

LONG-TIME EFFECT OF HARD COAL ASH ON THE CONTENT OF SOME ELEMENTS IN SOIL

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ABSTRACT

The aim of the study was to determine the long-time effect of meliorating doses of hard coal ash (0, 100, 200, 400, 600 and 800 t · ha⁻¹) on the content of some elements in soil with the application of different organic substances: manure, straw and bark. Nineteen years after the application of ash there was still an increase in the total content of all elements in soil. Its magnitude depended on soil horizon and it was highest in the humus horizon. The increase in the content of nutrients was, in general, proportional to the applied doses of ash. In the surface layer of soil, the increase was particularly high for sodium and subsequently for calcium, magnesium, sulphur, potassium and phosphorus, arranged in the order of decreasing values. The content of elements in deeper soil layers was significantly lower than in the 0–25 cm zone. A gradual reduction in the content, together with the increase in depth, was recorded only for magnesium and sulphur. The lowest concentration of phosphorus and calcium was detected in the 51–75 cm layer, while in the case of potassium it was in the 26–50 cm zone. The substances introduced into the soil in order to reduce the impact of ash generated by hard coal combustion did not exert any significant impact on the content of elements 19 years following their application.

Keywords: hard coal ash, manure, straw, bark, soil, elements.

INTRODUCTION

The current legal regulations on air protection in Poland have contributed to a significant reduction in dust emissions by the power engineering sector. The total emission estimated at 155 thousand tonnes in 2000 decreased to 61 thousand tonnes in 2010 (this data includes emissions from the occupational power industry, industrial and technological power engineering industry and does not cover local boiler houses, domestic furnaces, workshops and agriculture) [13]. These changes have mainly resulted from the installation of increasingly efficacious dust removal

equipment. Reduction in dust emissions generates an increase in the volume of volatile ash disposed on storage yards near power engineering plants. It is widely recognized that this ash poses a serious hazard to the natural environment mainly due to higher content of trace elements [18]. However, the presence of macro- and microelements and compounds with strong adsorptive properties indicate a potential for their environmental utilization [17, 18]. Although the effects of volatile hard coal ash on the properties of soil and plants have been well investigated in the literature, there is a limited source of data on the persistence of changes caused by their introduction into soil.

The objective of the study was to determine a long-time effect of meliorating doses of hard coal ash on the content of elements in soil with the application of different organic substances: manure, straw and bark.

MATERIALS AND METHODS

The studies were based on a field experiment by Prof. dr. hab. Grzegorz Nowak and Prof. dr. hab. Zdzisław Ciećko, the University of Agriculture and Technology in Olsztyn (presently, University of Warmia and Mazury in Olsztyn), in autumn, 1984 in a randomized sub-block model within Łęg Starościński village (Lelis commune) situated in the Ostrołęckie county (Poland) on soil classified as poor rye complex with a granule size composition of loamy sand. The soil was moderately abundant in available phosphorus ($55 \text{ mg P} \cdot \text{kg}^{-1} \text{ d.m.}$), with a high content of available potassium ($152 \text{ mg K} \cdot \text{kg}^{-1} \text{ d.m.}$), available magnesium ($55 \text{ mg Mg} \cdot \text{kg}^{-1} \text{ d.m.}$) and total boron ($0.45 \text{ mg B} \cdot \text{kg}^{-1} \text{ d.m.}$), average content of total manganese ($20.5 \text{ mg Mn} \cdot \text{kg}^{-1} \text{ d.m.}$) and total zinc ($4.16 \text{ mg Zn} \cdot \text{kg}^{-1} \text{ d.m.}$) and with low content of copper ($1.75 \text{ mg Cu} \cdot \text{kg}^{-1} \text{ d.m.}$). The sorption capacity was $125 \text{ mmol}(+) \cdot \text{kg}^{-1} \text{ d.m.}$ and the pH in water and in $1 \text{ mol KCl} \cdot \text{dm}^{-3}$ was 6.5 and 5.6, respectively. The experiment was conducted in a randomized block model in four repetitions with the inclusion of two experimental factors using incremental doses of ash (0, 100, 200, 400, 600 and $800 \text{ t} \cdot \text{ha}^{-1}$). In order to reduce the impact of ash, different substances were introduced into the soil in amounts equivalent to 10 tonnes d.m. $\cdot \text{ha}^{-1}$. The studies were carried out in four series: without substances and with the application of manure, straw and bark. The hard coal ash and organic compounds were introduced to the soil once in autumn in 1984 (at the time of experiment setting). The content of elements in hard coal ash and organic substances was presented in Table 1.

The ash was collected directly from the electro-filters at the “Ostrołęka” Power Plant Complex. The ash contained highest concentration of magnesium, iron, manganese, copper and cobalt. The reaction of ash measured in $1 \text{ mol KCl} \cdot \text{dm}^{-3}$ was 9.2. Manure was obtained from a nearby swine operation and bark from the paper and cellulose production plant located in Ostrołęka. Manure contained highest amounts of phosphorus and zinc; oat straw – nitrogen and potassium and bark – calcium. The surface of each experimental plot was 54 m^2 with a 1 m width of protective zones between the plots and 3 m between the sub-blocks. During the first six years of the studies, typical agricultural plants were cultivated (potatoes – 1985; oat for forage + lupine for forage – 1986; rye for forage + legumes-grass mixture for forage – 1987; legumes-grass mixture for forage – 1988–1991) and subsequently, starting from 1992, it was used as rough grazing land, non-fertilized with mineral fertilizers. Mineral fertilization with NPK and agricultural engineering procedures was identical on all experimental objects and NPK doses for 19 years equals 1215 kg N , 500 P and 1220 kg K per hectare.

After 19 years, in order to determine the long-time effect of ash on the selected soil parameters, samples from all objects and from 4 horizons (i.e. 0–25, 26–50, 51–75 and 76–100 cm) were collected. Following drying at room temperature and sieving through a 1 mm mesh, the total content of phosphorus with vanadium-molybdenum method was determined and the concentration of other elements (potassium, calcium, magnesium, sulphur and sodium) was measured with an atomic absorption spectrophotometer Unicam 939 Solar. In order to determine concentrations of elements, the soil was wet mineralized in a mixture of perchloric acid and nitric acid.

The results were statistically processed with Statistica 10 software using an ANOVA two-way analysis of variance [14]. The relations between the soil horizons and the content of elements in

Table 1. Content of some elements in hard coal ash, manure, straw and bark at the start of experiment in autumn 1984

| Hard coal ash and organic substances | N | P | K | Ca | Mg | Fe | Mn | Cu | Zn | Co |
|--------------------------------------|--------------------------------|-----|------|------|-----|------|---------------------------------|------|-------|------|
| | [g · kg ⁻¹ of d.m.] | | | | | | [mg · kg ⁻¹ of d.m.] | | | |
| Hard coal ash | - | 1.7 | 2.9 | 15.0 | 7.1 | 27.9 | 496.0 | 61.0 | 48.0 | 13.0 |
| Manure | 5.3 | 2.5 | 3.1 | 3.6 | 1.3 | 2.15 | 235.4 | 16.4 | 151.2 | 1.33 |
| Straw | 5.6 | 1.5 | 17.2 | 3.9 | 1.0 | 0.16 | 80.3 | 6.1 | 46.3 | 0.14 |
| Bark | 0.5 | 0.7 | 1.3 | 20.3 | 0.8 | 0.87 | 124.2 | 7.3 | 46.8 | 0.74 |



the soil expressed as simple Pearson's correlation coefficients and the standard deviation for average content of elements in soil were calculated with Microsoft Excel 2010 [11].

RESULTS AND DISCUSSION

The analysis of the content of elements in the soil demonstrated that, despite the period of 19

years that had passed from the moment of application, the incremental doses of ash generated an increase in the total content of all elements in the soil (Tables 2 and 3). The magnitude of this increase depended on soil horizon – it was highest in the surface layer of the soil. Within this horizon, the increase was particularly high for sodium and, in the case of other elements, it decreased in the following order: calcium, magnesium, sulphur, potassium and phosphorus. However, it

Table 2. Long-time effect of hard coal ash on the total content of phosphorus, potassium, calcium and magnesium in the soil (the average from four series) [$\text{g} \cdot \text{kg}^{-1}$ of soil]

| Hard coal ash dose [$\text{t} \cdot \text{ha}^{-1}$] | Soil horizon [cm] | | | | r |
|--|-------------------|-----------|-----------|-----------|-----------|
| | 0-25 | 26-50 | 51-75 | 76-100 | |
| Total phosphorus [$\text{g} \cdot \text{kg}^{-1}$ of soil] | | | | | |
| 0 | 0.56 | 0.33 | 0.17 | 0.20 | -0.902 ** |
| 100 | 0.61 | 0.33 | 0.17 | 0.20 | -0.894 ** |
| 200 | 0.63 | 0.34 | 0.17 | 0.19 | -0.906 ** |
| 400 | 0.65 | 0.34 | 0.18 | 0.20 | -0.898 ** |
| 600 | 0.67 | 0.34 | 0.19 | 0.20 | -0.899 ** |
| 800 | 0.68 | 0.35 | 0.20 | 0.20 | -0.907 ** |
| Average | 0.63±0.04 | 0.34±0.01 | 0.18±0.01 | 0.20±0.01 | -0.902 ** |
| LSD _{0.05} for: hard coal ash dose - 0.022; soil horizon - 0.018; interaction - n.s. | | | | | |
| Total potassium [$\text{g} \cdot \text{kg}^{-1}$ of soil] | | | | | |
| 0 | 0.36 | 0.38 | 0.40 | 0.38 | 0.632 * |
| 100 | 0.44 | 0.39 | 0.41 | 0.39 | -0.710 ** |
| 200 | 0.47 | 0.40 | 0.42 | 0.43 | -0.439 |
| 400 | 0.52 | 0.40 | 0.41 | 0.44 | -0.546 |
| 600 | 0.53 | 0.40 | 0.41 | 0.45 | -0.502 |
| 800 | 0.55 | 0.39 | 0.41 | 0.50 | -0.222 |
| Average | 0.48±0.07 | 0.39±0.01 | 0.41±0.01 | 0.43±0.04 | -0.432 |
| LSD _{0.05} for: hard coal ash dose - 0.024; soil horizon - 0.020; interaction - 0.049 | | | | | |
| Total calcium [$\text{g} \cdot \text{kg}^{-1}$ of soil] | | | | | |
| 0 | 1.11 | 0.66 | 0.41 | 0.43 | -0.909 ** |
| 100 | 1.35 | 0.81 | 0.48 | 0.51 | -0.912 ** |
| 200 | 1.65 | 1.03 | 0.53 | 0.62 | -0.908 ** |
| 400 | 2.38 | 1.27 | 0.69 | 0.73 | -0.907 ** |
| 600 | 3.09 | 1.36 | 0.70 | 0.82 | -0.874 ** |
| 800 | 3.44 | 1.44 | 0.72 | 0.91 | -0.861 ** |
| Average | 2.17±0.96 | 1.10±0.31 | 0.59±0.13 | 0.67±0.18 | -0.888 ** |
| LSD _{0.05} for: hard coal ash dose - 0.079; soil horizon - 0.064; interaction - 0.160 | | | | | |
| Total magnesium [$\text{g} \cdot \text{kg}^{-1}$ of soil] | | | | | |
| 0 | 0.34 | 0.31 | 0.29 | 0.24 | -0.983 ** |
| 100 | 0.40 | 0.32 | 0.29 | 0.29 | -0.894 ** |
| 200 | 0.47 | 0.33 | 0.30 | 0.29 | -0.882 ** |
| 400 | 0.78 | 0.42 | 0.31 | 0.30 | -0.889 ** |
| 600 | 0.87 | 0.44 | 0.31 | 0.31 | -0.880 ** |
| 800 | 0.93 | 0.46 | 0.31 | 0.32 | -0.877 ** |
| Average | 0.63±0.26 | 0.38±0.07 | 0.30±0.01 | 0.29±0.03 | -0.894 ** |
| LSD _{0.05} for: hard coal ash dose - 0.025; soil horizon - 0.020; interaction - 0.050 | | | | | |

Explanation: r – correlation coefficient; differences significant for: * – $P \leq 0.05$; ** – $P \leq 0.01$.

Table 3. The long-time effect of hard coal ash on the total content of sulphur and sodium in the soil (the average from four series) [$\text{g} \cdot \text{kg}^{-1}$ of soil]

| Hard coal ash dose [$\text{t} \cdot \text{ha}^{-1}$] | Soil horizon [cm] | | | | Average | r |
|--|-------------------|-------------|-------------|-------------|-------------|-----------|
| | 0-25 | 26-50 | 51-75 | 76-100 | | |
| Total sulphur [$\text{g} \cdot \text{kg}^{-1}$ of soil] | | | | | | |
| 0 | 0.27 | 0.08 | 0.06 | 0.04 | 0.11 | -0.863 ** |
| 100 | 0.30 | 0.17 | 0.09 | 0.04 | 0.15 | -0.979 ** |
| 200 | 0.34 | 0.14 | 0.07 | 0.04 | 0.15 | -0.928 ** |
| 400 | 0.43 | 0.14 | 0.07 | 0.04 | 0.17 | -0.898 ** |
| 600 | 0.46 | 0.13 | 0.06 | 0.04 | 0.17 | -0.878 ** |
| 800 | 0.48 | 0.14 | 0.06 | 0.04 | 0.18 | -0.883 ** |
| Average | 0.38±0.09 | 0.13±0.03 | 0.07±0.01 | 0.04±0.00 | 0.16±0.02 | -0.905 ** |
| LSD _{0.05} for: hard coal ash dose - 0.012; soil horizon - 0.010; interaction - 0.024 | | | | | | |
| Total sodium [$\text{g} \cdot \text{kg}^{-1}$ of soil] | | | | | | |
| 0 | 0.019 | 0.021 | 0.301 | 0.013 | 0.089 | 0.239 |
| 100 | 0.147 | 0.021 | 0.276 | 0.015 | 0.115 | -0.147 |
| 200 | 0.443 | 0.037 | 0.262 | 0.001 | 0.186 | -0.687 ** |
| 400 | 1.529 | 0.039 | 0.307 | 0.006 | 0.470 | -0.773 ** |
| 600 | 1.341 | 0.029 | 0.105 | 0.047 | 0.381 | -0.766 ** |
| 800 | 0.562 | 0.034 | 0.031 | 0.004 | 0.158 | -0.802 ** |
| Average | 0.674±0.624 | 0.030±0.008 | 0.214±0.116 | 0.014±0.017 | 0.233±0.155 | -0.754 ** |
| LSD _{0.05} for: hard coal ash dose - 0.026; soil horizon - 0.021; interaction - 0.052 | | | | | | |

Explanation: r – correlation coefficient; differences significant for: * – $P=0.05$; ** – $P=0.01$.

should be noted that the increase in the content of sodium was detected only up to the dose of $400 \text{ t} \cdot \text{ha}^{-1}$ and was 80-fold in comparison with the control object (without ash).

The increase in the total content of calcium and magnesium in the surface soil layer was linear and amounted to 210% and 174%, respectively, on the object fertilized with $800 \text{ t} \cdot \text{ha}^{-1}$ in comparison with the control object. As impacted by the application of ash, the increase in the content of sulphur was also directly proportional to their doses. It amounted to max. 78% as compared to the control object. In the case of potassium and phosphorus, the increase in their concentration in the surface layer of the soil was significantly lower: under the dose of 800 tonnes of ash per ha it amounted to, respectively, 53% and 21%.

In the subsequent horizon of soil, an increase of all elements was observed. It was smaller than in surface soil layer. In other horizons of soil, the highest increase in contents was observed in case of magnesium and potassium. Within the zones 26–50 and 76–100 cm, calcium was lower by nearly half than in surface layer, while it amounted to 76% in the 51–75 cm zone.

In other three soil horizons (26–50, 51–75 and 76–100 cm), the increase in the content of total

magnesium was directly proportional to the dose of ash reaching, respectively, 48%, 7% and 33%.

The content of analyzed elements was positively correlated with soil pH and negatively with soil hydrolytic acidity [3]. The increase in pH_{KCl} (from 5.2 to 7.2) and decrease in hydrolytic activity (2.5 times) in the surface soil layer was observed in the object fertilized with $800 \text{ t} \cdot \text{ha}^{-1}$ in comparison with the control object. In 26–50 cm horizon, the changes of pH_{KCl} were the same but hydrolytic activity smaller than in surface soil layer.

The content of elements in deeper soil layers was significantly lower than in the 0–25 cm zone (Tables 2 and 3, Figure 1).

It should be emphasized that a gradual reduction in the content, together with increasing soil depth was recorded only for magnesium (correlation between soil horizons and content of magnesium in soil, $r = -0.894$) and sulphur ($r = -0.905$). The lowest concentration of phosphorus and calcium was detected in the 51–75 cm layer while potassium was in the 26–50 cm zone. The biggest differences between the 0–25 and 76–100 cm layers were recorded for the content of sodium and sulphur, whereas the lowest differentiation between the examined zones was detected for



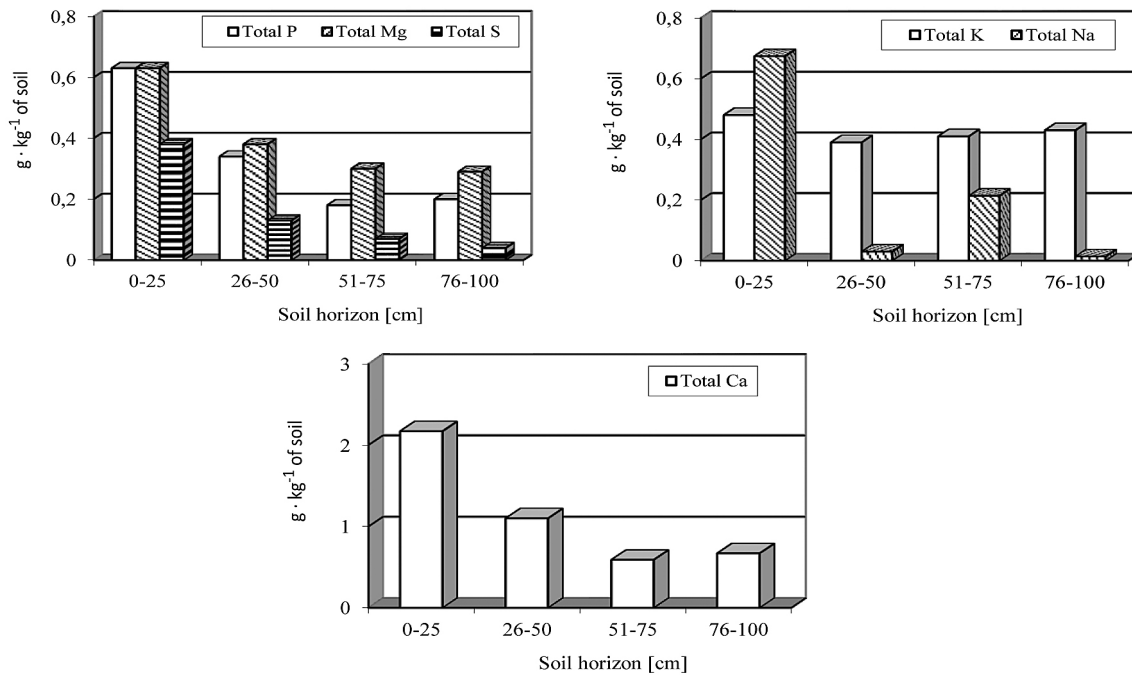


Figure 1. Total content of elements in the soil profile regardless of ash dose (the average for the individual horizons) [$g \cdot kg^{-1}$ of soil]

potassium. The substances applied to the soil, in order to reduce the impact of ash generated by the combustion of hard coal, did not influence significantly the content of elements in the soil 19 years after their application.

The increase in the total content of tested elements recorded in the present study confirms the findings reported by other authors. The changes in the concentration of phosphorus and potassium in the soil are consistent with the results reported by Właśniewski [19] and Lee et al. [7, 8]. Właśniewski [19] demonstrated that application of the highest dose of ash ($134 t \cdot ha^{-1}$) caused a marked increase in total content of phosphorus by 361%, magnesium by 633%, and a slight increase in potassium content by 38% (compared to reference). Lee et al. [8] observed that the application of fly ash in the dose of 40, 80 and $120 t \cdot ha^{-1}$ in two paddy soils increased the available phosphorus significantly. An increase in the total content of potassium with fertilization with hard coal ash was indicated by Lee et al. [7]. Conversely, different results were reported by Matsi and Keramidas [9] who observed that over time following the application of furnace waste materials, the soil surface layer became depleted of potassium.

Mittra et al. [12] demonstrated that, together with ash, a substantial amount of potassium, calcium and magnesium were introduced into soil, for instance, 32 kg of P, 25 kg of K, 33 kg of Ca

and 17 kg of Mg were introduced with a dose of $10 t \cdot ha^{-1}$. The studies conducted by Kovacik et al. [6] demonstrated that ash-fly ash mixture statistically significant increase of the content of available calcium. An increase in the total content of calcium and sodium with fertilization with hard coal ash in the dose of $50-400 t \cdot ha^{-1}$ was also indicated by Gourab and Vadakepuram [4].

Hjemar [5] and Theis and Gardner [16] demonstrated that sodium that originated from ash introduced into soil diffused into the soil solution relatively quickly and passed deeper into the soil profile faster than potassium. Tejasvi and Kumar [15] reported a slight increase in the content of phosphorus, potassium, sulphur, calcium and magnesium following the application of ash.

The results of our studies confirm the findings by Meller [10] indicating that nutrients introduced into soil with ash become mobile at different rates depending on the degree of their solubility. The studies conducted by Meller [10] demonstrated that sodium, potassium, calcium and subsequently magnesium were most rapidly transformed into soluble forms as a result of precipitation water activity. Conversely, in an acidic environment calcium, manganese, magnesium and lead are the first quantitatively mobilized elements, followed by sodium and potassium [5, 10, 16]. Higher doses of ash have a large effect on chemical composition of plants [1, 2].

CONCLUSION

1. Nineteen years after the application of ash there was still an increase in the total content of all elements in the soil. Its magnitude depended on the soil horizon and it was highest in the humus horizon. The increase in the content of nutrients was in general proportional to the applied doses of ash.
2. In the surface layer of the soil, the increase was particularly high for sodium and subsequently for calcium, magnesium, sulphur, potassium and phosphorus, arranged in the order of decreasing values.
3. The content of elements in deeper soil layers was significantly lower than in the 0–25 cm zone. A gradual reduction in the content together with the increase in depth was recorded only for magnesium and sulphur. The lowest concentration of phosphorus and calcium was detected in the 51–75 cm layer, while in the case of potassium it was in the 26–50 cm zone.
4. The substances introduced into the soil in order to reduce the impact of ash generated by hard coal combustion did not exert any significant impact on the content of elements 19 years following their application.

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