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# EFFECT OF LAND USE ON LEAD AND NICKEL CONTENT AND DISTRIBUTION IN RENDZINA AND RUSTY SOIL PROFILES

## WPŁYW SPOSOBU UŻYTKOWANIA NA ZAWARTOŚĆ I ROZMIESZCZENIE OŁOWIU I NIKLU W PROFILACH RĘDZIN I GLEB RDZAWYCH

**Abstract:** The objective of the present researches was to analyze a content and distribution of lead (Pb) and nickel (Ni) in the profiles of variously utilized rendzinas and rusty soils (forest, arable soils).

The investigations were carried out in the Lublin Upland (rendzinas) and the Sandomierz Basin (rusty soils). Within each soil type, 10 profiles were sampled (5 profiles from arable and 5 from forest soils). Beside the basic properties, there was established a total Pb and Ni content in the concentrated acid mixture $HNO_3$ and $HClO_4$ (1:1). The samples were also examined for the determination of lead and nickel soluble in 1 mol $HCl \cdot dm^{-3}$. The elements were determined using the AAS technique, FAAS method.

A lead content in rendzina soils ranged between 21.0 and 54.5 $mg \cdot kg^{-1}$, whereas in rusty soils from 3 up to 32.0 $mg \cdot kg^{-1}$. Lead soluble in 1 mol hydrochloric acid accounted for 33.1–59.6 % in rendzinas, while in rusty soils – from 3.9 up to 59.4 %.

A total Ni level in rendzinas was found within 22.0 and 46.1 $mg \cdot kg^{-1}$, whereas in rusty soils 0.5–5.0 $mg \cdot kg^{-1}$. Hydrochloric acid-soluble forms of nickel constituted 11.4–34.0 % of its total content in rendzina soils while between 0 and 42.8 % in rusty soils. Both, rendzinas and rusty soils displayed the highest lead content in the humus horizons and a steady quantity decrease with the depth. The changes observed in a nickel content were not so pronounced, but in majority of profiles a lower Ni content was shown in the parent material as compared with humus horizons.

Land use has not affected significantly a content of both analyzed elements in the soil horizons under study.

**Keywords:** rendzina, rusty soil, lead, nickel, forest, arable land

Heavy metal contents in natural soils in Poland prove to be low. Occurrence and content of trace elements in soils are related with the mineral composition of parent

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material, soil properties, numerous climatic conditions and occasionally biological, chemical and physicochemical factors. The recent years have been marked with widely different kinds of human interventions that affect soil conditions [1]. Alike, different land use (arable land, forest) may produce some changes in the physical, chemical and physicochemical properties as well as in content of macro- and microelements in soils. Nevertheless, these soils have the same pedogenesis, granulometry and mineralogical composition [2–5]. Natural contents of heavy metals in soils and the current norms in force should be taken into account while evaluating environmental pollution with trace elements and their joint effect in ecosystem [6, 7].

It is assumed that Pb occurrence in soil, an element very toxic for human, is mostly associated with the anthropogenic factors constituting the major sources of soil pollution in Poland [8]. Nickel is a very abundant natural element whose amount is also conditioned by a clay fraction content [9].

The present study aimed at the analysis of Pb and Ni content and distribution in the profiles of rendzina and rusty soils under various agricultural utilization (forest, arable land).

## Material and methods

The soils under study were located in two physiographical regions: the Lublin Upland (the Zamosc Depression) and the Sandomierz Basin (the Bilgoraj Plain). At each physiographical region, 10 profiles were selected, ie 5 forest profiles and 5 in the immediate vicinity of arable land. The soil samples were collected in autumn, after crop harvest. There were examined a total of 20 soil profiles of diverse typology, formed on chalk marls and sands. The soils developed from chalk marls are classed as rendzina type, subtype: typical, kind: chalk marls, soil textural group: clay loams [10]. According to the WRB, they belong to *Rendzic Leptosols*. The forest associations were classified into subcontinental hornbeam forest *Tilio-carpinetum typicum*, forest site type – fresh forest.

Soils derived from fluvioglacial sands are classed to rust soil type, kind: loose and coarse sands [10], whereas in the WRB system as *Haplic Arenosols*.

As far as phytosociology is concerned, the forest associations from the *Vaccinio--Piceetea* class were classified to the *Peucedano-Pinetum* association (subcontinental fresh coniferous forest).

The single soil samples collected from the analyzed horizons were examined for the granulometric composition using the Casagrande and Proszynski modified aerometric Bouyoucos method, the pH was measured in redistilled water and in 1 mol · $dm^{-3}$ KCl solution by potentiometric method, hydrolytic acidity by a titration method after extraction with the solution of 1 mol $CH_3COONa$ · $dm^{-3}$ (Kappen method), a content of exchangeable cations was established through the extraction with the solution of 1 mol $CH_3COONH_4$ · $dm^{-3}$ of pH = 7, organic carbon level with the Tiurin method modified by Simakow.

After soil samples mineralization in the concentrated acid mixture (nitric(V) and chloric(VII) acids) [11], there was determined a total Pb and Ni content with the FAAS analytical method application, a content of Pb and Ni forms soluble in 1 mol HCl · $dm^{-3}$ was established by FAAS procedure.

The obtained research findings were used to calculate total sorptive capacity, enrichment index called concentration index as a ratio of total metal content in the horizon A to its total average content in the horizon C [12] as well as relative topsoil enhancement index RTE as a relation between total content in the horizon A and its total content in the horizon B [13].

## Results

The investigated rendzina soils, both forest and arable, prove to be heavy soils of granulometric composition characteristic of clay loams with over 57 % of clay fraction in the humus horizons of forest soils and 66 % in arable ones (Table 1). Generally, the top horizons of forest rendzinas showed weakly acidic or neutral reaction (pH in KCl 6.0–6.9), while in the transition horizons – a reaction ranged between neutral and basic. The humus levels of arable rendzinas, similar to underlying (transition) ones, showed a neutral reaction. A parent material reaction in both forest and arable rendzinas appeared to be basic and was found within 7.4–7.7 and 7.2–7.4, respectively (Table 1).

Table 1

Selected physicochemical and chemical properties of rendzinas (average values)

| Properties of soils | | | Forest soils | | | Arable soils | | |
|---|---|---|---|---|---|---|---|---|
| | | | Aca | ACca | Cca | Apca | ACca | Cca |
| 1–0.1 | [mm] | Share of fractions [%] | 21–32*<br>23** | 0–22<br>11 | — | 4–27<br>13 | 13–16<br>14 | — |
| 0.1–0.02 | [mm] | Share of fractions [%] | 14–24<br>20 | 14–22<br>18 | — | 16–31<br>21 | 12–21<br>17 | — |
| < 0.02 | [mm] | Share of fractions [%] | 54–59<br>57 | 57–85<br>71 | — | 52–77<br>66 | 63–75<br>69 | — |
| pH in $H_2O$<br>pH in KCl | Range | | 6.2–7.1<br>6.0–6.9 | 6.8–7.8<br>6.8–7.6 | 7.6–8.1<br>7.4–7.7 | 7.4–7.7<br>6.9–7.2 | 7.6<br>6.9–7.1 | 7.5–7.8<br>7.2–7.4 |
| Organic C | [g · $kg^{-1}$] | | 30.8–45.2<br>37.68 | 6.0–15.0<br>11.16 | 2.4–16.2<br>7.44 | 12.6–33.0<br>20.58 | 7.8–9.6<br>8.60 | 1.2–9.0<br>5.16 |
| Hh | [mmol(+) · $kg^{-1}$] | | 10.7–55.9<br>25.4 | 7.5–12.0<br>8.8 | 6.0–8.2<br>6.7 | 6.0–10.5<br>8.7 | 6.5–8.2<br>7.5 | 6.6–8.2<br>7.2 |
| CEC | [mmol(+) · $kg^{-1}$] | | 396–908<br>633 | 957–1327<br>1230 | 1155–1447<br>1290 | 647–1166<br>990 | 1121–1284<br>1217 | 1285–1412<br>1343 |

* – range, ** – average from 5 examined points.

In forest rendzinas, a mean content of organic carbon in the humus horizons averaged 37.68 g · $kg^{-1}$ and was found within 30.8–45.2 g · $kg^{-1}$. It appeared to be higher than that established in arable rendzina soils (mean 20.58 g · $kg^{-1}$, a range between 12.6–33.0 g · $kg^{1}$) (Table 1).

Hydrolytic acidity in the forest rendzina humus horizons amounted to average 25.4 mmol(+) · kg$^{-1}$, while in the arable – 8.7 mmol(+) · kg$^{-1}$. The obtained research findings reveal this feature value to decrease with the depth (Table 1). Sorptive capacity in the forest rendzina humus horizons were lower as compared with the arable ones and its value was growing with depth (Table 1).

Rusty soils belonged to very light soils derived from loose and coarse sands, with a clay fraction content under 4 %. Humus horizons in the forest soils and arable soils showed a strongly acidic or acidic reaction, while the parent material was acidic in reaction (Table 2).

Table 2

Selected physicochemical and chemical properties of rusty soils (average values)

| Properties of soils | | | Forest soils | | | Arable soils | | |
|---|---|---|---|---|---|---|---|---|
| | | | A | Bv | C | A | Bv | C |
| 1–0.1 | [mm] | Share of fractions [%] | 88–93*<br>91** | 91–94<br>92 | 92–96<br>93 | 83–95<br>89 | 81–93<br>88 | 88–96<br>93 |
| 0.1–0.02 | | | 4–11<br>7 | 3–6<br>5 | 2–7<br>4 | 3–11<br>7 | 3–13<br>8 | 1–5<br>3 |
| < 0.02 | | | 0–3<br>2 | 2–4<br>3 | 0–5<br>3 | 2–7<br>4 | 2–6<br>4 | 3–7<br>4 |
| pH in $H_2O$<br>pH in KCl | | Range | 4.2–5.9<br>3.6–5.1 | 4.6–6.0<br>4.3–5.4 | 5.0–5.9<br>4.7–5.4 | 4.7–5.6<br>3.9–4.9 | 5.0–6.1<br>4.6–5.6 | 5.5–5.9<br>4.7–5.2 |
| Organic C | | [g · kg$^{-1}$] | 4.2–12.0<br>8.4 | 1.3–5.6<br>3.56 | 0 | 5.6–20.4<br>13.16 | 2.0–4.8<br>3.04 | 0 |
| Hh | | [mmol(+) · kg$^{-1}$] | 24.0–55.5<br>40.8 | 15.0–39.0<br>27.3 | 9.0–15.0<br>12.3 | 21.0–70.5<br>45.9 | 15.0–39.0<br>24.6 | 9.0–12.0<br>11.4 |
| CEC | | | 25.1–57.2<br>43.3 | 16.4–40.6<br>29.0 | 10.8–15.6<br>13.6 | 25.8–75.0<br>51.2 | 21.1–41.1<br>28.0 | 11.9–16.1<br>13.7 |

* – range, ** – average from 5 examined points.

In the forest soil humus levels, an organic carbon content ranged within 4.2–12.0 g · kg$^{-1}$ (average 8.4 g · kg$^{-1}$), whereas in the arable soils from 5.6–20.4 g · kg$^{-1}$ (average13.16 g · kg$^{-1}$).

Hydrolytic acidity in the humus horizons of rusty forest soils was lower than in arable soils and amounted to 40.8 mmol(+) · kg$^{-1}$ and 45.9 mmol(+) · kg$^{-1}$, respectively, in both land uses, its value decreased with depth (Table 2). Alike, sorptive capacity in forest soil humus horizons that averaged 43.3 mmol(+) · kg$^{-1}$ proved to be lower as compared with arable soils (average 51.2 mmol(+) · kg$^{-1}$). As for parent material, sorptive capacity was similar, irrespective of land use. Rusty soil humus levels as against the parent rock were characterized with higher hydrolytic acidity and sorptive capacity (Table 2).

Total lead content in rendzina humus horizons was within 37.5–54.5 mg · kg$^{-1}$ range, its differentiation was dependent on a sampling site but not land use (Table 3).This content decreased steadily with the profile depth.

Table 3

Average content of lead and nickel in examined rendzinas

| Parameter | | Forest soils | | | Arable soils | | |
|---|---|---|---|---|---|---|---|
| | | Aca | ACca | Cca | Apca | ACca | Cca |
| Pb total | [mg · kg$^{-1}$] | 42.5–51.0*<br>45.3** | 37.0–42.5<br>40.0 | 24.5–35.5<br>28.8 | 37.5–54.5<br>44.1 | 37.0–40.0<br>38.7 | 21.0–39.5<br>30.8 |
| Pb in 1 mol HCl · dm$^{-3}$ | [mg · kg$^{-1}$] | 18.4–26.8<br>23.1 | 13.7–23.1<br>17.36 | 9.3–12.9<br>11.6 | 17.5–23.6<br>20.36 | 13.7–19.4<br>16.53 | 9.4–13.5<br>12.88 |
| Mobility coefficient | | 42.8–59.6<br>50.98 | 35.1–54.4<br>43.1 | 36.1–52.7<br>40.98 | 39.8–51.9<br>46.58 | 37.0–42.3<br>42.6 | 33.1–51.9<br>42.86 |
| RTE | | 1.07–1.26<br>1.13 | | | 0.96–1.47<br>1.14 | | |
| Accumulation coefficient | | | | 1.28–1.76<br>1.59 | | | 0.96–2.59<br>1.55 |
| Ni total | [mg · kg$^{-1}$] | 25.0–38.5<br>32.4 | 31.3–36.0<br>33.1 | 22.0–32.5<br>29.8 | 22.5–40.0<br>29.8 | 34.0–46.1<br>40.67 | 23.5–40.0<br>31.4 |
| Ni in 1 mol HCl · dm$^{-3}$ | [mg · kg$^{-1}$] | 5.6–9.2<br>7.64 | 6.3–8.0<br>7.24 | 5.1–7.3<br>6.58 | 3.6–9.1<br>7.36 | 5.3–8.4<br>7.07 | 6.3–7.4<br>7.14 |
| Mobility coefficient | | 17.4–26.7<br>23.36 | 17.5–25.0<br>21.98 | 15.4–31.8<br>22.66 | 16.0–34.3<br>24.98 | 11.4–24.7<br>18.07 | 17.7–31.5<br>23.86 |
| RTE | | 0.79–1.12<br>0.99 | | | 0.48–1.12<br>0.93 | | |
| Accumulation coefficient | | | | 1.0–1.18<br>1.10 | | | 0.56–1.13<br>0.98 |

* – range; ** – average from 5 examined points; RTE – relative enhancement index.

A content of lead soluble in 1 mol HCl · dm$^{-3}$ was similar. Its content range in humus levels was from 17.5–26.8 mg · kg$^{-1}$ that accounted for 39.8–59.6 % of total Pb content (named as mobility coefficient representing a percentage of this lead form in its total content). Besides, a content of this lead form also declined consistently with depth of the studied soil horizons.

The index of relative enhancement of lead (RTE expressing a ratio between total metal content and its content in the underlying profile) in the humus horizons in both forest and cultivated soils was similar and averaged 1.13. There was noted substantial scatter of the index for cultivated soils. Alike, the concentration index (accumulation coefficient) expressing a ratio of total lead content in the humus horizons to its concentration in parent rock material, was on average 1.59 in forest soils and 1.55 in the arable.

Irrespective of rendzina use, total Ni content in rendzina humus profiles was found within 22.5–40.0 mg · kg$^{-1}$. Under both management ways, the rendzina transition horizons showed higher mean nickel contents than the humus profiles and parent material.

Content of 1 mol · dm$^{-3}$ hydrochloric acid soluble nickel in humus horizons of examined rendzinas was in the range of 3.6–9.2 mg · kg$^{-1}$ that constituted 16.0–34.3 %

of its total content (Table 3). This Ni form concentration was affected by neither land use nor genetic horizon.

RTE index appeared to be below 1, whereas concentration index in forest soils averaged 1.1 and 0.98 in cultivated soils.

Total lead content in the humus horizons of forest rusty soils amounted to mean 22 $mg \cdot kg^{-1}$, whereas in arable soils – 17.1 $mg \cdot kg^{-1}$ (Table 4). In the soils under both utilization ways, there was observed this element decrease with depth.

Table 4

Average content of lead and nickel in examined rusty soils

| Parameter | | Forest soils | | | Arable soils | | |
|---|---|---|---|---|---|---|---|
| | | A | Bv | C | Ap | Bv | C |
| Pb total | $[mg \cdot kg^{-1}]$ | 15.0–27.0<br>22 | 11.0–32.0<br>17.7 | 4.0–7.1<br>5.42 | 9.0–24.0<br>17.1 | 5.0–15.5<br>10.9 | 3.0–9.0<br>6.9 |
| Pb in 1 mol $HCl \cdot dm^{-3}$ | $[mg \cdot kg^{-1}]$ | 7.1–9.7<br>8.10 | 3.5–7.9<br>5.68 | 0.5–1.3<br>0.96 | 4.5–10.7<br>8.6 | 1.5–6.9<br>3.8 | 0.3–2.3<br>1.3 |
| Mobility coefficient | | 27.3–64.7<br>39.3 | 24.7–44.3<br>33.8 | 12.7–26.0<br>18.1 | 35.4–69<br>52.0 | 26.1–49.3<br>34.4 | 3.9–31.7<br>18.7 |
| RTE | | 0.8–2.0<br>1.38 | | | 1.4–1.8<br>1.60 | | |
| Accumulation coefficient | | | | 3.03–6.75<br>4.29 | | | 1.89–3.16<br>2.57 |
| Ni total | $[mg \cdot kg^{-1}]$ | 1.0–3.0<br>2.0 | 1.0–3.5<br>2.0 | 0.5 | 1.0–5.0<br>2.3 | 1.5–5.0<br>2.3 | 0.5–2.5<br>0.9 |
| Ni in 1 mol $HCl \cdot dm^{-3}$ | $[mg \cdot kg^{-1}]$ | 0–1.5<br>0.54 | 0–1.5<br>0.5 | 0 | 0–1.2<br>0.5 | 0–1.5<br>0.4 | 0–0.7<br>0.1 |
| Mobility coefficient | | 0–50<br>21 | 0–42.8<br>20.2 | 0 | 0–39.3<br>12.7 | 0–30.0<br>11.9 | 0–28.0<br>5.6 |
| RTE | | 0.5–1.5<br>1.08 | | | 0.5–1.65<br>0.96 | | |
| Accumulation coefficient | | | | 2.0–6.0<br>4.0 | | | 2.0–5.6<br>2.92 |

* – range; ** – average from 5 examined points; RTE – relative enhancement index.

Content of 1 mol $\cdot$ $dm^{-3}$ hydrochloric acid soluble lead in humus profiles was reported to be similar and this element amount declined with depth. Mobility factor in the forest soil humus horizons averaged 39.3 %, while in arable soils – 52 %.This factor tended to decrease with depth and it had similar values for both utilization ways.

A relative enrichment index of lead in the humus horizons of forest soils reached 1.38 on average, whereas in arable – 1.60. A mean concentration index in forest soils was markedly higher than in arable and amounted to 4.29 and 2.57, respectively (Table 4).

A nickel content in the studied rusty soils was very low and did not exceed 5 $mg \cdot kg^{-1}$. Parent material of these soils appeared to be substantially poorer as compared both with humus and rusting horizons. Mean content of 1 mol · $dm^{-3}$ hydrochloric acid soluble nickel in the humus and rusting profiles averaged ca 0.5 mg · $kg^{-1}$, regardless land use, that in forest soils constituted 21.0 and 20.2 % of total content, while in arable soils 12.7 and 11.9 %, respectively.

The RTE index reached mean value 1.08 in forest soils and 0.96 in arable. Similarly for lead, a concentration index reported for forest soils proved to be notably higher than for arable (Table 4).

## Discussion

Naturally occurring metals level in loamy soils is 70 mg Pb · $kg^{-1}$ and 50 mg Ni · $kg^{-1}$, while in light soils – 30 mg · $kg^{-1}$ and 10 mg · $kg^{-1}$, respectively [14]. Considering the limit numbers, the rendzina and rusty soils under study should be classed into soils of natural lead and nickel content ($0^o$ of pollution).

Analyzing lead distribution in the profiles of rendzinas and rusty soils, both forest and arable, there was found its higher level in the humus horizons than in parent rock material. That gives evidence of anthropogenic origin of this element. Similar research findings were reported by other authors [15, 16].

Land use did not exert any significant impact on Pb content and distribution in the studied soil horizons. Rusty soils tended to show a lower lead content in arable ones. According to other studies [17, 18] humus profiles of forest soils were characterized with an elevated lead content as compared with arable ones.

Average mobility factor (MF) expressing a percentage of nickel soluble in 1 mol · $dm^{-3}$ HCl in its total content, appeared to be higher in humus horizons of both soils as compared with those underlying them. While in rendzinas, the MF obtained higher values than in rusty soils.

In rendzina soils, irrespective of land use, the transition horizons were shown to have higher Ni contents as against the humus ones and parent material, whereas in rusty soils, the lowest nickel content was detected in the parent rock material. Nickel mobility in rendzinas was markedly higher in rusty soils as mobility factor displayed. These research results were consistent with those presented by other authors [19, 20].

RTE – relative topsoil enhancement index [13] for lead and nickel in the investigated soil types was low but higher for lead. While concentration index calculated from a ratio of element content in humus horizon to its content in parent material for Pb and Ni in rendzinas turned out to be similar, regardless agricultural use. Similar value of this index for other metals in black soils was reported by Dabkowska-Naskret et al [12]. In rusty soils, this index was close to that for Pb and Ni but markedly higher than in rendzinas. In these soils concentration index value varied subject to land use. The forest soils showed the index nearly twice that of arable soils.

## Conclusion

1. Total content of lead and nickel in the studied rendzinas and rusty soils was characteristic of soils with the metals occurring naturally ($0^o$ of pollution).

2. Humus horizons of rendzina and rusty soils displayed higher Pb content than the underlying ones and steady decline of its amount with depth. Changes in Ni levels were not so marked, but in majority of profiles there was observed a lower content of the element in parent material compared with humus horizons.

3. Land use did not have a significant influence on both elements content in soil profiles analyzed.

4. In rendzinas, average lead and nickel concentration index appeared to be substantially lower as against rusty soils.

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## WPŁYW SPOSOBU UŻYTKOWANIA NA ZAWARTOŚĆ I ROZMIESZCZENIE OŁOWIU I NIKLU W PROFILACH RĘDZIN I GLEB RDZAWYCH


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**Abstrakt:** Celem przeprowadzonych badań była analiza zawartości i rozmieszczenia ołowiu i niklu w profilach rędzin i gleb rdzawych różnie użytkowanych (las, pole uprawne).

Badania przeprowadzono na Wyżynie Lubelskiej (rędziny) i w Kotlinie Sandomierskiej (gleby rdzawe). Z każdego typu gleb pobrano próbki z 10 profili (po 5 profili gleb uprawnych i po 5 profili gleb leśnych). Oprócz podstawowych właściwości oznaczono całkowitą zawartość ołowiu i niklu po mineralizacji gleby w mieszaninie stężonych kwasów $HNO_3$ i $HClO_4$ (1:1). W pobranych próbkach oznaczono również formy ołowiu i niklu rozpuszczalne w 1 mol · $dm^{-3}$ HCl. Pierwiastki te oznaczono techniką ASA metodą FAAS.

Zawartość ołowiu w rędzinach zawierała się w przedziale 21,0–55,9 mg · $kg^{-1}$, a w glebach rdzawych od 3 do 32,0 mg · $kg^{-1}$. Ołów rozpuszczalny w 1-molowym kwasie solnym stanowił od 33,1 do 59,6 % w rędzinach i od 3,9 do 59,4 % w glebach rdzawych. Całkowita zawartość niklu w rędzinach wahała się od 22,0 do 46,5 mg · $kg^{-1}$, a w glebach rdzawych od 0,5–5,0 mg · $kg^{-1}$. Formy niklu rozpuszczalne w kwasie solnym stanowiły w rędzinach od 11,4 do 34,0% całkowitej zawartości, a w glebach rdzawych od 0 do 42,8 %.

Zarówno rędziny, jak i gleby rdzawe charakteryzowały się największą zawartością ołowiu w poziomach próchnicznych i jego ilości systematycznie zmniejszała się wraz z głębokością. Zmiany w zawartości niklu nie były tak jednoznaczne, chociaż w większości profili obserwowano mniejszą zawartość tego pierwiastka w skale macierzystej niż w poziomach próchnicznych.

Sposób użytkowania nie miał istotnego wpływu na zawartość obu analizowanych pierwiastków w profilach badanych gleb.

**Słowa kluczowe:** rędziny, gleby rdzawe, ołów, nikiel, las, pole uprawne