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CONTENT OF SULPHATE SULPHUR IN DIFFERENT TYPES OF SOILS IN THE PODKARPACKIE REGION

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Abstract. The aim of the investigation was the estimation of sulphate sulphur in soils in the Podkarpackie Province. The content of sulphate sulphur within the soils developed on flysch works subject to strong spatial variability of 0.87 g kg⁻¹ in the Przemyśl Foothills to 2.00 g kg⁻¹ in the Cieżkowickie and Strzyżowskie Foothills. The content of sulphate sulphur in soils is positively correlated with the content of humus in the Western Bieszczady Mountains and the content of colloidal clay fraction within the Tarnogrodzki Plateau and Rzeszów Foothills. In soil types: Haplic Cambisol, Haplic Cambisol (Dystric), Haplic Cambisol Podzolised, Haplic Podzol and Haplic Luvisol found in the Podkarpackie Province there is no significant variation of the sulphate sulphur content (average 1.73-1.93 mg 100g⁻¹), but less sulphur was found in Haplic Cambisol (Eutric) soils.

Sulphur is an element which commonly occurs in nature and is necessary for proper functioning of living organisms. Its total content in the soils of Poland ranges from 70 to 1070 mg kg⁻¹ [11] and depends on the type of parent rock, organic matter content, as well as fertilization [18]. The greatest amounts of total sulphur are included in chernozem soils, alluvial soils and black earth. A deficit of sulphur occurs in soils derived from light loamy sands and weakly loamy sands, which is related to their small content of organic matter. The easily soluble sulphate fraction of sulphur typically constitutes a small percentage of its total content. Some researchers have investigated the problem of sulphur shortages in soils under heavy agricultural usage [10]. Others have researched the anthropogenic emission of sulphur into the atmosphere, which induces local soil contamination and, in consequence, leads to chemical degradation of soils [21]. The aim of this research was to assess the content of sulphur in the soils of the Podkarpackie Region in the regional and typological sense according to the physical and physical-chemical properties of these soils.

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MATERIAL AND METHODS

The analysis of the spatial differentiation of the content of sulphate sulphur in the soils of the Podkarpackie Region was carried out based on the results of tests of 2061 soil samples taken at the Regional Chemical-Agricultural Station in Rzeszów (Fig. 1). These samples were taken from the soils of agricultural areas (arable and permanent grassland) and the specific location of the sample was determined by the knots of the square-based net with 2 km long sides. During the field work, the soil type was determined acc. to FAO classification [4] and the samples were taken from the 0-20 cm (n = 1 678), and 20-40 cm (n = 383) depths.



Fig. 1. Mezoregions in Podkarpackie Province according to Kondracki [7] – with modification. Explanations: Roztocze Wschodnie – 343.23 (n=10); Pogórze Strzyżowskie – 513.63 (n=33); Nizina Nadwiślańska – 512.41 (n=24); Pogórze Synowskie – 513.64 (n=414); Płaskowyż Tarnowski – 512.43 (n=5); Pogórze Przemyskie – 513.65 (n= 60); Dolina Dolnej Wisłoki – 512.44 (n=40); Kotlina Jasielsko-Sanocka – 513.67 (n=49); Dolina Dolnego Sanu – 512.46 (n=62); Pogórze Jasielskie – 513.68 (n=70); Równina Biłgorajska – 512.47 (n=5); Pogórze Bukowskie – 513.69 (n=78); Płaskowyż Kolbuszowski – 512.48 (n=184); Beskid Niski – 513.71 (n=59); Płaskowyż Tarnogrodzki – 512.49 (n=106); Płaskowyż Chyrowski – 521.11 (n=3); Pradolina Podkarpacka – 512.51 (n=62); Góry Sanocko-Turczańskie – 522.11 (n=74); Podgórze Rzeszowskie – 512.52 (n=242); Bieszczady Zachodnie – 522.12 (n=72); Pogórze Ciężkowickie – 513.62 (n=25); n – number of samples.

The mean content of sulphate sulphur in the particular soil types and physiographic units are presented in Table 1. The types and units with the count below 10 were excluded from further statistical analysis or were incorporated into the adhering units.

The Podkarpackie Region shows a clear differentiation in terms of climate conditions and the landscape, which is related to its genesis. The northern part of the region, with the exception of Roztocze, is located within the Sandomierska Basin macro-region and is of a plain character formed by glacier sediments and is

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						Soil 1	types					;
Physico-geographical regic	suc	1	2	3	4	5	9	7	8	6	10	Mean
Nizina Nadwiślańska and	А	1.38	ı	I	1.63	ı	ı	2.36	ı	1.81	2.29	1.89
Dolnej Wisłoki	В	1.38-1.38	ı	ı	0.17-3.0	ı	ı	2.13-2.65	0.37-3.76	0.12-2.88	1.2-5.13	0.12-5.13
, , , ,	А	1.80	ı	ı	1.58	ı	I	0.75	0.90	0.17	1.76	1.07
Dolina Dolnego Sanu	В	0.42-3.70	ı	ı	0.05-3.87	ı	ı	0.75-0.75	0.12-1.67	0.17-0.17	0.3 - 4.0	0.05-4.0
:	А	1.59	ı	0.77	1.65	3.38	I	2.85	1.56	2.45	1.93	2.02
Płaskowyż Kolbuszowski	В	0.15-4.35	1	0.62-0.92	0.17-4.0	2.5-4.25	ı	1.62-5.50	0.5-3.62	0.3-4.25	0.17-6.0	0.15-5.50
	А	1.90	ı	1	1.32		I	3.09	3.25	ı	1.91	2.29
Płaskowyż Tarnogrodzki	В	0.12-8.12	ı	ı	0.2-2.55	ı	ı	0.43-7.50	1.2-7.33	ı	0.43-4.30	0.12-8.12
:	А	1.58	ı	ı	1.69		0.12	1.22	1.32	1.51	1.60	1.29
Pradolina Podkarpacka	В	0.1-3.8	ı	ı	0.12-7.63	ı	0.12-0.12	0.8-1.50	0.12-2.62	0.07-5.75	0.3-0.3	0.07-7.63
	А	1.80	ı	2.29	1.68	2.18	1.81	2.12	1.19	1.80	1.75	1.85
Podgórze Rzeszowskie	В	0.12-6.12	ı	0.75-2.37	0.11-8.25	1.87-2.87	0.05-5.37	2.12-2.12	0.15-7.5	0.13-12	0.17-2.37	0.05-12
Pogórze Cieżkowickie	A	2.02	2.47	ı	1.91	1.71	ı	ı	2.38	ı	1.53	2.00
And Strzyżowskie	В	0.1-4.07	1.5-3.4	ı	0.37-4.5	0.3-2.4	ı	ı	0.15-3.25	ı	0.8-2.3	0.1-4.5
	Α	1.68	1.97	2.30	1.51	1.72	2.10	0.13	1.65	1.43	1.28	1.58
Pogorze Dynowskie	В	0.1-4.25	0.5-5.5	2.30-2.30	0.07-5.12	0.3-4.25	2.10-2.10	0.13-0.13	0.05-4.76	0.05-3.5	0.12-6	0.05-6
	A	0.89	I	I	1.22	I	1.31	I	0.05	I	I	0.87
Pogorze Przemyskie	В	0.15-2.50	,	ı	0.12-4.12	,	0.2-2.42	ı	0.05-0.05	ı	ı	0.05-4.12

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Physico-geographical regic	suc	1	2	3	4	5	9	7	8	6	10	Mean
	Α	1.74	1.74	0.08	1.82	1.68	ı	2.12	1.66	ı	2.37	1.65
Kotlina Jasielsko-Sanocka	В	0.92-2.37	0.87-3.5	0.05-0.1	0.25-3.8	0.05-3.0	ı	2.12-2.12	0.25-3.25	ı	2.37-2.37	0.05-3.8
	Α	2.00	1.37	1.50	1.32	1.75	I	1.37	2.82	ı	1.87	1.75
Pogorze Jasielskie	В	0.65-3.25	1.37-1.37	1.50-1.50	0.12-6.5	0.05-7.25	I	1.37-1.37	0.2-7.12	ı	1.87-1.87	0.05-7.25
- - - -	А	0.12	1.70	1.19	1.17	1.67	I	I	0.51	0.20	1.64	1.03
Pogorze Bukowskie	В	0.12-0.12	1.07-2.33	0.25-2	0.05-3	0.05-6.37	I	I	0.2-1.25	0.20-0.20	1.3-2.12	0.05-6.37
	Α	I	I	I	1.61	1.40	I	I	1.29	1.60	1.08	1.40
Beskid Niski	В	I	I	ı	0.12-5	0.5-3.17	ı	I	0.89-2.05	0.25-2.9	0.2-1.55	0.12-5
Góry	Α	1.62	1.82	0.15	1.45	1.70	I	I	1.22	I	ı	1.32
Sanocko-Turczańskie	В	0.12-3.12	1.37-2.37	0.15-0.15	0.12-3.7	0.1-5.5	I	I	0.37-2.12	I	ı	0.1-5.5
	A	0.13	1.29	2.35	1.25	1.94	I	I	1.22	1.45	ı	1.38
Bieszczady Zachodnie	В	0.13-0.13	0.37-3.75	0.25-4.75	0.18-3.5	0.25-5.24	ı	I	0.17-2.45	0.8-2.3	ı	0.13-5.24
Mean		1.35	2.00	1.27	1.52	1.91	1.34	1.78	1.50	1.38	1.75	1.56
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*Soil types: 1 - Haplic Podzol, n=271; 2 - Haplic Luvisol, n= 48; 3 - Haplic Cambisol, n= 41; 4 - Haplic Cambisol (Eutric), n= 609; 5 - Haplic Cambisol (Dystric), n= 157; 6 - Haplic Chernozem, n=40; 7 - Gleyic Chernozem, n=21; 8 - Haplic Fluvisol, n=138; 9 - Endofluvic Phaseozem, n= 98; 10 - Haplic Cambisol (Spodic), n=210. n - numer of samples.

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characterized by long warm summers, relatively mild winters and a small yearly sum of precipitation (700 mm in the Kolbuszowski Plateau). Within its area, there are wide river valleys of the Vistula, Wisłoka and San. The southern part is composed of the Karpathian flysh detritus with a hilly terrain (Pogórze Środkowobeskidzkie) and mid-range mountain terrain (Beskidy Środkowe and Beskidy Lesiste).

The climate becomes more raw (daily and yearly air temperature amplitudes increase) with the increasing elevation above sea level, where the rainfall reaches 1200 mm. The grain size distribution was assessed in the soil samples using the Cassagrande method as modified by Prószyński, the reaction using the potentiometer method in a 1 M KCl solution, the content of organic carbon using the Tiurin method and the content of sulphate sulphur using the Bardsley and Lancaster method used in monitoring research [1].

The results were statistically analyzed including the calculation of correlations between the content of S-SO₄ in the investigated soils and the basic properties of these soils. In cases of significant correlations, regression equations were estimated using linear and multiple regression at the significance level of p=0.05. The regression equations containing the reaction (pH) can only be used for estimating the direction of the changes in the content of sulphate sulphur in the soils and cannot be used to assess its content. In addition, an analysis of variability was carried out and the significance of the differences between the sulphur content in the region, types of soils and the particular groups of soil reaction were assessed. The analyses were performed using Statistica 8 software.

RESULTS AND DISCUSSION

The soils of the northern part of the Podkarpackie Region, derived from post-glacial formations, are classified as light soils in terms of their grain-size distribution. In the Kolbuszowski Plateau, representative for this region, sands constitute 81%, loams 14% and silt formations 5%. The light post-glacial sediments are intensely washed out; therefore, the highly acidic and acidic soils dominate in these areas. In the relatively big region of the Tarnogrodzki Plateau, the percentage of highly acidic soils is 33%, acidic 33%, neutral 16% and there are no soils with a basic reaction. In the soils of the northern part of the Region, organic matter is subject to processes of intensive decomposition, which leads to the relatively fast mineralization. The content of humus in the surface horizon of these soils is, on average, from 1.27% in Roztocze to 1.88% in the Kolbuszowski Plateau.

The southern part of the Podkarpackie Region, covered by the *in situ* detritus of the Karpathian flysh, is characterized by a high content of heavy soils. In the Beskid Niski area, clay formations constitute 36%, loams 61% and the remaining

3% are silts. The soils derived from the flysh detritus have lower acidity than those derived from post-glacial sediments. In some regions, areas of basic reaction soils occur. In the region of Pogórze Jasielskie, adhering to Beskid Niski, the content of highly acidic soils is 33%, acidic 36%, while neutral and basic soils represent 18%. In the conditions of a more extreme climate and at higher humidity levels compared to the northern part of the Region, the greatest content of organic matter becomes humified. Thus, the content of humus in the soils of the southern part of the Region reaches 3.57% (in Beskid Niski).

The climate-flora-soil conditions promote the occurrence of the zonal brown soils in the Podkarpackie Region. Local rainfall and temperature, as well as the permeability of the parent rock differentiate the morphological picture of the brown soil profile, which is accompanied by further features of the other soil-formation processes (Table 1).

In the northern part of the Region, in the Kolbuszowski Plateau, the highest content is that of brown soils Haplic Cambisol – 51%, brown leached soils Haplic Cambisol (Eutric) – 19% and proper podzolic soils Haplic Podzol – 16%. In the southern part, in Beskid Niski, brown leached soils Haplic Cambisol (Eutric) represent 56% and the acidic brown soils Haplic Cambisol (Dystric) – 10%.

The content of sulphate sulphur in the soils of the selected regions of the Podkarpackie Region, measured in the surface horizon 0-20 cm was differentiated (Table 1). The highest mean values of S-SO₄ occurred in the soils of the northwestern part of the Region, in the Tarnogrodzki Plateau – 2.29 mg 100 g⁻¹ of the soil, as well as in the Kolbuszowski Plateau – 2.02 mg 100 g⁻¹. The lowest mean values were observed in the southeastern part of the Region, in the soils of the Przemyskie Foothills - 0.87 mg 100 g⁻¹ of the soil, Bukowskie Foothills – 1.03 mg 100 g⁻¹ and the Lower San River Valley – 1.07 mg 100 g⁻¹ (Table 1).

The collected analytical material, after verifying the counts, allowed for distinguishing three groups of uniform regions. The group with the lowest sulphate sulphur content in the soil (below 1.5) included Przemyskie Foothills, Bukowskie Foothills, Beskid Niski, Sanocko-Turczańskie Mountains and the Podkarpacka Proglacial Stream Valley. Higher sulphur contents (1.6-1.7 mg S-SO₄ g⁻¹) were found in the soils of the Western Bieszczady, Jasielsko-Sanocka Basin, Lower San River Valley and Jasielskie Foothills. The highest sulphate sulphur contents (above 1.8 mg 100 g⁻¹) were observed in the soils of the Kolbuszowski Plateau, Tarnogrodzki Plateau, Ciężkowicko-Strzyżowskie Foothills, Nadwiślańska Valley and Wisłoka Valley.

Motowicka-Teralak and Terelak [11] stated that the mean content of sulphate sulphur in Polish soils is 17.9 mg kg⁻¹ of soil. Other research [17, 18] indicates much higher contents (up to 500 mg kg⁻¹) of this fraction of sulphur in the soils. Koter *et al.* [8] found from trace amounts to 15 mg S-SO₄ kg⁻¹ of soil. Values similar to the above literature were obtained by Rejman-Czajkowska [12].

Wlaśniewski *et al.* [19], while investigating the soils of the Kolbuszowski region, stated that the measured mean content of sulphate sulphur 2.19 mg 100 g⁻¹ is a low natural content, while in the soils of the Kolbuszowa county the value of 3.15 mg 100 g⁻¹ is a high natural content. The content observed in the town of Zarębki (>3.5 mg 100 g⁻¹) was described as elevated due to anthropogenic pressure. According to these authors, this zonal differentiation is a result of the activity of local sources of SO₂ emission. Szulc *et al.* [16] investigated the content of sulphate sulphur according to the systems of soil cultivation and showed that the highest content of S-SO₄ in the soil (34 mg g⁻¹) occurred in the conditions of deep tillage performed every 5 years. The lowest content (27.2 mg g⁻¹) was found in the combination, in which simplified cultivation with direct sowing was used.

In the authors research on the soils of the Podkarpackie Region it was found that there was a great differentiation of the mean contents of sulphate sulphur depending on the genetic type of the soil. The highest means were found in grey-brown podzolic soils (Table 1), in which it was 2.00 mg 100 g⁻¹ of soil. In acidic brown soils, this content was 1.91 mg 100 g⁻¹ g and in proper black earth 1.78 mg 100 g⁻¹ g. In the remaining soil types, these values were as follows: 1.75 mg in brown podzolic soils; 1.52 in brown leached soils; 1.50 in proper alluvial soils; 1.38 in chernozem alluvial soils; 1.35 in proper podzolic soils; 1.34 in proper chernozems; and 1.27 mg 100 g⁻¹ of soil in proper brown soils.

The analysis of the variability on the verified count of the analytical material showed significant differences in the content of sulphate sulphur in the selected soil types of the Podkarpackie Region. Lower contents of sulphate sulphur were observed in brown leached soils (mean of $1.52 \text{ mg } 100 \text{ g}^{-1}$), while a significantly higher content ($1.73-1.93 \text{ mg } 100 \text{ g}^{-1}$) was found in the uniform group of the following types: acidic brown, proper and podzolized brown, and proper and grey brown podzolic soils.

The content of sulphate sulphur is influenced by numerous processes occurring in the soil, such as the process of washing. Measurement of the loss of sulphur caused by washing is difficult due to the fact that the intensity of washing depends on many factors, such as: soil type; content of iron and aluminum oxides; concentration of sulphates; pH of the soil; and the amount of atmospheric precipitation [15]. In general, it is assumed that the process of washing of sulphur is the most intensified in sandy soil, which is related mainly to their low sorptive capacity [6]. The distribution of sulphate sulphur in the soil profile may be related to the process of pedogenesis. While investigating podzolic soils in the Tatra Mountains, Zadrożny *et al.* [20] showed that the sub-surface levels spodic contained much higher amounts of this element than the surface levels albic.

The high number of the analyzed soil samples allowed also a more detailed interpretation of the content of sulphate sulphur based on the basic physical-chemical properties. This interpretation is limited to the statistically significant relationships. In the group of highly acidic soils, the mean content of sulphate sulphur was the highest $-2.02 \text{ mg } 100 \text{ g}^{-1}$ regardless of the type of the soil process or mezoregion (Fig. 2). In the group of acidic soils, it was 1.59 mg 100 g⁻¹ and was higher than the sulphur content in the group of lightly acidic and neutral soils (which did not show significant differences), in which it was 1.42 and 1.24 mg 100 g⁻¹ respectively.

In the soils of the following regions, a negative correlation between the content of sulphate sulphur and the soil reaction was found: Dynowskie Foothills (-0.25); Przemyskie Foothills (-0.25); Rzeszowskie Foothills (-0.30); Sanocko-Turczańskie Mountains (-0.40); Kolbuszowski Plateau (-0.21); Podkarpacka Proglacial Stream Valley (-0.44); and Lower San River Valley (-0.26). This corresponds with the results presented by Motowicka-Terelak and Terelak [11] in terms of the strong correlation between these soil properties. Singh *et al.* [14] explain that lowering the soil pH leads to an increase in the sorption of sulphate ions by the particles of the solid phase. Opposite results were obtained by Kulczycki and Patorczyk-Pytlik [9], who observed a significant positive relationship between the content of sulphate sulphur and the reaction in the 5-20 cm soil horizon (the reaction represented 12% in the assessment of the components of the variance).

In the soils of Western Bieszczady, a positive correlation between the content of sulphate sulphur and humus was stated. This is in accordance with the thesis of Eriksen *et al.* [3], who stated that the amount of easily soluble sulphates in the soil profile is dependent upon the content of organic matter. Diamond and Hanley [2] and Kulczycki and Patorczyk-Pytlik [9] indicated the high correlation between the content of sulphate sulphur and the organic carbon in the surface horizon (up to 20 cm). Similar relationship was observed by Terelak *et al.* [17].

Moreover, in the cultivated soils of Western Bieszczady, in the region characterized by one of the highest mean contents of humus (3.27%), the content sulphate sulphur was negatively correlated with the soil reaction. This relationship may be described by the following regression equation: $S-SO_4=3.70+0.13\%$ humus-0.38 pH. From the analysis of the soils of the Tarnogrodzki Plateau



Fig. 2. The average standard deviation and content of sulphate sulphur in soils of Podkarpackie Province. Explanations: 1 – very acid soils, 2 – acid soils, 3 – weakly acid soils, 4 – neutral soils.

and Rzeszowskie Foothills, a positive correlation was observed between the content of sulphate and the content of the fraction of colloidal clay, which allowed to formulate the following regression equation: $S-SO_4=1.41+0.04\%$ of the fraction of colloidal clay. Jakubus and Czekała [5] and Koter *et al.* [8] did not find a relationship between the content of sulphate sulphur and the amount of washable parts.

Among the following soil types: proper podzolic; proper brown; leached brown; acid brown; and podzolized brown of the Podkarpackie Region, there was a negative correlation between the content of $S-SO_4$ and the pH. Moreover, in the grey-brown podzolic soils and acid brown soils, the content of sulphur sulphate was positively correlated with the humus content.

In the soils of the Podkarpackie Region, the mean content of sulphate sulphur in the 0-20 cm soil horizon is, on average, higher by about 10% than that of the 20-40 cm horizon. In the soils of the Dynowskie Foothills, in the 20-40 cm layer, the content of sulphur is negatively correlated with the pH and the regression equation is as follows: $S-SO_4=2.35-0.17$ pH. In addition, in the brown leached soils in that region, there was a negative correlation between the content of sulphate sulphur with the pH in both layers and a stronger relationship was observed in the surface horizon: $S-SO_4=3.19-0.32$ pH as compared to the 20-40 cm layer: S-SO₄=2.45-0.22 pH. In the Kolbuszowski Plateau mezoregion, in the 20-40 cm layer, there was a positive correlation between the content of sulphate sulphur with the content of the colloidal clay fraction, which allowed to formulate the following regression equation: $S-SO_4=1.40+0.03\%$ of the colloidal clay fraction. Investigating the relationships between the content of sulphate sulphur and the particular features of the soil types, it was stated that in the proper podzolic soils, in the surface horizon, the content of sulphate sulphur could be described with the following equation: $S-SO_4=2.21-0.23$ pH+0.04% of the colloidal clay fraction, while in the 20-40 cm layer the equation is: $S-SO_4 = 2.71-0.31 \text{ pH}+0.03\%$ of the colloidal clay fraction. In addition, in the surface horizon of the leached brown soils, a negative correlation between the content of sulphur and pH was stated, which is described by the following equation: $S-SO_4=2.78-0.25$ pH.

CONCLUSIONS

1. The content of sulphate sulphur in the 0-20 cm horizon in the soils derived from the flysh formation is highly differentiated: on average, 0.87 mg kg⁻¹ in the Przemyskie Foothills to 2.00 mg kg⁻¹ in the Ciężkowickie and Strzyżowskie Foothills.

2. In the soils derived from the sediments of the Karpathian Flysh, the content of sulphur is negatively correlated with their reaction, while in post-glacial sediments the sulphur content is not correlated with the pH.

3. The content of sulphate sulphur in the soils is positively correlated with the content of humus in Western Bieszczady and the content of the colloidal clay fraction in the Tarnogrodzki Plateau.

4. In the proper brown, acidic and podzolized, as well as proper podzolic and grey-brown podzolic soils, occurring in the Podkarpackie Region, there was no significant differentiation in the content of sulphate sulphur $(1.73-1.93 \text{ mg } 100 \text{ g}^{-1}, \text{ on average})$. Less sulphur was stated in the leached brown soils $-1.52 \text{ mg } 100 \text{ g}^{-1}$.

5. In the most highly represented soil types: brown leached; proper podzolic; and brown podzolized, regardless of the region, the content of sulphur could be described with the following multiple regression equations: $S-SO_4=2.89-0.26$ pH; $S-SO_4=2.88-0.21$ pH+2.02% colloidal clay fraction; $S-SO_4=2.90-0.24$ pH.

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ZAWARTOŚĆ SIARKI SIARCZANOWEJ W RÓŻNYCH TYPACH GLEB PODKARPACIA

Celem badań była ocena zawartości siarki siarczanowej w różnych typach gleb woj. podkarpackiego. Zawartość S-SO₄ w glebach wytworzonych z fliszu karpackiego była bardzo zróżnicowana i wynosiła średnio od 0,87 g·kg⁻¹ na Pogórzu Przemyskim do 2 g·kg⁻¹ na Pogórzu Ciężkowickim i Strzyżowskim. W glebach wytworzonych z osadów fliszowych zawartość siarki siarczanowej była ujemnie skorelowana z odczynem. Zależności takiej nie stwierdzono w glebach wytworzonych z utworów polodowcowych.