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## SULPHUR IN THE FOREST SOILS OF THE OJCOW NATIONAL PARK

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**Abstract:** The aim of this study was to determine the effect of the pedogenesis on the sulfur content in the forest soils of the Ojców National Park (OPN). The study was carried out on soils representing the main units of OPN soil cover: brown rendzinas and soils lessives. Studied soils were characterized by a high variability of sulphate sulfur content within the profiles. The surface OI horizons contained the highest amount of SO<sub>4</sub>-S (in rendzinas 104.2–248.0 mg · kg<sup>-1</sup>, in soils lessives 101.0–232.0 mg · kg<sup>-1</sup>) and a significantly higher than deeper horizons. The concentration of sulfur in the humus A horizons was lower (in rendzinas 14.1–91.4 mg · kg<sup>-1</sup>, in soils lessives 16.5–35.5 mg · kg<sup>-1</sup>) and similar to the values in the horizons of parent rock (in rendzinas 12.5–26.9 mg · kg<sup>-1</sup>, in soils lessives 9.1–67.5 mg · kg<sup>-1</sup>). Content of SO<sub>4</sub>-S was not varied between the Et eluvial horizons (15.9–47.3 mg kg<sup>-1</sup>) and illuvial Bt horizons (12.3–49.8 mg · kg<sup>-1</sup>). The direction of pedogenesis had no effect on the vertical distribution of sulfur. This set was caused probably by a high variability of relief and profiles diversity within a type unit. Moreover, the content of the analyzed component was determined by a geographical location of soils and specific microclimatic conditions of the Ojców National Park.

**Keywords:** sulphur, soils, the Ojców National Park

### Introduction

The Ojców National Park (OPN) is considered as one of the most polluted national parks in Poland for more than last three decades [1–5]. The location in the neighborhood of Silesian and Cracow agglomeration and specific climate conditions, associated with the local terrain relief, is the main reason of the high concentration of pollutants in the OPN [4, 6].

Atmospheric sulfur infiltrates into the soil with precipitation and occurs in soil in the form of sulphides and sulphates or is bound with soil organic matter. Sulphate ions may be leached from the soil or adsorbed by humic and fulvic acids, sesquioxides, clay

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minerals, as well as occluded by calcite. Transformation of sulfur is highly dependent on soil-forming processes, as well as on climatic and habitat conditions [7–11].

The study was aimed to determine the effect of the pedogenesis on the sulfur content in soils of the Ojców National Park.

## Material and methods

The soil material was taken from horizons of 23 profiles located in the Ojców National Park. Studied soils represented the main units of soil cover of the Ojców National Park: brown rendzinas (15 profiles) and soils lessives (8 profiles) (Fig. 1) [12, 13].

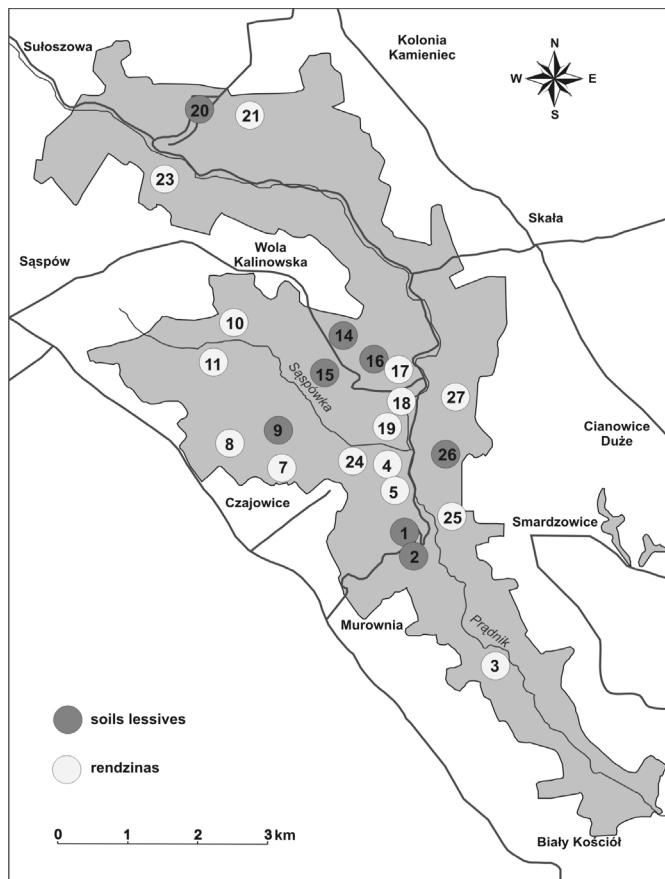


Fig. 1. Location of studied soils profiles in the Ojców National Park

Rendzinas have been derived from Jurassic limestones and soils lessives were developed on loess sediments, underlaid by limestones. Soil profiles were located only in forests.

Soil material was dried at room temperature and sieved through a sieve with a mesh of 2 mm. The sulphate sulfur in soil was determined using the ICP-AES method after earlier extraction with a  $0.3 \text{ mol} \cdot \text{dm}^{-3}$  HCl solution with the addition of activated carbon [9].

Spearman rank correlation coefficients were calculated between main soil parameters and sulphur content using Statistica 10.1 software [14]. The statistical differences in the sulfur content of corresponding horizons of soils lessives and rendzinas were determined using the Kruskal-Wallis test. Profile distribution of sulfur in studied soils was evaluated as well.

The sulfur accumulation index (AI) was also calculated as the ratio of its content in surface horizon (O1 or A) and in horizon of the parent rock. The maps of sulfur spatial distribution in O1 and A horizons were performed using kriging method in Surfer 8.0 software.

## Results and discussion

Studied soils were characterized by a high variability of sulphate sulfur content within the profiles, what was confirmed statistically (Table 1).

Table 1

Sulphur content in studied soils (minimum, maximum, mean). Means followed by the same letters do not differ significantly ( $p = 0.05$ ) in Kruskal-Wallis test

Horizon	Rendzinias [mg · kg <sup>-1</sup> ]	Horizon	Soils lessives [mg · kg <sup>-1</sup> ]
O1	<u>104.2–248.0</u> 160.6 (a)	O1	<u>101.0–232.0</u> 157.1 (a)
A	<u>14.1–91.4</u> 27.8 (b)	A	<u>16.5–35.1</u> 26.2 (b)
Cca	<u>12.5–26.9</u> 19.5 (b)	Et	<u>15.9–47.3</u> 27.8 (b)
		Bt	<u>12.3–49.8</u> 25.6 (b)
		C	<u>9.1–67.5</u> 31.5 (b)

The highest amounts of SO<sub>4</sub>-S contained the organic surface O1 horizons. The content of sulfur in the organic horizons of rendzinias ranged from 104.2 to 248.0 mg · kg<sup>-1</sup>, and in the organic horizons of soils lessives from 101.0 to 232.0 mg · kg<sup>-1</sup>. In the organic horizons of soils of the Tatra National Park were determined similar values of SO<sub>4</sub>-S content – 55.4–280 mg · kg<sup>-1</sup> [15].

Sulphur content in the humus horizons was significantly lower than in the organic horizons and ranged in rendzinias from 14.1 to 91.4 mg · kg<sup>-1</sup> and in soils lessives from 16.5 to 35.5 mg · kg<sup>-1</sup>. In the parent rock horizons were determined similar amounts of

$\text{SO}_4\text{-S}$  to the humus horizons – in rendzinas from 12.5 to 26.9  $\text{mg} \cdot \text{kg}^{-1}$ , and in soils lessives from 9.1 to 67.5  $\text{mg} \cdot \text{kg}^{-1}$ . The decisive role as a barrier in sulphate sulfur transport into the deeper parts of the soil profile have the humus-rich surface horizons, what was reported in previous studies as well [16]. There were no statistically significant differences in the sulfur content between the corresponding horizons of soils lessives and rendzinas.

The accumulation of sulfur in humus horizons was statistically dependent on total nitrogen content ( $r_s = 0.6410$ ,  $p = 0.001$ ) and organic carbon content ( $r_s = 0.4454$ ,  $p = 0.05$ ) (Fig. 2). Similar correlation was found in soils of the Tatra National Park [15].

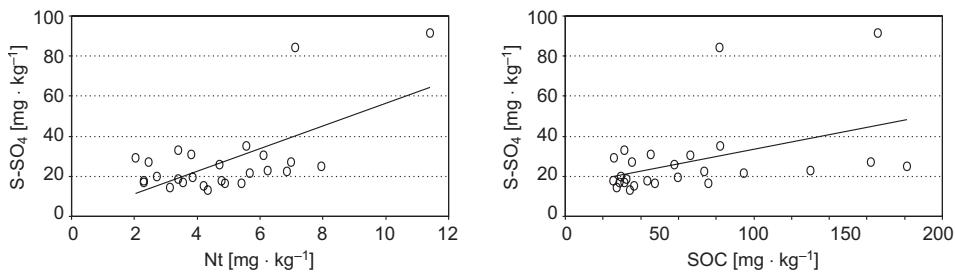


Fig. 2. Sulphur content related to total nitrogen content – Nt ( $r_s = 0.6410$ ,  $p = 0.001$ ) and organic carbon content – SOC ( $r_s = 0.4454$ ,  $p = 0.05$ )

Calculated accumulation index (AI) values for the organic Ol horizons were significantly higher than the values determined for corresponding humus horizons. The values of AI for rendzinas and soils lessives were similar (Fig. 3).

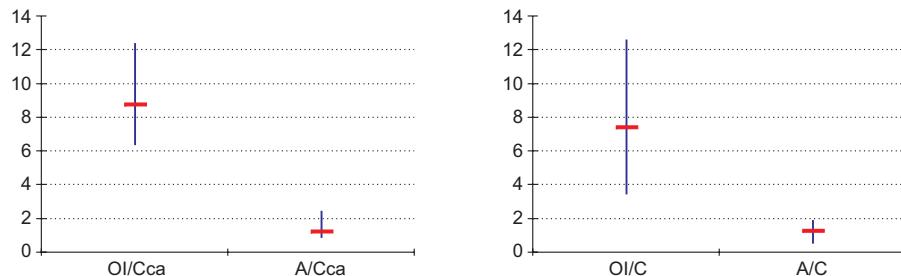


Fig. 3. Accumulation index (AI) calculated for investigated rendzinas (above) and soils lessives (below)

Sulphate sulfur content in soils was conditioned by the location of soils. The highest amounts of  $\text{SO}_4\text{-S}$  in organic horizons were found in soils located within the Pradnik Valley, in the section of the Ojców – Pradnik Korzkiewski. However, the largest values of  $\text{SO}_4\text{-S}$  in humus horizons were determined in soils of Wola Kalinowska village (Fig. 4).

The pedogenesis direction in soils lessives had no effect on the profile distribution of sulfur. Concentration of  $\text{SO}_4\text{-S}$  did not vary significant between eluvial (Et) and illuvial horizons (Bt), and ranged from 15.9 to 47.3  $\text{mg} \cdot \text{kg}^{-1}$  and from 12.3 to 49.8  $\text{mg} \cdot \text{kg}^{-1}$ ,

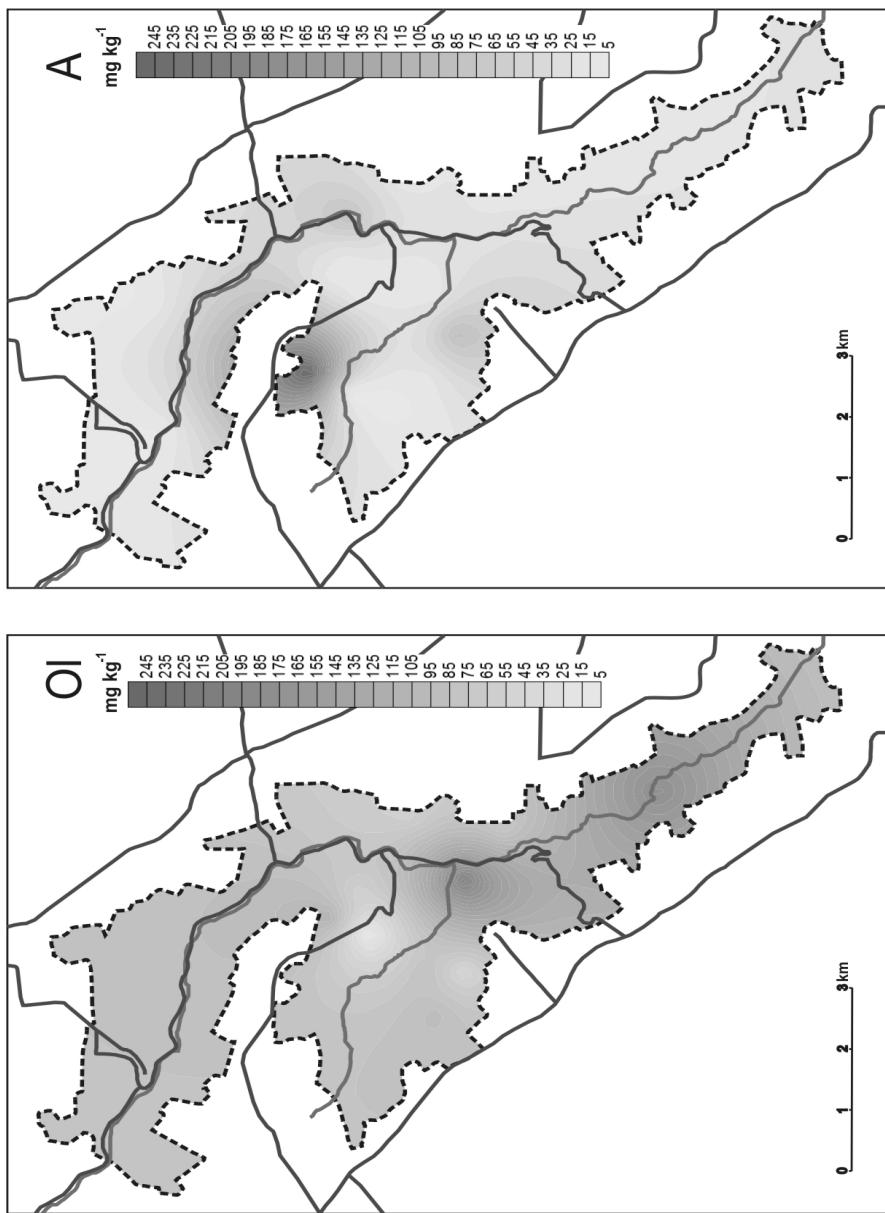


Fig. 4. Sulphur content [ $\text{mg} \cdot \text{kg}^{-1}$ ] in organic (OI) and humus (A) horizons of studied soils

respectively (Fig. 5). Differences in content of  $\text{SO}_4\text{-S}$  in genetic horizons are similar in all studied rendzinas profiles (Fig. 5). Profile distribution of sulphur in rendzinas was similar to soils lessives. Determined sulfur content in profiles of soils lessives and rendzinas was dependent mainly on the humus accumulation process [16].

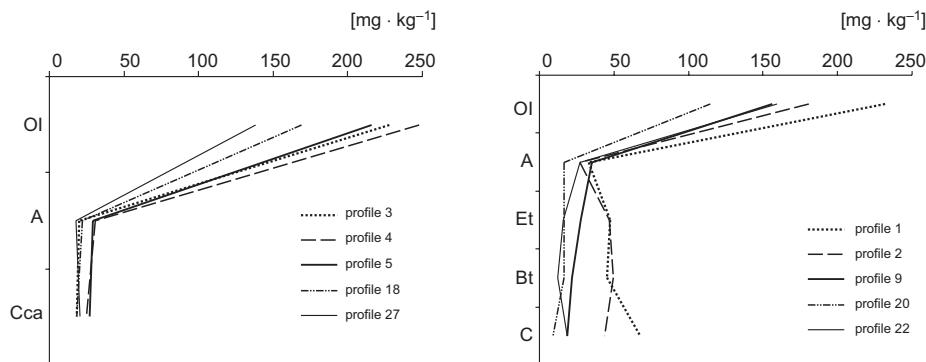


Fig. 5. Profile distribution of sulphur in chosen rendzinas (above) and soils lessives (below)

Therefore, there was no evident effect of soil direction development on the content of sulphate sulfur, what was previously reported by Skłodowski [9] in the soils lessives and by Zadrożny and Miechowka [15] in podzols. The high variability of relief and diversity within a soil type unit was the reason.

Moreover, the content of the analyzed component was determined primarily by the specific terrain relief and secondary by the geographical location of soils. The amount of deposited in soil air pollutants containing sulfur compounds was determined also by local climate conditions, which vary greatly on the area of the Ojców National Park [4, 13, 17].

## Conclusions

1. The highest content of sulphate sulfur in soils of the Ojców National Park was determined in organic OI horizons.
2. There were no significant differences in sulphate sulfur content, profile distribution and accumulation indices between soils lessives and rendzinas.
3. Organic horizons of soils located in the Pradnik Valley, within the section Ojców – Pradnik Korzkiewski, were characterized by a highest content of  $\text{SO}_4\text{-S}$ . The highest content of sulphur in humus horizons was determined in soils of the area of Wola Kalinowska village.

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## SIARKA W GLEBACH LEŚNYCH OJCOWSKIEGO PARKU NARODOWEGO

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**Abstrakt:** Celem pracy było określenie wpływu kierunku pedogenezy na zawartość siarki w glebach leśnych Ojcowskiego Parku Narodowego (OPN). Badaniami objęto gleby reprezentujące główne jednostki pokrywy glebowej OPN: rędziny brunatne i gleby płowe. Badane gleby charakteryzowały się dużą zmiennością zawartości siarki siarczanowej w obrębie profilu. Największe ilości  $\text{S-SO}_4$  zawierały powierzchniowe poziomy organiczne Ol (rędziny 104,2–248,0  $\text{mg} \cdot \text{kg}^{-1}$ , gleby płowe 101,0–232,0  $\text{mg} \cdot \text{kg}^{-1}$ ). W poziomach próchniczych A zawartość siarki była niższa (rędziny 14,1–91,4  $\text{mg} \cdot \text{kg}^{-1}$ , gleby płowe 16,5–35,5  $\text{mg} \cdot \text{kg}^{-1}$ ) i zbliżona do wartości w poziomach spagowych analizowanych profiliów (rędziny 12,5–26,9  $\text{mg} \cdot \text{kg}^{-1}$ , gleby płowe 9,1–67,5  $\text{mg} \cdot \text{kg}^{-1}$ ). W glebach płowych stwierdzono małe zróżnicowanie pomiędzy poziomami eluwialnymi (Et, 15,9–47,3  $\text{mg} \cdot \text{kg}^{-1}$ ) a iluwialnymi (Bt, 12,3–49,8  $\text{mg} \cdot \text{kg}^{-1}$ ). W badanych glebach nie stwierdzono wpływu kierunku pedogenezy i ich rozwoju na zawartość siarki siarczanowej. Było to prawdopodobnie spowodowane dużą zmiennością rzeźby i zróżnicowaniem badanych profiliów w obrębie danego typu. Ponadto wydaje się zasadne stwierdzenie, że zawartość analizowanego składnika była najbardziej determinowana specyfiką ukształtowania terenu i położeniem geograficznym badanych gleb.

**Słowa kluczowe:** siarka, gleby, Ojcowski Park Narodowy

