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# Selected properties of cobalt-contaminated soil following the application of neutralising substances

## Wybrane właściwości gleby zanieczyszczonej kobaltem po zastosowaniu substancji neutralizujących

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**Keywords:** cobalt, contamination, soil properties, neutralising substances
**Słowa kluczowe: kobalt, zanieczyszczenie,właściwości gleby, substancje neutralizujące**

**Abstract**
The aim of the study was to determine the influence of increasing cobalt soil contamination (0 mg·kg$^{-1}$, 20 mg·kg$^{-1}$, 40 mg·kg$^{-1}$, 80 mg·kg$^{-1}$, 160 mg·kg$^{-1}$, 320 mg·kg$^{-1}$) after the application of neutralising substances on selected soil properties. In the soil without an addition of neutralising substances, the highest doses of cobalt caused the pH, total exchangeable bases, cation exchange capacity and the degree of base saturation to decrease and the hydrolytic acidity of soil to increase. Among the substances used, zeolite and calcium oxide (particularly) had the most advantageous influence on the analysed soil properties. They caused the pH, total exchangeable bases and cation exchange capacity to increase and the hydrolytic acidity to decrease. Among the other substances, it was charcoal that had the greatest influence on the soil properties, but the way it influenced the total exchangeable bases, the cation exchange capacity of soil and the degree of base saturation were opposite to the way calcium oxide influenced these properties.



**Streszczenie**
Celem badań było określenie działania wzrastającego zanieczyszczenia gleby kobaltem (0, 20, 40, 80, 160, 320 mg·kg$^{-1}$) po zastosowaniu substancji neutralizujących na wybrane właściwości gleby. W glebie bez dodatku substancji neutralizujących najwyższe dawki kobaltu spowodowały zmniejszenie odczynu, sumy zasad wymiennych, całkowitej pojemności sorpcyjnej i stopnia wysycenia kompleksu sorpcyjnego gleb kationami o charakterze zasadowym oraz zwiększenie kwasowości hydrolitycznej gleby. Spośród zastosowanych substancji zeolit i zwłaszcza tlenek wapnia miały najbardziej korzystny wpływ na analizowane właściwości gleby. Spowodowały one wzrost odczynu, sumy zasad wymiennych, całkowitej pojemności sorpcyjnej i zmniejszenie kwasowości hydrolitycznej. Z pozostałych substancji największy wpływ na właściwości gleby miał węgiel drzewny, ale kierunek jego oddziaływania na sumę zasad wymiennych, całkowitą pojemność sorpcyjną gleby i stopień wysycenia kompleksu sorpcyjnego gleby kationami o charakterze zasadowym był przeciwny niż tlenku wapnia.

## 1. INTRODUCTION

Cobalt is one of the many trace metals occurring in the environment. Its sources naturally present in the Earth's crust include sulphide minerals, arsenide minerals and oxide minerals (of iron, nickel and copper) [Faucon *et al.* 2007]. Due to an increase in mining cobalt ore, inappropriate fertiliser use, waste water discharge and coal and motor fuel combustion processes, the amount of naturally occurring cobalt in the environment has increased [Saaltink *et al.* 2014]. The main forms of cobalt in soil are $Co^{2+}$ and $Co^{+3}$, although it can also occur in the form of $CoOH^{+}$, $Co(OH)^{-}_{3}$ and $Co(OH)_{2}^{0}$. The organic matter content in soil has a significant influence on the soil cobalt content, as the content of this element is greatest in loam soils and alluvial soils [Faucon *et al.* 2007]. Most often, the total cobalt content in normal soils ranges from 1 mg·kg$^{-1}$ to 40 mg·kg$^{-1}$, and less often from 1 mg·kg$^{-1}$ to 100 mg·kg$^{-1}$ [Chatterjee and Chatterjee 2002]. The greatest natural cobalt content in soil may reach 500 mg·kg$^{-1}$ of soil [Tappero *et al.* 2007]. However, the exceeding of the acceptable cobalt content in soil, water and air may pose a potential threat to plants, animals and also humans. It can also cause many potentially deadly illnesses [Taghipour *et al.* 2011, Wendling *et al.* 2009]. Trace metals, including cobalt, play a vital role in the lives of all living organisms [Wyszkowska and Wyszkowski 2002, Wyszkowski and Radziemska 2013, Wyszkowski and Wyszkowska 2009]. They are mainly responsible for biochemical processes and for increasing the activity of vitamins and hormones which influence the immune system [Moghaddas *et al.* 2013]. The incorporation of trace metals into the food chain starts from their uptake from the soil by plants with which they enter animal and human organisms [Fitamo *et al.* 2011]. However, the trace metal content in an animal or human organism depends on their availability in soil for plants. This availability is mostly influenced by the trace metal chemical properties and by soil properties [Basta *et al.* 2005, Mico *et al.* 2008, Reedy *et al.* 2011]. Cobalt contamination also causes changes in soil properties.

Table 1. Effect of cobalt on pH, hydrolytic acidity and total exchange bases in soil

| Cobalt dose in mg·kg$^{-1}$ of soil | Kind of substance neutralising the effect of cobalt | | | | | | |
|---|---|---|---|---|---|---|---|
| | Without additions | Manure | Loam | Charcoal | Zeolite | Calcium oxide | Average |
| $pH_{KCl}$ | | | | | | | |
| 0 | 6.19 | 6.14 | 5.97 | 5.94 | 6.58 | 7.46 | – |
| 20 | 5.83 | 6.54 | 5.89 | 5.60 | 6.65 | 7.47 | – |
| 40 | 6.30 | 6.26 | 5.49 | 5.85 | 6.64 | 7.43 | – |
| 80 | 6.22 | 6.35 | 5.85 | 5.68 | 6.76 | 7.54 | – |
| 160 | 5.73 | 6.18 | 5.63 | 5.72 | 6.52 | 7.47 | – |
| 320 | 5.38 | 6.04 | 5.51 | 6.40 | 6.33 | 7.53 | – |
| r | -0.83 | -0.61 | -0.64 | 0.74 | -0.81 | 0.56 | – |
| LSD for | Co dose — 0.05; kind of neutralising substance — 0.05; interaction — 0.12 | | | | | | |
| Hydrolytic acidity [mmol(+)·kg$^{-1}$ of soil] | | | | | | | |
| 0 | 26.78 | 29.77 | 28.98 | 28.82 | 28.98 | 15.28 | 26.43 |
| 20 | 29.93 | 26.46 | 29.61 | 28.35 | 24.41 | 12.44 | 25.20 |
| 40 | 26.62 | 31.50 | 39.06 | 27.09 | 26.93 | 13.86 | 27.51 |
| 80 | 25.52 | 26.93 | 30.56 | 33.23 | 24.10 | 16.85 | 26.20 |
| 160 | 30.87 | 28.04 | 36.07 | 33.86 | 28.35 | 20.48 | 29.61 |
| 320 | 34.97 | 30.08 | 32.76 | 27.72 | 30.08 | 21.58 | 29.53 |
| Average | 29.11 | 28.80 | 32.84 | 29.85 | 27.14 | 16.75 | 27.41 |
| r | 0.84 | 0.17 | 0.21 | 0.05 | 0.56 | 0.89 | 0.81 |
| LSD for | Co dose — 0.65; kind of neutralising substance — 0.65; interaction — 1.60 | | | | | | |
| Total exchangeable bases [mmol(+)·kg$^{-1}$ of soil] | | | | | | | |
| 0 | 84.26 | 63.53 | 63.63 | 84.95 | 56.86 | 110.88 | 77.35 |
| 20 | 66.05 | 73.13 | 62.53 | 62.06 | 55.23 | 119.02 | 73.00 |
| 40 | 66.78 | 66.10 | 58.75 | 54.50 | 51.45 | 106.68 | 67.38 |
| 80 | 68.36 | 64.94 | 57.54 | 30.40 | 78.86 | 104.16 | 67.38 |
| 160 | 52.34 | 60.32 | 56.44 | 15.23 | 62.21 | 89.20 | 55.96 |
| 320 | 48.46 | 58.64 | 54.44 | 14.60 | 30.24 | 119.65 | 54.34 |
| Average | 64.37 | 64.44 | 58.89 | 43.62 | 55.81 | 108.26 | 65.90 |
| r | -0.85 | -0.73 | -0.87 | -0.83 | -0.58 | 0.06 | -0.90 |
| LSD for | Co dose — 1.92; kind of neutralising substance — 1.92; interaction — 4.70 | | | | | | |

Explanations: r — correlation coefficient, LSD — least significant differences

For this reason, studies were conducted to determine the influence of increasing cobalt soil contamination after the application of neutralising substances on selected soil properties.

## 2. MATERIALS AND METHODS

The experiment was carried out in the vegetation hall of the University of Warmia and Mazury in Olsztyn in polyethylene pots which were filled with 9 kg of soil. Before the experiment, the soil had the following properties: pH in a 1 M KCl solution — 4.32; hydrolytic acidity (HA) — 46.50 mmol(+)·kg$^{-1}$; total exchangeable bases (TEBs) — 28.40 mmol(+)·kg$^{-1}$; cation exchange capacity (CEC) — 74.90 mmol(+)·kg$^{-1}$; degree of base saturation (BS) — 37.92%. The soil was contaminated with increasing doses of cobalt: 0 mg·kg$^{-1}$, 20 mg·kg$^{-1}$, 40 mg·kg$^{-1}$, 80 mg·kg$^{-1}$, 160 mg·kg$^{-1}$, 320 mg·kg$^{-1}$. An amount of 2% of manure, loam, charcoal and zeolite were used as neutralising substances based on the weight of the soil and calcium oxide in a dose corresponding to 1 HA. Natural zeolite with medium potassium, calcium and sodium content and very low phosphorus and magnesium content was used in the experiment. In order to secure the plants' nutritional requirements, all pots received the following additions: nitrogen — 100 mg N; phosphorus — 35 mg P; potassium — 100 mg K; magnesium — 50 mg Mg; boron — 0.33 mg B; manganese —

Table 2. Effect of cobalt on cation exchange capacity and base saturation in soil

| Cobalt dose in mg·kg$^{-1}$ of soil | Kind of substance neutralising the effect of cobalt | | | | | | |
|---|---|---|---|---|---|---|---|
| | Without additions | Manure | Loam | Charcoal | Zeolite | Calcium oxide | Average |
| Cation exchange capacity [mmol(+)·kg$^{-1}$ of soil] | | | | | | | |
| 0 | 111.04 | 93.29 | 92.61 | 113.77 | 85.84 | 126.16 | 103.78 |
| 20 | 95.97 | 99.59 | 92.14 | 90.41 | 79.64 | 131.46 | 98.20 |
| 40 | 93.40 | 97.60 | 97.81 | 81.59 | 78.38 | 120.54 | 94.89 |
| 80 | 93.87 | 91.88 | 88.10 | 63.63 | 102.95 | 121.01 | 93.57 |
| 160 | 83.21 | 88.36 | 92.51 | 49.09 | 90.56 | 109.68 | 85.57 |
| 320 | 83.42 | 88.72 | 87.20 | 42.32 | 60.32 | 141.23 | 83.87 |
| Average | 93.49 | 93.24 | 91.73 | 73.47 | 82.95 | 125.01 | 93.31 |
| r | -0.78 | -0.74 | -0.60 | -0.86 | -0.55 | 0.37 | -0.90 |
| LSD for | Co dose — 1.98; kind of neutralising substance — 1.98; interaction — 4.85 | | | | | | |
| Base saturation [%] | | | | | | | |
| 0 | 75.89 | 68.09 | 68.71 | 74.67 | 66.24 | 87.89 | 73.58 |
| 20 | 68.82 | 73.43 | 67.86 | 68.64 | 69.35 | 90.54 | 73.11 |
| 40 | 71.50 | 67.72 | 60.06 | 66.80 | 65.64 | 88.50 | 70.04 |
| 80 | 72.82 | 70.69 | 65.32 | 47.77 | 76.59 | 86.07 | 69.88 |
| 160 | 62.90 | 68.27 | 61.01 | 31.02 | 68.70 | 81.33 | 62.20 |
| 320 | 58.09 | 66.09 | 62.43 | 34.49 | 50.13 | 84.72 | 59.33 |
| Average | 68.34 | 69.05 | 64.23 | 53.90 | 66.11 | 86.51 | 68.02 |
| r | -0.91 | -0.58 | -0.51 | -0.85 | -0.72 | -0.66 | -0.95 |
| LSD for | Co dose — 1.11; kind of neutralising substance — 1.11; interaction — 2.71 | | | | | | |

Explanations: r — correlation coefficient, LSD — least significant differences

5 mg Mn and molybdenum — 5 mg Mo·kg$^{-1}$ of soil. The test plant was oat (*Avena sativa* L.), Polish variety Zuch. Soil samples for laboratory analyses were taken during oat harvest, at the hard dough stage.

Before the determinations were performed, the soil was dried and sieved through a sieve with a 1 mm ×1 mm mesh. The soil pH in a 1 M KCl solution was determined potentiometrically and HA and TEB were determined with Kappen's method [Ostrowska *et al.* 1991]. The CEC was calculated with the formula CEC = TEB + HA, and BS was calculated with the formula BS = (TEB·CEC$^{-1}$) · 100. The results were statistically analysed using a two-way analysis of variance with the Statistica software package (STATSOFT, 2014).

## 3. RESULTS AND DISCUSSION

The study found that both cobalt contamination and the selected neutralising substances had a significant influence on the tested soil properties. In the soil without added neutralising substances, the highest doses of cobalt caused the soil pH to be lowered from 6.19 to 5.38 and the HA to increase from 26.78 mmol(+)·kg$^{-1}$ to 34.97 mmol(+)·kg$^{-1}$ of soil (Table 1). Apart from this, cobalt contamination in the soil caused the TEBs to decrease from 84.26 mmol(+)·kg$^{-1}$ to 48.46 mmol(+)·kg$^{-1}$ of soil and the sorption capacity to decrease from 111.04 mmol(+)·kg$^{-1}$ to 83.42 mmol(+)·kg$^{-1}$ of soil. The BS also decreased from 75.89% to 58.09%. The influence of cobalt in the soil on the decrease in the soil pH was also confirmed by Bakkaus *et al.* [2008], Lange *et al.* [2014], Pathak and Choppin [2009]. The significant influence of cobalt on the decrease of the sorption capacity of soil was also found by Reedy *et al.* [2011] and Taghipour *et al.* [2011]. A decrease of the soil pH can thus have an influence on increased cobalt uptake from the soil by plants [Fitamo *et al.* 2011].

Among the substances used, calcium oxide had the most advantageous influence on the analysed soil properties (Table 2). Compared with the soil without an added neutralising substance, it caused soil pH to increase above the value of 7.4, which, according to Wendling *et al.* [2009], significantly contributes to immobilising cobalt in soil. This was also confirmed by Li *et al.* [2009], who found that the soil with pH 4.5 contained 0.01 mg Co·kg$^{-1}$ to 367 Co·kg$^{-1}$ of soil, while soil with pH 7.5 contained 0 mg Co·kg$^{-1}$ to 158 mg Co·kg$^{-1}$ of soil. The main study also found: an increase of TEBs, on average, for the series from 64.37 mmol(+)·kg$^{-1}$ to 108.26 mmol(+)·kg$^{-1}$ of soil, an increase in CEC from 93.49 mmol(+)·kg$^{-1}$ to 125.01 mmol(+)·kg$^{-1}$ of soil and an increase in BS from 68.34% to 86.51%, as well as a decrease in HA from 29.11 mmol(+)·kg$^{-1}$ to 16.75 mmol(+)·kg$^{-1}$ of soil. Apart from calcium oxide, a similar advantageous influence was also found by adding zeolite to soil. However, it has to be noted that the effect of calcium oxide was much stronger than that of zeolite. Among the other substances used, charcoal had the greatest influence on soil properties, but the way it influenced TEBs (a change by −32% on average), CEC of soil (−21%) and BS (−14%) was opposite to the way that calcium oxide influenced these properties (Table 2). Adding loam to soil also caused a small increase in HA (Table 1). Kumari and Singh [2003] found a tendency of the pH value and the electrical conductivity to decrease after introducing coal ash into the soil.

## 4. CONCLUSION

1. In the soil without an addition of neutralising substances, the highest doses of cobalt caused the pH, TEBs, CEC and BS to decrease and the HA of soil to increase.
2. Among the substances used, zeolite and calcium oxide (particularly) had the most advantageous influence on the analysed soil properties. They caused the pH, TEBs and CEC to increase and HA to decrease.
3. Among the other substances, it was charcoal that had the greatest influence on the soil properties, but the way it influenced TEBs, CEC of soil and BS were opposite to the way calcium oxide influenced these properties.

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