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LONG-TIME EFFECT OF HARD COAL FLY ASHES APPLICATION ON NITROGEN CONTENT IN THE SOIL

NASTĘPCZE ODDZIAŁYWANIE POPIOŁÓW Z WĘGLA KAMIENNEGO NA ZAWARTOŚĆ AZOTU W GLEBIE

Abstract: The paper discusses the long-term effect of hard coal fly ashes on the content of some nitrogen forms in soil. The study was based on a field experiment 19 years after it had been established. Fly ashes were dosed at rates of 0, 100, 200, 400, 600 and 800 Mg ha⁻¹, in the following four series: without organic substance, with farmyard manure, with straw and with tree bark. The results seem to prove that hard coal fly ashes as well as organic fertilizers applied in addition to fly ashes had a significant influence on the long-term content of the analyzed forms of nitrogen in soil. The effect of fly ashes was particularly evident in the arable horizon of the analyzed soil. In deeper soil layers, fly ashes were found to have no influence on the content of the analyzed nitrogen forms. Among the organic amendments tested in the experiment, irrespective of the depth at which soil samples were taken, tree bark had the strongest influence on N-NO₃, increasing its content. With respect to N-NH₄, the strongest influence on its content was produced by straw.

Keywords: hard coal fly ashes, nitrogen, ammonia nitrogen, nitrates

The regulations introduced to the Polish law over the last few years, regarding air pollution control, have resulted in considerably depressed emission of fly ashes from energy generating facilities. In 1990, about 1,430 thousand tonnes of fly ashes were emitted into the atmosphere, and that amount was reduced to about 112 thousand tonnes in 2006 (these data pertain to commercial energy plants, industrial energy generating facilities and technologies, but exclude local heat energy generating facilities, household fireplaces, small workshops or agriculture) [1]. These changes have taken place owing to implementation of high-performance dust separators. Such facilities can capture up to 98 % of the ashes produced during combustion processes. However, reduction in the emission of pollutants to air means an increase in amounts of fly ashes stored near power plants. It is estimated that in 2007 about 99.5 % of fly ash produced

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in energy and heat generating plants in Poland was captured and stored. This percentage corresponds to 19,914 thousand tonnes of such waste. Therefore, it is becoming increasingly important to recycle fly ash, a by-product of the energy generating industry. Fly ashes stored in bulk can act as an aggressive factor, adversely affecting ecosystems. However, the same fly ashes contain elements, which can be useful in agricultural practice. Therefore, they can be used as a component added to soil in order to improve its physiochemical properties [2, 3]. Such waste can also be used as fertilizers [3–7]. By introducing fly ashes to soil, it is possible to improve the balance of nutrients in environment and reduce the negative effect of excessive concentration of fly ashes near energy generating plants. The data found in the relevant references largely explain the immediate effect of hard coal fly ashes on the properties of soil and crop yields. In contrast, there is little information regarding the long-term changes caused by introduction of fly ashes to soil.

The results presented in this paper aimed at clarifying how fly ashes from energy generating plants can affect the total nitrogen abundance as well as the content of nitrogen mineral forms, ie ammonia nitrogen and nitrates, in soil. Another objective was to determine the interaction between fly ashes and organic amendments, such as farmyard manure, straw and tree bark, added to soil together with fly ashes. The analyses were performed 19 years after these substances had been introduced to soil, which enabled the authors to evaluate the duration of their influence on the selected forms of nitrogen in soil.

Material and methods

The study was based on a field experiment established in 1884 in the commune of Lelis, in the Mazowia province, on weak rye complex 6 soil. The arable horizon of the soil represented the grain size distribution defined as slightly loamy and silty sand [8]. The soil was moderately abundant in available phosphorus (55 mg P kg^{-1}) and rich in available potassium (152 mg K kg^{-1}) and magnesium (55 mg Mg kg^{-1}). The sorptive capacity of the soil was $12.3 \text{ cmol}(+) \text{ kg}^{-1}$, and the reaction measured in water and in 1 M KCl was 6.5 and 5.6, respectively.

The experiment was set up according to the random block design with four replications, including three experimental factors. The first order factor consisted of increasing doses of hard coal fly ashes from electrofilters in Ostrołęka Power Plant, introduced to soil in the following doses: 0, 100, 200, 400, 600 and $800 \text{ Mg} \cdot \text{ha}^{-1}$. The fly ashes used in the experiment contained 491 g SiO_2 , 1.7 g P, 2.9 g K, 15.0 g Ca and 7.1 Mg in 1 kg dm. Their reaction pH measured in 1 M KCl was 9.2. The second order factor comprised the organic amendments which were introduced to soil alongside fly ashes. They included farmyard manure (FYM), straw and tree bark, in the amount of 10 Mg dm per 1 ha. The depth of soil profile at which soil samples were collected made up the third order factor. Each plot covered 54 m^2 .

Fly ashes and organic amendments were added to soil in the autumn of 1984, before winter ploughing. The crops grown in the subsequent years were potatoes (1985), oat for green matter + lupine for green matter (1987), rye for green matter + a mixture of

legumes and grasses for green matter (1987), and a mixture of legumes and grasses for green matter in 1988–1991. All the crops received NPK fertilization in rates recommended in agronomy, identical during the entire experiment. In 1992, the field was used as permanent grassland, without mineral fertilization.

In 2003, nineteen years after fly ashes had been applied, soil samples were taken from particular objects at four depths: 0–25 cm, 26–50 cm, 51–75 cm and 76–100 cm. Samples were collected using a soil drill measuring $\varnothing = 50$ mm in diameter, from four different locations on each plot. These samples were then aggregated as one sample from each plot. Fresh soil collected for analyses was air dried, passed through a sieve of a $\varnothing = 1.0$ mm mesh size. The samples thus prepared underwent the following determinations: total nitrogen by Kjeldahl's method [9], having digested the soil with sulphuric acid in an open system, the content of ammonia nitrogen by colorimetry using Nessler's reagent in a Spekol 220 apparatus at wavelength $\lambda = 410$ nm, having previously extracted samples with 1 % K_2SO_4 , and the content of nitrate nitrogen by colorimetry using phenyl disulphonic acid [10], likewise in a Spekol apparatus at wavelength $\lambda = 220$ nm.

The results were processed statistically applying ANOVA test, at the level of significance $\alpha = 0.05$, with an aid of the software package Statistica v. 8.0 [11]. The correlation between a dose of fly ashes and the content of $N-NO_3$ and $N-NH_4$ was determined using a simple correlation coefficient [12].

Results and discussion

Fly ashes from power plants contain negligible amounts of nitrogen. During coal combustion, this element is released to the atmosphere as oxides. The total nitrogen amounts recorded in fly ashes are less than a few tenths of a per cent [13] and are not any larger source of nitrogen for plants. Nevertheless, the results presented in this paper have proven that application of fly ashes has significantly affected the level of nitrogen in soil. The increasing rates of fly ashes introduced to soil 19 years earlier have caused a highly significant increase in the content of N-total content in soil (Table 1).

Table 1

Total-N content in the soil 19 years after application of hard coal fly ash and organic amendments [$g \cdot kg^{-1}$ dm of soil]

Hard coal fly ash rate [$Mg \cdot ha^{-1}$]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
soil layer 0–25 cm				
0	0.89	0.95	1.03	1.01
100	1.17	1.29	1.23	1.26
200	1.20	1.22	1.26	1.17
400	1.32	1.40	1.21	1.19
600	1.15	1.17	1.12	1.07

Table 1 contd.

Hard coal fly ash rate [Mg · ha ⁻¹]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
800	1.13	1.17	1.20	1.04
LSD _{0.05} for:	hard coal fly ash rate – 0.020**; organic amendments – 0.017**; hard coal fly ash rate × organic amendments – 0.041**			
correlation coefficient	0.35 ns	0.21 ns	0.15 ns	–0.34 ns
soil layer 26–50 cm				
0	0.14	0.19	0.33	0.36
100	0.84	0.60	0.62	0.36
200	0.24	0.28	0.38	0.36
400	0.47	0.52	0.41	0.30
600	0.30	0.47	0.23	0.27
800	0.32	0.46	0.60	0.34
LSD _{0.05} for:	hard coal fly ash rate – 0.015**; organic amendments – 0.012*; hard coal fly ash rate × organic amendments – 0.030**			
correlation coefficient	–0.15 ns	0.38 ns	0.09 ns	–0.55 ns
soil layer 51–75 cm				
0	0.25	0.20	0.24	0.24
100	0.27	0.27	0.29	0.21
200	0.18	0.20	0.22	0.18
400	0.21	0.21	0.18	0.17
600	0.18	0.18	0.25	0.22
800	0.24	0.20	0.22	0.23
LSD for:	hard coal fly ash rate – 0.022**; organic amendments – 0.018*; hard coal fly ash rate × organic amendments – 0.045*			
correlation coefficient	–0.24 ns	–0.43 ns	–0.28 ns	0.04 ns
soil layer 76–100 cm				
0	0.19	0.18	0.17	0.18
100	0.17	0.18	0.18	0.15
200	0.18	0.21	0.23	0.21
400	0.17	0.19	0.18	0.15
600	0.22	0.20	0.19	0.20
800	0.25	0.19	0.15	0.19
LSD _{0.05} for:	hard coal fly ash rate – ns; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.56 ns	0.21 ns	–0.34 ns	0.24 ns

Two-way ANOVA: ** – significant at $\alpha < 0.01$, * – significant at $\alpha < 0.05$, ns – not significant.

Such correlation was most evidently revealed in soil collected from the arable layer 0–25 cm. In the series without added organic amendments, increasing doses of fly ashes

have raised the total nitrogen content from 0.89 g N kg^{-1} of soil in the control treatment to 1.32 g N kg^{-1} soil in the object which had received the dose of fly ashes equal 400 Mg ha^{-1} . Higher doses of fly ashes did not lead to further increase in the N-total content. As the depth of sample collecting increased, the total N content declined. In the control series – without added organic amendments – total nitrogen reached 1.14, 0.39, 0.22 and 0.20 g kg^{-1} of soil in the subsequent soil horizons. This effect was accompanied by concomitant disappearance of the effect of the applied fly ashes on total nitrogen in soil. In the deepest soil profile layer, ie 76–100 cm, no effect of the applied fly ashes on the total nitrogen content in soil was determined.

Similarly, additional application of organic amendments had a significant influence on modelling the long-term effect expressed as the total N content in soil. The analysis of variance run with respect to total nitrogen revealed a highly significant dependence of this trait on the applied organic amendments at the depths of 0–15 cm and 26–50 cm. Weaker effect was observed at the depth of 51–75 cm, while at the deepest layer, 76–100 cm, no such effect was evidenced. When analyzing the average values, it has been verified that among the tested organic substances, the total N content in soil was raised versus the control value (1.14 g N kg^{-1}) by FYM (1.20 g N kg^{-1}) and straw (1.18 g N kg^{-1}). Tree bark, in contrast, depressed the total N content (1.12 g N kg^{-1}).

Although fly ashes alone do not contain nitrogen as a fertilizer component, over the many years they have contributed to an increase in the content of nitrogen in soil. This effect is attributable to improved growing conditions for plants, created by fly ashes and their properties. Under such improved conditions lasting for many years, owing to deeper and more intensive root development the soil naturally gathered more post-harvest residue, which is now a valuable source of available nitrogen to aftercrops. The fact that N-total increases in soil following application of fly ashes has been also demonstrated by Kawecki and Tomaszewska [14, 15], Giedrojc and Fatyga [16] and Wojcieszczuk et al [17].

The fly ashes tested in this experiment had a significant effect on the content of nitrate nitrogen in soil (Table 2).

When comparing the soil profile horizons, it became evident that the content of N- NO_3 was the highest in the soil's arable layer, 0–25 cm deep. In the control series (with no amendments added to soil), it ranged from 2.32 to 4.57 mg kg^{-1} of soil. Analogously to total N, the content of this form of nitrogen tended to decline in deeper layers of soil and the influence produced by application of fly ashes on this form of nitrogen in soil weakened. In the deepest layer, 75–100 cm, no effect of fly ashes on the content of N- NO_3 in soil was determined.

In the arable layer of soil, the highest content of nitrates was found in the series with added tree bark, on average $4.07 \text{ mg N-NO}_3 \text{ kg}^{-1}$. Less N- NO_3 appeared in the series supplemented with straw (3.64 mg kg^{-1} soil) and the lowest content of this form of nitrogen was determined in the objects treated with farmyard manure (3.46 mg kg^{-1} soil).

Table 2

N-NO₃ content in the soil 19 years after application of hard coal fly ash
and organic amendments [mg · kg⁻¹ dm of soil]

Hard coal fly ash rate [Mg · ha ⁻¹]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
soil layer 0–25 cm				
0	2.32	2.69	2.33	3.93
100	3.75	3.15	3.80	3.76
200	3.75	3.67	4.08	4.25
400	4.57	4.40	4.27	4.43
600	4.57	3.89	3.59	4.20
800	4.00	2.98	3.75	3.86
LSD _{0.05} for:	hard coal fly ash rate – 0.65**; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.64 ns	0.16 ns	0.34 ns	0.12 ns
soil layer 26–50 cm				
0	1.94	2.41	2.16	2.75
100	2.86	3.48	1.34	1.55
200	1.26	1.71	1.06	1.29
400	1.43	2.38	1.61	1.42
600	1.07	1.20	1.10	1.53
800	1.09	2.69	1.80	1.72
LSD _{0.05} for:	hard coal fly ash rate – 0.37**; organic amendments – 0.30**; hard coal fly ash rate × organic amendments – 0.74**			
correlation coefficient	–0.67 ns	–0.24 ns	–0.12 ns	–0.38 ns
soil layer 51–75 cm				
0	2.62	1.23	1.03	2.61
100	1.41	1.79	2.01	2.55
200	2.91	1.75	1.91	1.12
400	0.95	1.16	2.25	1.67
600	1.88	2.28	1.21	1.83
800	1.80	1.71	1.08	1.22
LSD for:	hard coal fly ash rate – ns; organic amendments – ns; hard coal fly ash rate × organic amendments – 1.27*			
correlation coefficient	–0.28 ns	0.25 ns	–0.22 ns	–0.57 ns
soil layer 76–100 cm				
0	1.74	3.21	1.77	2.89
100	1.85	1.69	1.95	1.62
200	1.48	0.93	0.59	1.26
400	1.53	1.34	1.23	2.30
600	1.60	1.70	1.86	2.30
800	1.21	1.94	2.16	1.95
LSD _{0.05} for:	hard coal fly ash rate – 0.48**; organic amendments – 0.39**; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.36 ns	0.00 ns	0.06 ns	0.02 ns

Two-way ANOVA: ** – significant at $\alpha < 0.01$, * – significant at $\alpha < 0.05$, ns – not significant.

The content of ammonia nitrogen in soil was varied and depended on such factors as a rate of fly ashes, the applied organic substance and the depth of collecting soil samples (Table 3).

Table 3

N-NH₄ content in the soil 19 years after application of hard coal fly ash and organic amendments [mg · kg⁻¹ dm of soil]

Hard coal fly ash rate [Mg · ha ⁻¹]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
soil layer 0–25 cm				
0	8.82	8.00	10.28	6.77
100	7.69	9.27	9.78	7.77
200	11.36	10.72	12.00	7.23
400	11.94	11.56	12.85	11.02
600	13.79	16.79	14.66	14.29
800	13.83	13.68	12.67	12.09
LSD _{0.05} for:	hard coal fly ash rate – 1.50**; organic amendments – 1.22**; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.85 ns	0.77 ns	0.66 ns	0.88 ns
soil layer 26–50 cm				
0	9.37	8.70	10.24	9.78
100	5.89	6.61	6.00	6.11
200	7.04	6.42	7.33	6.62
400	6.09	6.94	5.45	6.99
600	5.29	6.05	7.06	7.06
800	6.68	6.00	5.69	5.80
LSD _{0.05} for:	hard coal fly ash rate – 0.77**; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	–0.52 ns	–0.59 ns	–0.54 ns	–0.51 ns
soil layer 51–75 cm				
0	10.65	12.68	11.33	10.15
100	11.08	10.66	10.47	9.52
200	8.00	8.53	7.56	5.75
400	6.18	4.72	7.58	7.02
600	7.19	4.19	5.88	7.02
800	6.88	5.79	3.33	4.17
LSD for:	hard coal fly ash rate – 1.16**; organic amendments – ns; hard coal fly ash rate × organic amendments – 2.33*			
correlation coefficient	–0.73 ns	–0.83 ns	–0.92 ns	–0.74 ns
soil layer 76–100 cm				
0	5.15	7.20	4.34	4.39
100	4.48	4.99	4.10	4.71
200	4.61	5.67	6.57	7.00

Table 3 contd.

Hard coal fly ash rate [Mg · ha ⁻¹]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
400	3.76	4.16	4.37	3.72
600	4.93	6.80	3.50	4.50
800	6.57	6.34	4.97	6.07
LSD _{0.05} for:	hard coal fly ash rate – ns; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.46 ns	0.06 ns	–0.09 ns	0.09 ns

Two-way ANOVA: ** – significant at $\alpha < 0.01$, * – significant at $\alpha < 0.05$, ns – not significant.

Fly ashes evidently, in a nearly linear fashion, raised the content of this form of nitrogen in the series without additional organic amendments and in the series fertilized with manure or tree bark up to 600 Mg ha⁻¹. Such dependence was not confirmed for the series with straw, although straw introduced to soil resulted in the highest mean accumulation of N-NH₄ in soil (12.04 mg kg⁻¹). In the series with FYM, the determined concentration of ammonia nitrogen was 11.67 mg kg⁻¹, while in the control treatment, this amount reached 11.24 mg kg⁻¹. Tree bark strongly reduced the amount of N-NH₄, down to 9.86 mg kg⁻¹. The influence of fly ashes added to soil 19 years earlier on ammonia nitrogen was observable down to the depth of 51–75 cm, although the dependence between a dose of fly ashes and the content of N-NH₄ in this soil layer was reverse. Higher levels of ammonia nitrogen were found in the plots which had received smaller doses of fly ashes. In the deepest layer, 76–100 cm, none of the dependences mentioned above occurred.

The present study has demonstrated that N-NH₄ prevailed over N-NO₃ in soil collected from all the treatments. These observations are divergent from the literature data, which imply a reverse dependence, ie prevalence of nitrates over the ammonia form of nitrogen [18]. The prevalence of ammonia form over nitrates is typical for soils in Poland. This fact proves that there are conditions which limit the nitrification process [19, 20].

Conclusions

1. Hard coal fly ashes and organic amendments added to soil together with ashes have contributed to the increase in the analyzed forms of nitrogen in soil, mainly in its arable horizon.
2. Among the tested organic amendments, irrespective of the depth of collecting soil samples, tree bark had the strongest effect on the content of N-NO₃, raising its concentration in soil.
3. Regarding N-NH₄, the most desirable effect was produced by straw as a soil amending substance, as it depressed the level of this form of nitrogen in soil.

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NASTĘPCZE ODDZIAŁYWANIE POPIOŁÓW Z WĘGLA KAMIENNEGO NA ZAWARTOŚĆ AZOTU W GLEBIE

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Abstrakt: Pracę poświęcono wyjaśnieniu następczego oddziaływania popiołów z węgla kamiennego na zawartość wybranych form azotu w glebie. Badania wykonano, korzystając z doświadczenia polowego po 19 latach od jego założenia. Popioły stosowano w dawkach 0, 100, 200, 400, 600 i 800 Mg · ha⁻¹ z uwzględnieniem czterech serii: bez dodatku substancji organicznej, z obornikiem, ze słomą i z korą drzewną. Uzyskane wyniki badań wskazują, że popioły z węgla kamiennego oraz wprowadzane wraz z nimi dodatki nawozów organicznych znacznie wpłynęły na długookresowe kształtowanie się zawartości badanych form azotu w glebie. Działanie popiołów uwidoczniło się przede wszystkim w warstwie ornej badanej gleby. W głębszych warstwach nie stwierdzono wpływu popiołów na zmiany zawartości badanych form azotu. Spośród zastosowanych dodatków organicznych niezależnie od poziomu pobrania próbek gleby na zawartość N-NO₃ najsilniej wpływała kora drzewna, powodując wzrost jego ilości. W odniesieniu do formy N-NH₄ najsilniejszy wpływ na zawartość tej formy azotu miała słoma.

Słowa kluczowe: popioły lotne z węgla kamiennego, azot, N-amonowy, N-azotanowy