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MERCURY CONTENT IN SOILS OF THE OJCOW NATIONAL PARK

ZAWARTOŚĆ RTĘCI W GLEBACH OJCOWSKIEGO PARKU NARODOWEGO

Abstract: The aim of the study was to evaluate the total mercury content in genetic horizons of soils of the Ojcow National Park (ONP). Most part of all 27 examined soils showed low Hg content, which resulted in classifying them as not polluted soils. The highest concentration of Hg was found in organic horizons of lessive soils. Based on statistical analyze it was found that lessive soils were more polluted in humus horizons than rendzinas. Most part of studied soils humus horizons was characterized by a higher Hg content in comparison with geochemical background, what evidence is accumulation index (AI) values more than 1. Mercury content in examined soils was depended on the content of organic carbon, total nitrogen and C:N ratio.

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

Geographical position of the Ojcow National Park (ONP) within the pollutant range of large industrial centres (Upper Silesian Industrial Region, Olkusz, Jaworzno, Trzebinia-Siersza), a considerable number of windless periods and small wind speed favour persistent air pollution in the park flowing from the west and south-west [1].

According to Grodzinska [2], who in the eighties investigated the problem of contamination in national parks in Poland, the Ojcow National Park was counted among the groups of parks strongly polluted with heavy metals. Moreover, Grodzinska demonstrated that contamination of the Ojcow National Park was the highest among the analyzed parks.

Presented research aimed at determining the total content of mercury in soils of the Ojcow National Park and establishing the degree of these soils pollution with the discussed element.

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Material and methods

The soil material for analyses was collected from 27 soil profiles located in the area of the Ojcow National Park (Fig. 1).

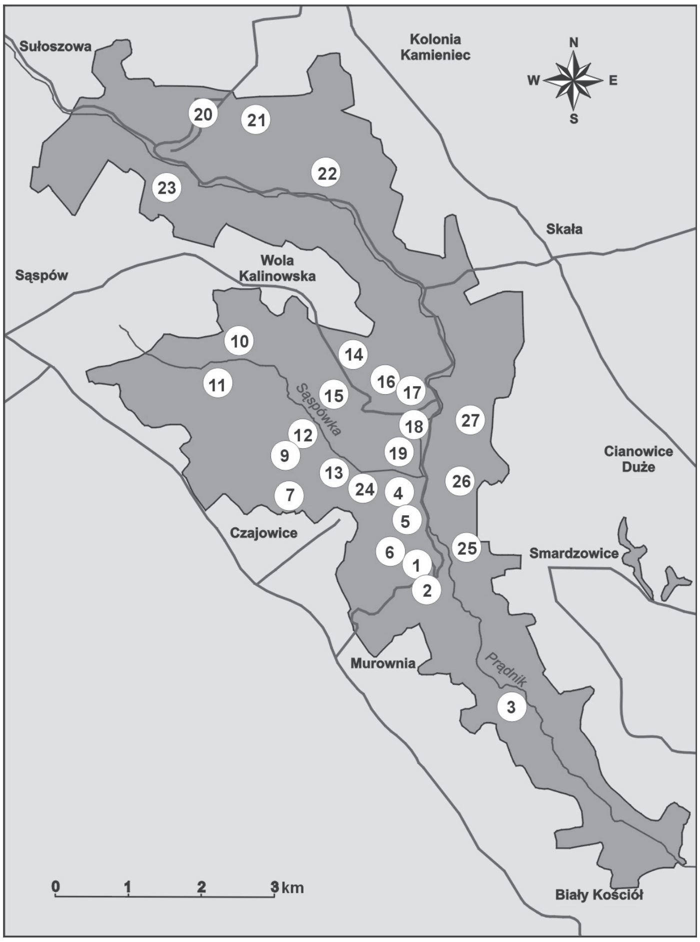

Fig. 1. Location of soil profiles on the Ojcow National Park area

The researched soils represented 5 types [3]:
– rendzinas (16 profiles),
– brown soils (1 profile),
– lessive soils (8 profiles),
– pseudogley soils (1 profile),
– river alluvial soils (1 profile).

Rendzinas were developed from the Jura limestones, brown soils, lessive soils and pseudogley soils formed from loesses deposited on limestones, whereas river alluvial soils from alluvia. The soil profiles were situated in the forest areas and only river alluvial soil (profile 13) was situated on grassland.

Laboratory analyses were conducted on the samples collected from 87 soil genetic horizons. The soil material was dried at room temperature and sifted through a sieve with 1 mm mesh, and subsequently basic physicochemical and chemical properties were determined:

– pH in distilled water using potentiometric method,
– total nitrogen using Kjeldahl method on Kjeltec apparatus (Tecator),
– organic carbon using Tiurin method modified by Oleksynowa,
– granulometric composition using Casagrande method modified by Proszynski,
– total mercury content using atomic absorption spectrometry (AAS) in AMA 254 mercury analyzer (Altech).

The obtained results were subjected to statistical analysis using Statistica 6.1 software; simple correlation coefficients were computed and their significance determined using t-Student test. RIR Tukey test was used to compare mercury contents in rendzinas and lessive soils. Mercury accumulation indices (AI) were also computed as a ratio of the element content in the surface and bottom horizons of the profiles.

Results and discussion

Analyzed rendzinas were characterized by a considerable skeletal content. Granulometric composition of rendzinas was strongly diversified and resulted from the thickness of loess layer lying on carbonate rocks (mixed rendzinas) (Table 1) [4].

Table 1

Chemical and physico-chemical properties of investigated soils

Soil type, profiles number	Horizon	Share of fraction [%] with diameter [mm]				pH (H_2O)	Organic C	Total N
		1–0.1	0.1–0.02	< 0.02	< 0.002		[$g \cdot kg^{-1}$]	
Rendzinas (16)	O A	— 0–45.5	— 30.5–56	— 19–56	— 3–22	6.0–7.4 5.7–7.8	118.2–326.9 25.4–81.8	1.14–1.63 2.0–7.1
Lessive soils (8)	O A	 0.5–24	 46–81	 29–53	 5–15	3.5–5.3 3.2–5.2	204.0–375.0 25.9–82.0	7.0–23.5 2.5–5.6
Brown soils (1)	A	1	56	43	10	4.6	30.1	3.6
Ground gley soils (1)	A	7	55	38	8	3.6	94.6	5.7
River alluvial soils (1)	A	6	62	32	7	6.1	32.3	3.4

A majority of rendzinas revealed granulation of clayey silt, three profiles has clay granulation, one loamy and one sandy granulation. On the other hand, lessive soils were characterized by ordinary silt or clayey silt granulation.

Rendzinas in the surface horizons revealed neutral or alkaline reaction, slightly acid reaction was determined in two profiles and acid reaction in three profiles. Lessive soils were more strongly acidified (strongly acid or acid reaction). Also in surface horizons of brown soil and pseudogley soil strongly acid reaction was determined. On the other hand, river alluvial soil was characterized by a neutral reaction in the surface horizon, whereas in deeper horizons the reaction was alkaline.

A considerable diversification in organic carbon content was found in soils of the Ojcow National Park. The lowest content of organic carbon in organic horizon, amounting 118.2 g · kg^{-1}, was assessed in proper rendzina (profile 7) and the highest, 375.0 g · kg^{-1}, in pseudogley lessive soil (profile 14). On the other hand, in humus horizons organic carbon contents fluctuated from 25.4 g · kg^{-1} in proper rendzina (profile 12) to 94.6 g · kg^{-1} in pseudogley soil (profile 22). Mean carbon contents in organic horizons of lessive soils were higher than in the analogous horizons of rendzinas and reached: 280.4 g · kg^{-1} and 208.5 g · kg^{-1}, respectively. The situation looked similar for humus horizons, where mean content of organic carbon was also higher in lessive soils, i.e. 57.0 g · kg^{-1} and 44.6 g · kg^{-1} for rendzinas.

Nitrogen content in humus horizons remained on a level from 2.0 g · kg^{-1} in proper rendzina (profile 5) to 7.1 g · kg^{-1} in brown rendzina (profile 19). Mean content of total nitrogen in humus horizons of lessive soils was 4.2 g · kg^{-1} and was slightly lower than in rendzinas, ie 4.3 g · kg^{-1}.

Total mercury content in individual genetic horizons of soils in the Ojcow National Park was diversified (Table 2).

Table 2

Mercury content [mg · kg^{-1}] in investigated soils

Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]	Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]
Rendzinas				Lessive soils			
3 brown	A1h	2–4	0.07	1 glossic	Ol	1–2	0.17
	A2h	4–25	0.04		Ah	2–10	0.14
	BbrC1ca	25–58	0.04		AEet	10–35	0.04
	BbrC2ca	58–80	0.05		Eet	35–48	0.02
4 brown	Ah	1–8	0.06		Eet/Btg	48–115	0.02
	BbrCca	8–30	0.05		BtCg	115–150	0.01
5 typical	Ah	2–15	0.08	2 glossic	Ol	2–4	0.19
	ACca	15–25	0.04		Ah	4–12	0.13
	Cca	25–45	0.04		BtCg	80–150	0.02
6 brown	Ah	2–10	0.11	9 typical	Ol	2–6	0.39
7 typical	O1Cca	2–10	0.36		Ah	6–12	0.39
	O2Cca	10–45	0.29		IIBtC	> 75	0.06
8 typical	A1Cca	2–8	0.19	14 pseudo-gley	Ol	1–4	0.25
	A2Cca	8–35	0.18		Oh	4–7	0.30
10 typical	AhCca	2–15	0.07		AEet	7–13	0.12
11 brown	Ah	1–19	0.14		Eet	13–52	0.04
	AhBbr	19–40	0.12		BtCg	52–125	0.02

Table 2 contd.

Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]	Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]
12 typical	Ah	5–20	0.07	15 pseudo-gley	Ol	1–4	0.31
17 brown	Ol	1–2	0.21		Ah	4–7	0.17
	ACca	2–28	0.16		BtCg	20–100	0.01
	BbrCca	28–40	0.04	16 pseudo-gley	Ol	1–3	0.32
18 inicial	A1Cca	1–6	0.16		Ah	3–9	0.25
	A2Ccaan	6–20	0.13		BtCg	35–100	0.02
19 brown	Ol	1–3	0.16	20 pseudo-gley	A1h	3–6	0.34
	A1Cca	3–20	0.20		IICca	> 59	0.16
	BbrCca	28–48	0.07	26 pseudo-gley	Ol	1–3	0.25
23 brown	Ah	1–16	0.20		Oh	3–6	0.54
	BbrCca	16–38	0.13		AEet	6–35	0.03
24 brown	A1Cca	1–12	0.12		Btg	35–80	0.03
	BbrCca	30–60	0.06		C	80–115	0.02
25 brown	Ah	1–14	0.16		IIC	> 115	0.02
	BbrCca	25–40	0.09	Pseudogley soils			
27 typical	A1Cca	1–10	0.16	21 typical	A1h	2–6	0.23
	A2Cca	10–40	0.13		Gg	12–38	0.03
Brown soils				River alluvial soils			
22 typical	Ah	2–16	0.13	13 typical	Ah	2–10	0.05
	IICca	33–55	0.08		IIG	43–80	0.02

In organic horizons Ol mercury contents ranged between 0.16 and 0.39 mg · kg^{-1} and exceeded natural mean content of this metal in soil, ie 0.1 mg · kg^{-1} [5]. Organic horizons Oh of lessive soils (profiles 14 and 26) revealed high contents of mercury, 0.30 and 0.54 mg · kg^{-1}, respectively. Demers et al [6] point to potential of "internal" mercury binding in O horizons, which escapes in a gaseous form from mineral soil horizons. A lower mercury accumulation was observed in humus horizons in comparison with organic horizons. In their humus horizons rendzinas revealed low contents of the discussed element and 0.20 mg · kg^{-1} was registered only in two profiles (no. 19 and 23). In lessive soils mercury concentration was the highest and reached value 0.39 mg · kg^{-1} (profile 9).

Mean mercury contents computed for humus horizons of rendzinas and lessive soils were 0.13 and 0.24 mg · kg^{-1}, respectively. A statistically significant difference was determined between mercury content in humus horizons of rendzinas and lessive soils at significance level $p = 0.05$ (RIR Tukey test).

In compliance with the Regulation of the Minister of the Environment of 9th September 2002 on soil standards and earth standards, mercury contents in the soils of protected areas cannot exceed 0.5 mg · kg^{-1} [7]. Therefore, the soils of the Ojcow National Park should be considered as unpolluted with the discussed metal. Only in one profile (profile 26) the content of 0.54 mg · kg^{-1} assessed in organic Oh horizon exceeded the admissible value.

Mercury contents determined in soils of the Ojcow National Park were compared with this element contents in black earths from the city area of Krakow and from the southern part of the Nida Basin [8]. Mercury contents in surface horizons of soils from the Nida Basin ranged from 0.078 to 0.390 mg · kg^{-1}, which shows a certain similarity with the park soils, were the values fluctuated from 0.05 to 0.54 mg · kg^{-1}. Mercury content in soils close to the Krakow Gate was slightly higher than in the park and varied within a narrower range (from 0.436 to 0.538 mg · kg^{-1}).

Lower content of mercury was found in surface horizons of forest soils on the Wielun Uppland (from 0.003 to 0.190 mg · kg^{-1}) and on the Tarnobrzeg Plain (from 0.005 to 0.240 mg · kg^{-1}) [9, 10].

Average mercury content in organic horizons of the Babiogorski National Park (BgNP) is 0.32 mg · kg^{-1} and is higher than in soils of the Ojcow National Park (ONP) (0.29 mg · kg^{-1}) [11]. The highest mercury concentrations in the areas of these parks were assessed in the organic horizons: in BgNP it was 0.79 mg · kg^{-1} (the soil covered with spruce trees) and in ONP – 0.54 mg · kg^{-1} (under mixed coniferous forest). In humus horizons, higher mercury contents were found in the soils of ONP than in BgNP and the values were: 0.16 and 0.12 mg · kg^{-1}, respectively.

Profile distribution of Hg contents was different for rendzinas and lessive soil, which is due to different permeability of these soils (Fig. 2).

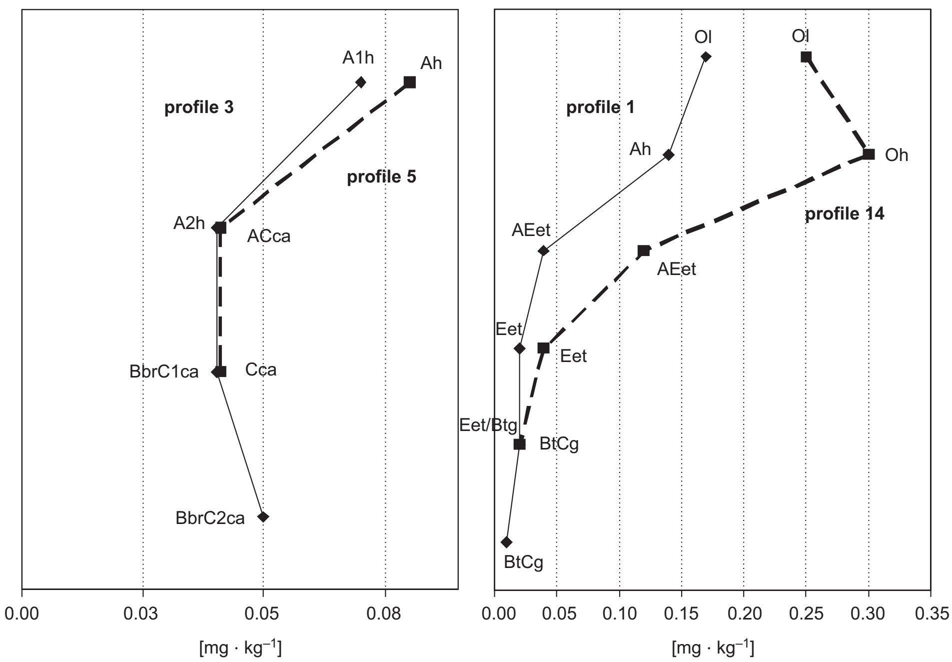

Fig. 2. Mercury profile distribution in chosen rendzinas (profiles 3 and 5) and lessive soils (profiles 1 and 14)

In lessive soils the highest Hg concentrations were found in organic and humus horizons. In deeper, poorly permeable horizons, this element content visibly diminished. In permeable rendzina profiles, mercury content usually varied little in the surface and bottom horizons. Grimaldi et al [12] obtained similar results showing that profile distribution of mercury depends on soil water permeability.

Accumulation indices computed for the analyzed soils of ONP ranged from 1.05 to 16.34 (Fig. 3). Average value of AI determined for lessive soils was 9.32 which is a five-fold higher value in comparison with mean index computed for rendzinas (1.82). Rendzinas are characterized by a high permeability and therefore mercury translocation into deeper horizons is facilitated.

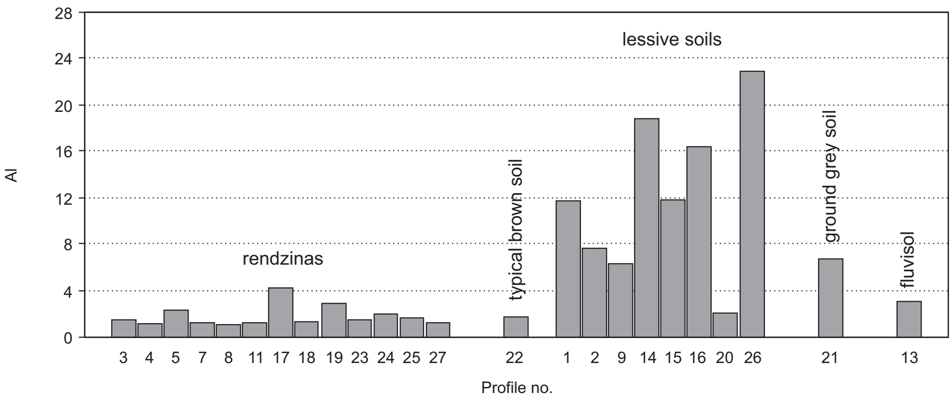

Fig. 3. Accumulation index (AI) calculated for investigated soils

On the basis of computed accumulation indices it may be assumed that the analyzed soil revealed elevated mercury contents as evidenced by AI value higher than assessed in all investigated soil profiles.

Table 3

Linear correlation coefficients between mercury content and some properties of humus horizons of investigated soils

Soil properties	Linear correlation coefficient (r)		
	Rendzinas (16 profiles)	Lessive soils (8 profiles)	Total (27 profiles)
pH (H_2O)	–0.04	0.04	–0.45
Organic C content	0.73***	0.97***	0.87***
Total N content	0.79***	0.96***	0.66***
C:N ratio	–0.27	0.79*	0.60***
Share of fraction < 0.02 mm	0.03	–0.38	–0.22
Share of fraction < 0.002 mm	–0.30	–0.34	–0.33

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

Total mercury contents in all analyzed soils were statistically significantly affected by organic carbon and total nitrogen content, as well as C:N ratio, whereas simple correlation coefficients (significant at $p = 0.001$) computed for these relationships were: $r = 0.87$, 0.66 and 0.60, respectively (Table 3). It corroborates previous research results evidencing the strongest Hg binding by soil humus and clayey minerals [13].

In rendzinas the content of discussed element was strictly (significant at $p = 0.001$) dependant on contents of organic carbon ($r = 0.73$) and total nitrogen ($r = 0.79$), similarly as in lessive soils where simple correlation coefficients (significant at $p = 0.001$) were $r = 0.97$ and 0.96, respectively. Moreover in lessive soils statistical analysis revealed weakly significant (at $p = 0.05$) positive correlation with C:N ratio ($r = 0.79$). Strongly significant correlation between C:N ratio and mercury content in the all analyzed soils shows that the lower the degree of organic matter decomposition in humus horizons, the greater mercury accumulation.

Conclusions

1. A majority of the analyzed soils of the Ojcow National Park were characterized by a low content of mercury but the value of accumulation index AI higher than 1 evidence an artificial enrichment of the surface horizons.
2. Mercury content in the analyzed soils was higher in organic horizons than in humus horizons.
3. Accumulation indices revealed higher values for lessive soils than for rendzinas.
4. Mercury content in all investigated soils strictly depended on the contents of organic carbon, total nitrogen and C:N ratio.

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ZAWARTOŚĆ RTĘCI W GLEBACH OJCOWSKIEGO PARKU NARODOWEGO

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Abstrakt: Celem pracy było oznaczenie całkowitej zawartości rtęci w poziomach genetycznych gleb Ojcowskiego Parku Narodowego oraz określenie zależności między wybranymi właściwościami badanych gleb a ilością tego pierwiastka w glebie. Większość badanych gleb charakteryzowała się małą zawartością rtęci. Największą koncentrację tego pierwiastka stwierdzono w poziomie organicznym gleby płowej (0,54 $mg \cdot kg^{-1}$). Na postawie analizy statystycznej stwierdzono, że gleby płowe w porównaniu z rędzinami charakteryzowały się większą zawartością rtęci w poziomach próchnicznych. W porównaniu z tłem geochemicznym większość badanych gleb wykazywała podwyższoną zawartość rtęci, czego dowodem były wartości współczynnika akumulacji (WA) większe od 1. Zawartość rtęci we wszystkich badanych glebach była uzależniona od zawartości węgla organicznego i azotu ogólnego oraz stosunku C:N.

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