

Received: November 4, 2019  
Accepted: June 1, 2020

ISSN 1857–9027  
e-ISSN 1857–9949  
UDC: 631.413.4:552.53(497.7)  
DOI: 10.20903/csnmbs.masa.2020.41.1.155

*Original scientific paper*

## CONTENT OF EXCHANGEABLE CATIONS OF SOILS FORMED ON GYPSUM ROCKS IN THE REPUBLIC OF MACEDONIA

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The current paper examines the content of exchangeable cations of soils formed on gypsum rocks in the Republic of Macedonia. The cation exchange capacity in gypsic rendzic leptosol ranges between 6.68 and 19.28 cmol(+)kg<sup>-1</sup> of soil while in gypsic pararendzina it ranges between 3.92 and 18.83cmol(+)kg<sup>-1</sup> of soil. The cation exchange capacity decreases with profile depth in gypsic pararendzina, which is a result of the reduction of humus content. In both soil types, the exchangeable Ca is dominant in the adsorption complex, followed by Mg, whereas the occurrence of K and Na is minimal.

**Key words:** cation-exchange capacity; exchangeable cation; gypsum rocks; soil; gypsic pararendzina; gypsic rendzic leptosol

### INTRODUCTION

Soils formed upon gypsum rocks are some of the least studied types of soil in our country. On a global scale they are poorly examined, too, with scarce data available. This is due to the narrow distribution of gypsum rocks on earth surface, which is a prerequisite for formation of these types of soil. According to [1], most of the landscapes where solid gypsum rocks occur are located in the northern hemisphere, primarily in Europe, less in Northern America and Asia. Owing to the distinctions in their morphological and chemical properties, soils constituted on gypsum rocks are divided into two groups, as follows: 1) soils of humid areas and 2) soils of semiarid continental and Mediterranean areas. The soils from the first group have been described in Russia, Poland, Germany and France while the semiarid variations have been described from Russia, Spain, Italy, the USA, Iran and Iraq. The soils to be dealt with in the current paper belong to the latter variation.

We [2] are the first to have conducted research into soils formed on gypsum rocks in the Balkan Peninsula. These soils are distributed in the vicinity of the villages of Dolno and Gorno Kosovrasti, Debar area, the Republic of Macedonia. A segment of the research referring to soil-forming conditions, morphological properties, genesis, evolution, classification, mechanical composition and a number of chemical properties was published in our preceding paper [3]. The current work will elaborate on the results from the study of content of exchangeable ions of gypsic rendzic leptosol and gypsic pararendzina for profiles identical with those observed in the earlier paper.

As mentioned above, there is very limited literature data concerning these types of soil, in particular data on the content of exchangeable ions. Therefore, we have set a goal to study the content of exchangeable ions of soils formed on gypsum rocks in the Republic of Macedonia. The content of exchangeable ions is an indicator of the conditions where soil genesis occurs, and it has a different im-

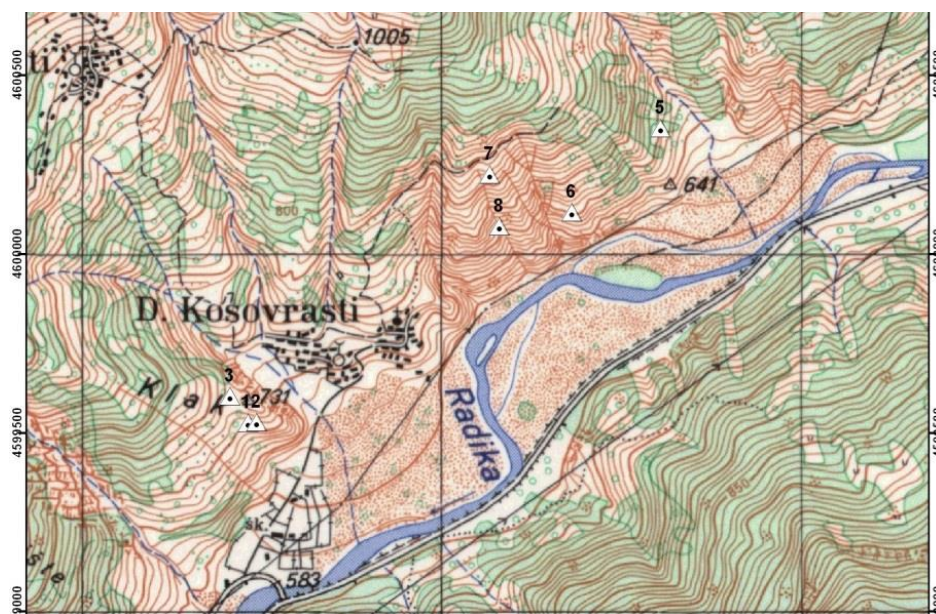
pect both on the soil-genesis direction and on soil fertility, genesis, evolution and properties of soils formed on gypsum rocks.

Field research and laboratory analyses have been conducted in compliance with the established methods [4, 5].

Data on the content of exchangeable ions of soils formed on gypsum rocks have been published in foreign literature by [1, 6–8].

## RESEARCH RESULTS

In the vicinity of the villages of Dolno and Gorno Kosovrasti (Debar area), 7 soil profiles on gypsum rocks (Map 1) were excavated, studied and morphologically described, whereof four profiles are gypsic rendzic leptosol with A-R profile and three profiles are gypsic pararendzina with A-AC-C profile.



Map 1. Profile location

### Cation-exchange capacity

The cation-exchange capacity is dependent on the total clay quantity, character of clay minerals, humus content and on the reaction of the solution for extraction of exchangeable ions during their identification.

Table 1 and 2 comprise data on the cation-exchange capacity of soils formed on gypsum rocks.

The cation-exchange capacity of gypsic rendzic leptosol is  $14.11 \text{ cmol}(+)\text{kg}^{-1}$  of soil on average varying from  $6.68$  до  $19.28 \text{ cmol}(+)\text{kg}^{-1}$  of soil.

These large differences are due to the distinctions in the content of clay and humus. According to the classification provided by Penkov [9], the studied gypsic rendzic leptosol possesses medium cation exchange capacity, apart from prof. 8, which has a small cation exchange capacity.

Table 1. Content of exchangeable cations of soils formed on gypsum rocks in the Republic of Macedonia (average values)

| Horizon                 | Exchangeable cations in $\text{cmol}(+)\text{kg}^{-1}$ of soil |                  |                |                 |       |       | Exchangeable cations in % of T |                  |                  |                |                 |
|-------------------------|--|------------------|----------------|-----------------|-------|-------|--------------------------------|------------------|------------------|----------------|-----------------|
|                         | $\text{Ca}^{2+}$   | $\text{Mg}^{2+}$ | $\text{K}^{+}$ | $\text{Na}^{+}$ | S     | T     | V%                             | $\text{Ca}^{2+}$ | $\text{Mg}^{2+}$ | $\text{K}^{+}$ | $\text{Na}^{+}$ |
| Gypsic rendzic leptosol |  |                  |                |                 |       |       |                                |                  |                  |                |                 |
| A                       | 11,32  | 2,27             | 0,30           | 0,22            | 14,11 | 14,11 |                                | 80,00            | 16,02            | 2,35           | 1,63            |
| Gypsic pararendzina     |  |                  |                |                 |       |       |                                |                  |                  |                |                 |
| A                       | 12,36  | 2,75             | 0,42           | 0,29            | 15,81 | 15,81 | 100,00                         | 77,88            | 17,32            | 2,84           | 1,94            |
| AC                      | 7,42   | 1,64             | 0,21           | 0,13            | 9,39  | 9,39  | 100,00                         | 78,88            | 17,18            | 2,52           | 1,42            |
| C                       | 3,26   | 0,69             | 0,07           | 0,03            | 4,05  | 4,05  | 100,00                         | 80,40            | 17,03            | 1,83           | 0,74            |

**Table 2.** Content of exchangeable cations of soils formed on gypsum rocks in the Republic of Macedonia

| No of prof              | Horizon and depth in cm | Exchangeable cations in cmol(+)kg <sup>-1</sup> of soil |                  |                |                 |       |       |     | Exchangeable cations in % of T |                  |                |                 |
|-------------------------|-------------------------|---|------------------|----------------|-----------------|-------|-------|-----|--------------------------------|------------------|----------------|-----------------|
|                         |                         | Ca <sup>2+</sup>  | Mg <sup>2+</sup> | K <sup>+</sup> | Na <sup>+</sup> | S     | T     | V%  | Ca <sup>2+</sup>               | Mg <sup>2+</sup> | K <sup>+</sup> | Na <sup>+</sup> |
| Gypsic rendzic leptosol |                         |   |                  |                |                 |       |       |     |                                |                  |                |                 |
| 1                       | A 0-18                  | 15.61   | 3.15             | 0.30           | 0.22            | 19.28 | 19.28 | 100 | 80.96                          | 16.34            | 1.56           | 1.14            |
| 3                       | A 0-16                  | 14.92   | 2.74             | 0.30           | 0.28            | 18.24 | 18.24 | 100 | 81.80                          | 15.02            | 1.64           | 1.54            |
| 5                       | A 0-21                  | 9.36  | 2.21             | 0.45           | 0.23            | 12.25 | 12.25 | 100 | 76.40                          | 18.05            | 3.67           | 1.87            |
| 8                       | A 0-17                  | 5.40  | 0.98             | 0.17           | 0.13            | 6.68  | 6.68  | 100 | 80.83                          | 14.67            | 2.54           | 1.95            |
| Gypsic pararendzina     |                         |   |                  |                |                 |       |       |     |                                |                  |                |                 |
| 2                       | A 0-19                  | 14.82   | 3.57             | 0.28           | 0.16            | 18.83 | 18.83 | 100 | 78.70                          | 18.96            | 1.49           | 0.85            |
| 2                       | AC 19-32                | 9.83  | 2.33             | 0.09           | 0.11            | 12.36 | 12.36 | 100 | 79.53                          | 18.85            | 0.73           | 0.89            |
| 6                       | A 0-15                  | 13.08   | 2.52             | 0.52           | 0.36            | 16.48 | 16.48 | 100 | 79.36                          | 15.29            | 3.15           | 2.18            |
| 6                       | AC 15-24                | 6.38  | 1.26             | 0.26           | 0.22            | 8.12  | 8.12  | 100 | 78.57                          | 15.51            | 3.20           | 2.71            |
| 6                       | C 24-50                 | 3.16  | 0.63             | 0.11           | 0.02            | 3.92  | 3.92  | 100 | 80.61                          | 16.07            | 2.81           | 0.51            |
| 6                       | C 50-80                 | 3.41  | 0.72             | 0.05           | 0.03            | 4.21  | 4.21  | 100 | 81.00                          | 17.10            | 1.19           | 0.71            |
| 7                       | A 0-15                  | 9.17  | 2.15             | 0.47           | 0.34            | 12.13 | 12.13 | 100 | 75.59                          | 17.72            | 3.87           | 2.80            |
| 7                       | AC 15-28                | 6.04  | 1.32             | 0.28           | 0.05            | 7.69  | 7.69  | 100 | 78.54                          | 17.17            | 3.64           | 0.65            |
| 7                       | C 28-43                 | 3.20  | 0.72             | 0.06           | 0.04            | 4.02  | 4.02  | 100 | 79.60                          | 17.91            | 1.49           | 1.00            |

The data on cation-exchange capacity in rendzina on hard limestones and dolomites from Jablanica Mt quoted by [10] are much higher compared to gypsic rendzic leptosol, and they come as a result of the higher content of clay and humus.

The cation-exchange capacity of gypsic pararendzina is the highest in the humus-accumulative horizon, and it is 15.81 cmol(+)kg<sup>-1</sup> of soil on average for the type, varying from 12.13 to 18.83 cmol(+)kg<sup>-1</sup> of soil. The values of the cation exchange capacity decrease from the humus-accumulative towards the transitional horizon and the parent material. On average, the cation-exchange capacity in the transitional horizon amounts to 9.39 cmol(+)kg<sup>-1</sup> of soil, varying from 7.69 to 12.36 cmol(+)kg<sup>-1</sup> of soil, and in the parent material its average value is 4.05 cmol(+)kg<sup>-1</sup> of soil, varying from 3.92 to 4.21 cmol(+)kg<sup>-1</sup> of soil. The cation-exchange capacity becomes reduced with profile depth as a result of humus content decrease. On the basis of the aforementioned classification, humus-accumulative horizons of gypsic pararendzina and the transitional horizon of prof. 2 have medium cation exchange capacity; the transitional horizons of prof. 6 and 7 have a small cation exchange capacity while horizon C of prof. 6 and 7 has very little cation exchange capacity. Similar values for soils resembling our gypsic pararendzina have been report-

ed by [6,8]. As maintained by [6], the cation exchange capacity in hor. A is 17, in hor. AC it is 16 and in hor. C it is 5.1 cmol(+)kg<sup>-1</sup> of soil. Kliment'ev *et al.*[8] state values that tend to decrease with profile depth, and they are 15.3, 11.4 and 10.00 cmol(+)kg<sup>-1</sup> of soil.

### Content of Exchangeable Cations

Data on exchangeable base cations in soils formed on gypsum rocks are provided in tables 1 and 2.

Judging by the data from tables 1 and 2, it may be ascertained that in gypsic rendzic leptosol, Ca<sup>2+</sup> is the overriding exchangeable base cation, followed by Mg<sup>2+</sup>, K<sup>+</sup> whereas Na<sup>+</sup> is the least present. The average content of exchangeable Ca<sup>2+</sup> is 11.32 cmol(+)kg<sup>-1</sup> of soil (5.4 to 15.61 cmol(+)kg<sup>-1</sup> of soil). Expressed in percentage of the cation exchange capacity, the exchangeable Ca<sup>2+</sup> is 80.00 % (76.4 to 81.8 %) on average.

Mg<sup>2+</sup> is the second most represented exchangeable cation in the adsorption complex. The content of the exchangeable Mg<sup>2+</sup> ranges between 0.98 to 3.15 cmol(+)kg<sup>-1</sup> of soil, the average is 2.27 cmol(+)kg<sup>-1</sup> of soil, or expressed in percentage of the cation exchange capacity - from 14.67 to 18.05 %, on average 16.02 %.

The exchangeable ions of  $K^+$  and  $Na^+$  are found in small quantities. The average content of exchangeable potassium amounts to  $0.30 \text{ cmol (+) kg}^{-1}$  of soil, varying from  $0.17$  to  $0.45 \text{ cmol (+) kg}^{-1}$  of soil, or expressed in percentage of the cation exchange capacity - on average  $2.35 \%$ , varying from  $1.56$  to  $3.67 \%$ . The content of exchangeable  $Na^+$  is the lowest, and it is  $0.22 \text{ cmol (+) kg}^{-1}$  of soil on average, with a variation interval from  $0.13$  to  $0.28 \text{ cmol (+) kg}^{-1}$  of soil. Expressed in percentage of the cation-exchange capacity, the exchangeable  $Na^+$  ranges from  $1.14$  to  $1.95 \%$ , on average  $1.63 \%$ .

If the content of exchangeable cations in gypsic rendzic leptosol and in rendzina on hard limestones and dolomites in Jablanica Mt is compared, the following will be established: both in gypsic rendzic leptosol and in rendzina on hard limestones and dolomites, the most represented base cation is calcium, then magnesium, potassium while sodium comes last. In gypsic rendzic leptosol because of the occurrence of  $CaCO_3$  and gypsum in certain profiles, there is absence of exchangeable ions of  $H^+$  and  $Al^{3+}$  while in rendzina on hard limestones and dolomites they are present. Therefore, base saturation percentage in gypsic rendzic leptosol is  $100 \%$  while in rendzina on hard limestones and dolomites it is  $73.6 \%$  on average.

Calcium is also the most prevailing in the adsorption complex of gypsic pararendzina. The average content in hor.A is the highest, and it is  $12.36 \text{ cmol (+) kg}^{-1}$  of soil ( $9.17$  to  $14.82 \text{ cmol (+) kg}^{-1}$  of soil), the transitional horizon  $7.42 \text{ cmol (+) kg}^{-1}$  of soil ( $6.04$  to  $9.83 \text{ cmol (+) kg}^{-1}$  of soil) and in hor. C  $3.26 \text{ cmol (+) kg}^{-1}$  of soil ( $3.16$  to  $3.41 \text{ cmol (+) kg}^{-1}$  of soil). Expressed in percentage of the cation-exchange capacity, the exchangeable calcium in hor.A is  $77.88 \%$  ( $75.59$  to  $79.36 \%$ ) on average, hor.AC  $78.88 \%$  ( $78.54$  to  $79.53 \%$ ) and hor.C  $80.40 \%$  ( $79.6$  to  $81 \%$ ). The amount of  $CaCO_3$  and gypsum increases with depth of profile in gypsic pararendzina, coupled by a rise in the percentage of exchangeable calcium in the adsorption complex.

The reasons for the greater occurrence of calcium in the adsorption complex of gypsic rendzic leptosol and gypsic pararendzina are the following: on the one hand, in some horizons,  $CaCO_3$  and gypsum occur in the profile and they saturate the adsorption complex with Ca, while, on the other hand, they neutralize all of the acids produced in the humification and mineralization process. The exchangeable property of calcium is greater than that of magnesium, which is the reason why it is harder to wash. In contrast to magnesium, it penetrates less in the crystal lattices of secondary clay minerals; hence, more remains for exchange.

Calcium is a major nutrient element in plant nutrition and it plays a significant role in creation of stable fine granular structure. Calcium converts phosphates in an insoluble form, thereby protecting them from washing. Magnesium comes second in terms of occurrence in the adsorption complex of gypsic pararendzina, too. The content of exchangeable magnesium is the highest in hor.A and it is  $2.75 \text{ cmol (+) kg}^{-1}$  of soil ( $2.15$  to  $3.57 \text{ cmol (+) kg}^{-1}$  of soil) on average, in AC horizon  $1.64 \text{ cmol (+) kg}^{-1}$  of soil ( $1.26$  to  $2.33 \text{ cmol (+) kg}^{-1}$  of soil) and in hor.C  $0.69 \text{ cmol (+) kg}^{-1}$  of soil ( $0.63$  to  $0.72 \text{ cmol (+) kg}^{-1}$  of soil). Expressed in percentage of the cation-exchange capacity, the exchangeable  $Mg^{2+}$  in hor. A is  $17.32 \%$  ( $15.29$  to  $18.96 \%$ ) on average, in hor.AC  $17.18 \%$  ( $15.51$  to  $18.85 \%$ ), and in hor.C  $17.03 \%$  ( $16.07$  to  $17.91 \%$ ).

Magnesium is also an essential nutrient element in plant nutrition. As claimed by [11], magnesium deficit has been noted in acid sandy soils, which contain less than  $0.2 \text{ cmol (+) kg}^{-1}$  of soil of exchangeable magnesium. Per the data obtained regarding exchangeable magnesium in gypsic rendzic leptosol and gypsic pararendzina, the conclusion is that there is no risk of a deficit of the quoted nutrient element.

The exchangeable  $K^+$  and  $Na^+$  are found in minor amounts. Exchangeable potassium is in the third place in terms of occurrence in the adsorption complex of gypsic pararendzina. The content of exchangeable  $K^+$  in hor. A in gypsic pararendzina is  $0.42 \text{ cmol (+) kg}^{-1}$  of soil ( $0.28$  to  $0.52 \text{ cmol (+) kg}^{-1}$  of soil) on average, in hor. AC  $0.21 \text{ cmol (+) kg}^{-1}$  of soil ( $0.09$  to  $0.28 \text{ cmol (+) kg}^{-1}$  of soil), and in hor. C  $0.07 \text{ cmol (+) kg}^{-1}$  of soil ( $0.05$  to  $0.11 \text{ cmol (+) kg}^{-1}$  of soil). Expressed in percentage of the cation-exchange capacity, the exchangeable  $K^+$  in hor. A is  $2.84 \%$  ( $1.49$  to  $3.87 \%$ ) on average, in hor.AC  $2.52 \%$  ( $0.73$  to  $3.64 \%$ ), and in hor. C  $1.83 \%$  ( $1.19$  to  $2.81 \%$ ).

The exchangeable  $Na^+$  comes last in terms of occurrence. In hor. A, exchangeable  $Na^+$  is found  $0.29 \text{ cmol (+) kg}^{-1}$  of soil ( $0.16$  to  $0.36 \text{ cmol (+) kg}^{-1}$  of soil) on average, in hor. AC  $0.13 \text{ cmol (+) kg}^{-1}$  of soil ( $0.05$  to  $0.22 \text{ cmol (+) kg}^{-1}$  of soil), and in hor. C  $0.03 \text{ cmol (+) kg}^{-1}$  of soil ( $0.02$  to  $0.04 \text{ cmol (+) kg}^{-1}$  of soil). Expressed in percentage of the cation-exchange capacity, the exchangeable  $Na^+$  occurs in hor. A  $1.94 \%$  ( $0.85$  to  $2.8 \%$ ) on average, in hor. AC  $1.42 \%$  ( $0.65$  to  $2.71 \%$ ), and in hor. C  $0.74 \%$  ( $0.51$  to  $1.00 \%$ ). According to [8], for a profile resembling gypsic pararendzina, the exchangeable Na ranges between  $1.7$  and  $2.1 \%$  of the cation-exchange capacity.

Similar to gypsic pararendzina, in calcareous pararendzina from Ovče Pole, it is calcium that is the most represented cation in the adsorption complex, followed by magnesium while potassium and sodium occur in minimum amounts [10]. Goryachkin *et al.* [7] provide data about exchangeable calcium, magnesium and hydrogen for soils formed on pure gypsic rocks from the boreal belt. Different from our soils on gypsic rocks, those do not contain CaCO<sub>3</sub> in the solum given that it is absent from the parent material. Ca is the most common cation in these soils, followed by H while magnesium comes last. Lafuente *et al.* [6] report on data from Spain for a profile akin to our gypsic pararendzina. Like our gypsic pararendzina, carbonates are also found in this profile whereas Ca is the most common cation, followed by Mg, Na and K.

The values of exchangeable sodium in gypsic rendzic leptosol and gypsic pararendzina are not detrimental to plants and they do not cause peptisation of colloids.

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### СОСТАВ НА РАЗМЕНЛИВИТЕ КАТЈОНИ НА ПОЧВИТЕ ОБРАЗУВАНИ ВРЗ ГИПСЕНИ СТЕНИ ВО РЕПУБЛИКА МАКЕДОНИЈА

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Во овој труд е проучен составот на разменливите катјони на почвите образувани врз гипсени стени во Република Македонија. Капацитетот на атсорпција на катјони во гипсените црници се движи од 6,68 до 19,28 cmol(+)kg<sup>-1</sup> почва, а во гипсените рендзини од 3,92 до 18,8 cmol(+)kg<sup>-1</sup> почва. Во гипсените рендзини по длабочина на профилот се намалува капацитетот на атсорпција на катјони и се должи на намалување на содржината на хумус. И во двата почвени типа, во атсорптивниот комплекс разменливиот Са е доминантен, следи Mg, а К и Na се минимално застапени.

**Клучни зборови:** капацитет на атсорпција на катјони, разменливи катјони, гипсени стени, почва, гипсена рендзина, гипсена црница