

Ryszard MAZUREK¹ and Paweł ZADROŻNY¹

CADMIUM IN SOILS OF THE OJCOW NATIONAL PARK

KADM W GLEBACH OJCOWSKIEGO PARKU NARODOWEGO

Abstract: The aim of the paper was to investigate cadmium contamination of soils of the Ojcow National Park and to evaluate influence of location, soil type and soil properties on contamination degree with this element. Investigations was conducted on soil samples from 24 profiles represented main types of the park soil cover: rendzinas (13 profiles), lessive soils (8 profiles), brown soils proper (1 profile), pseudogley soils (1 profile) and river alluvial soils (1 profile). Cadmium content ranged from 0.4 to 12.8 mg · kg⁻¹ in surface horizons of investigated soils. On the base of limit values proposed by IUNG and defined in Decree of the Minister of Environment of 9th September, 2002 on soil quality standards and earth quality standards, was stated that almost all soils (except 2 profiles of lessive soils) of the Ojcow National Park are polluted with cadmium. The highest cadmium concentration was analyzed in soils located close to the Czajowice village and the town of Skala. The higher content of analyzed element was measured in rendzinas than in lessive soils. In opposite was higher accumulation index in luvisols than in rendzinas. On the base of statistical analyze were state that soil reaction and below 0.02 mm fraction content are influenced on cadmium concentration in investigated soils.

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

Geographical location of the Ojcow National Park in within the large industrial centres operation range (Upper Silesia Industrial Region, Olkusz, Jaworzno and Trzebinia-Siersza), considerable number of windless periods and small wind velocity favour persistence of air pollutants flowing from the west, north-west and south-west [1].

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

Presented investigations focused on the assessment of cadmium pollution in the Ojcow National Park and determining the influence of its location, type and properties of soil on the degree of pollution with this element.

¹ Department of Soil Science and Soil Protection, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 70, email: rrmazure@cyf-kr.edu.pl

Material and methods

Soil material was collected from 24 soil profiles located in the area of the Ojców National Park (Fig. 1) and representing main typological units of the park soil cover: rendzinas (13 profiles); lessive soils (8 profiles), brown soils (1 profile), pseudogley soils (1 profile) and alluvial soils (profile) [3, 4].

Rendzinas developed from Jurassic limestones, whereas brown soils, soil lessives and pseudogley soils formed from loesses lying on limestones, and river alluvial soils from river alluvia. The soil profiles were situated in the forested areas, only the alluvial soils (profile 13) was a grassland.

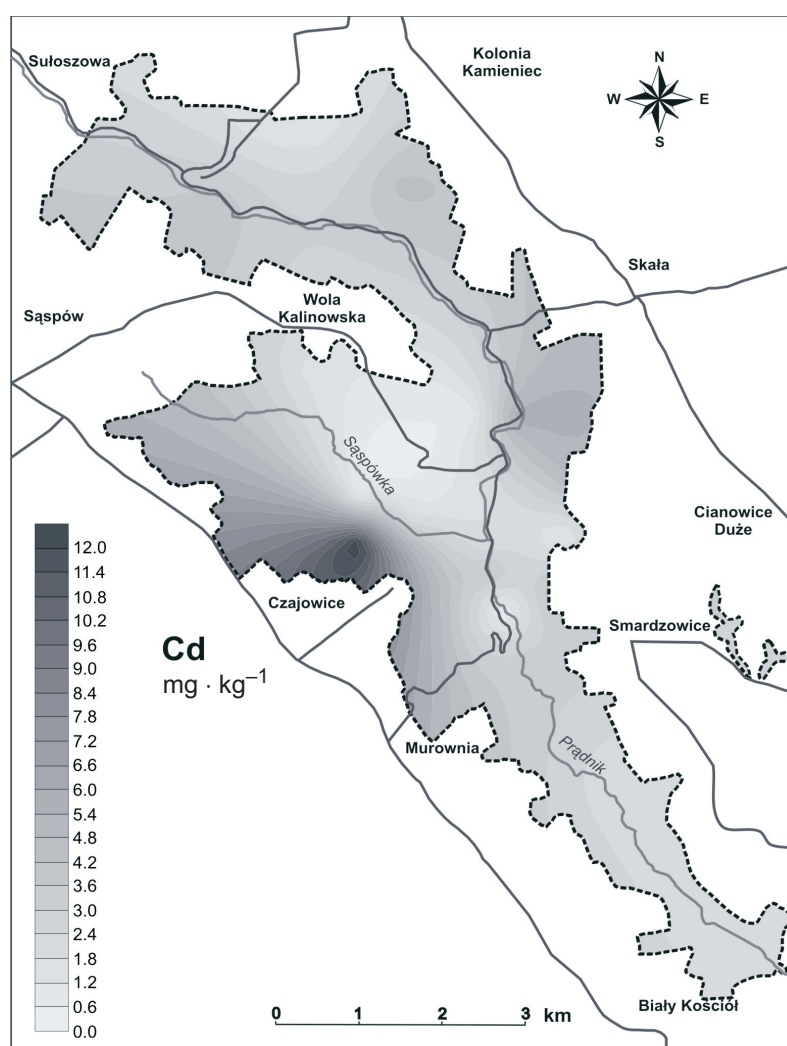


Fig. 1. Cadmium content in surface horizons of the Ojców National Park soils

The soil material was dried at room temperature and sifted through a sieve with 1 mm mesh. Subsequently basic physicochemical properties were determined:

- pH in distilled water with potentiometric method,
- total nitrogen with Kjeldahl method on Kjeltex apparatus (Tecator),
- organic carbon with Tiurin method in Oleksynowa's modification,
- granulometric composition with Casagrande method modified by Proszynski,
- total cadmium content with AAS method using acetylene-air flame for atomization (Philips PU 9100x apparatus) following previous soil solution in a mixture of concentrated nitric(V) and chloric(VII) acids in 2:1 ratio [5].

The obtained results were subjected to statistical analysis using Statistica 6.1 programme; simple correlation coefficients were computed and their significance was determined by t-Student test. Cadmium accumulation indices were also computed as a ratio of the element content in surface and bottom horizons of the profile. Surfer 8.0 software was used to create maps of cadmium occurrence in the park area.

Results and discussion

Cadmium content in surface horizons of the analyzed soils ranged from 0.4 to 12.8 $\text{mg} \cdot \text{kg}^{-1}$ (Table 1). In most cases it is a definitely higher content than mean cadmium concentrations in the soils of Poland, ie 0.2–2 $\text{mg} \cdot \text{kg}^{-1}$ [6]. Such high contents are due to the element deposition from the Olkusz region, which is the colour metal processing centre [7]. The results of investigations on the Ojcow National Park (ONP) soil pollution are identical with the analysis of heavy metal concentrations in moss tissues in the area of Poland conducted by Grodzinska [8] in the late nineties of the previous century. The highest cadmium contents (over 1.5 $\text{mg} \cdot \text{kg}^{-1}$) were assessed in plant samples collected in the Ojcow National Park.

Table 1

Cadmium content in surface horizons of the Ojców National Park soils

Soil type	Horizon	Range of cadmium content (average) [$\text{mg} \cdot \text{kg}^{-1}$]
Rendzinas	O	1.0–1.1 (1.11)
	A	0.4–3.0 (1.18)
Lessive soils	O	12.8
	A	1.7–7.0 (3.72)
Brown soil	A	4.4
Pseudogley soil	O	1.3
River alluvial soil	A	1.9

The highest cadmium content, on average 4.42 $\text{mg} \cdot \text{kg}^{-1}$ (ranging from 1.7–12.8 $\text{mg} \cdot \text{kg}^{-1}$) was characteristic for surface horizons of rendzinas, slightly lower quantities

of this element were found in lessive soils, respectively $1.15 \text{ mg} \cdot \text{kg}^{-1}$ ($0.4\text{--}3.0 \text{ mg} \cdot \text{kg}^{-1}$) (Table 1). The higher content of the analyzed element in rendzinas results from its elevated natural content in Jurassic limestones, which in the north-western part of the Malopolska region are in contact with Trias rocks constituting the source of colour metal ores [7].

In compliance with the Decree of the Minister of the Natural Environment on the soil quality standards and earth quality standards, the soils of national parks are classified to group A soils, where limit numbers for toxic substances content are especially strict [9]. Cadmium content in the group A, above which the soils are considered as polluted, is $1 \text{ mg} \cdot \text{kg}^{-1}$. On the basis of the above – mentioned regulation, as many as 21 profiles of the analyzed Ojcow National Park soils should be regarded as polluted with cadmium. Only 3 lessive soils profiles were characterized by the content lower than $1 \text{ mg} \cdot \text{kg}^{-1}$, therefore may be counted among the unpolluted soils.

When limit numbers for heavy metal content in arable soils as suggested by IUNG were applied, only 3 soils lessives profiles could be counted among the soils with natural cadmium concentrations [11]. 10 profiles (including 4 soils lessives profiles, 4 rendzinas profiles, brown soil and alluvial soil) were classified to the soils with elevated Cd concentrations (I category). 10 profiles of the tested soils, in which 9 were rendzinas were counted among weakly polluted soils (II category) and medium polluted (III category).

Analysis of the spatial distribution of Cd in the ONP area shows that the analyzed element accumulation was the highest in the park soils collected in the area of Czajowice and Skala villages (Fig. 1). Higher concentrations were assessed in the profiles collected in the hilltop parts of the park than in the Pradnik River or Saspowka River Valley. More exposed surface features of the park are more liable to deposition of pollutants flowing from the west.

Accumulation index (AI) computed for the analyzed soils was between 0.2 and 15.9 (Fig. 2). Mean accumulation index was higher for soils lessives (6.07) than for rendzinas (3.19) (Fig. 2). Soils lessives characterized by a relatively low Cd content in their surface horizons, were underlain by carbonate rocks in which higher heavy metal

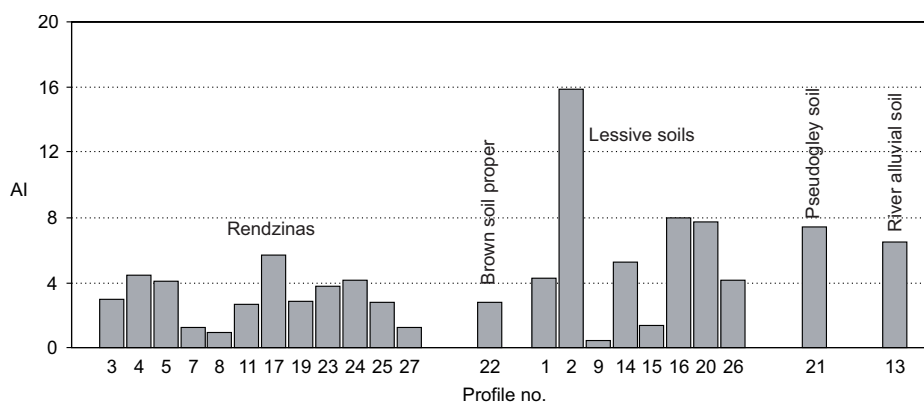


Fig. 2. Accumulation index (AI) calculated for investigated soils

concentrations occur [7]. Low values of AI in rendzinas result both from metal release also in the surface horizons and high permeability of these soils' profiles [12].

On the basis of limit numbers referring to AI suggested by Southerland [13], 5 profiles were counted among the soils with minimum accumulation, 11 to soils with moderate accumulation and 7 to soils with considerable metal accumulation (Table 2). As many as 9 profiles of the analysed rendzinas revealed a moderate or considerable heavy metal accumulation.

Table 2

Classification of cadmium accumulation degree in soils of the Ojcow National Park on the base of AI level

Cadmium accumulation degree	Soil type			Total
	Rendzinas	Lessive soils	Other	
Minimal	3	2	0	5
Moderate	8	2	1	11
High	1	4	2	7

On the basis of the conducted statistical analysis it was found that cadmium content in the investigated soils depended mainly on the soil pH (0.56**) and clay fraction content (< 0.02 mm) (0.48**) (Table 3). It corroborates the results of research on cadmium contamination in forest soils of France [12].

Table 3

Dependence of cadmium content and chosen soil properties

Soil properties	Linear correlation coefficients		
	Rendzinas (14 profiles)	Lessive soils (8 profiles)	Total (24 profiles)
pH _{H₂O}	-0.02	0.94***	0.56**
pH _{KCl}	-0.01	0.85**	0.56**
% C _{org}	0.90***	-0.21	0.28
% N	0.87***	-0.39	0.52
C/N	0.75**	0.26	0.03
% fraction < 0.02	0.08	-0.16	0.48**
% fraction < 0.002	0.90***	0.19	0.35

* significance level 0.05; ** significance level 0.01; *** significance level 0.001.

Conclusions

1. A majority of analysed soils of the Ojcow National Park was considered as polluted with cadmium. It was assessed that the analyzed element accumulation in the investigated soils was moderate or considerable.

2. Accumulation of the analysed element was the highest in the hilltop parts of the park situated in its northern and western regions.

3. Higher cadmium content was assessed in the surface horizons of rendzinas than in lessive soils, whereas the average accumulation index values were the opposite.

4. Cadmium concentrations in the analyzed soils depended mainly on soil reaction and clay fraction content (< 0.02 mm).

References

- [1] Schejbal-Chwastek M. and Marszałek M.: *Geologia Carpathica*, 1999, **50**(5), 409–412.
- [2] Grodzińska K.: [in:] *Zagrożenie Parków Narodowych w Polsce*. Wyd. Nauk. PWN, Warszawa 1985, 23–35.
- [3] Systematyka gleb Polski. *Roczn. Glebozn.* 1989, **40**(3), pp. 150.
- [4] Zalewa S.: [in:] *Badania naukowe w południowej części Wyżyny Krakowsko-Częstochowskiej, Materiały konferencyjne*, Ojców, 2001, 142–147.
- [5] Ostrowska A., Gawliński S. and Szczubiałka Z.: *Metody analizy i oceny właściwości gleb i roślin.*, Katalog. Instytut Ochrony Środowiska, Warszawa 1991, pp. 334.
- [6] Kabata-Pendias A. and Pendias H.: *Biogeochemia pierwiastków śladowych*. Wyd. Nauk. PWN, Warszawa 1999, pp. 400.
- [7] Gleby [in:] *Raport o stanie środowiska w województwie małopolskim w 2007 roku*. WIOŚ, Kraków 2008, 155–173.
- [8] Grodzińska K., Szarek-Lukaszewska G. and Godzik B.: *Sci. Total Environ.* 1999, **229**, 41–51.
- [9] Rozporządzenie Ministra Środowiska z 9 września 2002 roku w sprawie standardów jakości gleby oraz standardów jakości ziemi. *DzU* 2002, nr 165, poz. 1359.
- [11] Kabata-Pendias A., Motowicka-Terelak T., Piotrowska M., Terelak H. and Witek T.: *IUNG*, Puławy 1993, ser. **P 53**, 1–14.
- [12] Probst A., Hernandez L., Probst J.I. and Ulrich E.: *J. Phys. IV France* 2003, **107**, 1107–1110.
- [13] Southerland R.A.: *Environ. Geology* 2000, **39**, 611–627.

KADM W GLEBACH OJCOWSKIEGO PARKU NARODOWEGO

Katedra Gleboznawstwa i Ochrony Gleb
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem badań było określenie zanieczyszczenia kadmem gleb Ojcowskiego Parku Narodowego i określenie wpływu położenia, typu i właściwości gleb na stopień zanieczyszczenia tym pierwiastkiem. Badania zostały przeprowadzone na próbkach glebowych pochodzących z 24 profilów glebowych reprezentujących główne jednostki typologiczne pokrywy glebowej parku: rędziny (13 profilów), gleby płowe (8 profilów), gleby brunatne właściwe (1 profil), gleby opadowo-glejowe (1 profil) i mady (1 profil). Zawartość kadmu w poziomach powierzchniowych badanych gleb wynosiła od 0,4 do 12,8 mg · kg⁻¹. Na podstawie porównania z normami zaproponowanymi przez IUNG oraz zdefiniowanymi w Rozporządzeniu Ministra Środowiska z 2002 w sprawie standardów jakości gleby oraz standardów jakości ziemi, stwierdzono, że prawie wszystkie (oprócz 2 profilów gleb płowych) badane gleby (24 profile) Ojcowskiego Parku Narodowego należy uznać za zanieczyszczone kadmem. Zawartość kadmu była największa w glebach parku pobranych w rejonie Czajowic oraz Skały. W rędzinach oznaczono wyższą zawartość badanego pierwiastka niż w glebach płowych. Z kolei obliczony wskaźnik akumulacji był większy dla gleb płowych niż dla rędzin. Według przeprowadzonej analizy statystycznej stwierdzono, że zawartość kadmu w badanych glebach zależała od odczynu i zawartości frakcji $< 0,02$ mm.

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