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GROUNDWATER QUALITY IN TWO RURAL COMMUNITIES FROM CLUJ AND BISTRIȚA-NĂSĂUD COUNTIES – ROMANIA

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ABSTRACT. In Romania, there are rural areas where the access to safe drinking water sources is still an unsolved issue. The main objective of the present study was to assess the quality of several underground drinking water sources from two rural communities from Romania and to evaluate the suitability of using those water sources in drinking and agricultural purposes. The investigated parameters were: pH, redox potential (E_h), electrical conductivity (EC), total dissolved solids (TDS), salinity, dissolved ions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{-3}, SO_4^{-2}, Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and metals (Fe, Zn, Cr, Cu, Cd, Ni, Pb and Mn). The analyses indicated high levels of sulphates (up to 353.2 mg/l) in the wells from Cluj County and high concentrations of nitrates (up to 111.4 mg/l) and nitrites (up to 1.49 mg/l) in the wells from Bistrița-Năsăud County, these parameters frequently exceeded the safely limits imposed by national and international legislation. The levels of the other investigated parameters were generally below the maximum limits imposed by national and international legislation. Based on the sodium adsorption ratio, sodium percentage and magnesium adsorption ratio values, most of the investigated water sources can be safely used in agriculture purposes.

Key words: *rural communities, drinking water quality, water quality index, sodium adsorption ratio, sodium percentage*, *magnesium adsorption ratio*

INTRODUCTION

The access to safe drinking water supply in rural areas is an important national goal in many developing countries. Drinking water sources are susceptible to chemical, physical or biological contamination, depending on the geological conditions, agricultural, industrial, or other man-made activities. According to the European Commission, the groundwater pollution represents the most serious problem of the EU water resources policy (Llamas, 2004). As a consequence, in the new EU Water Framework Directive enacted in December 2000, great attention has been paid to the groundwater quality. In Romania, there are rural areas where the access to safe drinking water sources is still an unsolved issue. In many rural areas from Romania, the underground water is the only source of drinking water. As a consequence, the investigation of the underground water quality has a major importance. The main objectives of the present study were: (1) to investigate several physico-chemical (pH, redox potential, electrical conductivity, total dissolved solids, salinity) and chemical water quality parameters (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Fe, Zn, Cr, Cu, Cd, Ni, Pb and Mn) in 16 private wells from two rural areas located in Cluj County (Fizeșu Gherlii) and Bistrița-Năsăud County (Mărișelu); (2) to assess the monthly fluctuations of the quality parameters; (3) to evaluate the water quality by calculating the water quality index (WQI); and (4) to assess the suitability of using the water sources for agricultural purposes, by calculating specific indices.

MATERIALS AND METHODS

Sampling and processing

For the present study, a total of 48 samples were collected from 16 private wells from Fizeșu Gherlii village (Cluj County) and Mărișelu village (Bistrița-Năsăud County). The samples were collected during three campaigns, in November 2017, December 2017 and January 2018 (Roșu et al., 2018).

Fizeşu Gherlii is a commune in Cluj County, Romania. It lies between 47°01′41″ north latitudes and 23°59′16″ east longitudes, at an altitude of 265 m and it is composed of four villages: Bonț, Fizeșu Gherlii, Nicula and Săcălaia. The total surface is of 67.12 km², and it has a population of 2,631 inhabitants (according to the 2011 census), with a density of 39.51 inhabitants/km².

Mărișelu is a commune in Bistrița-Năsăud County, Romania. It lies between 47°01′46″ north latitudes and 24°29′39″ east longitudes, at an altitude of 357 m and it is composed of seven villages: Bârla, Domnești, Jeica, Măgurele, Mărișelu, Nețeni and Sântioana. The total surface is of 71.68 km², and it has a population of 2,383 inhabitants (according to the 2011 census), with a density of 33.24 inhabitants/km².

The analysed physico-chemical parameters were: pH, redox potential (E_h), electrical conductivity (EC), total dissolved solids (TDS) and salinity.

They were measured *in situ* using a portable multiparameter (WTW inolab 350i). The sampling and processing procedures were performed according to standard protocols (EN 25667-2; EN ISO 5667-3). The water samples were collected in polyethylene bottles and were filtered *in situ* using 0.45 µm syringe filters. The water samples used for metals analysis were acidified to a pH ≈ 2 (with HNO_3 65%). The samples were then transported to the laboratory, stored at dark and 4ºC, and analyzed within 48 hours from sampling. The dissolved ions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were analyzed by ion chromatography, using an IC1500 Dionex system. The total amount of heavy metals (Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni) were analyzed by atomic absorption spectrometry (AAS), using an AAS system ZeeNIT 700 (Analytik Jena) equipped with air-acetylene flame and graphite furnace.

Water quality index (WQI)

WQI was developed by Horton (1965) in United States by selecting the most commonly used water quality parameters like dissolved oxygen (DO), pH, coliforms, specific conductance, alkalinity, chloride, etc. and has been widely applied and accepted in many countries. Furthermore, new models for WQI, similar to Horton's index, have been developed by different scientific researcher groups.

In the present study, WQI was calculated based on fifteen parameters: pH, EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Fe, Zn, Ni and Mn, using the equations 1 – 3 (Thakov et al., 2011; Yogendra and Puttaiah, 2008; Srinivas et al., 2011):

$$\mathrm{WQI} = \frac{\sum_{i=1}^{n} q_i \cdot W_i}{\sum_{i=1}^{n} W_i} \quad (1)\,; \quad W_i = \frac{k}{S_i} \quad (2)\,; \quad q_i = \frac{V_a - V_i}{S_i - V_i} \cdot 100 \quad (3)$$

where, W_i is the weightage factor; k is the proportionality constant (k = 1); S_i is the standard value of the ith water quality parameter; n is the total number of water quality parameters; q_i is the quality rating for the ith water quality parameter; V_a is the value of the ith water quality parameter determinate in laboratory, V_i is the ideal value of the ith water quality parameter obtained from standard tables (V_i for pH = 7 and for the other parameter the V_i = 0) (Srinivas et al., 2011).

Possibility of using water sources for agricultural purposes

In order to assess the possibility of using the investigated water sources in agricultural purposes, three indices were calculated: the sodium adsorption ratio (**SAR**) (equation 4), the sodium percentage (**SP**) (equation 5) and magnesium adsorption ratio (**MAR**) (equation 6). SAR, is a parameter which influences the infiltration rate of water and it was calculated based on the sodium, calcium and magnesium concentrations (expressed in milliequivalent per liter) (Harront et al., 1983; WHO, 1984; WHO, 1989; BC Health Act Safe Drinking Water Regulation, 2001).

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \quad (4); \qquad SP = \frac{Na^{+}+K^{+}}{Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}} \cdot 100 \quad (5);$$

$$MAR = \frac{Mg^{2+}}{Ca^{2+}+Mg^{2+}} \cdot 100 \quad (6)$$

Based on the sodium, calcium, magnesium and potassium concentrations (expressed in milliequivalent per liter), the SP was calculated (Kelly, 1940; Wilcox, 1958), while the magnesium adsorption ratio was calculated using the magnesium and calcium content (expressed in milliequivalent per liter) (Paliwal, 1972).

RESULTS AND DISCUSSIONS

Physico-chemical and chemical parameters

The values of the investigated physico-chemical and chemical parameters are presented in Fig.1 and Fig. 2. The water samples proved to be neutral to slightly basic, having the pH within the permissible limits (6.5 – 9.5) set by the Romanian legislation (Drinking water law 458/2002). The redox potential had negative values (-14 – -85.4 mV) indicating the presence of anaerobic redox potential and reducing conditions in the aquifer. The redox potential was within the WHO (World Health Organization) and US-EPA (United States – Environmental Protection Agency) recommendation (-100 – +100 mV) for drinking water (US EPA, 1991; WHO, 1984; WHO, 2008). The analyzed waters had a low electrical conductivity, between 358 – 1,317 µS/cm, being lower than the limit (2,500 µS/cm) imposed by national legislation (Drinking water law 458/2002). The EC level was slightly higher in the water sampled from Cluj County (Fizeșu Gherlii) than those from Bistrița-Năsăud County (Mărișelu) (figure 1). The low level of EC, TDS (233 – 762 mg/l) and salinity (0.1 – 0.6‰) reflect the relatively low content of dissolved salts for the analysed drinking water sources.

The water samples had a low level of F^{-} (0.01 – 0.93 mg/l) and Cl^{-} (7.3 – 107.4 mg/l), being within the national permissible limits (1.2 mg/l and 250 mg/l) (Roșu et al., 2018). With the exception of one well from Cluj County

(Fizeșu Gherlii), the Na^+ content was considerably lower than the national limit (200 mg/l) (figure 1). The content of Mg^{2+} (11.0 – 49.1 mg/l) and Ca^{2+} (17.8 – 235.3 mg/l) were, with one exception, within the recommendations (50 mg/l and 200 mg/l) of international forums (BC Health Act Safe Drinking Water Regulation–Canada and World Health Organization, 2001; WHO, 1984; WHO, 2008; Roșu et al., 2018). Calcium and magnesium are two important macroelements for human body, and the Ca/Mg ratio has a great importance in drinking water. An optimal value for this ratio is 2:1, offering greater protection against cardiovascular disease (Feru, 2012). In the present study, the Ca/Mg ratio ranged between 0.9 and 9.6. In addition, high contents of calcium and magnesium increase the water hardness.

The analysed water sources proved to have a considerably high level of K^+, especially those from Cluj County (Fizeșu Gherlii) (4.1 – 303.3 mg/l), exceeding the limit (10 mg/l) recommended by the international forums (BC Health Act Safe Drinking Water Regulation–Canada and World Health Organization, 2001; WHO, 1984; WHO, 2008). It is possible that such high potassium level could be a consequence of the hydrogeological features of the two aquifers, but further investigations should be performed on this topic. There are studies (Diaconu et al., 2005) which indicated that the intake of high levels of sodium and potassium via water and food ingestion can be associated with increased incidence of hypertension. The optimal Na/K ratio is 3:1 (Feru, 2012). In the analysed water samples, the Na/K ratio was relatively low, ranging between 0.1 and 5.4, being generally below the optimal value.

Some of the investigated water sources proved to be contaminated with NO_2^- (0.08 – 1.49 mg/l), NO_3^- (0.7 – 111.4 mg/l) and SO_4^{2-} (17.5 – 353.2 mg/l), exceeding the limits imposed by national and international legislation (0.5 mg/l, 50 mg/l and 250 mg/l). The residents who use those water sources for drinking, cooking, recreational or agricultural purposes, should be informed in order to stop or restrict as much as possible the usage of those water sources, because of the possible negative impact on their health. The presence of high levels of SO_4^{2-} in some of the investigated wells can be a consequence of the presence of anthropogenic sources such as the application of fertilizers on cultivated lands (Khan et al., 2012). The ingestion of high levels of sulphates through drinking water may cause heath effect such as laxative action (WHO, 1996). The high level of NO_3^- and NO_2^- from some of the investigated wells can be a consequence of over-application of fertilizers, sewage disposal, or manure applications in the vicinity of the wells (Chowdary et al., 2005; Liu et al., 2005; Khan et al., 2012). Nitrites are classified as toxic to human body, and the exposure to high levels of NO_3^- and NO_2^- via water ingestion can lead to seriously health problems like methemoglobinemia (blue baby syndrome) (Gupta et al., 2000).

By comparing the two areas, the waters sampled from Cluj County (Fizeșu Gherlii) had a higher content of F^-, Na^+, SO_4^{2-}, K^+ than the water sources from Bistrița-Năsăud County (Mărișelu).

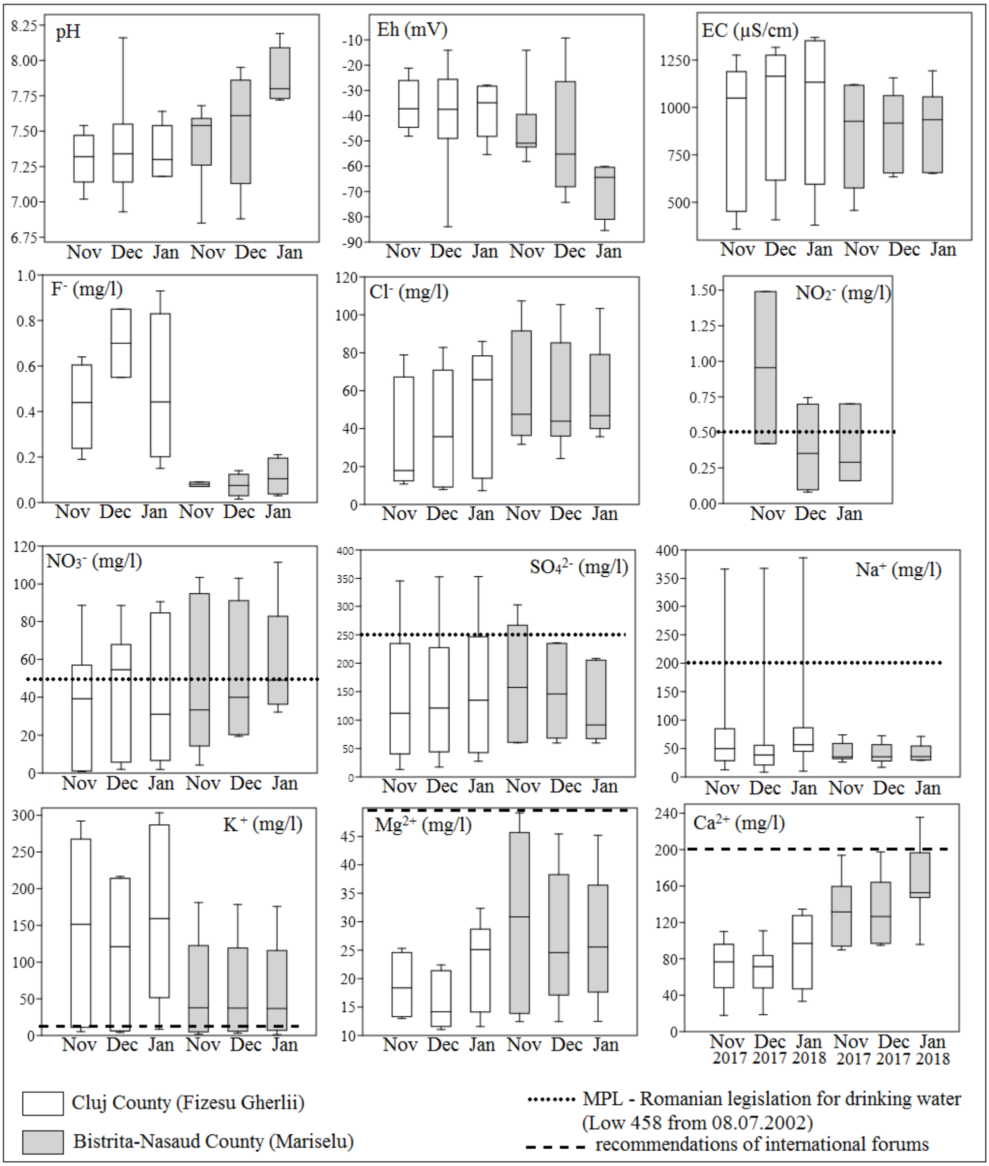

Fig. 1. *Monthly fluctuations of analysed physico-chemical parameters and dissolved ions*

The water sources proved to have low levels of metals, the presence of Cd, Cr, Pb, Cu, was not detected in any of the analysed water samples, while the content of Zn (0.001 – 0.092 mg/l), Fe (0.09 – 0.16 m/l) and Ni (0.005 – 0.019 mg/l) were within the national limits (5 mg/l for Zn, 0.2 mg/l for Fe and 0.02 mg/l for Ni) (Fig. 2). The level of Ni in some wells from Bistrița-Năsăud County (Mărișelu) should be carefully monitored because it is close to the maximum permissible limits. The continuous exposure to Ni via water ingestion could be a risk factor for resident's health, considering that Ni is classified as human carcinogenic. Manganese (0.02 – 0.09 mg/l) was detected only in two wells from Bistrița-Năsăud County (Mărișelu), exceeding in one water sources the national limit (0.05 mg/l).

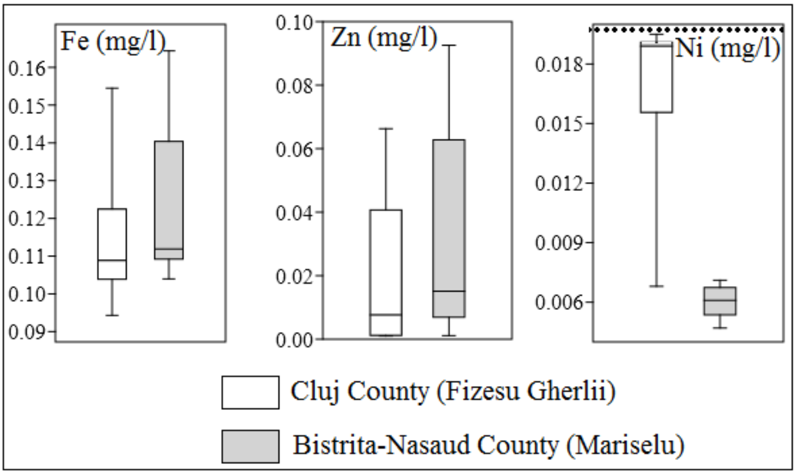

Fig. 2. *Metal content in the analysed water samples*

Generally, the chemical quality parameters presented low fluctuations during the three months of monitoring indicating a good hydrochemical stability of aquifers.

Water quality index

In order to evaluate the overall quality of the investigated drinking water sources, the **WQI** was calculated. The results are shown in figure 3.

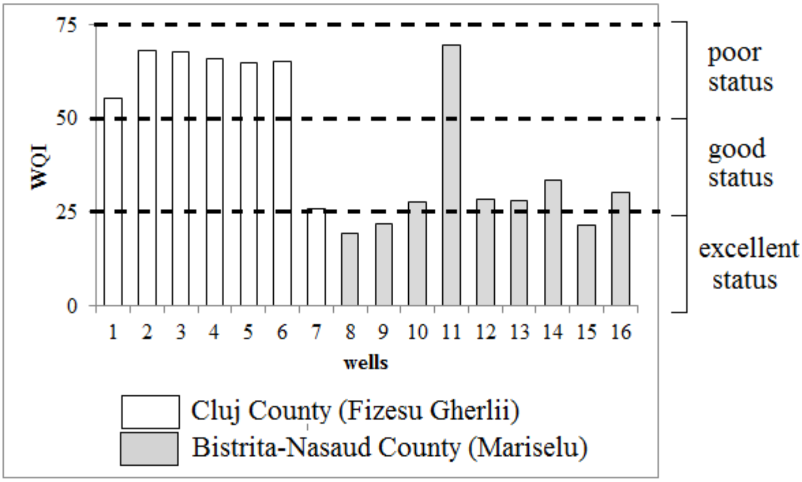

Fig. 3. *Water quality index for the investigated water sources*

Based on **WQI**, one of the wells from Fizeșu Gherlii (sample 7) (figure 3) can be classified as good water quality, while the other wells from the area, are classified as poor quality (because of the high levels of K^+, SO_4^{2-}, NO_3^-, NO_2^- and Ni). Three of the wells from Mărișelu (8, 9 and 15) had an excellent status and four of the wells (10, 12, 13, 14 and 16) had a good status being suitable for drinking purposes. Only one of the wells from Mărișelu area (11) had a poor water quality status (because of the high level of manganese which exceeded the permissible limits). The **WQI** values indicated that the waters sampled from Cluj County (Fizeșu Gherlii) had an inferior quality than those from Bistrița-Năsăud County (Mărișelu) (figure 3).

Possibility of using water sources for agricultural purposes

The content of sodium, potassium, calcium and magnesium are important factors in irrigation water quality assessment. Considering the high content of these elements in some of the investigated water sources, three indices were calculated (sodium adsorption ratio - **SAR**, sodium percentage - **SP** and magnesium adsorption ratio - **MAR**) in order to evaluate the suitability of using those water sources in agricultural purposes (figure 4).

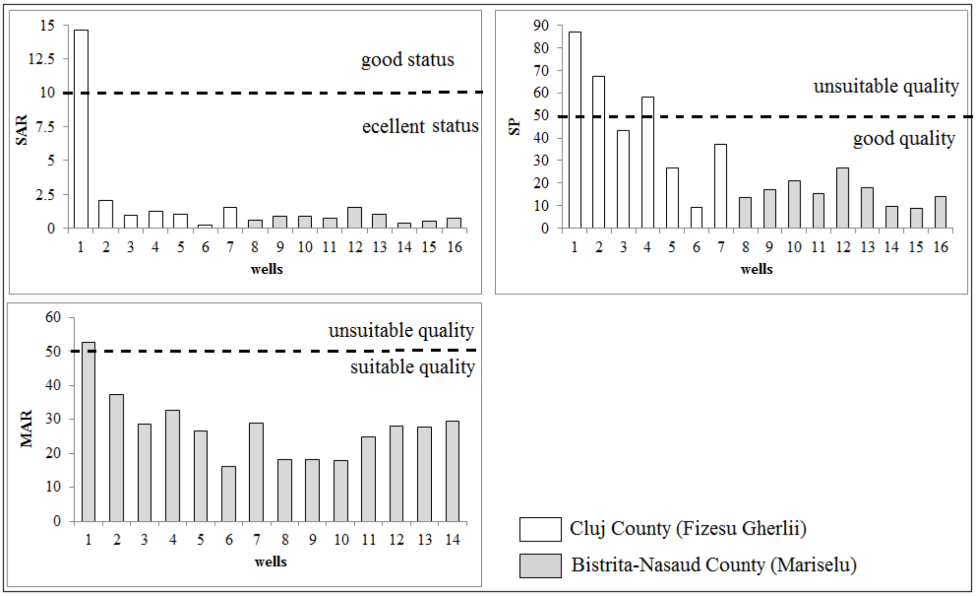

Fig. 4. *Water suitability for agricultural usages based on specific indices*

SAR ranged between 0.2 and 14.6, being below 10, with the exception of one well from Cluj County (Fizeșu Gherlii) (figure 4). If the **SAR** level is below 10, it is considered that the water has an excellent status and can be safely used in irrigations. With the exception of three wells from Fizeșu Gherlii, the level of **SP** was lower than 50%, which indicates a good water quality, being suitable for irrigations purposes. With the exception of one well from Fizeșu Gherlii, the analysed water sources had the **MAR** index below 50, indicating that their quality is suitable for agricultural usages.

Based on the **SAR**, **SP** and **MAR** values, it results that most of the investigated water sources can be safely used in agriculture purposes.

CONCLUSION

The results of the present study showed that there were identified several water sources, where the chemical quality parameter were within the permissible limits, and these waters can be safely used as drinking water sources. On the other hand, there were water sources where the content of NO_2^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mn exceeded the recommendations on national and international forums. The residents who use those water sources for drinking, cooking, recreational or agricultural purposes, should be informed in order to stop or restrict as much as possible the usage of those water sources, because of the possible negative impact on their health.

Generally, the chemical quality parameters presented low fluctuations during the three months of motorisation indicating a good hydrochemical stability of aquifers.

Based on **WQI**, most of the water sources from Cluj County (Fizeșu Gherlii) can be classified as poor quality, while the majority of water sources from Bistrița-Năsăud County (Mărișelu) belong to excellent to good quality class.

Based on the **SAR**, **SP** and **MAR** indices, it results that most of the investigated water sources had an excellent/good quality and they can be safely used in agriculture purposes.

The results have an important practical implication for rural communities in the areas as population has low information on the quality of their drinking water.

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