAL SOIL

HCFA dose [Mg ha^{-1}]	Available forms of elements [mg kg^{-1} of soil]				
	Zn_{av}	Cu_{av}	Mn_{av}	Fe_{av}	B_{av}
0	6.79^{a} ±0.31	1.89^{a} ±0.11	75.23^{a} ±4.87	2000^{a} ±26	0.39^{a} ±0.06
100	6.97^{a} ±0.16	2.80^{b} ±0.24	78.93^{a} ±3.85	2150^{b} ±37	0.43^{a} ±0.04
200	9.00^{b} ±0.58	3.40^{c} ±0.07	84.83^{a} ±5.10	2200^{b} ±33	1.07^{b} ±0.07
400	10.57^{c} ±0.54	3.89^{d} ±0.01	104.70^{b} ±7.80	2450^{c} ±42	2.21^{c} ±0.17
600	12.30^{d} ±0.42	4.21^{e} ±0.07	107.90^{b} ±6.94	2450^{c} ±80	2.29^{c} ±0.19
800	14.37^{e} ±0.29	5.02^{f} ±0.13	110.20^{b} ±12.41	2502^{c} ±53	3.33^{d} ±0.13
Average	10.00 ±2.78	3.53 ±1.01	93.63 ±16.13	2292 ±190	1.62 ± 1.08
$LSD_{(0.05)}$	0.89	0.28	16.11	78.86	0.27
r	0.98**	0.96**	0.85**	0.92**	0.97**

Values given are means of four replicates ± standard errors, different letters near value indicate significant differences between the treatments at P=0.05. Simple Pearson's correlation coefficient (r) between HCFA dose and elements content: * r – significant for α=0.05, ** – significant for α=0.01, ns – not significant; n=24

Me_{av} – available form of metal in soil.

The results prove firmly that the applied fly ash has contributed to a permanent increase in the soil content of the analyzed microelements. Noteworthy are the very high doses of HCFA used in the discussed experiment (from 100 to 800 Mg ha^{-1}) and yet the currently determined content of the analyzed elements (and especially the toxic ones, like cadmium, lead and chromium) are safe and within the geochemical background [18, 23].

For nature conservation and protection, and in particular, for remediation of soil polluted with heavy metals, it is extremely important to evaluate dependences between soil properties and the levels of available as well as bound forms of elements in the soil. In this study, the correlation power was assessed between selected chemical properties of soil. i.e. pH measured in H_2O and in 1 M of KCl solution, content of soil organic matter (SOM) and the C:N coefficient relative to the share of the soil-bound form of an element in its total content for such elements as manganese, copper, zinc and iron (Table 3).

TABLE 3. PEARSON'S SIMPLE CORRELATION COEFFICIENTS (*R*) BETWEEN SOIL CHEMICAL PROPERTIES AND SHARE OF ELEMENTS BOUND IN SOIL IN RELATION TO THE TOTAL CONTENT OF ELEMENTS IN SOIL 29 YEARS AFTER THE HCFA APPLICATION

Variable	1	2	3	4	5	6	7	8
1. pH H_2O		0.96**	0.92**	0.81**	0.08	-0.19	0.35	0.93**
2. pH KCl	0.96**		0.93**	0.83**	0.03	-0.23	0.39*	0.95**
3. SOM	0.92**	0.93**		0.91**	0.12	-0.32	0.38	0.94**
4. C:N	0.81**	0.83**	0.91**		0.28	-0.19	0.39*	0.87**
5. Mn_{bd}	0.08	0.03	0.12	0.28		0.00	0.07	0.07
6. Cu_{bd}	-0.19	-0.23	-0.32	-0.19	0.00		-0.67**	-0.18
7. Zn_{bd}	0.35	0.39*	0.38	0.39*	0.07	-0.67**		0.24
8. Fe_{bd}	0.93**	0.95**	0.94**	0.87**	0.07	-0.18	0.24	

* – correlation coefficient r significant for α=0.05; ** – correlation coefficient r significant for α=0.01; n=24

Me_{bd} – bound form of metal in soil.

The comparison demonstrated that all of the examined soil chemical properties (pH$\mathrm{H_2O}$, pHKCl, SOM, C:N) are strongly and positively correlated with one another, which is supported by the correlation coefficients r within the range of 0.81** – 0.96** [8, 11]. The participation of the bound form (Me_{bd}) in the case of Mn_{bd} was not correlated with any of the compared values. With respect to copper, the value of Cu_{bd} was not significantly dependent on any of the compared properties. However, it was shown that Cu_{bd} was highly significantly and negatively correlated with Zn_{bd} (r=-0,67**), which implicates antagonism between these elements. The relationship illustrated in Fig. 1 indicates that the ionic equilibrium between the two elements occurred at the Cu_{bd} in Cu_{tot} contribution = 56.72 %, at which the Zn_{bd} in Zn_{tot} share = 68.47%. The above suggests that the relative content of the forms of zinc and copper beyond this level tended to increase, although at the content of Cu_{bd}> 57%, the share of Zn_{bd} in the total content of this element in soil began to decline. An increase in the concentration of soil-bound copper versus the total copper content may therefore contribute to a rise in the pool of zinc available to plants, and vice versa, which is also supported by the literature [2, 13, 24, 26, 33].

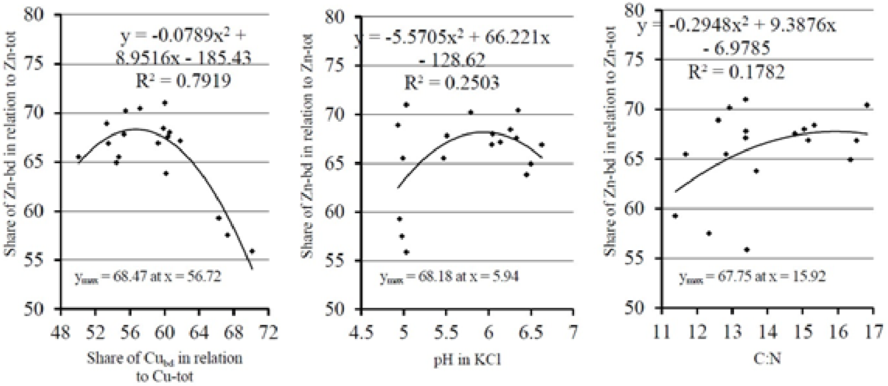

Fig. 1. Significant relationships between the share of Zn_{bd} in Zn_{tot} and soil properties.

The increase in the Zn_{bd} percentage in the total content of zinc found in our experiment was also significantly correlated with pH measured in 1M KCl (*r*=0.39*) and with the C:N ratio (*r*=0.39*; Table 3). While the measured soil reaction was increasing to 5.94, and the content of organic soil matter was rising, as a result of which the C:N ratio was widened to the value of 15.92, zinc soluble forms could undergo immobilization. Any excess of the values of the above parameters are associated with Zn_{bd} being transformed into Zn_{av}. No such dependences were noted in the case of Mn_{bd} and Cu_{bd}. The strongest dependences between the analyzed parameters were verified for iron. An increase in the Fe_{bd} form in Fe_{tot} was highly significantly and positively correlated with the soil reaction, increase in soil organic matter and the C: N ratio (Table 3, Figure 2). These results are indicative of the fact that iron belongs to elements whose solubility is largely dependent on the balance between H^+ and OH – ions, and on the content of organic carbon. As soil became less acidic and its carbon content increased, iron was bound in insoluble forms.

The results show that the increasingly higher doses of fly ash contributed to a change in the soil's reaction, thus affecting the soil content of carbon and nitrogen [11]. This way, they significantly influenced the relative shares of soluble and insoluble forms of the analyzed microelements in soil. Application of hard coal fly ash on farmland can contribute to the increase of the soil content of micronutrients as well as heavy metals. On the other hand, the high deacidifying power of fly ash resulting from its content of alkaline elements (Ca, Mg, K) and the physical properties of fly ash [1, 45] can help to reduce the uptake of harmful microelements, e.g. cadmium, by plants [25]. Many research projects on the applicability of HCFA in agriculture [35, 42, 43] demonstrate that fly ash contributes to higher yields of crops. A dose of 10 Mg HCFA ha^{-1} does not affect significantly the plants' uptake of such metals as Fe, Mn, Zn or Cu, while the plant content of Cd and Ni may even decrease [35]; in turn, a dose of 52 Mg HCFA ha^{-1} raises the soil content of heavy metals, but their concentrations usually remain within the permissible ranges, set by such environmental protection agencies as the US EPA (United States Environmental Protection Agency), EEC (European Environmental Commission), and MOE (Ministry of Environment of Ontario) [42]. Studies completed in Poland also indicate than an optimal dose of HCFA, enhancing the soil's richness in macro – and microelements, is the dose of 67.2 Mg ha^{-1} [43].

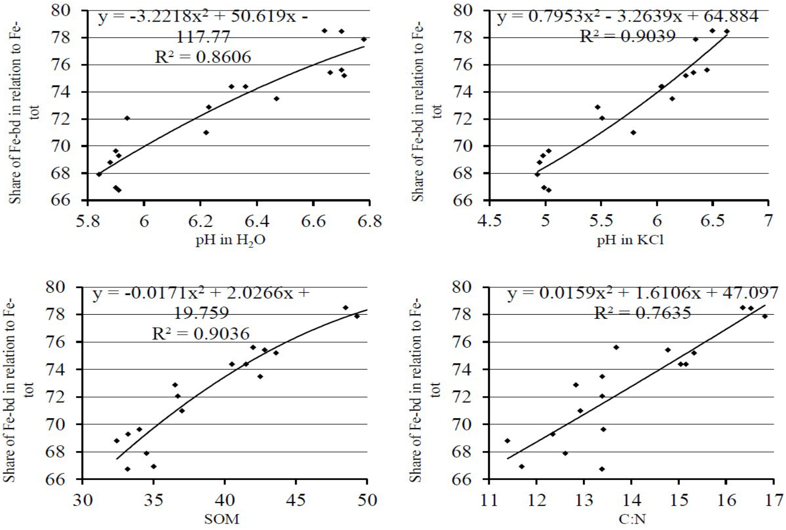

Fig. 2. Significant relationships between the share of Fe_{bd} in Fe_{tot} and soil properties.

Despite a number of advantages that can be gained from agricultural utilization of waste originating from combustion of hard coal, in the light of reports on other, less known effects of HCFA on the environment, e.g. on specific activities of U, Th, Ra and K radionuclides [3, 37], and in line with the Act of 5 April 2011, on R10 recovery process [17], only fly ash from combustion of peat and wood or straw can be used in agriculture.

CONCLUSIONS

1. Hard coal fly ash applied in soil ameliorating doses of 100–800 Mg HCFA ha^{-1} permanently raised, compared to the control treatment, the total content and concentrations of soluble forms of microelements in soil.

2. Twenty-nine years after the application of HCFA ameliorating doses, the trace elements determined in the soil did not seem to exceed the threshold levels set by the Polish regulations for land used for farming; moreover, the detected content was within the limits determined as the geochemical background.

3. The analysis of correlation showed that iron was an element most strongly connected with pH_{H_2O}, pH_{KCl}, SOM, C:N, with zinc being only slightly less correlated with these parameters. No such correlations were demonstrated for the other microelements.

4. It can be concluded in the light of the above results that changes within the soil content of trace elements and microelements detected twenty-nine years after the application of HCFA were beneficial, but because of the presence of some less known and harmful elements, the provisions of Act of 5 April 2011 on the process of recycling combustion by-products pertaining to hard coal fly ash should be re-affirmed

REFERENCES

[1] Adriano D.C., Weber, J.T.: J. Environ. Qual., **30**, 596, 2001
[2] Arora C.L., Sekhon G.S.: J. Agric. Sci., **99**, 185, 1982.
[3] Aytekin H., Baldik R.: Radiat. Prot. Dosimetry, **149**(2), 211, 2012.
[4] Bielińska E.J., Baran S. Stankowski S.: Inż. Roln., **6**(115), 7, 2009.
[5] Bogacz A., Chodak T., Szerszeń L.: Zesz. Probl. Post. Nauk Roln., **418**, 671, 1995.
[6] Burdzy J.: Tablice statystyczne. Wyd. Politechniki Lubelskiej, Lublin: 60, 1999.
[7] Ciećko Z., Rolka E., Najmowicz T., Archacka A., Grzybowski Ł.: Ecol. Chem. Eng., A, **16**(5–6), 523, 2009.
[8] Ciećko Z., Żołnowski A. C., Kulmaczewska J., Chełstowski A.: Zesz. Probl. Post. Nauk Roln., **535**, 73, 2009.
[9] Ciećko Z., Żołnowski A.C., Chełstowski A.: Application of Phytotechnologies for Cleanup of Industrial, Agricultural, and Wastewater Contamination. NATO Science for Peace and Security Series, 147, 2009.
[10] Ciećko Z., Żołnowski A.C., Chełstowski A.: Zesz. Probl. Post. Nauk Roln., **518**, 23, 2007.
[11] Ciećko Z., Żołnowski A.C., Madej M., Wasiak G., Lisowski J.: Polish J. Environ. Stud., (in press), 2015.
[12] Ciećko Z., Żołnowski A.C., Ostrowska E., Chełstowski A.: Ecol. Chem. Eng., **17**(6), 748, 2010.
[13] Dangarwala, R.T.: J. Ind. Soc. Soil Sci., **49**, 647, 2001.
[14] Directive 2001/80/EC of the European Parliament and of the Council: Official Journal of the European Communities L **309**/1, 2001.
[15] Directive 2010/75/EU of the European Parliament and of the Council: Official Journal of the European Union L **334**/17, 2010.
[16]Dz.U.: Regulation of the Minister of the Environment of 22 April 2011 r. on emission standards from facilities. Journal of Law **95**, 558, 2011.
[17] Dz.U:Regulation of the Minister of the Environment of 5 April 2011 r. on R10 recovery process. Journal of Law **86**, 476, 2011.
[18] Dz.U:Regulation of the Minister of the Environment of 9 September 2002 on Standards of Soil Quality Journal of Law **165**, 1359, 2002.

[19] Gaind S., Gaur A.C.: Bioresource Technol., **87**, 125, 2003.

[20] GUS Ochrona Środowiska: Central Statistical Office, 217, 2013.

[21] IUSS Working Group WRB. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome, 2014. www.fao.org/3/a-i3794e.pdf

[22] Jala S., Goyal D.: Bioresource Technol., **97**, 1136, 2006.

[23] Kabata-Pendias A., Piotrowska M.: Biblioteka Monitoringu Środowiska, PIOŚ, IUNG, Warszawa, 28, 1995.

[24] Kabata-Pendias A.: Trace Elements in Soils and Plants, Third Edition. CRC Press, 432, 2000.

[25] Kalembasa S., Kuziemska B., Adamiak E.A.: Polish J. Soil Sci., **43**(2), 165, 2010.

[26] Kumar R., Mehrotra N.K., Nautiyal B.D., Kumar P, Singh P.K.: J. Environ. Biol. **30**(4), 485, 2009.

[27] Lee H., Ha H.S. Lee C.H. Lee Y.B., Kim P.J.: Bioresource Technol., **97**, 1490, 2006.

[28] Mahale N.K., Patil A.D., Sarode D.B., Attarde A.B.: Pol. J. Environ. Stud., **21**, 1713, 2012.

[29] Meller E., Bilenda E.: Polit. Energ., **15**(3), 287, 2012.

[30] Meller E.: Fol. Univ. Agric. Stetin., Ser. Agricultura, **201**(78), 203, 1999.

[31] Microsoft: Excel 2010. 2010. www.microsoft.com.

[32] Murkowski A., Stankowski S.: Proc. IV Symp. ‘Breeding, cultivation and use of triticale’. Kołobrzeg, 29, 2002.

[33] Ondo J.A., Prudent P., Menye Biyogo R., Domeizel M., Vassalo L., Eba F.: Res. J. Chem. Sci., **2**(11), 45, 2012.

[34] Pandey V.C. Singh N.: Agric. Ecosys. Environ., **136**, 16, 2010.

[35] Rautaray S.K., Ghosh B.C., Mittra B.N.: Bioresource Technol., **90**, 275, 2003.

[36] Rolka E.: Zesz. Probl. Post. Nauk Roln., **576**, 99, 2014.

[37] Roper A.R., Stabin M.G., Delapp R.C., Kosson D.S.: Health Phys., **104**(3), 264, 2013.

[38] Sharma S.K., Kalra N.: J. Sci. Ind. Res., **65,** 383, 2006.

[39] Shibaoka M: Fuel, **65**(3), 449, 1986,

[40] Statsoft: Statistica v. 10.0 (data analysis sotware system). 2010. www.statsoft.com.

[41] Ukwattage N.L., Ranjith P.G., Bouazza M.: Fuel, **109**, 400, 2013.

[42] Veeresh H., Tripathy S., Chaudhuri D., Ghosh B.C., Hart B.R., Powell M.A.: Environ. Geol., **43**, 513, 2003.

[43] Właśniewski S. Ochr. Środ. Zas. Nat., **41**, 479, 2009.

[44] Wyszkowski M., Chełstowski A., Ciećko Z., Szostek R.: J. Ecol. Eng., **15**(1), 55, 2014.

[45] Yeledhalli N.A., Prakash S.S., Ravi M.V. Narayana Rao K.: J. Agric. Sci., **21**(4), 507, 2008.

[46] Żołnowski A.C., Busse M.K., Zając P.K.: J. Elem., **18**(3), 507, 2013.

[47] Żołnowski A.C., Ciećko Z., Najmowicz T.: Application of Phytotechnologies for Cleanup of Industrial, Agricultural and Wastewater Contamination. NATO Science for Peace and Security Series, 135, 2009.

NASTĘPCZY WPŁYW MELIORACYJNYCH DAWEK POPIOŁÓW LOTNYCH Z WĘGLA KAMIENNEGO NA KSZTAŁTOWANIE SIĘ ZAWARTOŚCI WYBRANYCH MIKROSKŁADNIKÓW W GLEBIE UŻYTKOWANEJ ROLNICZO

W doświadczeniu założonym w 1984 roku badano działanie melioracyjnych dawek popiołów ze spalania węgla kamiennego (hard coal fly ashes – HCFA) na właściwości fizykochemiczne gleby oraz na plonowanie i skład chemiczny roślin uprawnych. W pierwszych latach badań uprawiano typowe rośliny rolnicze, a w 1992 zmieniono charakter uprawy na trwały użytek zielony. Obecne badania wykonano po dwudziestu dziewięciu latach od zastosowania HCFA. Próbki gleby pobrano z poziomu 0–20 cm w nawiązaniu do porównywanych obiektów. Następcze działanie rosnących dawek HCFA od 100 do 800 $Mg \cdot ha^{-1}$ powodowało zarówno wyraźnie regularny wzrost zawartości całkowitej – Cd, Cr, Cu, Mn, Fe, Zn i Pb, jak i form rozpuszczalnych w 0.1 M HCl – Zn, Cu, Mn, Fe i B. Zawartość całkowita rozpatrywanych mikroskładników maksymalnie wzrosła o 30% w przypadku kadmu do 176 % w odniesieniu do cynku. Maksymalny wzrost zawartości form rozpuszczalnych kształtował się od 25 % w odniesieniu do żelaza do 760 % w przypadku boru. Udział Zn_{bd} tj. trwale związanego z glebą w stosunku do jego formy ogólnej Zn_{tot}, istotnie dodatnio korelował z pH w KCl i stosunek C:N oraz z Cu trwale związaną z glebą. W odniesieniu do udziału Fe_{bd} w Fe_{tot} wykazano korelacje z pH w H_2O, pH w KCl, SOM i C:N ratio. W odniesieniu do pozostałych badanych pierwiastków takich zależności nie wykazano.