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# CHEMICAL INDUSTROGENIC TRANSFORMATIONS OF SOILS ON THE SELECTED AREA OF PRZEDGÓRZE IŁŻECKE

ANNA ŚWIERCZ

Akademia Świętokrzyska, Instytut Geografii, ul. Świętokrzyska 15, 25-406 Kielce

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## PRZEMYSŁOWE CHEMICZNE PRZEKSZTAŁCENIA GLEB NA WYBRANYCH STANOWISKACH PRZEDGÓRZA IŁŻECKIEGO

Cementownia Ożarów S.A produkuje cement metodą suchą, zaopatrując rocznie ponad 15% rynku krajowego. Procesami szczególnie uciążliwymi dla środowiska są: wydobycie surowca, jego transport, rozdrabnianie, wypał, pakowanie i składowanie. Każdy z wymienionych etapów jest źródłem zorganizowanej i niezorganizowanej emisji pyłów i gazów. Celem pracy było określenie wpływu emisji z cementowni Ożarów na właściwości chemiczne gleb znajdujących się pod ich bezpośrednim wpływem. Wykonano 7 profili glebowych w zwartym kompleksie leśnym na wschód od cementowni. W próbach zbadano podstawowe właściwości fizykochemiczne gleb. Badane gleby zdefiniowano jako bielicowe i rdzawe bielicowe. Stwierdzono zmianę wartości pH gleby do 8,3 jednostki w poziomach organicznych, utrzymującą się zawartość $CaCO_3$ do głębokości 30–40 cm, wyraźne obniżenie kwasowości hydrolitycznej, glinu i wodoru wymiennego, wzrost wysycenia kompleksu sorpcyjnego głównie kationami $Ca^{2+}$ i $Mg^{2+}$, znaczne zasolenie poziomów organicznych do 270 mg KCl/100 g, wzrost troficzności, wzbogacenie poziomów powierzchniowych w metale ciężkie.

Summary

"Ożarów" Cement Plant manufactures cement with the application of dry method, thus supplying its products on more than 15% of the domestic market. The processes, especially troublesome for the environment, are as follows: raw material output, its transportation, grinding, burning, packaging and storage. The aim of this paper is to determine the influence of emission from "Ożarów" Cement Plant on the chemical properties of the soils being under its direct impact. There are seven soil profiles done in the forested complex at the South from the Cement Plant. In soils material content chemical properties were examined. On the basis of the profile structure the uncovered soils were defined as albic arenosol and haplic podzol soils. The following have been noticed: the change of pH value of soil from 8.3 in the organic horizons, the change of $CaCO_3$ at the depth of 30–40 cm, the considerable decrease in the hydrolytic acidity, aluminum and exchangeable hydrogen, the saturation of the sorption complex mainly by cations $Ca^{2+}$ and $Mg^{2+}$, the considerable salinity of the organic horizons from 270 mg KCl/100 g, the considerable trophic, considerable content trace elements in organic horizons.

## INTRODUCTION

At the region of Iłża and Przedgórze Iłżeckie there are two industrial plants: Ostrowiec Steelworks as well as "Ożarów" Cement Plant [15], which are the most troublesome to the environment. The Cement Plant, built in the area of Potok, has been in operation since 1978 and at present it covers the area of approx. 59 ha. In the close vicinity of the plant there is

Gliniany Lime Quarry from which the raw materials are extracted in the wall system (lime and marls) with the application of explosives. The closest villages are Dąbrówka and Potok situated at the distance of 1 km in the northern direction from the boarder of the Cement Plant. In a relatively small distance (up to 15 km) from the discussed industrial plant there are valuable natural beauty regions such as: "Zielonka" reserve, "Lisiny Bodzechowskie" forested reserve, "Ulów" flora reserve and "Krzemionki Opatowskie" reserve.

The "Ożarów" Cement Plant has been producing cement in a dry method to supply over 15% of the domestic market. The current level of gas and dust pollution in the close vicinity of the plant does not exceed the permitted value [15, 20]. Since 1995 the Cement Plant has been monitoring pollutants in 15 measuring points. On the basis of the research conducted by Eko-Labor from Kraków it is possible to state that in 2001 the total dust fall ranged from 140 to 75 $g/m^2$ (on average 62 $g/m^2$), annual average suspended dust fall was at the level of 35 $\mu g/m^3$ (at the standard value of 50 $\mu g/m^3$ ), whereas the emission of $SO_2$ and $NO_2$ would correspond to 7 $\mu g/m^3$ and 20 $\mu g/m^3$ (the permitted annual standard for those compounds at 40 $\mu g/m^3$). A visible huge drop in annual average concentration values of $SO_2$ has been observed since 1997, it is caused by the decrease of sulphur in Tarnobrzeg zone [15, 19, 20].

In the case of the decreased polluting emission in 2003 soil examination was conducted in the forested complexes located closely to the "Ożarów" Cement Plant. The aim was to determine the impact of the plant on the chemical properties of podzol soil.

The results of investigations were related to chemical properties of haplic podzol on the controlled area (in Holendry), out of reach of the emitter cement dust (profile "0" Tab. 1, 2).

## MATERIAL AND METHODS

There are seven soil horizons defined in the compact forested complex situated in the southern part of the Cement Plant at the distance from 200 to 1200 m. Excavations were dug to the depth of 200 cm, and 5–9 samples were collected for laboratory analysis from the designated soil horizons. In the dry air samples physical and chemical properties were examined [13]:

- gain of fraction > 0.1 mm by a wet sieving method (with the application of sieves in a wet method (with the application of sieves with the diameter of: 10, 5.0, 1.0 mm) and soil fraction < 0.1mm by Casagrande's method in Prószyński's modification; the material division into mechanical fractions and determination of mechanical groups were done on the basis of PTG;
- $pH_{H2O}$ and $pH_{KCl}$ by a potentiometric method;
- (Hh) by Kappen's hydrolith method;
- acidity substitution (Hw) and aluminium substitution ($Al^{3+}$) by Sokołow's method;
- organic carbon (Corg) by Tiurin's method in mineral samples and Altan's method in organic samples;
- nitrogen total (Ntot) modified by Kjeldahl's method in Kjeltec Auto analyzer 1030;
- $CaCO_3$ by Scheibler's method;
- soil salinity on the basis of results of electrolytic conductivity measurements $PEW_{25}$ soil extracts using the proportion of 1:5 (standard ISO-PN 11265);
- exchangeable cations in the solution of 1 M $CH_3COONH_4$ ($pH_{H2O} \leq 7.5$), the sum of exchangeable cations S, capacity of real exchangeable cations $PWK_r$ (ISO-PN 11260),

Table 1. Some chemical properties of investigated soils

| Profile No | Horizons | Depth | pH $H_2O$ | pH KCl | $CaCO_3$ | Corg. | N total | Soil salinity | $Al^{3+}$ | Hw | Hh | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Na^+$ | S | PWKr | Vpot |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | cm | | | % | | | KCl/100 g | cmol(+)/kg | | | | | | | | | % |
| 1 | Ol | 0–2 | 6.05 | 5.89 | 5.98 | 48.17 | 1.22 | 260.7 | 0.01 | 0.02 | 10.19 | 38.99 | 3.19 | 2.57 | 0.17 | 44.92 | 44.94 | 81.51 |
| | Ofh | 2–5 | 8.10 | 7.96 | 19.11 | 20.98 | 0.89 | 151.8 | 0 | 0 | 1.21 | 87.12 | 8.13 | 1.41 | 0.21 | 96.87 | 96.87 | 98.77 |
| | AEes | 5–14 | 7.98 | 7.24 | 4.63 | 1.12 | 0.05 | 27.7 | 0 | 0 | 0.32 | 25.12 | 1.04 | 0.32 | 0.10 | 26.58 | 26.58 | 98.81 |
| | Bv | 14–65 | 5.61 | 5.41 | 0.51 | 0.23 | 0.04 | 14.4 | 0.15 | 0.17 | 1.15 | 6.12 | 0.24 | 0.09 | 0.03 | 6.48 | 6.65 | 84.93 |
| | C | 65–120 | 4.51 | 4.47 | 0.0 | 0.08 | 0.01 | 36.2 | 0.69 | 0.77 | 2.11 | 0.55 | 0.06 | 0.02 | 0.00 | 0.63 | 1.4 | 22.99 |
| 2 | Ol | 0–2 | 6.22 | 6.07 | 6.11 | 52.11 | 1.08 | 250.3 | 0.02 | 0.03 | 11.23 | 40.34 | 3.00 | 2.34 | 0.11 | 45.79 | 45.82 | 80.31 |
| | Ofh | 2–4 | 8.11 | 8.02 | 15.91 | 27.20 | 0.81 | 141.7 | 0 | 0 | 2.10 | 51.90 | 4.11 | 1.34 | 0.09 | 57.44 | 57.44 | 96.47 |
| | AEes | 4–7 | 7.67 | 7.31 | 4.26 | 1.45 | 0.06 | 21.8 | 0 | 0 | 0.41 | 21.87 | 1.32 | 0.66 | 0.03 | 23.88 | 23.88 | 98.31 |
| | Ees | 7–17 | 6.55 | 6.42 | 1.10 | 0.20 | 0.04 | 18.5 | 0.04 | 0.06 | 0.83 | 9.78 | 0.45 | 0.07 | 0.02 | 10.32 | 10.38 | 92.56 |
| | Bhfe | 17–57 | 5.72 | 5.56 | 0.55 | 0.11 | 0.03 | 28.8 | 0.04 | 0.07 | 1.97 | 2.11 | 0.10 | 0.05 | 0.00 | 2.26 | 2.33 | 53.43 |
| | C | 57–100 | 4.51 | 4.48 | 0.0 | 0.05 | 0.01 | 30.2 | 0.21 | 0.27 | 2.76 | 0.78 | 0.08 | 0.05 | 0.00 | 0.91 | 1.18 | 24.80 |
| 3 | Ol | 0–2 | 6.11 | 6.10 | 2.35 | 48.34 | 0.96 | 270.3 | 0 | 0 | 16.10 | 38.12 | 4.11 | 2.23 | 0.15 | 44.61 | 44.61 | 73.48 |
| | Ofh | 2–4 | 8.24 | 8.11 | 7.15 | 29.32 | 0.85 | 136.2 | 0 | 0 | 2.15 | 86.23 | 4.98 | 1.53 | 0.17 | 92.91 | 92.91 | 97.74 |
| | AEes | 4–15 | 7.66 | 7.54 | 2.23 | 1.11 | 0.09 | 26.5 | 0 | 0 | 1.23 | 12.05 | 0.72 | 0.25 | 0.05 | 13.07 | 13.07 | 91.40 |
| | BvBfe | 15–28 | 5.71 | 5.63 | 1.30 | 0.78 | 0.09 | 7.3 | 0.07 | 0.12 | 2.45 | 6.54 | 0.09 | 0.07 | 0.02 | 6.72 | 6.84 | 73.28 |
| | Bv | 28–59 | 5.69 | 5.59 | 0.41 | 0.28 | 0.05 | 17.2 | 0.25 | 0.33 | 2.87 | 2.12 | 0.08 | 0.03 | 0.02 | 2.25 | 2.58 | 43.95 |
| | C | 59–110 | 4.78 | 4.62 | 0.00 | 0.06 | 0.02 | 24.2 | 0.49 | 0.59 | 3.12 | 0.31 | 0.04 | 0.03 | 0.01 | 0.39 | 0.98 | 11.11 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | Ol | 0–2 | 6.87 | 6.33 | 7.59 | 43.97 | 1.31 | 255.6 | 0.03 | 0.05 | 14.72 | 91.20 | 6.52 | 2.09 | 0.16 | 99.97 | 100.02 | 87.17 |
| | Ofh | 2–8 | 8.32 | 8.12 | 18.93 | 31.81 | 1.06 | 128.0 | 0 | 0 | 5.39 | 45.91 | 3.52 | 1.56 | 0.14 | 51.13 | 51.13 | 90.46 |
| | AEes | 8–12 | 8.22 | 8.00 | 7.11 | 0.49 | 0.04 | 25.7 | 0 | 0 | 0.33 | 7.98 | 0.27 | 0.23 | 0.06 | 8.54 | 8.54 | 96.28 |
| | Bv | 12–65 | 5.49 | 5.21 | 1.11 | 0.21 | 0.02 | 19.2 | 0.13 | 0.15 | 1.78 | 1.71 | 0.09 | 0.06 | 0.03 | 1.89 | 2.04 | 51.50 |
| | C | 65–100 | 4.21 | 4.10 | 0.21 | 0.14 | 0.01 | 21.1 | 0.61 | 0.65 | 1.99 | 0.51 | 0.05 | 0.03 | 0.01 | 0.6 | 1.25 | 23.17 |
| 5 | Ol | 0–2 | 6.10 | 6.05 | 6.43 | 49.23 | 0.92 | 220.3 | 0.05 | 0.08 | 17.71 | 37.00 | 3.98 | 2.00 | 0.16 | 43.14 | 43.22 | 70.90 |
| | Ofh | 2–4 | 7.99 | 7.78 | 7.15 | 21.13 | 0.75 | 111.0 | 0 | 0 | 2.98 | 84.50 | 3.17 | 1.43 | 0.21 | 89.31 | 89.31 | 96.77 |
| | AEes | 4–19 | 7.51 | 7.20 | 5.10 | 1.07 | 0.09 | 27.8 | 0 | 0 | 1.12 | 25.97 | 1.23 | 0.77 | 0.09 | 28.06 | 28.06 | 96.16 |
| | Bv | 19–60 | 5.55 | 5.13 | 0.22 | 0.40 | 0.08 | 21.3 | 0.12 | 0.19 | 2.45 | 2.75 | 0.24 | 0.07 | 0.02 | 3.08 | 3.27 | 55.70 |
| | C | 60–130 | 4.55 | 4.35 | 0.0 | 0.07 | 0.02 | 30.2 | 0.51 | 0.71 | 2.99 | 0.65 | 0.06 | 0.03 | 0.00 | 0.74 | 1.45 | 19.84 |
| 6 | Ol | 0–2 | 5.92 | 5.80 | 3.17 | 51.13 | 1.09 | 230.8 | 0.05 | 0 | 15.78 | 42.18 | 3.12 | 2.79 | 0.14 | 48.23 | 48.23 | 75.35 |
| | Ofh | 2–5 | 8.11 | 7.90 | 17.12 | 29.21 | 0.98 | 143.4 | 0 | 0 | 2.79 | 85.18 | 3.00 | 1.24 | 0.18 | 89.6 | 89.6 | 96.98 |
| | AEes | 5–12 | 8.00 | 7.85 | 6.41 | 0.95 | 0.11 | 29.6 | 0 | 0 | 0.37 | 27.18 | 1.10 | 0.21 | 0.03 | 28.52 | 28.52 | 98.72 |
| | Ees | 12–20 | 6.21 | 6.09 | 1.02 | 0.32 | 0.04 | 8.12 | 0.17 | 0.2 | 2.10 | 1.79 | 0.23 | 0.09 | 0.02 | 2.13 | 2.33 | 50.35 |
| | Bhfe | 20–60 | 5.11 | 5.08 | 0.0 | 0.09 | 0.02 | 19.9 | 0.19 | 0.41 | 2.45 | 1.98 | 0.13 | 0.05 | 0.02 | 2.18 | 2.59 | 47.08 |
| | C | 60–120 | 5.00 | 4.97 | 0.0 | 0.01 | 0.01 | 21.9 | 0.68 | 0.73 | 2.15 | 0.71 | 0.08 | 0.03 | 0.00 | 0.82 | 1.55 | 27.61 |
| 7 | Ol | 0–2 | 5.90 | 5.75 | 2.12 | 53.31 | 1.21 | 240.1 | 0 | 0 | 12.12 | 42.11 | 3.53 | 2.99 | 0.19 | 48.82 | 48.82 | 80.11 |
| | Ofh | 2–4 | 8.41 | 8.21 | 19.18 | 29.12 | 1.01 | 132.7 | 0 | 0 | 1.98 | 45.91 | 3.54 | 1.54 | 0.09 | 51.08 | 51.08 | 96.27 |
| | AEes | 4–10 | 8.12 | 8.00 | 4.11 | 2.41 | 0.14 | 31.1 | 0 | 0 | 0.41 | 30.19 | 1.09 | 0.98 | 0.11 | 32.37 | 32.37 | 98.75 |
| | Ees | 10–21 | 7.52 | 7.08 | 1.12 | 0.90 | 0.06 | 10.3 | 0 | 0 | 0.52 | 3.67 | 0.98 | 0.11 | 0.02 | 4.78 | 4.78 | 90.19 |
| | Bhfe | 21–58 | 5.90 | 5.64 | 0.40 | 0.32 | 0.03 | 23.4 | 0.21 | 0.24 | 2.13 | 1.89 | 0.12 | 0.07 | 0.01 | 2.09 | 2.33 | 49.53 |
| | C | 58–110 | 5.61 | 5.21 | 0.0 | 0.03 | 0.01 | 34.0 | 0.19 | 0.21 | 2.31 | 0.58 | 0.004 | 0.03 | 0.01 | 0.624 | 0.834 | 21.27 |
| "0" control area Holendry | Ol | 0–3 | 3.55 | 2.92 | 0 | 43.55 | 1.67 | 72.3 | 6.12 | 3.11 | 124.2 | 9.91 | 1.31 | 0.94 | 0.12 | 12.28 | 21.51 | 9.00 |
| | Ofh | 3–6 | 3.42 | 2.65 | 0 | 30.11 | 1.23 | 53.7 | 10.40 | 2.45 | 130.6 | 4.56 | 0.77 | 0.55 | 0.11 | 5.99 | 18.84 | 4.39 |
| | AEes | 6–15 | 3.40 | 3.00 | 0 | 4.11 | 0.32 | 21.1 | 6.08 | 1.09 | 26.7 | 0.51 | 0.11 | 0.19 | 0.07 | 0.88 | 8.05 | 3.19 |
| | Ees | 15–29 | 3.61 | 3.21 | 0 | 1.98 | 0.15 | 9.89 | 4.62 | 0.98 | 29.1 | 0.18 | 0.06 | 0.04 | 0.03 | 0.31 | 5.91 | 1.05 |
| | Bhfe | 29–70 | 4.41 | 4.09 | 0 | 0.96 | 0.05 | 20.1 | 3.87 | 0.90 | 9.1 | 0.21 | 0.05 | 0.03 | 0.02 | 0.31 | 5.08 | 3.29 |
| | C | 70–120 | 4.43 | 4.11 | 0 | 0.02 | 0.02 | 20.0 | 2.00 | 0.77 | 6.5 | 0.15 | 0.07 | 0.02 | 0.01 | 0.25 | 3.0 2 | 3.70 |

Table 2. Trophic index and trace elements contents in genetic horizons of investigated soils

| Profile No | Horizons | Depth cm | Index ITGL | Cr | Cu | Mn | Pb | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | | | | mg/kg d.w. of soil | | | | | |
| 1 | Ol | 0–2 | 40.1 | 10 | 12 | 620 | 87 | 16 | 134 |
| | Ofh | 2–5 | | 28 | 21 | 811 | 107 | 74 | 189 |
| | AEes | 5–14 | | 20 | 17 | 431 | 89 | 55 | 67 |
| | Bv | 14–65 | | 7 | 10 | 351 | 55 | 12 | 34 |
| | C | 65–120 | | 3 | 5 | 54 | 9 | 6 | 11 |
| 2 | Ol | 0–2 | 38.2 | 11 | 9 | 432 | 44 | 20 | 121 |
| | Ofh | 2–4 | | 19 | 14 | 947 | 62 | 55 | 181 |
| | AEes | 4–7 | | 2 | 2 | 195 | 10 | 3 | 9 |
| | Ees | 7–17 | | 3 | 3 | 90 | 13 | 3 | 11 |
| | Bhfe | 17–57 | | 2 | 2 | 195 | 10 | 6 | 18 |
| | C | 57–100 | | 3 | 2 | 67 | 4 | 2 | 10 |
| 3 | Ol | 0–2 | 30.0 | 15 | 8 | 556 | 51 | 15 | 100 |
| | Ofh | 2–4 | | 25 | 16 | 1196 | 91 | 65 | 239 |
| | AEes | 4–15 | | 19 | 14 | 440 | 29 | 17 | 48 |
| | BvBfe | 15–28 | | 6 | 4 | 334 | 7 | 6 | 9 |
| | Bv | 28–59 | | 5 | 3 | 95 | 3 | 5 | 10 |
| | C | 59–110 | | 2 | 1 | 64 | 2 | 3 | 12 |
| 4 | Ol | 0–2 | 29.1 | 13 | 11 | 621 | 85 | 17 | 131 |
| | Ofh | 2–8 | | 28 | 20 | 810 | 112 | 73 | 181 |
| | AEes | 8–12 | | 20 | 17 | 421 | 78 | 59 | 62 |
| | Bv | 12–65 | | 7 | 12 | 350 | 52 | 14 | 36 |
| | C | 65–100 | | 3 | 4 | 52 | 11 | 6 | 10 |
| 5 | Ol | 0–2 | 30.2 | 10 | 13 | 779 | 39 | 26 | 134 |
| | Ofh | 2–4 | | 22 | 21 | 1037 | 77 | 61 | 192 |
| | AEes | 4–19 | | 5 | 3 | 389 | 12 | 6 | 19 |
| | Bv | 19–60 | | 7 | 4 | 108 | 17 | 4 | 17 |
| | C | 60–130 | | 4 | 3 | 77 | 6 | 2 | 13 |
| 6 | Ol | 0–2 | 31.4 | 12 | 10 | 490 | 47 | 26 | 119 |
| | Ofh | 2–5 | | 18 | 15 | 943 | 65 | 57 | 192 |
| | AEes | 5–12 | | 3 | 4 | 192 | 14 | 4 | 11 |
| | Ees | 12–20 | | 3 | 3 | 93 | 14 | 4 | 12 |
| | Bhfe | 20–60 | | 2 | 3 | 185 | 11 | 7 | 20 |
| | C | 60–120 | | 3 | 2 | 64 | 3 | 3 | 11 |
| 7 | Ol | 0–2 | 30.5 | 13 | 12 | 439 | 67 | 31 | 142 |
| | Ofh | 2–4 | | 18 | 15 | 1003 | 109 | 59 | 199 |
| | AEes | 4–10 | | 4 | 5 | 267 | 67 | 8 | 51 |
| | Ees | 10–21 | | 3 | 4 | 98 | 44 | 7 | 22 |
| | Bhfe | 21–58 | | 3 | 4 | 185 | 21 | 9 | 21 |
| | C | 58–110 | | 3 | 2 | 64 | 6 | 3 | 14 |
| “0“ | Ol | 0–3 | 22.1 | 8 | 10 | 97 | 29 | 23 | 31 |
| control | Ofh | 3–6 | | 6 | 8 | 220 | 22 | 12 | 27 |
| area | AEes | 6–15 | | 5 | 4 | 68 | 14 | 7 | 10 |
| Holendry | Ees | 15–29 | | 3 | 5 | 60 | 2 | 8 | 8 |
| | Bhfe | 29–70 | | 3 | 3 | 62 | 3 | 3 | 4 |
| | C | 70–120 | | 3 | 2 | 68 | 2 | 3 | 4 |

potential saturation degree of the complex $V_{pot} = S/PWK_{8.2}*100\%$, where $PWK_{8.2} = S + Hh$ [2];
- heavy metals Cd, Cu, Cr, Mn, Pb, Sr, Zn with samples being burned in the electrical oven at the temperature of 480°C and dissolved in HCl-$HNO_3$ at the ratio of 3:1, by ICP-AES method with the application of Jobin-Yvon spectrometer, JY 70 PLUS.

For the soils analyzed the trophic index ITGL was calculated in compliance with Brożek's methodology [4, 5] on the basis of the weighing sum of indicators ($I_{suma}$) of the content of dust fraction ($I_{dust}$), floating parts ($I_{flot}$), reaction ($I_{pH}$), the exchangeable cations ($I_{cations}$) calculated per capacity unit, degree of organic matter decomposition ($I_{C:N}$), related to the mineral horizons of the tested soil.

The taxonomy of soil and humus was carried out on the basis of Forest Soil Classification [12].

## RESULTS AND DISCUSSION

The scope of research is within the physical geographical unit of Przedgórze Iłżeckie, in the eastern part of the "Ożarów" Cement Plant. Soil cover of the area is slightly varied since the input material for the soil is young of quaternary formations namely Eolithic sand with local dune formation [21]. The soils under discussion are forested with pine trees 20–60 years old [18] to a different degree of degradation.

The "Ożarów" Cement Plant produces pure Portland cement with the additive of fly ash. In the technological process there are dusts and gases manufactured (also as a result of fuel burning), which are transferred to the environment despite better and better protection. The primary emission is reinforced with the secondary emission generated by road traffic (cement forwarding) and that generated during product handling and packaging. The chemical composition of dust emitted by the "Ożarów" Cement Plant is close to the composition of dust generated in other cement plants located in the Świętokrzyski voivodship [18]. The dust fall in the tested area contains mainly: CaO 46.64%, $SiO_2$ 8.17%, $Al_2O_3$ 2.64%, $Fe_2O_3$ 1.21%, $K_2O$ 1.13%, MgO 0.83%, $Na_2O$ 0.14%, MnO 0.01% [19] and they strongly modify the soil properties.

All tested soils are classified as albic arenosols (profiles 1, 3, 4, 5) and haplic podzol soils (profiles 2, 6, 7) with the granulation composition of sand from loose to weakly argillaceous [12]. Soil humus (Ol-Ofh-AEes-) had a character of calci-drosomoder on the alkalization area or moder on the control area.

The tested soils showed various values of pH. Organic and mineral organic horizons showed the reaction with the range from 5.75 to 8.21 $pH_{KCl}$; whereas the reaction of mineral horizons below 7–10 cm was in the range from 4.10 to 6.42 $pH_{KCl}$ (Tab. 1). The designated values of pH are considerably higher than those stated for oligotrophic podzol soils [2, 3, 5, 8, 16], (Tab. 1). Such a high value of pH was conditioned by cement and lime dust emission containing over 46% CaO. The next consequence of the alkali increase in soil is the content of $CaCO_3$ stated in the soils tested to the depth of 100 cm. The highest numbers of carbonates from 7.15 to 19.18% contain the Ofh horizon, then the forest bed horizon from 2.12 to 7.59%. It is an unbeneficial phenomenon influencing forest plants, thus eliminating the plants from the *Vaccinio-Piccetea* group [19].

The content of carbonates in the tested soils is positively correlated with $pH_{KCl}$, the total content of oxygen, ions of lime and magnesium substitution and the content of heavy metals (Tab. 3).

Acidity substitution is shown by only a small number of tested mineral horizons (Tab. 1), below 50–60 cm. Hydrolytic acidity is also considerably low in comparison to the values stated for albic arenosols and haplic podzol soils [8, 9], (Tab. 1, Fig. 1). It ranges from 0.32 to 17.71 cmol(+)/kg, however, the highest values are typical of raw material horizon. Hydrolytic acidity considerably lowers together with the depth up to 50–60 cm, and then slightly increases to the parent rock horizon. Statistical analysis showed that acidity substitution was considerably correlated with $pH_{KCl}$, and the content of ion substitution with the designated heavy metals (Tab. 3).

Calcium dominates the exchangeable cations in the forested soil complex. The content of $Ca^{2+}$ ranges from 37.0 to 91.2 cmol(+)/kg in organic horizons and drops to 31–0.78 cmol(+)/kg at the C horizon. The content of cations is higher in the sorption complex of the tested albic arenosols in relation to its content in the haplic podzol soils (Fig. 1).

The content of $Mg^{2+}$ is considerable and of the following range 3.00–8.13 cmol(+)/kg (in Ol, Ofh horizons). The total sum of substituted cations is higher at the surface horizons and ranges from 8.54 to 99.97 cmol(+)/kg. In the C horizon it is considerably lower and in the range of 0.39–0.82 cmol(+)/kg.

Naturally the soil salinity is rare in Poland; usually in the agricultural areas it does not exceed 50 mg KCl/100 g [17]. Excessive salinity caused by alkalization can be a measurement of anthropogenic degradation of soils. In such conditions there is a disturbance of the ion balance and excessive concentration of soil solution, which consequently decreases water availability as well as substance availability for plants. This process is especially visible in the dry soil. Due to its properties lime and cement dusts are collected on the surface and they increase a shortage of water in soil in summer months [18].

High salinity in the tested surface horizons (from 111.0 to 270.3 mg KCl/100 g) causes that a considerable part of the designated cations is not absorbed in the ion substitution manner by a sorptive complex. In such a case the substituted ions appear in soil outside the sorptive complex in form of salts easily dissolved and they do not determine the size of the sorptive complex. Therefore, the sorptive complex features the capacity of real substituted ions PWKr [2]. In the acid samples PWKr is considerably lower than an exchangeable capacity of the potential ions PWKpot., whereas in the base samples those two values are close. The tested soils show high exchangeable capacity of PWKr in the limit from 48.82 to 100.02 cmol(+)/kg (in organic horizons) and from 0.83 to 1.40 cmol(+)/kg in the C horizons.

The conducted statistical analysis showed the essential correlation between the salinity of the soils and the content of Nog, Corg., exchangeable cations in the sorptive complex and the size of hydrolytic acidity (Tab. 3).

The content of organic carbon Corg. is at the level of Ol – 49.3%, in the Ofh horizon – 26.6%, in the AEes horizon – 1.5%. With the content of carbon there is a corresponding content of Ntot ranging from 1.31 to 0.04% (Tab. 1). The statistical analysis shows the intensified correlation between nitrogen and organic carbon with the content of exchangeable cations in the sorptive complex and the size of hydrolytic acidity.

The content of heavy metals in the soils reflects the status of the environment [1, 6, 7, 10, 11]. Usually the content of metals in the horizons is determined by: geochemical background (natural content of rock), soil formation processes, and anthropogenic deposits [6]. Sandy soils with low sorptive capacity and acid reaction in the natural environment absorb trace elements in a weak manner. Therefore, heavy metals occurring even in low

Table 3. Correlation coefficient (r) between some chemical properties of investigated soils and trace elements contents, p = 0.01

| Variables | $CaCO_3$ | N total | Soil salinity | Hw | Hh | $Ca^{+2}$ | $Mg^{+}$ | $K^{+}$ | $Na^{+}$ | Cr | Cu | Mn | Pb | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $pH_{KCl}$ | 0.7460 | | | -0.7574 | | 0.6314 | 0.5165 | | 0.5526 | 0.6763 | 0.6348 | 0.6796 | 0.6629 | 0.6991 | 0.6019 |
| $CaCO_3$ | 1.0000 | 0.6423 | | | | 0.7391 | 0.7190 | | 0.6359 | 0.7617 | 0.7300 | 0.7970 | 0.7507 | 0.8284 | 0.7997 |
| Corg. | | 0.9610 | 0.9848 | | 0.8496 | 0.6892 | 0.7809 | 0.9692 | 0.8072 | 0.5135 | 0.5194 | 0.6534 | 0.5729 | | 0.7663 |
| Nog. | | 1.0000 | 0.9500 | | 0.7143 | 0.8201 | 0.8728 | 0.9464 | 0.8698 | 0.6415 | 0.6353 | 0.7705 | 0.7041 | 0.5842 | 0.8750 |
| Soil salinity | | | 1.0000 | | 0.8546 | 0.6992 | 0.8072 | 0.9557 | 0.8048 | | | 0.6221 | 0.5613 | | 0.7376 |
| Hw | | | | 1.0000 | | -0.5432 | -0.5058 | -0.5103 | -0.5900 | -0.5213 | -0.5220 | -0.5767 | -0.5859 | | -0.5137 |
| Hh | | | | | 1.0000 | | 0.5127 | 0.7825 | 0.5319 | | | | | | |
| $Ca^{+2}$ | | | | | | 1.0000 | 0.9053 | 0.7262 | 0.9012 | 0.7458 | 0.7205 | 0.8673 | 0.7394 | 0.7234 | 0.8945 |
| $Mg^{+2}$ | | | | | | | 1.0000 | 0.7965 | 0.8681 | 0.7204 | 0.6779 | 0.7918 | 0.7364 | 0.6598 | 0.8584 |
| $K^{+}$ | | | | | | | | 1.0000 | 0.8612 | 0.5299 | 0.5366 | 0.6614 | 0.6209 | | 0.7685 |
| $Na^{+}$ | | | | | | | | | 1.0000 | 0.7551 | 0.7721 | 0.8291 | 0.7823 | 0.7047 | 0.8780 |

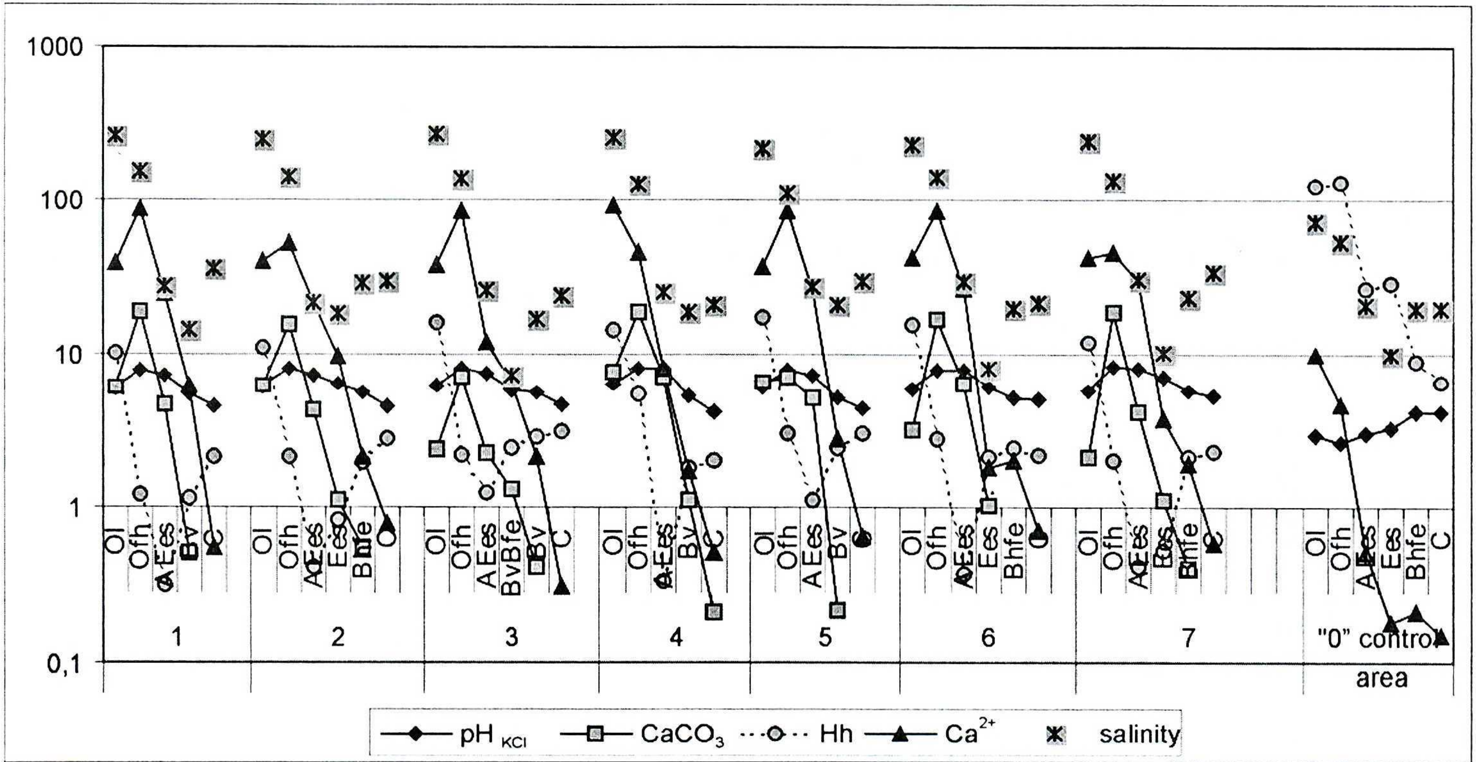


Fig. 1. Some chemical properties of anthropogenically transformed soils: $pH_{KCl}$, $CaCO_3$ (%), Hh, $Ca^{2+}$, (cmol(+)/kg), (cmol(+)/kg), salinity (KCl/100 g) in the relation to soil control area ("0")

concentrations can have a toxic influence on plants. Higher concentrations of heavy metals are conditioned by an increase in silty fractions, higher sorptive properties, increase in organic matter and basic reaction [10, 11].

Dusts occurring in technological processes of lime and cement industry do not contain the excessive amount of heavy metals in their content. They influence considerably the decrease in soil acidity and increase in sorptive capacity, which contributes to the accumulation of some metals in the tested soils (Tab. 2).

The content of chromium ranges from 3 to 28 mg/kg and it does not exceed the typical values for podzol soils [7, 10, 11] and permitted values of this element [14].

The statistical analysis showed highly essential correlation between Cr and the selected features of the tested soils (Tab. 3), with the power of correlation decrease in the following order: $CaCO_3 > Na^+ > Ca^{2+} > Mg^{2+} > pH_{KCl}$ > Nog > Corg. The content of copper is within the range of 1–21 mg/kg. These are typical values for podzol soils. The statistical analysis showed highly essential correlation between Cu and the selected features of the tested soils (Tab. 3), with the power of correlation decrease in the following order: $Na^+ > CaCO_3 > Ca^{2+} > Mg^{2+}$ > Nog > $pH_{KCl}$ > Corg.

The amount of manganese in the analyzed soil horizons ranges from 52 to 1196 mg/kg, whereas the highest concentrations were stated on the surface horizons. The designated values are higher (in the Ol and Ofh horizons twice) than those stated for podzol soils formed from sand. The statistical analysis showed highly essential correlation between Mn and the selected features of the tested soil (Tab. 3), with the power of correlation decrease in the following order: $Ca^{2+} > Na^+ > CaCO_3 > Mg^{2+} > K^+$ > Nog > $pH_{KCl}$ > Corg. > salinity.

The content of lead in the tested soil ranges from 6 mg/kg in the matter rock horizon to 112 mg/kg in the Ofh horizon. In all tested surface horizons and in some horizons of AEes (in the profiles 1, 4, 7) the concentration of leas exceeds the permitted value at the level of 50 mg/kg [14] and is a result of anthropogenic pollution. The statistical analysis showed highly essential correlation between Pb and the selected features of the tested soil (Tab. 3), with the power of correlation decrease in the following order: $Na^+ > CaCO_3 > Ca^{2+} > Mg^{2+}$ > Nog > $pH_{KCl} > K^+$ > Corg. > salinity.

The amount of strontium in the tested soil ranges from 6 to 74 mg/kg (Tab. 2). The permitted content of this element in the sandy soil is assumed to be 30 mg/kg [14] which would show a slight increase of this element in the tested Ofh and Aees horizons. In podzol soils in Poland the content of Sr ranges from 10 to 80 mg/kg [6, 7]. The statistical analysis showed highly essential correlation between Sr and the selected features of the tested soil (Tab. 3), with the power of correlation decrease in the following order: $CaCO_3 > Ca^{2+} > Na^+ > pH_{KCl} > Mg^{2+}$ > Nog.

The content of zinc is in the range from 9 to 199 mg/kg. The values are considerably higher from those stated as natural for the sandy soils [10, 11] and they exceed the values of permitted concentration of Zn in the soil [14]. The statistical analysis showed highly essential correlation between Zn and the selected features of the tested soil (Tab. 3), with the power of correlation decrease in the following order: $Ca^{2+} > Na^+$ > Nog > $CaCO_3$ > Corg > K > $pH_{KCl}$.

The largest amount of heavy metals is stated in the horizons of Ofh, then Ol and AEes all investigated soils, which confirms the results obtained by other authors [1, 7, 10]. The highest content of metallic elements in the surface horizons was a result of the natural biological accumulation and the anthropogenic impact on soil. This phenomenon is well visible in comparison to the properties of soil "O" on the Holendry area.

The calculated trophic indexes for the analyzed soil horizons ITGL (Tab. 3) range from 30.0 to 40.1 which would show unnatural trophic height [5]. They are much higher in comparison to the ITGL index soil situated out of reach of the emitter dust.

## CONCLUSION

The chemical properties of haplic podzol soils and albic arenosol formed in the sandy formation were strongly modified by a long lasting emission of alkali dust. It has been found:

1. pH value change of soil to 8.3 units in the organic horizons.
2. The high level of $CaCO_3$ (up to 19% in the Ofh horizon and to 1.2% in the Bv horizon).
3. The visible decrease of hydrolytic acidity of aluminium and substituted hydrogen.
4. Increase in saturation of the sorptive complex with ions $Ca^{2+}$ and $Mg^{2+}$ and 80–90% (organic horizons) and in 20–40% (mineral horizons).
5. Increase of salinity in organic horizons to 270 mg KCl/100 g.
6. Considerable increase in trophic settlements with high indexes ITGL.
7. Enrichment of surface horizons in heavy metals especially in the case of manganese, lead and zinc.

## REFERENCES

[1] Angelone M., C. Bini: *Trace Element Concentrations in Soils and Plants of Western Europe*, [in:] Biogeochemistry of Trace Metals, D.C. Adriano (ed.), Lewis Publishers, London, Tokyo 1992, 19–61.

[2] Bednarek R., H. Dziadowiec, U. Pokojska, Z. Prusinkiewicz: *Badania ekologiczno-gleboznawcze*, PWN, Warszawa 2004.

[3] Borowiec S., Z. Zabłocki: *Wpływ niektórych pyłów przemysłowych na właściwości chemiczne gleb leśnych*, Rocz. Glebozn., **24**(3),3–19 (1983).

[4] Brożek S.: *Indeks trofizmu gleb leśnych*, Acta Agr. et Silv. Ser. Silv., 39, 15–33 (2001).

[5] Brożek S., M. Zwydak: *Atlas gleb leśnych Polski*, Centrum Informacyjne Lasów Państwowych, Warszawa 2002.

[6] Czarnowska K: *Ogólna zawartość metali ciężkich w skałach macierzystych jako tło geochemiczne gleb*, Rocz. Glebozn., **47**, supl. 43–50, (1996).

[7] Czępińska-Kamińska D., E. Janowska: *Metale ciężkie w wybranych krajobrazach geochemicznych Kampinoskiego Parku Narodowego jako wskaźnik antropogenizacji środowiska*, Zesz. Prob. Post. Nauk Rol., 471, 895–902 (2000).

[8] Degórski M: *Przestrzenna zmienność właściwości gleb bielicoziemnych środkowej i Północnej Europy a geograficzne zróżnicowanie czynników pedogenicznych*, PAN, Instytut GIPZ, Prace geogr., 182, 1–189 (2002).

[9] Janowska E: *Geneza i właściwości gleb rdzawych na obszarze zlodowacenia środkowopolskiego*, Fundacja Rozwój SGGW, 2001, 75 ss.

[10] Kabata-Pendias A., T. Motowicka-Terelak, H. Piotrowska, T. Witek: *Ocena stopnia zanieczyszczenia gleb i roślin metalami ciężkimi i siarką*, Ramowe wytyczne dla rolnictwa, IUNG, Puławy, 1–20, 1993.

[11] Kabata-Pendias A., H. Pendias: *Biogeochemia pierwiastków śladowych*, PWN, Warszawa 1999.

[12] *Klasyfikacja gleb leśnych Polski*, Centrum Informacyjne Lasów Państwowych, 2000.

[13] Ostrowska A., S. Gawliński, Z. Szczubiałka: *Metody analizy chemicznej i oceny właściwości gleb i roślin*, Instytut Ochrony Środowiska, Warszawa 1991.

[14] *Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi z dnia 21.03.2002r. w sprawie dopuszczalnych stężeń metali ciężkich zanieczyszczających glebę*, Dz. U. 2002, nr 37, poz. 344, 2683–2684.

[15] *Stan środowiska w województwie świętokrzyskim w roku 2000*, Raport 2001, IOŚ, WIOŚ, Biblioteka

Monitoringu Środowiska, Kielce 2001.
[16] Prusinkiewicz Z., R. Bednarek, U. Pokojska: *Gleby bielicoziemne w Polsce*, Przegl. Geogr., **52**(1),103-113 (1980).
[17] Siuta J: *Gleba diagnozowanie stanu i zagrożenia*, IOŚ, Warszawa 1995.
[18] Świercz A: *Wpływ emisji alkalicznej na gleby i zbiorowiska roślinne borów sosnowych w „Białym Zagłębiu"*, cz. I, PAN Oddział w Krakowie, KTN, Kielce 1997, 205 ss.
[19] Świercz A: *Chemical Properties of Soil in the Region of Ożarów Cement Plant (Administrative district: Świętokrzyski, Poland)*, [in:] J. Sobocka, P. Jambor (eds.), Podoznalecke Dni v SR, Stara Lesna, Soc. Pedologica Slovaca, Bratislava 2003, 405–409.
[20] Walaszek J., A. Radomski: *System ciągłego monitorowania stanu powietrza jako element zarządzania środowiskiem w Cementowni „Ożarów" S.A.*, Biblioteka Monitoringu Środowiska, Kielce 2001, 151-161.
[21] Złonkiewicz Z.: *Szczegółowa Mapa Geologiczna Polski 1:50 000. Arkusz Ożarów*, Państwowy Instytut Geologiczny Oddział Świętokrzyski, 1997.

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