

# Long-Term Effects of Hard Coal Fly Ash on Selected Soil Properties

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## Abstract

This research reports and analyzes results of a field experiment started in 1984, when hard coal fly ash (HCFA) was added to soil at doses of 0 to 800 Mg·ha<sup>-1</sup>. During the first years of the experiment, traditional crops were grown in the plots, which in 1992 were converted into permanent grassland. Twenty-nine years after the application of fly ash, soil samples from the 0-20 cm soil layer were collected to determine chemical properties of soil. The results showed an elevated soil reaction, and high contents of available forms of P, K, and Mg, plus mineral forms of nitrogen and high soil organic matter. Under increased ash doses, analysed soils increased the C:N ratio and shares of N-NO<sub>3</sub> and N-NH<sub>4</sub> in total nitrogen content. These results justify that fly ash from combustion of hard coal in a power plant can produce long-term impact on soil, contributing to a certain improvement of its chemical, physical, and biological properties, which stimulate the sequestration of carbon in soil.

**Keywords:** hard coal fly ash, SOM, total N, N-NO<sub>3</sub>, NH<sub>4</sub>

## Introduction

The legal regulations in Europe pertaining to the protection of air stipulate that the permissible levels of fly ash emissions from hard coal combustion in power plants generating <500MW and >500MW are 100 and 50 mg·m<sup>-3</sup>, respectively [1-3]. Once implemented, these threshold limits have largely restrained dust emissions from the power generation sector and other industries. For example, ash emissions in Poland fell from about 115,000 tons in 2000 to 76,000 tons in 2011 (the data encompass power generating plants, heat generating plants, industrial power plants, and industrial technologies, but exclude local boilers, household furnaces, small workshops, agricultural facilities, etc.) [4]. Such a large reduction has been possible owing to high-

efficiency dust collectors, able to remove up to 98% of dust produced during the combustion of solid fuels, such as hard or brown coal. However, reduction in the dust emission increases the amounts of fly ash deposited on landfills near energy-generating plants. Covering more and more land, such dumping sites reduce the total surface of healthy and sustainable terrestrial habitats [5, 6]. It is estimated that in 2011, about 99.7% of the dust mass generated all over Poland was captured and removed through dust collectors [7], indicating that more than 75,000 tons of this waste was deposited in landfills at power and heat generating plants. Hence, the proper management and utilization of fly ash, a by-product of electricity or heat generation, is important. While containing elements that can be useful to soil and plants, fly ash gathered in heaps on landfills acts as an aggressive and adverse factor toward ecosystems [8]. A large share of alkaline elements in the chemical compo-

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Table 1. Some physicochemical properties of soil used in the experiment.

Soil/ Properties	pH <sub>KCl</sub>	pH <sub>H<sub>2</sub>O</sub>	Hydrolytic acidity	Bases Alkaline Cations	Cation Exchange Capacity CEC	Total Base Saturation [%]
			[cmol·kg <sup>-1</sup> ]			
Fluvisol	5.60	6.50	3.56	8.90	12.46	71.42
	Available forms of nutrients [mg·kg <sup>-1</sup> ]					
	P	K	Mg	B		
	55	152	55	0.45		

Table 2. Some physicochemical properties of ash used in the experiment.

Ash/properties	pH <sub>KCl</sub>	Total forms of macronutrients [g·kg <sup>-1</sup> ]					
		SiO <sub>2</sub>	P	K	Ca	Mg	Fe
	9.20	491	1.7	2.9	15.0	7.1	27.9
HCFA	Total forms of micronutrients [mg·kg <sup>-1</sup> ]						
	Mn	Cu	Zn	Co			
	496	61	48	13			

sition of fly ash (6.0-23.4% CaO and 0.9-2.0% MgO [9]) suggests that this waste can be used to neutralize the reaction of acid soils [8, 10-19]. In some European countries, for example Germany, Denmark, France, and the UK (as well as in the USA), more than 70% of fly ash on average is used as raw material in the construction industry. In Asian countries, on the other hand, such usage is less common, e.g. just 38% of fly ash in India and 45% in China is recycled by the building industry [20, 21]. The question of using fly ash by agriculture is highly controversial. One reason is the potential risk of polluting the natural environment with heavy metals like Cu, Sr, Ni, Cr, Zn, Cd, Mo, Se, Pb, As, V, Hg, Ba, Th, and B [8, 11, 21-23]. The direct effect of fly ash from hard coal on soil properties has been investigated rather thoroughly [11, 16, 24]. In contrast, reports on the lasting effects of fly ash on the chemical properties of soils are scarce.

Our objective has been to determine whether fly ash obtained by burning hard coal in power generating plants produces a long-term effect on the soil reaction and its content of macronutrients and humus. This thesis has been verified against the background of a null hypothesis stating that no difference between the analyzed objects would occur 29 years after the application of fly ash.

## Materials and Methods

### Experimental Design

In 1984 a field experiment was established in the village of Łęg Starościński in the province of Mazowsze (53°11'30.81"N; 21°57'20.20"E). The soil was fluvisol

(FL) with the textural composition of sandy loam (SL) (63% sand, 30% silt, and 7% clay) according to World Reference Base [25]. Physicochemical properties of soil at the beginning of the experiment are shown in Table 1.

The experiment was designed in line with the random block method including four replications. The first experimental factor consisted of increasing doses (0, 100, 200, 400, 600, and 800 Mg·ha<sup>-1</sup>) of hard coal fly ash (HCFA) from electrofilters working at the Ostrołęka Power Plants. The total content of elements per 1 kg of dry matter of HCFA are shown in Table 2.

The second experimental factor included organic soil amendments: farmyard manure, straw and tree bark applied to soil together with fly ash, in the amount of 10 t dry matter per ha. The analyses performed in 2003 did not reveal any significant differences between the experimental series in which different organic substances had been used, which is why since then the experiment has been treated as a single factor one, in which the only factor considered was the difference in the doses of fly ash, and the treatments in the individual series were perceived as four replications. The plots (each 54 m<sup>2</sup> in area) which composed a single block were separated from one another with 1 m wide belts, while the blocks were divided by 3 m wide belts. Hard coal fly ash was applied in autumn 1984 under winter ploughing, by mixing with the arable layer of soil. In the consecutive six years, the plots were cropped with typical agricultural plants: potatoes (1985), oat for green mass+lupine for green mass (1986), rye for green mass+a mix of legumes and grasses for green mass (1987), and a legume-grass mix for green mass in 1988-91. Since 1992, the whole field has been maintained as permanent grassland and not fertilized with mineral fertilizers.

## Soil Sampling

In 2013, that is 29 years after the application of fly ash, soil samples were taken from all treatments at a depth of 0-20 cm. The sampling was done with an Egner's core sampler. Samples were collected from four sites on each plot and then averaged into an aggregated sample. Consequently, four separate replications were obtained for each treatment. Soil samples collected for analyses were placed on trays and air dried, after which they were passed through a sieve with a 1.0 mm diameter. Samples thus prepared for analyses were kept in airtight plastic containers.

## Soil Analyses

The soil reaction was determined by potentiometry in 1M KCl and H<sub>2</sub>O in a 1:2.5 soil-to-solution ratio [26]. The determinations were done potentiometrically after 24 hours, with an HI 221 potentiometer (Hanna Instruments).

The contents of available P and K were determined after the extraction of soil with calcium lactate solution [27]. Having been transformed into phosphorus molybdenum blue, phosphorus in the soil extract was determined by the colorimetric method, in a reaction with ammonium molybdate and Photorex and with stannous chloride SnCl<sub>2</sub> on a Merck SQ118spectrocolorimeter (Merck KGaA, Germany). Potassium was determined by atomic emission spectroscopy (FAES) on Flapho 4, (Carl Zeiss Jena, Germany), after calcium had been precipitated and the sample had been passed through a filter.

The content of available Mg was determined after soil extraction with a solution of 0.0125 M CaCl<sub>2</sub>, at a soil-to-solution m:v ratio of 1:10 [28]. Magnesium was determined using flame atomic absorption spectroscopy (FAAS) on an AAS 1 apparatus (Carl Zeiss Jena, Germany).

The content of total nitrogen (ToN) was determined with a modified Kjeldahl's method [29], having mineralized the soil samples in infrared in Turbotherm TT 125 Rapid Digestion Systems (Gerhardt Fabrik und Lager Chemischer Apparate GmbH & Co. KG Germany). Samples were mineralized in concentrated sulphuric acid, using selenium mixture in the form of tablets (3.5 g K<sub>2</sub>SO<sub>4</sub>+0.0035 g Se) as a catalyst. A Büchi B-324 (BÜCHILabortechnik AG, Switzerland) distillation unit was employed for the distillation of nitrogen. Samples were titrated with 0.1 MNaOH solution titrated against the Tashiro reagent (POCh Gliwice, Poland) as an indicator. The reaction was carried out on a Schott TITRONIC universal apparatus (SCHOTT-GERÄTE GmbH, Germany).

N-NO<sub>3</sub><sup>-</sup> and N-NH<sub>4</sub><sup>+</sup> in soil samples were determined after soil extraction with 1% K<sub>2</sub>SO<sub>4</sub> solution, using the continuous flow analysis (CFA) technique with spectrometric detection on a Skalar<sup>++</sup> apparatus and a chemical section SA 3000/5000 (Skalar Analytical B.V., the Netherlands) according to Skalar methods [30, 31].

The content of organic carbon (OC) in soil was determined with a modified Tiurin's method on a Spectronic GENESYS 6 spectrocolorimeter (Thermo Electron

Scientific Instruments LLC, Madison, WI, USA) [32]. The content of soil organic matter (SOM) was derived from the content of OC using Van Bemmelen's index = 1.724, whose value had been calculated from the assumption that SOM contained 58% of OC [33].

## Statistical Analysis

The results underwent statistical processing according to the one-way analysis of variance at the level of significance  $P = 0.05$ , using the statistical calculation module of Statistica v. 10.0 [34]. The limit ranges (LSD) were determined with the one-dimensional Duncan's test, while the homogenous groups were distinguished with the Newman-Keuluss's test. The standard error ( $\pm$ SE) and power of the correlation between a dose of fly ash and soil chemical properties, expressed by Pearson's simple correlation coefficient was calculated with the aid of MS Excel 2010 [35]. The statistical significance of correlation coefficients at  $n-2$  degrees of freedom was assessed according to tables of critical values [36] at the levels of significance  $\alpha=0.05$  (\*) and  $\alpha=0.01$  (\*\*), at which point the correlation was significant or highly significant, respectively. Frequency of the pairs of observations ( $n$ ) of the above determinations is explained in the description underneath the tables and figures.

## Results and Discussion

### Soil Reaction and Available Phosphorus, Potassium, and Magnesium

The influence of HCFA on soil 29 years after its application of chemical properties is shown in Table 3. In response to HCFA introduced to soil in doses over 100 Mg·ha<sup>-1</sup>, a significant increase was noticed in the soil pH, measured in both H<sub>2</sub>O and 1M KCl. This de-acidifying effect on the soil reaction determined in water was noticed up to the dose of 600 Mg HCFA·ha<sup>-1</sup>. As regards pH in 1 M KCl, the effect continued up to the dose of 800 Mg HCFA·ha<sup>-1</sup>. The lasting de-acidifying influence of HCFA was further confirmed by highly significant coefficients of the correlation ( $r$ ) between a dose of fly ash and reaction of soil samples (Table 3). Ainsworth and Rai [37] claim that that the de-acidifying power of fly ash depends, among others, on the type and origin of coal from which the ash was obtained, on its chemical composition, including Si, Al, and Fe, as well as alkaline cations such as Ca, K, Na, and Ti. The reaction of raw ash can range from 4.5 to 12.0 (in our study, the pH in 1 M KCl was 9.2). The pH of fly ash is mostly dependent on the content of sulphur and its ratio to calcium [37]. In the vast majority of cases, combustion of hard coal generates alkaline ash, and the calcium it contains can enter in lasting interactions with the soil components that are acidic, e.g. sulphur, boron, or molybdenum. According to Bielińska et al. [8], ash can be an alternative substance to classical liming materials, at no detriment to important metabolic processes that shape the quality of soil, as demonstrated by the present study, where permanent and

Table 3. Effects of HCFA on soil pH and available forms of macronutrient content in surface soil layer after 29 years of ash application.

HCFA dose [Mg·ha <sup>-1</sup> ]	pH		Available forms [mg·kg <sup>-1</sup> ]		
	H <sub>2</sub> O	1M KCl	P	K	Mg
0	5.88 <sup>a</sup> ±0.03	5.01 <sup>a</sup> ±0.05	56.35 <sup>a</sup> ±4.83	61.45 <sup>a</sup> ±15.26	63.50 <sup>a</sup> ±4.50
100	5.88 <sup>a</sup> ±0.03	4.98 <sup>a</sup> ±0.04	70.02 <sup>b</sup> ±5.36	94.14 <sup>b</sup> ±11.63	64.25 <sup>a</sup> ±4.44
200	6.15 <sup>b</sup> ±0.12	5.54 <sup>b</sup> ±0.15	72.43 <sup>b</sup> ±10.87	94.60 <sup>b</sup> ±3.73	93.25 <sup>b</sup> ±5.36
400	6.43 <sup>c</sup> ±0.10	6.10 <sup>c</sup> ±0.05	83.43 <sup>c</sup> ±5.13	95.48 <sup>b</sup> ±3.85	115.75 <sup>c</sup> ±9.65
600	6.70 <sup>d</sup> ±0.02	6.28 <sup>d</sup> ±0.14	87.28 <sup>c</sup> ±2.90	96.74 <sup>b</sup> ±4.43	130.00 <sup>d</sup> ±5.00
800	6.72 <sup>d</sup> ±0.06	6.48 <sup>c</sup> ±0.10	94.10 <sup>c</sup> ±2.51	98.03 <sup>b</sup> ±13.82	121.75 <sup>cd</sup> ±6.94
Average	6.29±0.36	5.73±0.60	77.27±13.82	90.07±16.33	98.08±27.36
LSD <sub>(0.05)</sub>	0.12	0.17	10.19	17.27	10.74
<i>r</i>	0.90**	0.89**	0.87**	0.50*	0.88**

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 investigated parameters: \**r* – significant for  $\alpha=0.05$ , \*\**r* – significant for  $\alpha=0.01$ , ns – not significant; n=24

beneficial changes in the soil reaction were proven. The positive effect of fly ash on soil comprises other physical characteristics and the content of nutrients in soil [38]. The HCFA applied 29 years before continued to affect the content of available forms of phosphorus, potassium, and magnesium in soil. It has been demonstrated that doses of 100 and 400 Mg HCFA·ha<sup>-1</sup> acted beneficially on the content of phosphorus, raising the level of available P forms by 13.67 and 27.05 mg·kg<sup>-1</sup> of soil, respectively, compared to the control soil. Panthan et al. [39] also showed a 2.5- to 4.5-fold increase in the content of extractable phosphorus in response to the application of HCFA compared to the control (not treated with fly ash). In our investigations, the content of available potassium increased under the influence of HCFA, but only when 100 Mg HCFA·ha<sup>-1</sup> had been applied.

Although higher doses of fly ash did not change the soil content of available potassium significantly, they did alter the soil content of extractable magnesium. For example an application of 200 Mg HCFA·ha<sup>-1</sup> as well as 400 and 600 Mg HCFA·ha<sup>-1</sup> resulted in a significant rise in the content of Mg *versus* the control soil. Despite the 29-year lapse of time since the application of fly ash, high coefficients of the correlation between HCFA dose and content of available P and Mg ( $r=0.87^{**}$ ,  $r=0.88^{*}$ ) as well as K ( $r=0.50^{*}$ ) prove that HCFA maintained a strong residual effect on the above nutrients. The observed positive influence of fly ash on the elevated concentrations of macroelements in soil is verified by literature [10, 23, 40], and this finding gains importance in the context of possible utilization of ash from biomass combustion [17, 41].

#### Content of Total Nitrogen and Mineral Nitrogen Forms

The total nitrogen content (ToN) and mineral nitrogen forms in soil from the analyzed plots varied. Despite being unable to demonstrate significant differences between the

plots in terms of ToN, we can point to a highly significant correlation coefficient ( $r=0.59^{**}$ ) implicating a strong and previously verified [13] relationship between the ToN content and a dose of HCFA (Fig. 1). The content of nitrate nitrogen (N-NO<sub>3</sub>) in the analyzed soil samples was significantly elevated, on average by 20.3, 25.9, and 31.9% *versus* the CS, following the application of 400, 600, and 800 Mg HCFA·ha<sup>-1</sup>, respectively. The stimulating effect of HCFA was even stronger in the case of ammonia nitrogen. The content of N-NH<sub>4</sub><sup>+</sup> relative to the CS was 24.6 and 39.4% higher after the application of 400 and 800 Mg HCFA·ha<sup>-1</sup>, respectively. The strong relationship between the dose of HCFA and the content of mineral forms of nitrogen is confirmed by highly significant correlation coefficients ( $r=0.96^{**}$  and  $r=0.97^{**}$  for the sum of N-NO<sub>3</sub>+N-NH<sub>4</sub><sup>+</sup>). The higher abundance of N-NO<sub>3</sub> and N-NH<sub>4</sub><sup>+</sup> may be a consequence of the limited leaching of mineral nitrogen forms from soils treated with HCFA. This thesis is supported by the lysimetric experiments conducted by Panthan et al. [39], where the accumulated leaching of N-NO<sub>3</sub> and N-NH<sub>4</sub> from plots with a 20% contribution of fly ash into the surface layer of soil was approximately 2.0 (N-NO<sub>3</sub>) and 0.2 mg·m<sup>-2</sup> (N-NH<sub>4</sub>) lower than from the control object, without fly ash. Although the above authors did not show a significant effect of fly ash application on the content of extractable forms of N-NO<sub>3</sub> and N-NH<sub>4</sub>, a clear tendency appeared for a higher soil content of these forms of nitrogen in response to the amelioration of soil with HCFA. In the present study, the ameliorating doses of fly ash applied 29 years earlier also elevated the share of the mineral nitrogen forms in ToN. It was shown that the dose significantly raising this share was the amount of 400 Mg HCFA·ha<sup>-1</sup> (Fig. 2).

Hard coal fly ash as waste produced by heat and power generating plants contains minute quantities of nitrogen. During the combustion process, nitrogen is mostly emitted to the atmosphere in the form of oxides, and the N-total amount in fly ash is no more than a few tenths of a percent

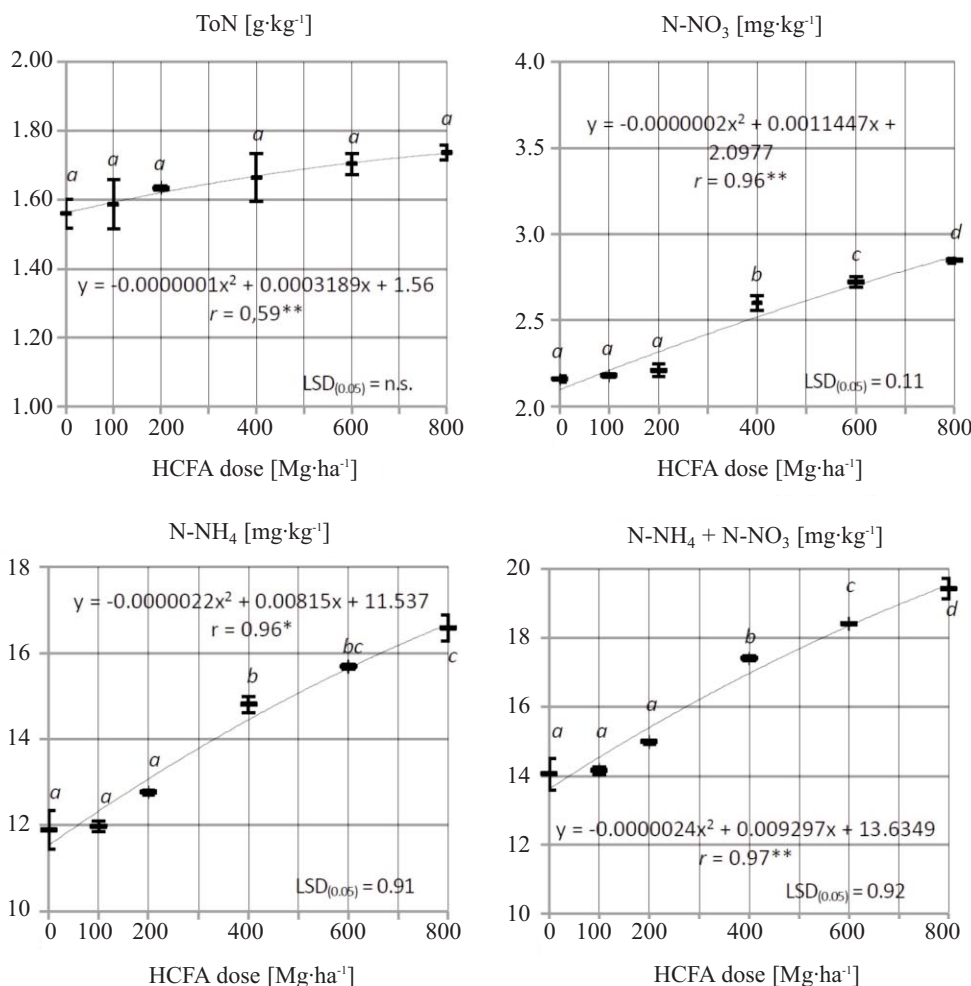


Fig. 1. Effect of HCFA on ToN, N-NO<sub>3</sub>, and N-NH<sub>4</sub> content in surface soil layer 29 years after ash application. Different letters on the marks indicate significant differences between the treatments. Pearson's simple correlation coefficient (*r*) between HCFA dose and nitrogen forms content: \**r* – significant for  $\alpha=0.05$ , \*\**r* – significant for  $\alpha=0.01$ , ns – not significant; n=24.

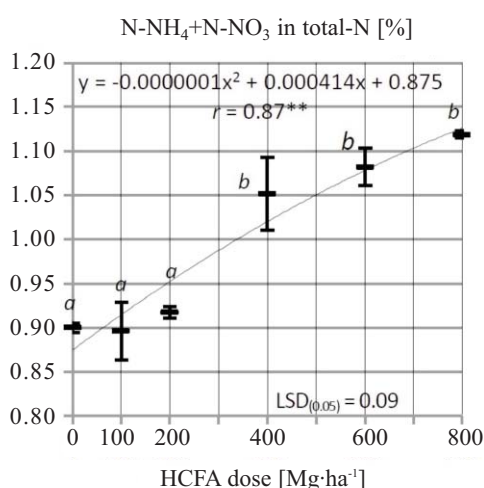


Fig. 2. Effect of HCFA on the share of N-NH<sub>4</sub>+N-NO<sub>3</sub> in ToN in the surface soil layer 29 years after ash application. Different letters on the marks indicate significant differences between the treatments. Simple Pearson's correlation coefficient (*r*) between HCFA dose and nitrogen forms content: \**r* – significant for  $\alpha=0.05$ , \*\**r* – significant for  $\alpha=0.01$ , ns – not significant; n=24

(ToN 0.2%) [42]. In this context, HCFA cannot be perceived as a source of nitrogen for plants. Notwithstanding this, our study has shown that incremental HCFA doses applied in the distant past significantly differentiate the content of ToN, N-NO<sub>3</sub>, and N-NH<sub>4</sub> in soil. Adriano and Weber [43] claim that the betterment of conditions for the growth and development of plants induced by HCFA fertilization is caused by a change in the physical properties of soil. The cited researchers used fly ash in doses between 280 and 1120 Mg·ha<sup>-1</sup>, and reported a significant increase in the water-holding capacity (WCH) as well as the content of water available to plants. Besides the higher WHC of soil in response to fly ash, Yeledhalli et al. [44] demonstrated that HCFA in soil improved soil porosity. Such changes result in improved air and water conditions in soil, which in our research, for example, led to the formation of deeper and more abundant root systems by all the cultivated plant species. Some earlier studies by Ciećko et al. [45] proved a positive effect of HCFA applied in doses of 200 t·ha<sup>-1</sup> on meadow sward, which produced higher yields. This observation has been verified by several other studies on the agricultural utilization of ash from power

generating plants. As reported by Jala and Goyal [16], higher yields owing to fly ash fertilization have been achieved by such plants as alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*), Bermuda grass (*Cynodon dactylon*), and white clover (*Trifolium repens*). Grewal et al. [46] showed that a 5-20% addition of fly ashes to the topsoil layer (0-15 cm) resulted in higher yields of grain and straw from pearl millet (*Pennisetum* sp.) grown after wheat. Positive results were also obtained while growing teak trees (*Tectona grandis*) and leucaena (*Leucaena leucocephala*) [47]. In our experiment, higher plant yields have led to higher accumulation of plant residue in soil, which is a valuable source of available nitrogen for subsequent plants. Owing to the increased soil porosity and water holding capacity, the leaching of mineral N forms is limited, as reported by Pathan et al. [39].

### Soil Organic Matter and C:N Ratio

The fly ash originating from a power plant and added to soil 29 years prior to our analyses affected the content of SOM. It has been demonstrated that the plots amended with 200 Mg HCFA·ha<sup>-1</sup> had a higher content of humus compared to the CS. The increase reached 3.54 g SOM·kg<sup>-1</sup>, which corresponds to 10.7%. The plots amended with higher doses of HCFA, i.e. 400 and 600 Mg HCFA·ha<sup>-1</sup>, composed a statistically homogenous group and were characterized by an average 27.0% increase in the humus content versus the CS. Another significant rise in the SOM content was achieved on the plot fertilized with 800 Mg HCFA·ha<sup>-1</sup>. There, the SOM content was 16.77 g·kg<sup>-1</sup> of soil, which was 50.5% higher than in the soil not treated with HCFA. The SOM content was significantly positively correlated with all the analyzed parameters except potassium content (Fig. 3).

The soil samples were also compared with respect to the C:N ratio. In Polish soils, typical values of this parameter are from 7.4 to 17.4, and the average value is 10.4 [48].

In our investigations, the C:N ratio in the soil samples was within 12.4-16.6. The applied ash significantly widened this ratio, which was demonstrated in the soils fertilized with 200, 400, and 800 Mg HCFA·ha<sup>-1</sup>. The C:N ratio was significantly positively correlated with almost all the analyzed parameters except the content of potassium and nitrogen (Table 4). The widening of the C:N ratio in plots amended with HCFA points to processes associated with a more intensive carbon sequestration, stimulated by the aforementioned higher accumulation of plant residue and roots in soil. A number of studies on HCFA carried out worldwide imply the significant influence of this waste material on the accumulation of organic and inorganic carbon in soil, which may follow a different course and occur with a different degree of intensity [49]. Such changes depend on the chemical and physical characteristics of both fly ash and soil. More intensive sequestration of OC in HCFA-treated soils is mostly a result of the microbiological decomposition of plant and animal waste to simple sugars, amino acids, and cellulose. At subsequent stages, however, these substances are decomposed by soil-borne microorganisms to simple compounds, including CO<sub>2</sub> released to the atmosphere. When viewing the above transformations in the long run, it can be concluded that parallel processes of synthesis connected with the humification of organic matter in HCFA-treated objects leads to the formation of soil organic matter that is more resistant to decomposition by microorganisms, which is explained by specific interactions with the soil's mineral phase and its structure [11, 50].

### Conclusions

1. Fly ash originating from combustion of hard coal and applied in the form of ameliorating doses between 200-800 Mg HCFA·ha<sup>-1</sup> permanently raised the soil pH and content of available forms of phosphorus, potassium, and magnesium in soil.

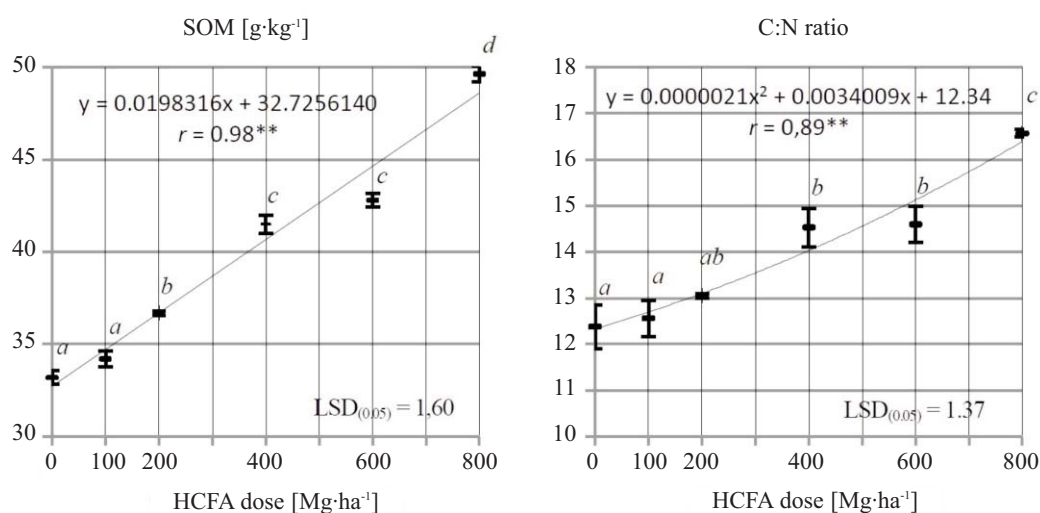


Fig. 3. Effect of HCFA on SOM content and C:N ratio in surface soil layer 29 years after ash application.

Different letters on the marks indicate significant differences between the treatments. Simple Pearson's correlation coefficient ( $r$ ) between HCFA dose and nitrogen forms content: \* $r$  – significant for  $\alpha=0.05$ , \*\* $r$  – significant for  $\alpha=0.01$ , ns – not significant;  $n=24$ .

Table 4. Pearson's simple correlation coefficients between soil chemical properties 29 years after HCFA application.

Variable	1	2	3	4	5	6	7	8	9	10	11
1. pH <sub>H<sub>2</sub>O</sub>											
2. pH <sub>KCl</sub>	0.96**										
3. P	0.87**	0.89**									
4. K	0.37	0.38	0.55**								
5. Mg	0.94**	0.97**	0.82**	0.38							
6. Total N	0.61**	0.61**	0.53**	0.18	0.61**						
7. NH <sub>4</sub>	0.94**	0.95**	0.84**	0.32	0.91**	0.65**					
8. N-NO <sub>3</sub>	0.94**	0.93**	0.81**	0.33	0.90**	0.61**	0.96**				
9. NH <sub>4</sub> +N-NO <sub>3</sub>	0.94**	0.95**	0.84**	0.33	0.91**	0.65**	1.00**	0.97**			
10. N-NH <sub>4</sub> +N-NO <sub>3</sub> in 3 ToN	0.83**	0.85**	0.75**	0.33	0.80**	0.23	0.88**	0.87**	0.89**		
11. SOM	0.92**	0.93**	0.86**	0.36	0.85**	0.61**	0.94**	0.94**	0.95**	0.84**	
12. C:N	0.81**	0.83**	0.78**	0.36	0.74**	0.22	0.82**	0.83**	0.82**	0.91**	0.91**

\* – correlation coefficient r significant for  $\alpha=0.05$ ; \*\* – correlation coefficient r significant for  $\alpha=0.01$ ; n=24

- The HCFA incorporated into soil 29 years before were not found to have affected significantly the content of ToN in soil, although concentrations of N-NO<sub>3</sub> and N-NH<sub>4</sub> were shown to have been significantly increased, and the share of mineral N forms in the pool of ToN was higher as well.
- Fly ash introduced to soil in doses above 200 Mg HCFA·ha<sup>-1</sup> significantly increased the SOM content of soil while contributing to a significant widening of the C:N ratio, which may implicate a significant, residual, and stimulating effect of HCFA on sequestration of carbon in soil.
- The lasting changes in the chemical composition of the analyzed soils, found 29 years after the application of fly ash, cannot be attributed to any direct impact of HCFA but result from indirect effects such as improved physicochemical properties of soil, which created more suitable conditions for accumulation of available elements, mineral nitrogen forms, and organic carbon in soil.

### Abbreviations

HCFA – hard coal fly ash,  
ToN – total nitrogen,  
OC – organic carbon,  
SOM – soil organic matter,  
CS – the control soil without addition of HCFA

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