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MERCURY CONTENT IN SOILS OF THE PIENINY NATIONAL PARK

ZAWARTOŚĆ RTĘCI W GLEBACH PIENIŃSKIEGO PARKU NARODOWEGO

Abstract: The work aimed at determining total mercury content in soils of the Pieniny National Park and relationship between properties of studied soils and mercury content. Soil samples used in the studies were collected from all genetic horizons of 12 profiles. Mercury concentrations in most part of investigated profiles (11 of 12) did not exceed limit content permissible for unpolluted soils. Mercury pollution was deposited mainly in organic and humus horizons. The highest content of mercury was determined in organic and humus horizons of some mountain humic rendzina on the top of the Biala Skala. Some of physical-chemical properties influenced profile distribution of mercury. Based on statistical analysis correlations were found between mercury accumulation and soil reaction (pH measured in 1 mol KCl $\cdot$ dm^{-3}), content of organic carbon and total nitrogen as well as clay fraction content (< 0.002 mm) in granulometric composition.

Keywords: mercury, soil, pollution, the Pieniny National Park

Mercury presence in soils is conditioned by natural factors (the content in the parent rock or volcanic eruptions) and by anthropogenic ones (gases and dusts from fuel combustion and technological processes) [1, 2]. Heavy metal accumulation in the area of the Pieniny National Park is mainly influenced by mountainous surface features, relatively heavy rainfall and location close to industrialized regions of Krakow and Silesia. Heavy metals, including mercury penetrate to the park area mainly as gases or dusts [3]. The most serious dust emitters in the park territory are home furnaces and petrol fumes, inevitably connected with intensified tourist traffic in this area [4].

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The paper aimed at an assessment of the total mercury content in soils of the Pieniny National Park and determining relationships between selected properties of the analyzed soils and degree of this element accumulation in soil.

Material and methods

The investigations were conducted on soil material collected from genetic horizons of 12 soil profiles located on the territory of the Pieniny National Park (Fig. 1). Individual soil pits represent the following taxonomic units: brown rendzinas (1 profile), mountain humic rendzina (1 profile), brown pararendzinas (4 profiles), typical brown soils (1 profile), gleyed brown soils (2 profiles), leached brown soils (2 profiles) and ground gley soils (1 profile).

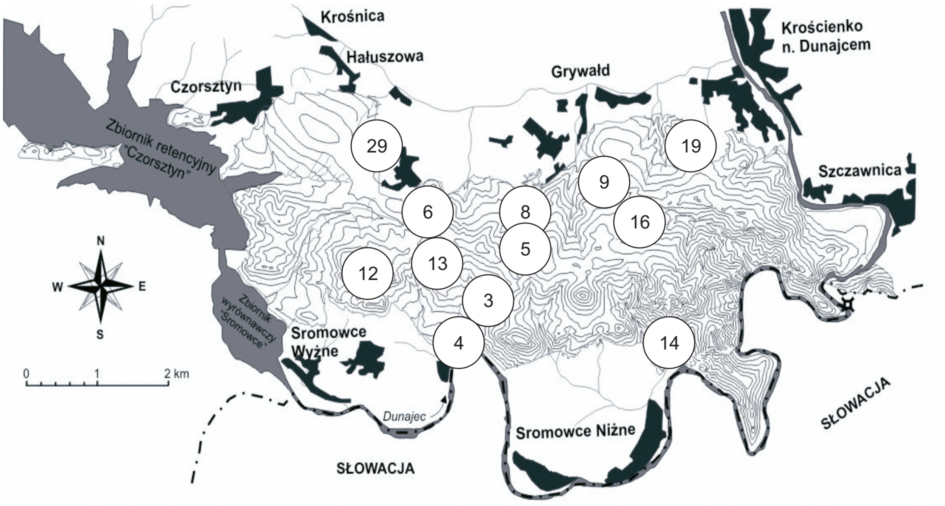

Fig. 1. Location of soil profiles

The soil material taken from individual genetic horizons was dried and sifted through a sieve with 2 mm mesh. The following assessments were made in the prepared soil samples:

– pH in distilled water and 1 mol · dm^{-3} KCl solution with potentiometric method,

– total nitrogen using Kjeldahl method in Kjeltec apparatus (Tecator),

– organic carbon according to Tiurin method modified by Oleksynowa,

– soil texture composition using Casagrande method in Proszynski's modification

– mercury content using atomic absorption spectrometry AAS in AMA 254 mercury analyzer (Altech).

The obtained results were verified statistically using Statistica 6.1 software; simple correlation coefficients were calculated and their significance was determined by t-Student test. Mercury accumulation indices (AI) were computed as a ratio of the element contents in the surface horizon and parent rock horizon of the profiles.

Results and discussion

A common characteristic of the analyzed soil from the Pieniny National Park was considerable content of skeleton in genetic horizons. Rendzinas (profiles 4 and 12) revealed granulation of light and heavy loams passing into clayey deposits in deeper profile horizons (Table 1).

Table 1

Physicochemical properties of investigated soils

Soil type, profiles number	Horizon	Content of fraction [%] with diameter [mm]				pH		Organic C	Total N
		1–0.1	0.1–0.02	< 0.02	< 0.002	H_2O	KCl	[g · kg^{-1}]	
Rendzinas (2)	O A	— 18–38	— 12–34	— 26–36	— 2–34	5.4–6.7 7.5–7.7	6.9–7.1 5.1–6.4	203.2–251.2 31.4–59.2	16.0–18.9 3.6–7.0
Brown para-rendzinas (4)	A	7–37	18–44	23–51	5–18	3.8–7.9	3.0–7.0	6.0–58.5	1.0–5.2
Typical brown soils (5)	O A	— 10–34	— 29–46	— 27–42	— 0–21	4.7 3.9–7.0	3.6 3.1–5.7	105.7 6.2–7.52	7.7 1.9–6.1
Ground gley soil (1)	A	46–50	23–32	16–22	1–0	5.0–6.4	4.7–6.1	65.9–74.2	3.8–5.6

In brown pararendzinas (profiles 6, 9, 14 and 19) determined granulation changed from light loams to clayey deposits. Brown soils (profiles 3, 5, 13, 16 and 29) were characterized by a granulation from light and medium loams in the surface horizons to heavy loams in their bottom horizons. A considerable part of sandy parts was visible among the fine parts of the analyzed ground gley soil (profile 8).

Table 2

Mercury content in genetic horizons of investigated soils

Profile nr	Soil type and subtype	Depth [cm]	Horizon symbol	Hg [mg · kg^{-1}]
4	Brown rendzina	0–22	AhBbr	0.22
		22–40	BbrCca	0.09
12	Mountain humus rendzina	0–3	Ofh	0.32
		3–8	Oh	0.98
		8–55	AhCca	0.92
6	Brown pararendzina	0–10	Ah	0.24
		28–50	BbrCca	0.11
		50–110	Cca	0.10
9	Brown pararendzina	1–7	A	0.29
		7–29	BbrC	0.14
		29–42	IICca	0.34
		0–5	Ah	0.09

Table 2 contd.

Profile nr	Soil type and subtype	Depth [cm]	Horizon symbol	Hg [mg · kg^{-1}]
		5–16	ABbr1	0.08
		16–44	ABbr2	0.08
14	Brown pararendzina	44–73	ABbr3	0.10
		73–84	ABbrCca	0.09
		2–20	Ah	0.11
		20–44	ABbr	0.10
19	Brown pararendzina	44–62	BbrC1	0.13
		62–80	BbrC2	0.24
		0–12	Ah	0.09
		12–45	Bbrg	0.10
3	Gleyed typical brown soil	45–67	BbrCgg	0.08
		1–9	Ah	0.26
		9–21	AhBbr	0.16
5	Leached typical brown soil	21–52	Bbr	0.13
		52–90	BbrCca	0.10
		0–4	Ah	0.12
		4–26	ABbr1	0.11
		26–39	ABbr2	0.12
13	Typical brown soil	39–72	ABbrCca	0.13
		72–85	IICca	0.08
		0–2	O	0.18
		2–12	Ah	0.12
		12–28	ABbr	0.09
16	Leached typical brown soil	28–50	ABbrC	0.10
		> 50	C	0.14
		0–18	Ah	0.24
		18–36	ABbr	0.14
29	Gleyed typical brown soil	82–100	Cg	0.10
		0–30	Ahgg	0.15
8	Ground gley soil (humic)	30–44	AG	0.09

Rendzinas revealed reaction from acid to neutral in the organic horizons (pH_{H2O} 5.4–6.7) and alkaline in the humus horizons (pH_{H2O} ranged from 7.5 to 7.7). In the humus horizons of the analyzed pararendzinas the reaction fluctuated from very acid to alkaline (pH_{H2O} 3.8–7.9). Brown soils revealed acid reaction in their organic horizons whereas in humus horizons the reaction varied from very acid to neutral. Ground gley soil was characterized by acid to slightly acid reaction in the humus horizons.

The highest content of organic carbon was assessed in organic horizons of the rendzinas (from 203.2 to 251.2 g · kg^{-1}). The highest content of organic carbon in humus horizons ranging from 65.9 to 74.2 g · kg^{-1} was characteristic for ground gley soil, lower contents were assessed in brown soils and pararendzinas, 6.2–75.2 g · kg^{-1} and 6.0–58.5 g · kg^{-1}, respectively (Table 1).

The analyzed soils of the Pieniny National Park (except profile 1) were characterized by mercury content lower than 0.5 g · kg^{-1}, which is a permissible value for protected area soils (Table 2) [5]. The highest mercury content (from 0.32 to 0.98 mg · kg^{-1}) was measured in rendzinas organic horizons. The content of mercury in the medium and bottom part of the mountain humic rendzina (profile 12) was the highest and exceeded the value of 0.90 mg · kg^{-1}. This profile was located on Biala Skala (805 m a.s.l.) in the western part of the Pieniny National Park and was particularly exposed to accumulation of pollutants carried from the Silesia Region. Mercury accumulation in genetic horizons of the analyzed rendzina was undoubtedly connected with this element absorption by raw organic horizons, which especially easily bind heavy metals [6].

In pararendzinas humus horizons A revealed Hg content between 0.09 and 0.29 mg · kg^{-1}, whereas elevated mercury content between 0.09 and 0.34 mg · kg^{-1} was assessed in parent rock Cca horizons. Small thickness of solum and considerable skeletal content affected free translocation of mercury into the soil profile and its accumulation in bottom horizons [7].

Mercury content assessed in organic and humus horizons of the investigated soils is approximate to this element content in other forest soils of southern Poland [8].

Characteristic elevated content of mercury in organic and humus horizons is connected with this element accumulation by organic matter at a low stage of decomposition. These horizons are a filter absorbing anthropogenic pollution (dusts), including mercury in the form of oxides and ions [1, 6, 9].

Computed values of accumulation index (AI) are low, which evidences a low mercury accumulation in the analyzed soils. Accumulation index values higher than 2 assessed for profiles: 4, 5, 6 and 29 prove a considerable accumulation of mercury in surface horizons as compared with the bottom ones (Fig. 2).

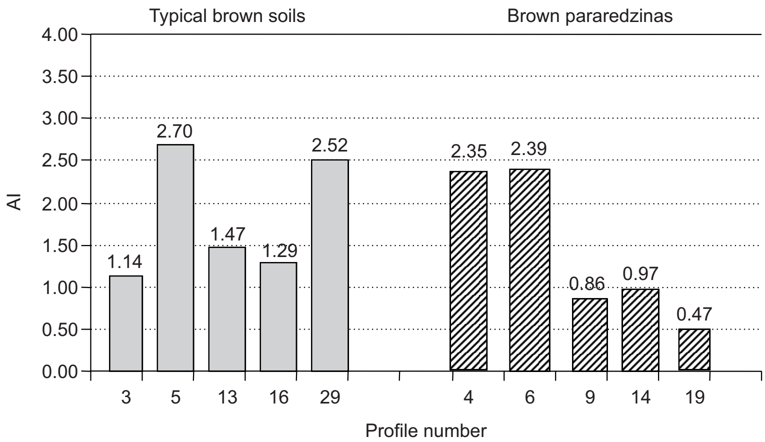

Fig. 2. Comparison of accumulation index (AI) calculated for brown soils proper and brown pararendzinas

In case of profile 3 among the analyzed brown pararendzinas it may be noticed that the value for accumulation index is lower than 1, which testifies an easy mercury translocation into the profile and accumulation mainly in bottom horizons of soil profiles.

Most soils in the Malopolska region is characterized by elevated mercury concentrations in comparison with the geochemical background, as shown by AI values higher than 1 [10]. Elevated accumulation indices (from 1.3 to 3.0) were also registered in the area of the Pieniny National Park for other heavy metals, ie Cd, Cu, Cr, Mn, Pb, Zn and Ni. It evidences slightly raised heavy metal accumulation in soils of this area [11].

Mercury content in organic horizons O and humus horizons A was connected with organic carbon and total nitrogen contents, and simple correlation coefficients calculated for these relationships were $r_{0.01} = 0.58$ and $r_{0.001} = 0.63$, respectively (Table 3). The other properties which positively affected mercury accumulation in the profile were: soil pH in KCl ($r_{0.05} = 0.43$) and the content of < 0.002 mm fraction ($r_{0.01} = 0.53$). The relationship between mercury content in soils, organic carbon content, share of floatable particles and additionally with sorption capacity and hydrolytic acidity was also confirmed by other authors [12, 13].

Table 3

Linear correlation coefficient between mercury content in organic (O) and humus (A) horizons and properties of investigated soils

Soil properties	Linear correlation coefficient (r)
pH H_2O	0.27
pH KCl	0.43*
Organic C content	0.58**
Total N content	0.63***
C:N ratio	0.26
Content of fraction < 0.02 mm	0.36
Content of fraction < 0.002 mm	0.53**

Significance level: * – α = 0.05***; ** – α = 0.01; – α = 0.001.

Conclusions

1. A majority of soils in the Pieniny National Park revealed lower contents of mercury than the limit value assumed for the protected areas.

2. The greatest content of mercury was assessed in organic and humus horizons of the analyzed rendzinas.

3. Values of accumulation index (AI) show that a majority of the analyzed soils was characterized by an elevated content of mercury in comparison with geochemical background.

4. On the basis of statistical analysis it was demonstrated that mercury content in organic and humus horizons of the soils was positively correlated with the contents of organic carbon, total nitrogen, soil pH in KCl and the share of floatable particles (< 0.002 mm).

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ZAWARTOŚĆ RTĘCI W GLEBACH PIENIŃSKIEGO PARKU NARODOWEGO

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Abstrakt: Celem pracy było oznaczenie całkowitej zawartości rtęci w glebach Pienińskiego Parku Narodowego oraz określenie zależności między wybranymi właściwościami badanych gleb a stopniem akumulacji tego pierwiastka w glebie. Do badań pobrano próbki ze wszystkich poziomów genetycznych 12 profilów gleb. Większość profilów (11 spośród 12) charakteryzowała się mniejszą zawartością rtęci niż wartość przyjęta dla niezanieczyszczonych gleb obszarów chronionych. Największe zawartości rtęci zanotowano w poziomach organicznych i próchnicznych badanych gleb. Niektóre właściwości fizyczne i chemiczne gleb wpłynęły na przestrzenne rozmieszczenie rtęci w profilach glebowych. Biorąc pod uwagę współczynnik akumulacji (WA), większość badanych gleb charakteryzowała się podwyższoną zawartością rtęci w porównaniu z tłem geochemicznym. Na podstawie analizy statystycznej stwierdzono, że zawartość rtęci w poziomach organicznych i próchnicznych badanych gleb była skorelowana z wartością pH (mierzoną w 1 mol $KCl \cdot dm^{-3}$), zawartością węgla organicznego i azotu ogólnego oraz z udziałem części spławianych (< 0.02 mm) w składzie granulometrycznym.

Słowa kluczowe: rtęć, gleby, zanieczyszczenie, Pieniński Park Narodowy