Trace Metals in Auto- and Semihydrogenic Soils Found in Three Forest Site Types of Bialowieza National Park

B. Gworek¹, M. Degórski², Z. Brogowski³

¹ Institute of Environmental Protection, Krucza Str. 5/11, Warsaw, Poland
² Polish Academy of Sciences, Twarda Str. 51/55, Warsaw, Poland
³ Agricultural Academy of Warsaw, Rakowiecka Str. 26/30, Warsaw, Poland

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Abstract

The aim of this work was to determine the content of Mn, Zn, Cu, Pb, Cr, Ni and Cd in auto- and semihydrogenic soils of Bialowieza National Park and to find relationships between their occurrence and litho-and pedogenic features of these soils. Based on geometric mean contents of the elements studied a quantitative series of their occurrence was established as follows: Mn $(297) > \text{Zn } (29) > \text{Cr } (16) > \text{Pb } (12) > \text{Ni } (10) > \text{Cu } (8.0) > \text{Cd } (0.29) \text{ mg kg}^{"1} \text{ d.w.}$

The distribution of the above trace elements in soil profiles is linked to the direction of progress of the soil-forming processes and, to some extent, to the variability of soil texture (especially in not completely developed soils). In general, the mineral-organic (A) horizons were least abundant in Cr, Ni, Cu, Zn and Cd, followed by the illuvial (Eet) and bedrock (C) horizons of the soils studied.

Statistical analysis shows a significant correlation between the contents of Cr, Ni and Zn and clay and colloidal particle amounts, and between the content of Pb and the amount of organic carbon.

Keywords: soils, forest, trace elements, Bialowieza National Park

Introduction

This work constitutes a successive stage of the study on soils of Bialowieza National Park, an area which so far has seen only light impact from human activities and is focused on the determination of soil trace metal contents. Results of this study will be of essential importance for the assessment of changes in soil contamination by heavy metals.

The aim of this work is to estimate contents of manganese - Mn, zinc - Zn, copper - Cu, nickel - Ni, chromium - Cr, and cadmium - Cd in soils of three forest site types of Bialowieza National Park and to determine relationships between these contents and litho- and pedogenic features of the soils under study.

Materials and Methods

The study was made using auto- and semihydrogenic

soils developed from sediment rocks of glacial origin. In terms of lithogenics within these soils are clayey sands, boulder clays and loamy materials of glacial accumulation.

Soil trace metals were determined in 20% HC1 extract after ashing of organic substance at 480°C. Heavy metals in thus prepared extracts were determined by AAS technique.

The following soils were studied in respective forest site types: gray brown podzolic soils (luwisole) developed from medium boulder clays (profiles 2, 5 and 6) in the oakhornbeam forest with hedge woundwort (*Tilio-Carpi-netum stacheytosum silvaticae*); acid brown soils (cambiso-le) developed from light silty boulder clays (profiles 3, 4 and 9) in the typical oak-hornbeam forest (*Tilio-Carpinetum typicum*) and proper gley soils (planosole) developed from light silty boulder clays (profiles 1, 7 and 8) in the oak-hornbeam forest with remote sedge {*Tilio-Carpinetum caricetosum remotae*).

For statistical computations use was made of the material presented in an earlier reference where both location of

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Table 1. Trace element contents in soil profiles in Bialowieza National Park.

| Profile | Genetic | Depth | Mn | Zn | Cu | Pb | Ni | Cr |
|---------|----------------|----------|---------------|------------------|------------------|------|------|------|
| No | horizon | (cm) | | | mg · | kg-1 | | |
| 11 | | . Combre | Tilio – Carpi | netum stacheyto | osum silvatiacae | | | |
| 2 | 0 | 0-1 | 363.8 | 26.5 | 7.82 | 9.2 | 3.2 | 12.1 |
| | A | 1-8 | 325.4 | 21.7 | 5.10 | 8.3 | 2.8 | 9.4 |
| | Eet | 8-18 | 229.0 | 29.8 | 7.32 | 8.6 | 12.5 | 12.3 |
| | Bt | 18-40 | 393.8 | 54.3 | 11.75 | 9.4 | 15.7 | 20.9 |
| | Cg | 40-46 | 229.4 | 34.3 | 12.10 | 9.0 | 17.5 | 23.6 |
| | D | < 46 | 260.0 | 61.4 | 14.85 | 15.7 | 24.7 | 31.9 |
| 5 | 0 | 0-1 | 727.2 | 37.0 | 7.80 | 19.0 | 6.5 | 9.6 |
| | A | 1-10 | 598.5 | 32.3 | 7.05 | 14.0 | 4.2 | 8.2 |
| | Eet | 10-34 | 250.4 | 23.3 | 6.37 | 9.2 | 8.2 | 11.6 |
| | BtD | 34-70 | 292.3 | 52.5 | 19.65 | 13.5 | 19.7 | 32.2 |
| | D | < 70 | 316.5 | 39.5 | 13.75 | 13.7 | 18.0 | 32.0 |
| 6 | 0 | 0-4 | 678.5 | 26.0 | 3.30 | 18.0 | 6.7 | 7.9 |
| 0.70 | A | 4-23 | 396.5 | 19.5 | 0.35 | 8.2 | 5.8 | 8.4 |
| | Eet | 23-37 | 97.5 | 15.6 | 1.00 | 8.4 | 9.2 | 9.1 |
| | Eet Bt | 37-46 | 90.5 | 11.7 | 0.36 | 3.7 | 4.3 | 7.8 |
| | Bt | 46-78 | 354.4 | 39.6 | 9.87 | 11.5 | 19.5 | 32.9 |
| | D | < 78 | 333.8 | 42.9 | 10.72 | 12.5 | 19.5 | 30.1 |
| - 2 | | | Tilio | – Carpinetum | typicum | | | |
| 3 | 0 | 0-4 | 625.2 | 27.0 | 6.65 | 16.2 | 4.8 | 9.1 |
| * | A | 4-9 | 265.1 | 19.8 | 4.90 | 13.2 | 6.2 | 8.7 |
| | Bbr | 9-35 | 151.2 | 30.1 | 9.45 | 9.4 | 13.5 | 16.4 |
| | CDg | 35-52 | 60.4 | 14.6 | 3.27 | 8.7 | 4.2 | 7.9 |
| | D | < 52 | 191.0 | 41.0 | 15.70 | 12.0 | 22.7 | 28.6 |
| 4 | 0 | 0-4 | | | | | | |
| | A | 4-15 | 151.7 | 15.2 | 4.60 | 11.5 | 3.8 | 9.6 |
| | A Eet | 15-18 | 225.8 | 17.1 | 4.80 | 10.0 | 3.2 | 8.3 |
| | Bbr | 18-43 | 224.3 | 19.8 | 8.12 | 9.4 | 2.8 | 12.1 |
| | Cg | 43-51 | 119.7 | 16.6 | 7.34 | 8.2 | 3.0 | 13.4 |
| | D | < 51 | 252.3 | 39.6 | 10.77 | 11.7 | 15.7 | 27.6 |
| 9 | 0 | 0-5 | 736.7 | 29.5 | 6.20 | 13.7 | 3.2 | 8.2 |
| | Α | 5-14 | 663.2 | 24.7 | 5.57 | 12.0 | 5.7 | 8.2 |
| | Bbr | 14-38 | 267.5 | 24.9 | 6.20 | 9.6 | 2.4 | 7.6 |
| | Cg | 38-54 | 26.4 | 10.4 | 4.10 | 5.4 | 6.5 | 8.3 |
| | Di | 54-160 | 22.7 | 10.4 | 5.22 | 5.2 | 3.0 | 7.3 |
| | D_2 | < 160 | 19.2 | 8.3 | 4.67 | 4.3 | 2.8 | 8.7 |
| | | | Tilio-Car | pinetum cariceto | osum remotae | · | | MI |
| 1 | 0 | 0-3 | 119.3 | 28.1 | 4.37 | 25.2 | 6.5 | 6.5 |
| | Α | 3-15 | 23.5 | 3.1 | 0.97 | 10.0 | 3.4 | 7.3 |
| | BCg | 15-48 | 47.9 | 20.5 | 1.62 | 12.6 | 3.2 | 9.1 |
| | Dg | 48-80 | 247.7 | 52.0 | 12.60 | 11.2 | 15.0 | 29.3 |
| | DG | < 80 | 190.4 | 31.1 | 10.27 | 9.3 | 13.0 | 24.0 |
| 7 | 0 | 0-3 | 480.3 | 26.7 | 2.32 | 15.5 | 3.8 | 6.7 |
| | A | 3-12 | 48.4 | 14.8 | 0.75 | 4.2 | 2.4 | 6.6 |
| | Cg | 12-41 | 69.8 | 17.2 | 1.00 | 5.0 | 8.5 | 8.4 |
| | DG | < 41 | 133.1 | 55.2 | 6.87 | 6.0 | 13.0 | 21.1 |
| 8 | 0 | 0-5 | 141.7 | 36.7 | 7.87 | 24.5 | 6.2 | 8.7 |
| | A | 5-32 | 41.4 | 23.2 | 5.37 | 6.0 | 8.0 | 8.0 |
| | BCg | 32-45 | 234.2 | 23.7 | 5.10 | 4.2 | 6.5 | 8.6 |
| | Cg | 45-70 | 366.9 | 18.6 | 5.95 | 6.0 | 10.5 | 8.5 |
| | $\mathbf{D_i}$ | 70-110 | 217.5 | 30.2 | 12.17 | 11.0 | 15.0 | 17.2 |
| | D_2 | < 110 | 176.1 | 47.3 | 13.92 | 11.5 | 4.3 | 26.7 |

profiles and a detailed characteristics of soils examined were also given [5].

Results and Discussion

Contents of soluble elements in 20% HCl and their distribution in soil profiles are given in Table 1, while geometric mean contents in soil genetic horizons can be found in Table 2. The range of element content, irrespective of soil types examined, fluctuates within the limits as follows: for manganese from 19 to 737; zinc from 3 to 61; copper from 0.3 to 19.6; lead from 3.7 to 25.2; nickel from 2.4 to 24.7, chromium from 6 to 36 and for cadmium from 0.09 to 0.34 mg kg⁻¹ d.w.

The geometric mean contents of trace elements in the soils under study can be arranged in the following series:

Mn (297) > Zn (29) > Cr (16) > Pb (12) > Ni (10) > Cu $(8.0) > Cd (0.29) \text{ mg kg}^{-1}$

Similar values were given by other authors [1-9] who studied the trace element content of soils developed from glacial formations. The distribution of trace elements in soil profiles is linked to the direction of progress of soil forming processes and, to some extent, to the variability of soil texture (especially in not completely developed soils).

Element contents determined in individual genetic horizons may be arranged in the following series: manganese: O(427) > Bt(373) > Bbr(333) > A(276) >

 $> D(194) > Eet(186) > C(115) \text{ mg kg}^{-1}$

zinc: Bt(46) > D(39) > Bbr(33) > O(26) > Eet(20) > $> A = C(19) \text{ mg kg}^{-1}$

copper: Bt(12.6) > D(9.0) > Bbr(7.6) > C(5.4) > O(5.0) >> Eet(3.9) > A(3.8) mg kg⁻¹

lead: 0(14.6) > D(13.6) > Bt(10.6) > A = Bbr(9.4) >

> Eet(9.0) > C(7.2) mg kg nickel: Bt(18.6) > D(13.0) > Eet(ll.O) > C(7.9) > Bbr(6.4)

 $> 0(4.3) > A(4.2) \text{ mg kg}^{-1}$

chromium: Bt(2.6) > D(21) > Eet(13) > C = Bbr(11) > $> O = A(8) \text{ mg kg}^{-1}$

cadmium: Bt(0.36) > D(0.34) > C(0.31) > O(0.3) >> Bbr(0.28) > A(0.21) > Eet(0.2) mg kg⁻¹.

The above set of series point out clearly to illuvial horizons (Bt) of gray brown podzolic soils as the ones which contain greatest amounts of trace elements except for manganese and lead, followed by horizons of underlying rock (D). Element accumulation in the illuvial horizons should

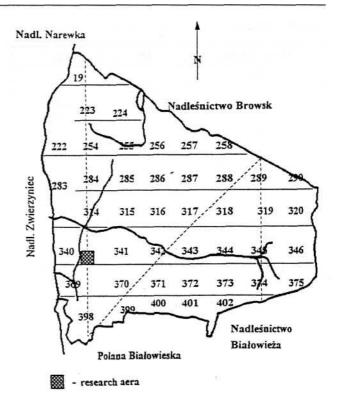


Fig. 1. Localization of the research area in Bialowieza National Park.

be ascribed to soil forming processes as well as to phenomena which occur under periglacial conditions and lead to vertical variability of soil texture. While element content in the horizons of underlying rock is linked to the soil lithogenesis [5].

Mineral-organic horizons (A) are generally poorest in chromium, nickel, copper, zinc and cadmium, except for manganese and lead, followed by the illuvial horizons (Eet) and bedrock (C). Noteworthy is the similarity of series occurrence of nickel and chromium in the analyzed genetic horizons. The latter regularity has often been emphasized in various references [3, 4, 7] as a result of geochemical similarity of the above elements.

Correlation coefficients (r) given in Table 3 show a significant relationship between trace element distribution in

| Table 2 Geometric mean contents of trace elements in genetic horizons of soils studied | Table 2. | Geometric | mean content | s of trace | e elements | in gene | etic | horizons | of soi | ls studied | 1. |
|--|----------|-----------|--------------|------------|------------|---------|------|----------|--------|------------|----|
|--|----------|-----------|--------------|------------|------------|---------|------|----------|--------|------------|----|

| | Mn | Zn | Cu | Pb | Ni | Cr | Cd | | | |
|-----------------|-----------------------|----|------|------|------|----|------|--|--|--|
| Genetic horizon | mg · kg ⁻¹ | | | | | | | | | |
| 0 | 427 | 26 | 5.0 | 14.6 | 4.3 | 8 | 0.30 | | | |
| A | 276 | 19 | 3.8 | 9.4 | 4.2 | 8 | 0.21 | | | |
| Eet | 186 | 20 | 3.9 | 9.0 | 11.0 | 13 | 0.20 | | | |
| Bt | 373 | 46 | 12.6 | 10.6 | 18.6 | 26 | 0.36 | | | |
| Bbr | 333 | 33 | 7.6 | 9.4 | 6.4 | 11 | 0.28 | | | |
| С | 115 | 19 | 5.4 | 7.2 | 7.9 | 11 | 0.31 | | | |
| D | 196 | 39 | 9.0 | 13.6 | 13.0 | 21 | 0.34 | | | |

Table 3. Correlation (r) coefficients between trace elements and their total contents and soil properties.

| Trace elements | Mn | Zn | Cu | Pb | Ni | Cr |
|------------------|--------|----------|-------|----------------|---------|----------|
| Mn | - 2 | X 11/2 | - | 120 | 929 | |
| Zn | 0.304 | (=) | | | 348 | 23 |
| Cu | -0.034 | 0.221 | |) = | * | - |
| Pb | 0.446 | 0.390 | 0.034 | - | | · ** |
| Ni | 0.020 | 0.727**) | 0.188 | 0.121 | - | 15.0 |
| Cr | 0.050 | 0.787**) | 0.344 | 0.108 | 0.858*) | - |
| Diameter < 0.02 | -0.093 | 0.484*) | 0.336 | -0.336 | 0.589*) | 0.701**) |
| Diameter < 0.002 | -0.018 | 0.560*) | 0.280 | 0.028 | 0.634*) | 0.722**) |
| Organic carbon | 0.110 | 0.110 | 0.002 | 0.653*) | -0.109 | -0.312 |

^{*)} P_{0.05} **) P_{0.01}

soils and soil texture. The coefficients may be arranged in the following series:

* for particles of a diameter < 0.02 mm -

 $Cr(0.701^{**}) > Ni(0.589^{**}) > Zn(0.484^{*})$

* for particles of a diameter < 0.002 mm -

 $Cr(0.722^{**}) > Ni(0.634^{*}) > Zn(0.560^{*})$

The above relationships approximate those which were referred to in earlier works [1-4] concerning trace element occurrence in soils developed from glacial formations. Likewise, statistical computations for the occurrence of elements under study show positive correlations only between zinc, chromium and nickel.

Basing upon the calculated correlation coefficients between organic carbon content and trace element amounts, the significance correlation was found solely for lead. The latter relationship can be explained by human activity impact rather than by lithogenic or pedogenic factors.

The results obtained confirm that the soils of Bialowieza National Park are not contaminated by the studied trace elements and that the distribution of these elements in soil profiles is linked to litho- and pedogenic processes.

Conclusions

- 1. Mean contents of Mn, Zn, Cu, Pb, Cr, Ni and Cd in soils of Bialowieza National Park amount respectively to: 297, 29, 8, 12, 16, 10, and 0.29 mg kg⁻¹ of soil.
- 2. Trace metals contents in organic (O) and mine ral-organic horizons (A), as compared to those contents in the remaining genetic horizons, do not testify to a negative impact of human activity on the soil environment, howe ver, there is a tendency to lead accumulation in the litter horizon.
 - 3. Trace elements distribution fractions smaller than

0.02 and 0.002 mm in soil profiles is linked to pedogenic processes and to soil lithogenesis.

4. Statistical analysis has revealed that there is a significant correlation between the occurrence of trace metals and the amount of only in the case of chromium, nickel and zinc. A positive correlation was found between the occurrence of organic carbon and lead.

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