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CONTENT OF HUMUS OF SOILS FORMED ON GYPSUM ROCKS IN THE REPUBLIC OF MACEDONIA

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This paper examines the humus content of soils formed on gypsum rocks in the Republic of Macedonia. The average content of humic acids is lower than that of fulvic acids in these soils (Gypsic pararendzina, Gypsic rendzic Leptosol). The ratio of humic acids to fulvic acids is less than 1 for both soil types. Due to the presence of $CaCO_3$ and $CaSO_4$ in the solum of the studied soils, the fractions of humic and fulvic acids bound to calcium are the most dominant. In these soils, humic acids bound to calcium, sesquioxides, and clay (the stable fraction of humus) are much more prevalent than the mobile fractions, making the humus highly stable.

Key words: content of humus; gypsum rocks; soil; gypsic pararendzina; gypsic rendzic leptosol

INTRODUCTION

Soils formed on gypsum rocks are among the least studied types of soil in our country and are also poorly examined on a global scale, with limited data available. This is primarily due to the narrow distribution of gypsum rocks on the Earth's surface, which is a prerequisite for the formation of these soil types. According to [1], most landscapes where solid gypsum rocks occur are located in the northern hemisphere, primarily in Europe, with fewer occurrences in North America and Asia. Due to distinctions in their morphological and chemical properties, soils formed on gypsum rocks are divided into two groups: 1) soils of humid areas and 2) soils of semiarid continental and Mediterranean areas. The soils in the current study belong to the latter group.

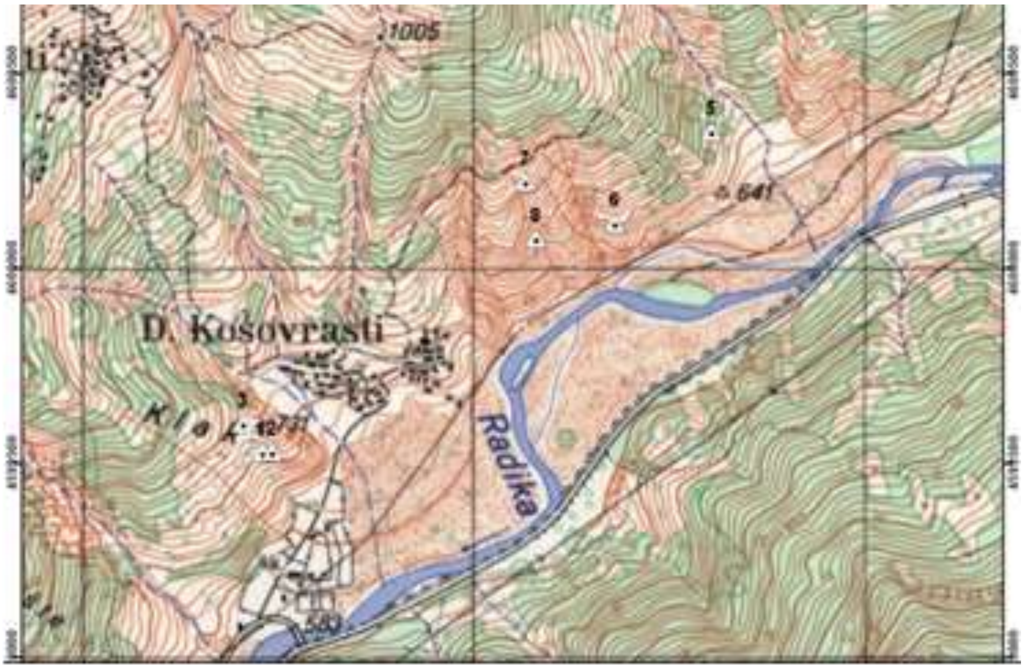
Filipovski & Andreevski [2] were the first to conduct research on soils formed on gypsum rocks in the Balkan Peninsula. These soils are found in the vicinity of the villages of Dolno and Gorno Kosovrasti in the Debar area, Republic of Macedonia. A segment of this research, which covers soil-forming conditions, morphological properties, genesis, evolution, classification, mechanical composition, chemical properties, and the content of exchangeable cations, was published in our previous papers [3, 4]. The present study will elaborate on the results regarding the humus content of gypsic rendzic leptosol and gypsic pararendzina profiles, identical to those observed in the earlier studies.

As previously mentioned, there is very limited literature on these types of soils, particularly regarding humus content. Therefore, the aim of this study is to examine the humus content in soils formed on gypsum rocks in the Republic of Macedonia. Humus content is an important indicator of soil genesis conditions, and it influences soil formation, fertility, and the overall properties of soils formed on gypsum rocks.

Field research and laboratory analyses were conducted following established methods [5, 6]. Data on humus content in soils formed on gypsum rocks have been published in foreign literature by [1, 7].

RESEARCH RESULTS

In the vicinity of the villages of Dolno and Gorno Kosovrasti (Debar area), seven soil profiles formed on gypsum rocks (Map 1) were excavated, studied, and morphologically described. Four of these profiles are Gypsic rendzic Leptosol with an A-R profile, while three profiles are Gypsic pararendzina with an A-AC-C profile.



Map 1. Profile location

Humus composition

The results of the analyses of the humus composition in Gypsic rendzic Leptosols and Gypsic pararendzina are presented in Tables 1, 2, and 3. Data on the humus composition of soils formed on gypsum rocks have been reported in the works of [1, 7], which focus on soils formed on pure gypsum from the boreal zone. One limitation of these studies is that the method used to determine the humus composition was less accurate compared to the method we applied.

The content of humic acids in Gypsic rendzic Leptosols averages 28.36 % (as a percentage of total carbon), with a range from 19 % to 37.93 %. In Gypsic pararendzina, the highest content of humic acids is found in the humus-accumulative horizon. Humic acids decrease from horizon A to horizon C, both absolutely and relatively. The content of humic acids in horizon A averages 29.52 % (ranging from 26.29 % to 33.14 %); horizon AC contains an average of 21.60 % humic acids, with a variation from 19.51 % to 25.72 %; and horizon C contains an average of 21.05 % (ranging from 18.00 % to 25.15 %).

Fraction 1 of humic acids consists of free humic acids and humic acids bound to mobile sesquioxides. From Table 1, it can be observed that fraction 1 is the least represented fraction of humic acids in both Gypsic rendzic Leptosols and Gypsic pararendzina. Fraction 2 of humic acids (humic acids bound to calcium) is significantly more prevalent than fraction 1 in both Gypsic rendzic Leptosols and Gypsic pararendzina.

In all profiles of Gypsic rendzic Leptosols and Gypsic pararendzina, $CaCO_3$ is present, and in some profiles, gypsum is also found. Calcium dominates the sorptive complex, and as a result, humification occurs in a base-saturated environment, where humic acids bind with calcium. Fraction 3 of humic acids (humic acids bound to clay and stable forms of sesquioxides) is quite similar to fraction 2 of humic acids in both Gypsic rendzic Leptosols and Gypsic pararendzina.

Table 1. The composition of humus in soils formed on gypsum rocks in the Republic of Macedonia (average values)

Horizon	Total C	Humic acids				Fulvic acids					Humin	Cha/
		1	2	3	S	1a	1	2	3	S		Cfa
						Gypsic rendizc Leptosols						
A	2.53*	0.09	0.36	0.34	0.78	0.15	0.04	0.38	0.31	0.88	0.86	0.83
	100**	2.79	12.87	12.70	28.36	6.27	1.41	16.43	12.76	36.87	34.77	
						Gypsic pararendzina						
A	3.19	0.12	0.41	0.43	0.96	0.19	0.06	0.55	0.38	1.18	1.06	0.81
	100	3.67	12.55	13.30	29.52	5.64	1.53	18.45	12.16	37.79	32.70	
AC	1.12	0.02	0.13	0.12	0.26	0.11	0.01	0.22	0.13	0.46	0.40	0.50
	100	1.30	11.06	9.24	21.60	10.54	0.57	22.50	12.99	46.60	31.80	
C	0.23	0.01	0.02	0.02	0.05	0.03	0.00	0.07	0.02	0.12	0.06	0.40
	100	2.22	10.02	8.81	21.05	13.79	1.60	27.94	10.02	53.35	25.60	

*in % of fineearth; **in % of total carbon

Table 2. The composition of humus in soils formed on gypsum rocks in the Republic of Macedonia

Prof. No.	Horizon and depth, cm	Totoal C	Humic acids				Fulvic acids					Humin	Cha/
			1	2	3	S	1a	1	2	3	S		Cfa
							Gypsic rendizc Leptosols						
1	A 0-18	3,63*	0.14	0.51	0.53	1.18	0.21	0.06	0.49	0.39	1.15	1.3	1.03
		100**	3.85	14.04	14.6	32.49	5.79	1.65	13.5	10.74	31.68	35.83	
3	A 0-16	3.19	0.17	0.52	0.52	1.21	0.16	0.09	0.38	0.31	0.94	1.04	1.29
		100	5.33	16.3	16.3	37.93	5.01	2.82	11.91	9.72	29.46	32.61	
5	A 0-21	2.39	0.026	0.322	0.226	0.574	0.147	0.023	0.483	0.396	1.049	0.767	0.55
		100	1.09	13.47	9.46	24.02	6.15	0.96	20.21	16.57	43.89	32.09	
8	A 0-17	0.9	0.008	0.069	0.094	0.171	0.073	0.002	0.181	0.126	0.382	0.347	0.45
			0.89	7.67	10.44	19	8.11	0.22	20.11	14	42.44	38.56	
							Gypsic pararendzina						
2	A 0-19	3.59	0.19	0.49	0.51	1.19	0.22	0.09	0.39	0.37	1.07	1.33	1.11
		100	5.29	13.64	14.21	33.14	6.13	2.51	10.86	10.31	29.81	37.05	
2	AC 19-32	2.06	0.03	0.25	0.25	0.53	0.17	0.02	0.3	0.2	0.69	0.84	0.77
		100	1.46	12.13	12.13	25.72	8.25	0.97	14.56	9.71	33.49	40.79	
6	A 0-15	3.7	0.089	0.486	0.503	1.078	0.235	0.071	0.658	0.464	1.428	1.19	0.75
			2.4	13.13	13.59	29.12	6.35	1.92	17.78	12.54	38.59	32.29	
6	AC 15-24	0.62	0.008	0.073	0.04	0.121	0.064	0.002	0.136	0.097	0.299	0.2	0.4
			1.29	11.77	6.45	19.51	10.32	0.32	21.93	15.64	48.21	32.28	
6	C 24-50	0.2	0.005	0.017	0.014	0.036	0.02	0.006	0.043	0.022	0.091	0.073	0.4
			2.5	8.5	7	18	10	3	21.5	11	45.5	36.5	
6	C 50-80	0.17	0.004	0.015	0.015	0.034	0.025	0.002	0.056	0.018	0.101	0.035	0.34
			2.35	8.82	8.82	19.99	14.7	1.18	32.94	10.59	59.41	20.6	
7	A 0-15	2.29	0.076	0.249	0.277	0.602	0.102	0.004	0.612	0.312	1.03	0.658	0.58
			3.31	10.87	12.09	26.29	4.45	0.17	26.72	13.62	44.96	28.75	
7	AC 15-28	0.69	0.008	0.064	0.063	0.135	0.09	0.003	0.214	0.094	0.401	0.154	0.34
			1.16	9.27	9.13	19.56	13.04	0.43	31.01	13.62	58.1	22.34	
7	C 28-43	0.33	0.006	0.042	0.035	0.083	0.055	0.002	0.097	0.028	0.182	0.065	0.46
			1.82	12.73	10.61	25.15	16.67	0.61	29.39	8.48	55.15	19.7	

*in % of fineearth, **in% of total C

The low representation of fraction 1 of humic acids in Gypsic rendzic Leptosols and Gypsic pararendzina can also be inferred from the ratio of humic acid fractions 2 + 3 to fraction 1 (Table 3). This ratio in Gypsic rendzic Leptosols averages 9.16, in horizon A of Gypsic pararendzina 7.05, in horizon AC 15.57, and in horizon C 8.47.

Table 3. Some indicators of the humus composition of soils formed on gypsum rocks (average values)

Horizon	Humic acids 2+3/1	Sum of fraction 2 humus acids	Sum of fraction 3 humus acids	Mobile fractions of humus acids	Humus acids 2+3	Fulic acids 2+3/1a+1	Humin and 3 fractions of humic acids
			Gypsic rendizc Leptosols				
A	9.16	29.30	25.46	10.47	54.76	3.80	47.47
			Gypsic pararendzina				
A	7.05	31.00	25.45	10.84	56.45	4.27	45.99
AC	15.57	33.56	22.23	12.41	55.78	3.19	41.04
C	8.47	37.96	18.83	17.61	56.79	2.47	34.41

The sum of humic acids bound to calcium (fraction 2) in Gypsic rendzic Leptosols averages 29.30 %. In Gypsic pararendzina, this fraction increases from the humus-accumulative horizon toward the transitional horizon and the parent substrate. As the depth of the gypsic pararendzina profile increases, the sum of $CaCO_3$ and gypsum, as well as the percentage of adsorbed calcium in the adsorptive complex, also increase. Consequently, at greater depths, humus acids interact with a higher concentration of calcium salts and adsorbed calcium, resulting in an increased sum of humic acids bound to Ca.

The sum of fraction 3 (humic acids bound to clay and stable sesquioxides) is almost equal in the humus-accumulative horizons of both Gypsic rendzic Leptosols and Gypsic pararendzina. However, as the depth increases in Gypsic pararendzina, the sum of fraction 3 decreases. Data on the clay content in Gypsic pararendzina shows that the clay content in horizons A and AC is nearly double that of horizon C, thus the sum of fraction 3 is higher in horizons A and AC compared to horizon C, as humic acids interact with more clay.

The fulvic acid content in Gypsic rendzic Leptosols shows that profiles 5 and 8 have more fulvic acids than humic acids, whereas profiles 1 and 3 have less. In Gypsic pararendzina, fulvic acids are more prevalent in all horizons except for horizon A of profile 2. Overall, the content of fulvic acids in both soil types is high. The average fulvic acid content in Gypsic rendzic Leptosols is 36.87 %, ranging from 29.46 % to 43.89 %. In Gypsic pararendzina, the average content in horizon A is 37.79 % (ranging from 29.81 % to 44.96 %), in horizon AC 46.6 % (33.49 % to 58.1 %), and in horizon C 53.35 % (45.5 % to 59.41 %).

Fraction 1a (the aggressive fraction) consists of free fulvic acids and fulvic acids bound to mobile sesquioxides. The average content of this aggressive fraction in Gypsic rendzic Leptosols (as a percentage of total C) is 6.27 %, ranging from 5.01 % to 8.11 %. In Gypsic pararendzina, the aggressive fraction increases from the humus-accumulative horizon towards the transitional horizon and parent substrate. In horizon A, the average is 5.64 % (ranging from 4.45 % to 6.35 %), in horizon AC 10.54 % (ranging from 8.25 % to 13.04 %), and in horizon C 13.79 % (ranging from 10.00 % to 16.67 %). The increased presence of the aggressive fraction in the lower parts of the profile is due to its high mobility, migrating from the upper part of the profile.

The ratio of fulvic acids bound to calcium, sesquioxides, and clay to free fulvic acids (fraction 1a + 1) is much wider in both Gypsic rendzic Leptosols and Gypsic pararendzina. In Gypsic rendzic Leptosols, this ratio is 3.80. In Gypsic pararendzina, this ratio is widest in horizon A at 4.27 and narrows with depth. In horizon AC, it averages 3.19, and in horizon C, it is 2.47. From this ratio, it can be concluded that most fulvic acids are bound to calcium, sesquioxides, and clay.

The mobile part of humus consists of humic acids fraction 1 and fulvic acids fraction 1 and 1a. In Gypsic rendzic Leptosols, these fractions average 10.47 %, in horizon A of Gypsic pararendzina 10.84 %, in horizon AC 12.41 %, and in horizon C 17.61 %. The opposite trend is observed for humus acid fractions 2+3 (humus acids bound to calcium, sesquioxides, and clay, which represent the more stable part of humus). In Gypsic rendzic Leptosols, these fractions average 54.76 %, in horizon A of Gypsic pararendzina 56.45 %, in horizon AC 55.78 %, and in horizon C 56.79 %. These results suggest that, in both Gypsic rendzic Leptosols and Gypsic pararendzina, humus acids bound to Ca, sesquioxides, and clay (the more stable part of humus) are much more prevalent than the mobile fractions of humus acids, indicating that the humus in these soils is highly stable.

An important parameter in studying the composition of humus is the ratio of humic to fulvic acids (Cha/Cfa). On average, the Cha/Cfa ratio in Gypsic rendzic Leptosols is 0.83. In profiles 1 and 3, this ratio is above 1, while in profiles 5 and 8, it is below 1. In Gypsic pararendzina, only horizon A of profile 2 has a Cha/Cfa ratio greater than 1, while all other horizons are below 1. The Cha/Cfa ratio narrows with depth in Gypsic pararendzina. On average, horizon A of Gypsic pararendzina has a Cha/Cfa ratio of 0.81, horizon AC 0.50, and horizon C 0.40. According to [5], if Cha/Cfa > 2, the humus is classified as humate; from 1 to 2, it is fulvate-humate; from 1 to 0.5, humate-fulvate; and < 0.5, fulvate. Based on this classification, Gypsic rendzic Leptosols have the following types of humus: profiles 1 and 3 are fulvate-humate, profile 5 is humate-fulvate, and profile 8 is fulvate. Gypsic pararendzina have the following types of humus: horizon A of profile 2 is fulvate-humate, horizon AC of profile 2, horizon A of profiles 6 and 7 are humate-fulvate, and horizons AC, C1, and C2 of profile 6 and horizons AC and C of profile 7 are fulvate humus. For soils formed on pure gypsum rocks from the boreal zone [7], the Cha/Cfa ratio ranges from 0.06 to 0.80.

In chemical terms, humin (the insoluble residue) is not a distinct group of humus compounds. In fact, humin consists of humic acids that are tightly bound to clay minerals. The content of humin in Gypsic rendzic Leptosols averages 34.77 % (ranging from 32.09 % to 38.56 %). In Gypsic pararendzina, the humin content decreases with depth. In horizon A, the average is 32.70 % (ranging from 28.75 % to 37.05 %), in horizon AC 31.80 % (ranging from 22.34 % to 40.79 %), and in horizon C 25.60 % (ranging from 19.7 % to 36.5 %). The clay content in horizons A and AC of Gypsic pararendzina is almost double that of horizon C. Since humic acids are in contact with more clay, the humin content is higher in horizons A and AC. Manusheva [8] points out that as the amount of clay increases, so does the amount of humin. Our research also confirms that the upper, more clayey part of the profile contains more humin.

The stable, inert part of humus, which is resistant to biodegradation, consists of humin and the third fraction of humic acids bound to clay and stable forms of sesquioxides. In Gypsic rendzic Leptosols, the stable part of humus averages 47.47 %. Similar to humin, the stable part of humus in Gypsic pararendzina is higher in the upper part of the profile. The stable humus content in horizon A averages 45.99 %, in horizon AC 41.04 %, and in horizon C 34.41 %.

Comparing the humus composition of Gypsic rendzic Leptosols with that of limestone-dolomite Rendzic Leptosols from the Jablanica mountain [9], which are distributed in similar climatic conditions, we find the following: the sum of humic acids, the sum of fulvic acids, the Cha/Cfa ratio, and the humin content are very close in both soil types. From this, we can conclude that in terms of the group composition of humus, climatic conditions play a decisive role in the humus composition of limestone-dolomite Rendzic Leptosols and Gypsic rendzic Leptosols. However, there are significant differences in the group-fractional composition of humus. In limestone-dolomite Rendzic Leptosols, Fraction 1 of humic acids (free humic acids and humic acids bound to mobile sesquioxides) is the most prevalent, followed by Fraction 3 (humic acids bound to clay and stable sesquioxides), with Fraction 2 (humic acids bound to calcium) being the least represented. In Gypsic redzic Leptosols, the order is reversed, with Fraction 2 being the most prevalent, followed by Fraction 3, and Fraction 1 being the least represented with minimal presence. As a result of this distribution of humic acid fractions, the ratio of humic acids 2+3/1 is much wider in Gypsic rendzic Leptosols. The mobile fractions of humus acids are about 2.5 times less prevalent in gypsic rendzic Leptosols, while the sum of fractions 2 and 3 (the more stable part of humus) is more prominent in gypsic rendzic Leptosols. The ratio of fulvic acids bound to calcium, sesquioxides, and clay to the free ones (fractions 1a + 1) is much wider in gypsic rendzic Leptosols. Unlike in limestone dolomitic rendzic Leptosols, in gypsic rendzic Leptosols, due to the presence of calcium salts in the solum, humification occurs in a soil environment saturated with bases, which explains the clear differences in the group fractional composition of humus between these two soil types.

The humus composition of gypsic pararendzina will be compared with that of carbonate rendzina from the Cemovsko Field, Montenegro, under humid climate conditions [10]. In both rendzinas, fulvic acids are more prevalent than humic acids, resulting in a humic to fulvic acid ratio (Cha/Cfa) of less than 1. In both rendzinas, fraction 2 of humic acids is the most dominant, while fraction 1 is the least represented. The stable fractions of humic and fulvic acids (humus acid fractions 2+3) are much more prevalent than the mobile fractions of humus acids.

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СОСТАВ НА ХУМУСОТ НА ПОЧВИТЕ ОБРАЗУВАНИ ВРЗ ГИПСЕНИ СТЕНИ ВО РЕПУБЛИКА МАКЕДОНИЈА

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Во овој труд е проучен составот на хумусот на почвите образувани врз гипсени стени во Република Македонија. Просечната содржина на хумински киселини е пониска од содржината на фулво киселини во почвите образувани врз гипсени стени (гипсена рендзина, гипсена црница). Односот на хумински киселини спрема фулво киселини е понизок од 1 и за двата почвени типа. Поради присуството на $CaCO_3$ и $Ca\ SO_4$ во солумот на испитуваните почви, фракциите на хумински и фулво киселини сврзани со Са се најзастапени фракции. Во испитуваните почви, хумусните киселини сврзани со Са, сесквиоксиди и глина (стабилен дел на хумусот) се многу позастапени од мобилните фракции хумусни киселини, затоа хумусот се одликува со голема стабилност.

Клучни зборови: состав на хумусот; гипсени стени; почва; гипсена рендзина; гипсена црница