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ASSESSMENT OF GROUNDWATER QUALITY IN NW OF ROMANIA AND ITS SUITABILITY FOR DRINKING AND AGRICULTURAL PURPOSES

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Abstract

In the present study it was investigated the chemistry of groundwater and its suitability for drinking and irrigation purposes in several urban and rural areas from Cluj, Sălaj, Satu Mare and Alba counties (NW of Romania). In order to evaluate whether the samples are drinkable or not, water quality index (WQI) and daily intakes (DI) were calculated. Water suitability for irrigation was estimated based on specific indices as sodium adsorption ratio (SAR), sodium percentage (% Na) and residual sodium carbonate (RSC). Piper and Gibbs diagrams and chloro-alkaline indices were used to emphasize the hydrogeochemical features of the aquifers. Generally, the wells correspond to Ca – HCO_3 and Ca-Mg-Cl type. Based on the WQI values (10 - 152) a total of 24% of the investigated wells corresponds to an excellent quality status, 16% have a good quality status, 51% have a poor and very poor water quality, while 9% of the wells are unsuitable for drinking. The nitrate proved to be the main contaminant for the analysed wells, having values between 0.2 and 447.1 mg/L. For some samples the DI for NO_2^- (0.33 – 110.67 µg/day/kg bw) and NO_3^- (0.13 - $14.90 \cdot 10^3$ µg/day/kg bw) exceeded the acceptable daily intake. The values of the specific indices SAR (0.1 – 3.6), Na% (1.9 – 58.4%) and RCS (-18.6 – 2.3), showed that all the wells can be safely used for irrigation purposes.

Keywords: aquifer hydrogeochemistry, groundwater quality, health risk assessment, Romania, WQI

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1. Introduction

In both developed and developing countries, there are rural areas, where the groundwater is the main source used for drinking, cooking, agricultural, or recreational purposes (Elsayed Gabr et al., 2020; Zektser and Everett, 2004). Globally, more than one-third of the population uses groundwater for drinking (Al-Ahmadi, 2013), which makes groundwater a vital source in these areas. For many communities there is a tendency to use groundwater as an alternative for the irrigation purpose (Ismail et al., 2020). The pollution increasing and the climatic changes from the last decades had a significant impact in terms of freshwater quality degradation, leading to an increasing of groundwater usages (Elsayed Gabr et al., 2020; Nistor, 2020). A poor water quality is linked to public health concerns, because of the transmission of waterborne diseases (Biglari et al., 2016; Elsayed Gabr et al., 2020). Therefore, the assessment of

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groundwater, in terms of suitability for irrigation and drinking, is extremely important for the safety of the environment and inhabitant's health. These data are very useful for all the decision-makers.

In many rural communities, the general perception is that the groundwater from the wells is cleaner than the surface water or the water from the local distribution supply (FAO, 2016). The chemical and microbiological analyses have often shown the opposite (Elsayed Gabr et al., 2020). The groundwater can be sometimes highly contaminated compared to the local distribution network. The chemical contaminants that are commonly found in the wells water are nitrate, nitrite, ammonium, chlorine, sulphates and heavy metals (Alam, 2013; Bird et al., 2009; EC, 1997; Elsayed Gabr et al., 2020; EFSA, 2015; FAO, 2016; Raju et al., 2011; Stigter et al, 2006; Zektser and Everett, 2004). The groundwater can be polluted by both natural processes (rock-water interaction, evaporation, etc.) and anthropogenic activities (landfills, agricultural practices, etc.).

The main objectives of the present study were: (1) to evaluate the quality of several private wells located in four counties (Cluj, Sălaj, Satu Mare and Alba) from the north-western part of Romania, by analyzing the general physico-chemical parameters and the content of the dissolved ions and metals; (2) to identify the main hydro chemical features of the aquifers; (3) to evaluate their suitability for drinking and irrigation purposes based on specific indices. To our knowledge, no similar study has been performed for some of the investigated areas.

2. Investigated areas

The private wells are located in eleven villages (in Satu Mare, Sălaj, Cluj and Alba counties) and three urban areas (in Alba and Cluj counties) (Fig. 1) (Table 1). The rural areas consist of small to medium communities, with 106 – 3,622 inhabitants, while the urban areas have 350 – 47,744 inhabitants (Table 1) (INS, 2013).

Satu Mare County has an area of 4,418 km^2 in the north-western part of Romania. It has a low relief and its topography increases through north-eastern part, where Oaş and Gutâi Mountains are located (Bird et al., 2009). The investigated localities are situated on Someş Plain which contains specific characteristics in terms of hydrographic network and underground waters. The evolution of the aquatic systems is linked with the formation of the Pannonian Basin and of the volcanic landforms. In the subsoil of Someş Plain a thick stack of different structures has been accumulated influencing the hydrogeological conditions. Thus, two different environments were separated: a deeper one and one located closer to the surface. The last one is formed into the Pleistocene and Holocene deposits which contain an alternation of sedimentary materials represented by pebbles, clays, loamy sands, sandy clays, loess, slimes a.o. These deposits have a great influence on the quality and quantity of underground waters (Sanislai et al., 2018).

Sălaj County is situated in the north-western part of Romania, between Eastern Carpathians and Apuseni Mountains, on the Someșan Plateau. This plateau is characterized by the unity of the fluvial system, a relatively chilly and moist climate and luvisols with different levels of clay migration (Sorocovschi et al., 2011). The studied area is situated at the basal part of the Meseș Mountains being formed by young sedimentary formations (Pliocene in age) containing clays, sands and marls eroded in some parts and revealing crystalline formations (Bilașco et al., 2009).

The localities from Cluj County are situated in the western part of the Transylvanian Basin, which is part of the Central Paratethys being a 200 km long and 250 km wide semi-isolated back-arc basin (Krézsek et al., 2010). Most of its filling consists of Miocene deposits. In the studied area the Sarmatian deposits are widespread and comprise siliciclastics materials, such as marls and sandstones, subordinate conglomerates and evaporites (Krézsek et al., 2010).

Table 1. Location and characterization of the investigated private wells

Investigated area		***Inhabitants***(1)	***Well depth (m)***	***Well age***	***Water usage***	***Chemical treatment***
Satu – Mare County (SM)	Botiz village (Botiz commune)	3.622	6 – 10	40 – 60 years	domestic, recreational and agricultural purposes	no chemical treatment
	Micula village (Micula commune)	3.040				
Sălaj County (SJ)	Hereclean village (Hereclean commune)	446	6 – 11	12 – 50 years		
Cluj County (CJ)	Mureșenii de Câmpie village (Palatca commune)	106	6 – 15	2 months – 170 years		
	Petea village (Palatca commune)	127				
	Sava village (Palatca commune)	199				
	Bărăi village (Căianu commune)	276				
	Căianu Vamă village (Căianu commune)	353				
	Vaida Cămăraș village (Căianu commune)	811				
	Ceanu Mare village (Ceanu Mare commune)	910				
	Câmpia Turzii urban area	22.223				
	Turda urban area	47.744				
Alba County (AB)	Mihăceni village (Unirea commune)	274	7 – 15	15 – 60 years		
	Recea urban area (Alba Iulia)	350				

(1)based on 2011 census (INS, 2013)

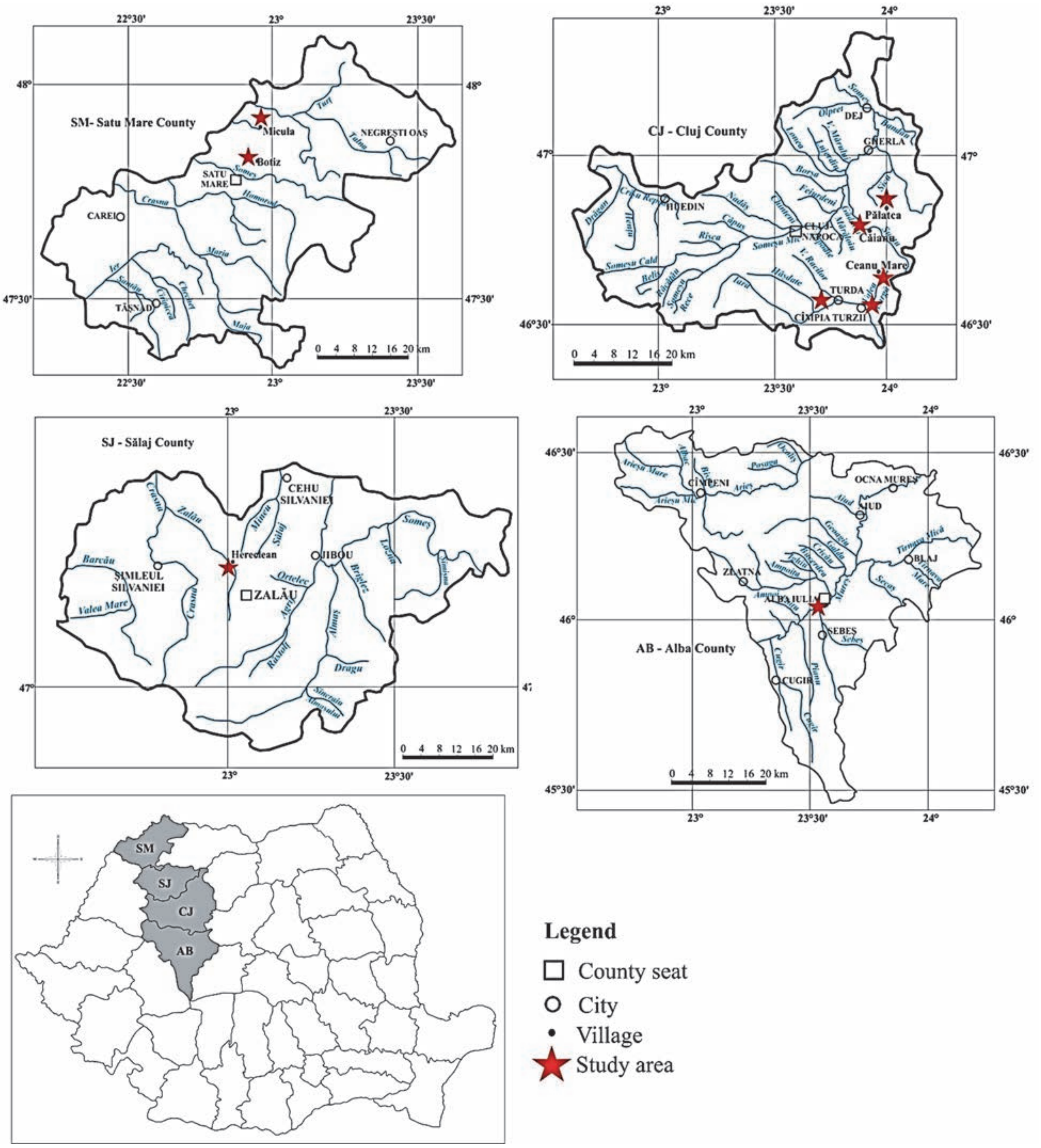

Fig. 1. Location of the investigated areas

Măhăceni area (Alba County) is located in the central-north-western part of Romania at the contact between Trascău Mountains and the Transylvanian Basin. From geological point of view, this area consists of Miocene formations revealing Badenian (marls, sand marls, sandstones) and Sarmatian deposits (sandstones, marl clays and sandstones) (Onac et al., 2008). Recea is part of Alba-Iulia city (Alba County) and it is situated on the Mureș River first terrace where the fertile aluviosols were developed. In this area, Mureș River looks like an accumulation intermountain plain. It is situated between two different lithological units: crystalline and eruptive rocks in the northern part and crystalline and sedimentary rocks in the southern part. On the first terrace the underground water is situated at 3.9 – 5.4 m in depth (Popescu et al., 2013).

3. Material and methods

3.1. Sampling, sample processing and analysis

A total of 69 samples were collected from private wells, which have a relatively low depth, between 6 and 15 m (Table 1). Generally, the wells are 12 to 60 years old, no chemical treatment is applied and the water is used for domestic, recreational and agricultural purposes. For some of the investigated communities there are no local supply networks and the private wells are the main source of drinking water. The waters were sampled during the summer season (2018).

The water samples were filtered through nylon syringe filters (0.45 μm) and placed in clean polyethylene vials. The samples collected for cations and metals analyses were acidified at a pH ≈ 2 (with HCl and HNO_3 respectively) in order to prevent their precipitation/adsorption during storage in dark and cold (4°C) conditions. Before ions analysis, the samples were diluted with ultrapure water (18.2 MΩ·cm) to an EC ≈ 100 μS/cm, in order to protect the column and to avoid the detector oversaturation.

The analyzed physico-chemicals parameters were pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS) and salinity. They were measured *in situ* by a portable multiparameter (WTW Inolab 320i, Germany).

The dissolved ions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}) were analysed by using an ion chromatograph system (IC 1500 Dionex, USA). Based on calcium and magnesium concentrations, the total hardness (TH) was calculated. The analyses for CO_3^{2-} and HCO_3^- were performed by titration with HCl (0.1M) in the presence of phenolphthalein and methyl orange as indicators. The metals (Cu, Zn, Fe, Cr, Cd, Pb, Ni) were analysed by atomic absorption spectrometry (AAS) using a ZeeNIT 700 system (Analytik Jena, Germany) equipped with a single-element hollow cathode lamp, an air-acetylene burner and a graphite furnace.

3.2. Hydrogeochemical features of the aquifers

Piper and Gibbs diagrams were used to highlight the hydrogeochemical features of the groundwater in the studied areas (Gibbs, 1970; Piper, 1944). All the concentrations were in meq/L. Piper diagram is used to emphasize the water facies based on the dominant ions. Gibbs diagrams were plotted in order to identify the impact of atmospheric precipitation, rock–water interaction and evaporation over groundwater geochemistry.

Chloro-alkaline indices (CAI 1 and CAI 2) were calculated in order to investigate the ion exchange reaction (Schoeller, 1965). The indices were calculated based on the Eqs. (1-2), where all the concentrations are expressed in meq/L (Ismail et al., 2020; Schoeller, 1965):

$$CAI\ 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{1}$$

$$CAI\ 2 = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-} \tag{2}$$

Positive values of CAI 1 and CAI 2 indices, indicate that sodium and potassium ions are exchanged with magnesium and calcium ions in water, while negative values indicate that magnesium and calcium are exchanged with sodium and potassium ions. Negative values for CAI 1 and CAI 2 reflect a chloro – alkaline disequilibrium (Ismail et al., 2020).

3.3. Water suitability for drinking purposes

The analysed physico-chemical and chemical parameters were used to calculate the water quality index (WQI) (Gharibi et al., 2012). WQI is a complex index which is very useful to present data regarding the water quality status to both, the general public and policy makers. WQI was calculated based on the arithmetic index method (Horton, 1965) as it is shown in Eqs. (3–6).

$$WQI = \frac{\sum_{i=1}^{n} q_i \cdot W_i}{\sum_{i=1}^{n} W_i} \tag{3}$$

$$q_i = \left(\frac{V_a - V_i}{S_i - V_i}\right) \cdot 100 \tag{4}$$

$$W_i = \frac{k}{S_i} \tag{5}$$

$$k = \frac{1}{\sum_{i=1}^{n} \frac{1}{S_i}} \tag{6}$$

where: q_i is the quality rating for ith parameter; W_i is the unit weightage of the ith parameter; *n* is the number of quality parameters; V_a is the analyzed value of the parameter; V_i is the ideal value of the parameter (7 for pH and 0 for the other parameters) (Tripaty and Sahu, 2005); S_i is the maximum permissible limit of the ith parameter, according to drinking water standards and *k* is the constant of proportionality.

Based on *WQI* values, there are five water quality classes: excellent (<25), good (26 – 50), poor (51 – 75), very poor (76 – 100) and unsuitable for drinking (>100) (Horton, 1965). The potential health risk associated to the contaminants intake via the water ingestion was evaluated by calculating the daily intake (DI) (USEPA, 1989) (Eq. 7):

$$DI = \frac{C \cdot IR}{BW} \tag{7}$$

where, *DI* is the daily intake (mg/day/kg bw); *C* is the element concentration in water (mg/L); *IR* is the water ingestion rate (2 L/person/day); and *BW* is the average adult body weight (60 kg for an adult person in Europe, according to FAO–WHO (2014)).

The results were compared with the adequate daily intake (ADI) or with the tolerable daily intake (TDI).

3.4. Water suitability for agricultural purposes

An excess of Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-} or HCO_3^- in the irrigation water can affect the quality of soil, by reducing the soil permeability, it can also change the balance between Na^+, Ca^{2+} and Mg^{2+}, which will inhibit the plant growth (He et al., 2019; Jain and Vaid, 2018; Song and Yang, 2017). In order to evaluate if the water from the private wells is suitable for agricultural purposes, the following indices were calculated (see Eqs. 8–10): sodium adsorption ratio (SAR) (Karanth, 1987), sodium percentage (%Na) (Wilcox, 1955) and residual sodium carbonate (RSC) (Eaton, 1950):

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (8)$$

$$\%Na = \frac{Na^{+} + K^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \cdot 100 \quad (9)$$

$$RCS = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}) \quad (10)$$

where, all the ions concentrations are expressed in meq/L.

4. Results and discussion

4.1. General physico-chemical parameters and the content of dissolved ions and metals

The analyzed waters had a neutral pH, with no significant fluctuations among the investigated areas (Fig. 2). Three wells from Botiz village (SM) and three wells from Ceanu Mare village (CJ) had a more acidic pH than the national and international recommendation for the drinking water (6.5 – 9.5 and 6.5 – 8.5) (Law 458/2002; WHO, 2011). The wells from Cluj and Sălaj counties proved to have a higher EC, TDS and salinity than those from Satu Mare and Alba Counties, indicating a higher content of dissolved ions (especially Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-}) (Fig. 3 and 4). A possible cause of the EC, TDS and salinity fluctuation might be the interaction between rock and water and/or due the agricultural activities (Abbasnia et al., 2018a). For all the analysed wells, the EC was within the safe limit of 2,500 μS/cm (Law 458/2002). Based on the total hardness value, the majority (94%) of the analysed waters were soft (TH < 60 mg $CaCO_3$/l) and 6% of the wells had moderately hard water (TH between 60 and 120 mg $CaCO_3$/l) (Sharma et al., 2016; Singh, 2019).

Several ions (Li^{+}, NH_4^{+}, F^{-}, Br^{-}, PO_4^{3-} and CO_3^{2-}) were not detected in the analysed waters. The abundance of ions was $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$ (Fig. 3) and $HCO_3^{-} > SO_4^{2-} > Cl^{-} > NO_3^{-} > NO_2^{-}$ (Fig. 4). For some wells, the content of the dissolved ions exceeded the safety limits recommended for the drinking water.

Exceedances were registered in the case of NO_3^{-} (34%), Ca^{2+} (28%), Cl^{-} (15%), SO_4^{2-} (9%), NO_2^{-} (7%), Mg^{2+} (3%) and Na^{+} (1%) (Figs. 3 and 4). The chemical features of the aquifers can reflect the geographical and pedological features of the area, the geological and tectonic characteristics of the aquifers, the mineralogical composition of the aquifer, the water-rock interaction time, the water flow table, the anthropogenic effect etc. Further research is needed in order to make assumptions about the fluctuation of the chemical characteristics of each aquifer.

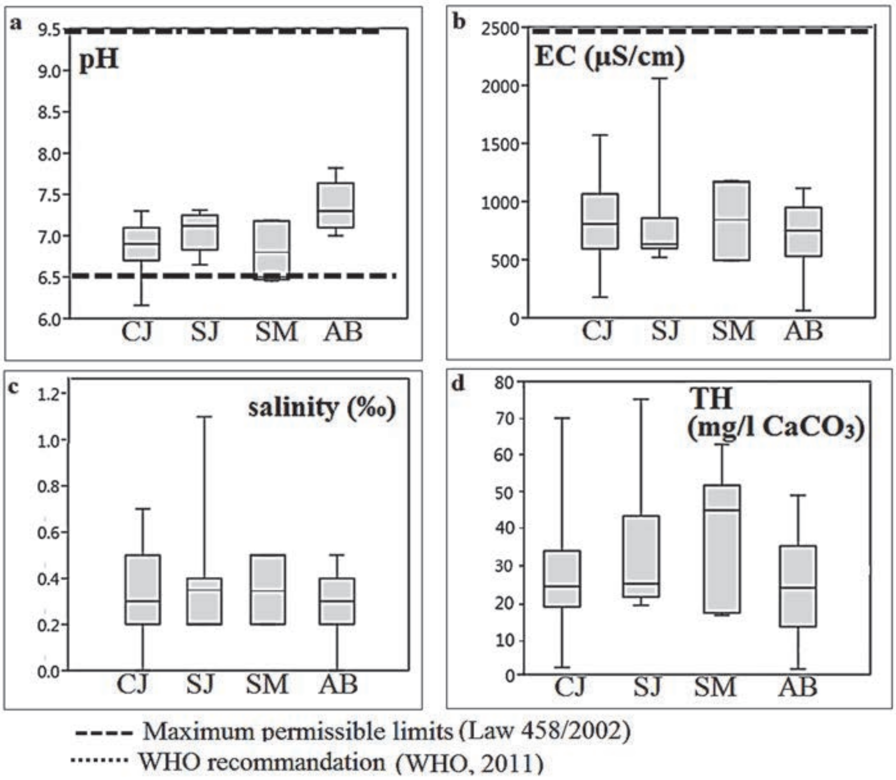

Fig. 2. The fluctuation of pH (a), electrical conductivity (b), salinity (c) and total hardness, (d), depending on the investigated areas

The nitrate proved to be the main contaminant (34%) for the analyzed wells, having concentrations between 0.2 and 447.1 mg/L, exceeding the safe limit for drinking water (50 mg/L). Nitrite was identified in 48% of the wells and had values between 0.01 and 5.3 mg/L. For 7% of the wells, the content of nitrite exceeded the safe limit (0.5 mg/L) for drinking water. For the investigated wells, the main sources of NO_2^- and NO_3^- contamination are the agricultural activities, the inappropriate practices for manure storage, unsanitary systems of sewage disposal and the presence of septic tanks in the wells proximity. Similar studies, like the one performed by Abbasnia et al. (2018a), Elsayed Gabr et al. (2020) or Breaban and Breaban (2020), associate the presence of nitrates and nitrites in the groundwater with these sources. The presence of high levels of nitrite and nitrate in drinking water can be a real threat for consumers' health, considering that these substances are probably carcinogenic to humans (IARC, 2010). High concentration of nitrates was reported in the southern (Breaban and Breaban, 2020) and eastern part of Romania (Paiu and Breaban, 2016).

According to the results of the present study, this scenario is also confirmed in areas located in the north and north-western part of Transylvania. Possible solutions for limiting the nitrate or nitrite contamination/migration into the groundwater include the drilling at greater depths (Minea, 2020), the usage of barriers walls like the double sheet pile sand (Elsayed Gabr et al., 2020), the aerobic granular sludge technology (Hurtado-Martinez et al., 2020) etc. In the analyzed waters, the metals abundance follows the sequence Zn > Fe > Cu > Cr > Ni > Pb > Cd (Fig. 5). The content of Zn, Cu, Cr was within the maximum permissible limits for all the analysed wells, while the level of Pb, Ni, Fe and Cd exceeded the safe limits for 23%, 17%, 13% and 6% of the analysed samples (Fig. 5).

A special attention should be paid to the wells contaminated with Cd (classified by IARC as human carcinogen – group 1), Pb and Ni (possibly carcinogenic to humans – group 2B). As it is mentioned in some studies (Oni and Hassan, 2013), the presence of elevated levels of Pb in wells samples in areas with no industrial activities, can be linked to improper disposal of Pb-containing domestic waste within the surroundings. The presence of cadmium in groundwater can be associated with the usage of natural (manure) and inorganic fertilizers into the agricultural soils from surroundings (Nicholson et al., 2003). Generally, the heavy metals pollution of groundwater, in rural areas, is associated with agricultural activities, through three main components: pastures, vegetable and animal production.

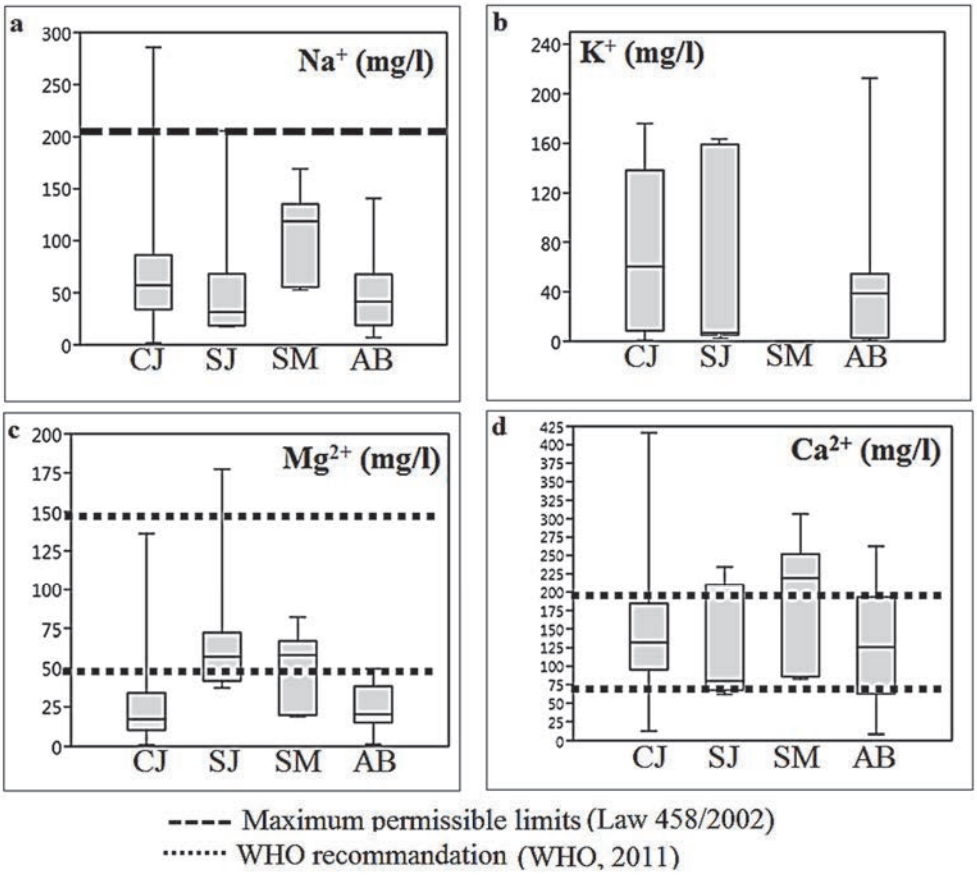

Fig. 3. The fluctuation of sodium (a), potassium (b), magnesium (c) and calcium (d), depending on the investigated areas

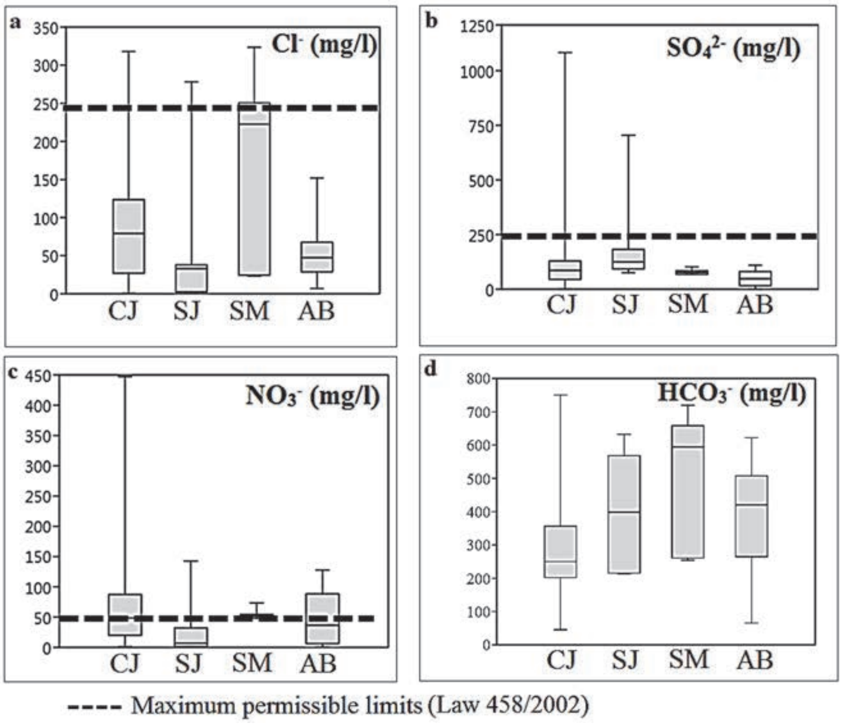

Fig. 4. The fluctuation of chloride (a), sulfate (b), nitrate (c) and bicarbonate (d), depending on the investigated areas

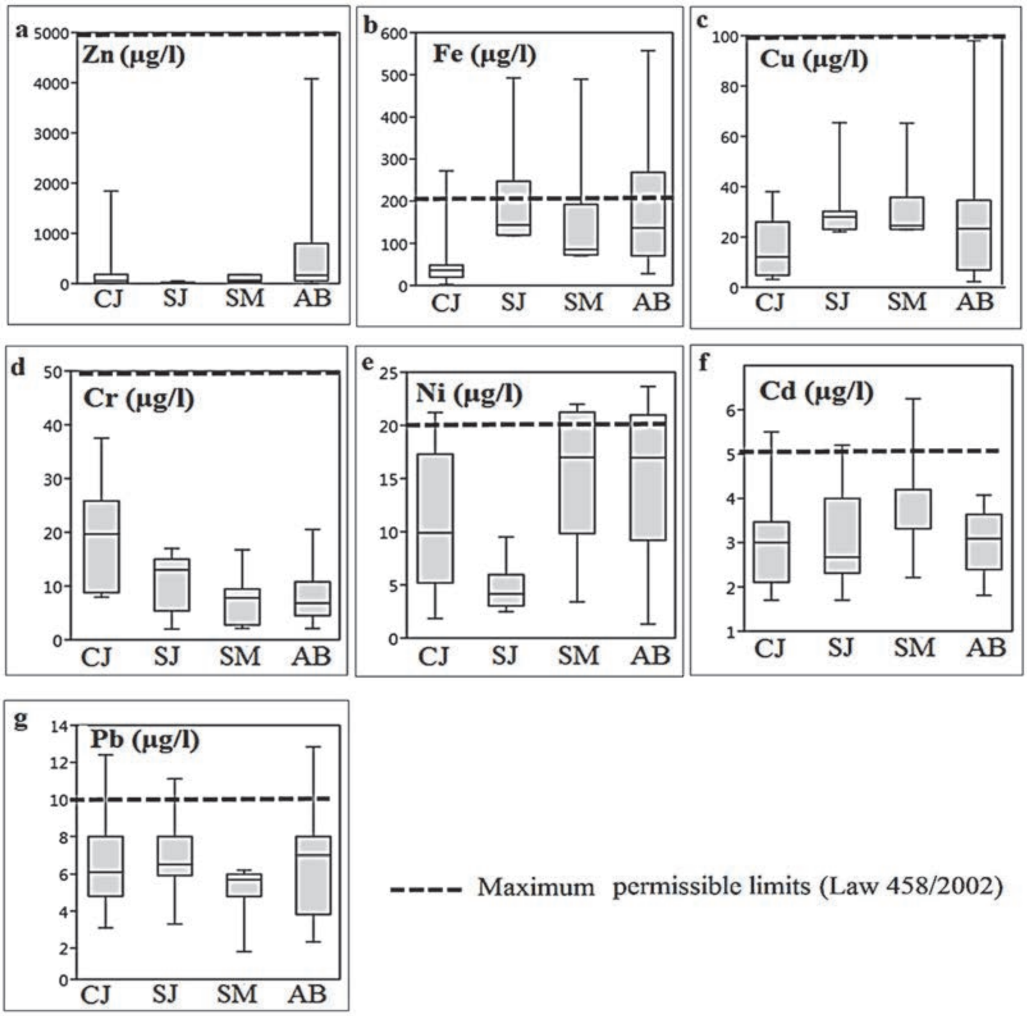

Fig. 5. Fluctuation of zinc (a), iron (b), copper (c), chromium (d), nickel (e), cadmium (f) and lead (g) in analyzed wells, depending on the investigated areas

The excess of chemical fertilizers and organic chemicals used to protect crops and/or presence of faeces, urine and grassland degradation due to the animal growth, can have a significant negative impact on the groundwater quality from rural areas (Burtea et al., 2015; Briciu et al., 2016; Capatina and Simionescu, 2008; Cojocariu et al., 2012).

4.2. Hydrogeochemical features of the aquifers

The main hydrochemical facies of the investigated groundwater were highlighted by plotting the Piper diagram, using the concentration of major ions expressed in meq/l (Fig. 6). The data showed that most of the wells from Cluj County correspond to Ca – HCO_3 and Ca – Mg – Cl type, and only few samples are classified as Ca – Cl type (Fig. 6). The wells from Sălaj County belong to Ca – HCO_3 and Ca – Mg – Cl type. The wells from Satu Mare correspond to Ca – HCO_3 facies, while the wells from Alba County are Ca – HCO_3 and Ca – Na – HCO_3 type. The abundances of Ca – HCO_3 and Ca – Mg – Cl waters can be associated with the presence of marls and clays in those areas. The dominance of HCO_3^- ions indicates a freshwater environment, emphasizing the fact that the area is a recharge zone (Raoa and Chaudhary, 2019).

The Gibbs diagrams (Fig. 7) showed that the rock weathering and water–rock interaction are the main processes, which control the hydrogeochemical evolution of groundwater in the investigated areas. In the case of one sample from Sălaj County and two samples from Alba County, the hydrogeochemistry is dominated by the evaporation and precipitation processes (Fig. 7).

The results of the present study are similar to those reported in other studies (Alam, 2013; Raju et al., 2011; Madhav et al., 2018), which confirm that in alluvial plains, the groundwater chemistry is dominated by the rock–water interface.

The CAI indices ranged between -0.67 and 0.56, having negative values for 65% of the analysed samples. It results that for 65% of the investigated wells the chemistry is governed by the indirect base-exchange reaction, in which Mg^{2+} and Ca^{2+} are exchanged with Na^+ and K^+ from rocks, indicating a chloro-alkaline disequilibrium (Ismail et al., 2020; Schoeller, 1965). For the other 35% of the wells, which have positive ratios, the direct base-exchange reaction are dominant, in this case Na^+ and K^+ are exchanged with Mg^{2+} and Ca^{2+} in water (Ismail et al., 2020; Schoeller, 1965).

4.3. Water suitability for drinking purposes

The WQI ranged between 10 – 119 (Cluj County), 28 – 152 (Sălaj County), 32 – 91 (Satu Mare County) and 12 – 129 (Alba County) (Fig. 8). Based on the WQI, a total of 24% of the investigated wells corresponds to an excellent quality status, 16% are classified as good quality status, 48% have a poor water quality, 3% of the wells have a very poor water quality, while 9% of the wells are unsuitable for drinking. In conclusion, WQI emphasizes that only 40% of the private wells are suitable for drinking (having an excellent and good quality status), while 60% are not recommended to be used for drinking in high quantities and for a long time (having a "poor", "very poor" and "unsuitable for drinking" status).

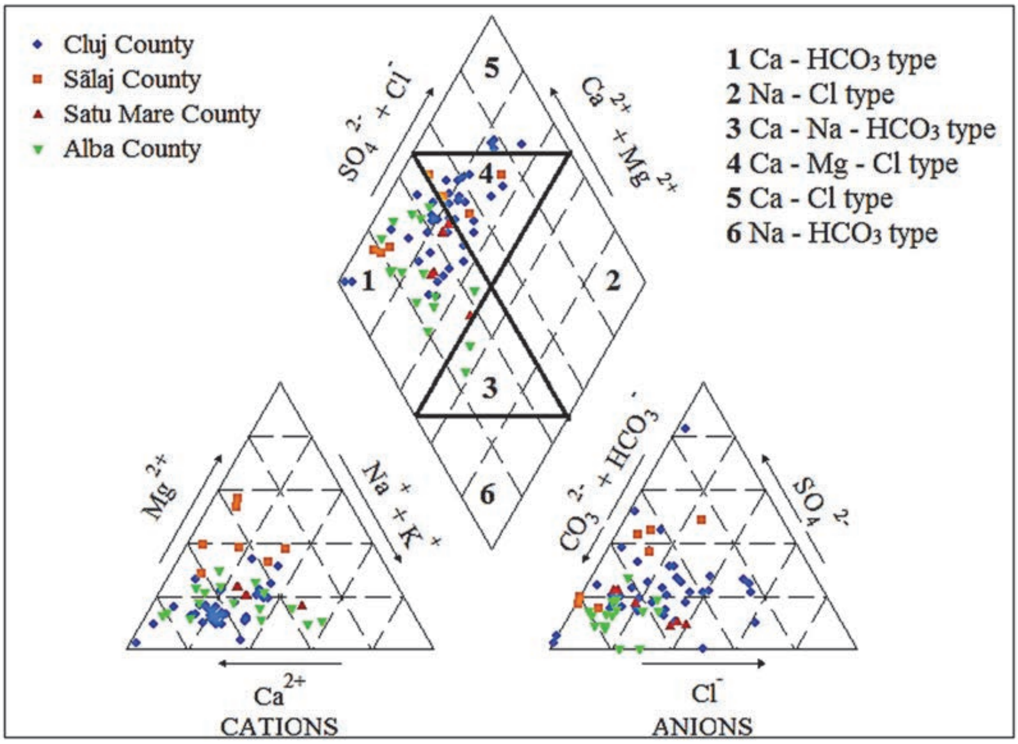

Fig. 6. Piper diagram showing the hydrochemical facies of groundwater samples

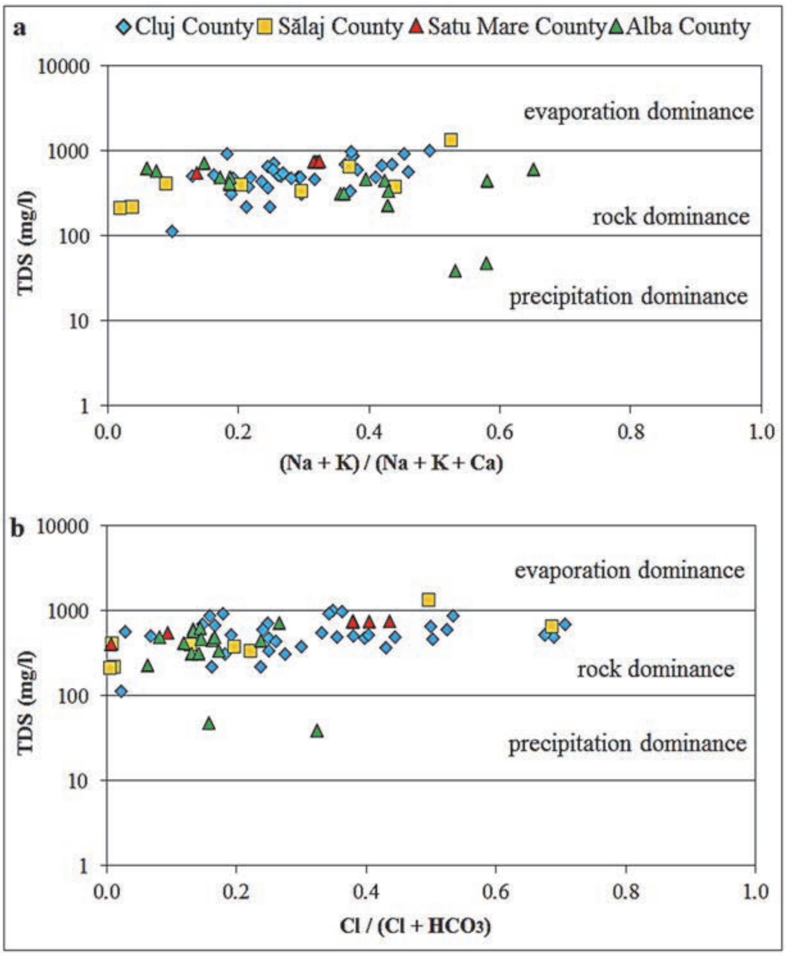

Fig. 7. Gibbs diagrams showing the main mechanism which controls the groundwater chemistry, based on cations (a) and anions (b) concentration

The poor quality of these waters is associated with the presence of high levels of nitrate, nitrite and heavy metals. In the case of these wells, the locals should use the water from local supply networks, or other sources. There are studies, in which the WQI showed a poor groundwater quality comparing to the present study; for example, in Barand area (Hungary) (Mester et al., 2020), Campina de Faro and Campina da Luz (Portugal) (Stigter et al., 2006), or in Tiruchirappalli (India) (Jha et al., 2020). There are areas, where the WQI of the groundwater indicated a superior quality, like villages of Chabahr city, Sistan and Baluchistan province (Iran) (Abbasnia et al., 2018a; Abbasnia et al., 2018b), Dagu River Basin (China) (Fang et al., 2020) or Sanganer Tehsil Jaipur (India) (Shahnawaz et al., 2020).

The data regarding the daily intake of ions and metals via water ingestion are synthetized in Table 2. For 1.5% of the analysed wells, the DI_NO_2^- exceeded the acceptable daily intake (60/70 µg/day/kg bw) recommended by the European Commission's Scientific Committee on Food (SCF) (EC 1992; EC 1997) and the Joint Expert Committee of the Food and Agriculture (JEFCA) of the United Nations/World Health Organization (WHO) (EFSA 2008; FAO/WHO 2003). For 10.3% of the investigated wells, the intake of nitrate via water consumption proved to be higher than the acceptable daily intake ($3.7 \cdot 10^3$ µg/day/kg bw) (EFSA 2008; FAO/WHO 2003).

The ingested dose indicates that the continuous consumption of water from some of the investigated private wells represents a significant risk for human health, because of the high content of nitrite and nitrate. Immediate intervention is required to prevent the long-term exposure of locals.

For the wells where the content of Pb, Ni, Fe and Cd exceeded the permissible limits, the DI showed that if these waters are used in reasonable quantities (2 l/day) for drinking, they do not pose a significant threat for consumer health. People who use these wells should be informed to restrict the usage of these sources as much as possible.

4.4. Water suitability for agricultural purposes

Water suitability for irrigation purposes was evaluated based on specific indices. The results are synthetically presented in Table 3. The calculated indices showed that all the investigated wells can be safely used for irrigation purposes, having a suitable quality for this type of usage.

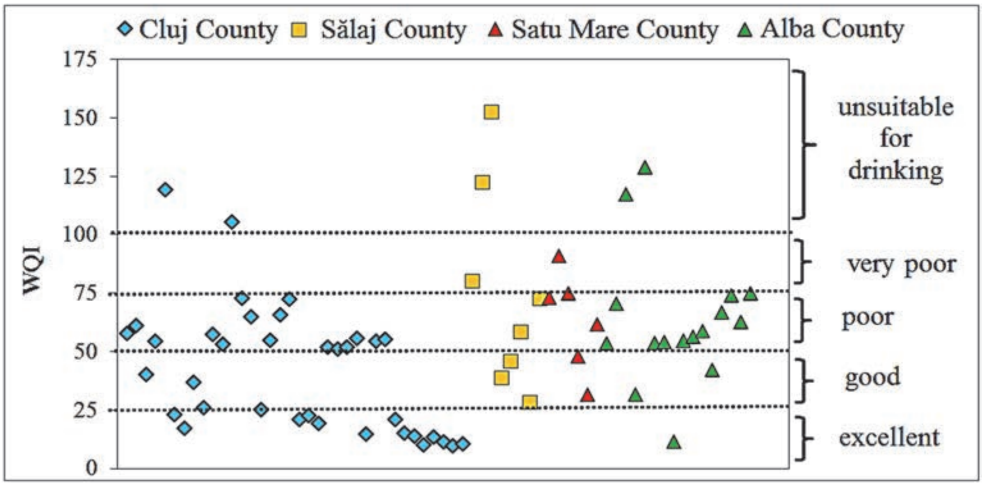

Fig. 8. Water quality status based on WQI

Table 2. The daily intake of ions and metals via water ingestion

Parameter	*DI (μg/day/kg bw)*				*Recommendation (μg/day/kg bw)*	*Total exceeding (%)*
	Cluj	*Sălaj*	*Satu Mare*	*Alba*		
NO_2^-	0.67 – **110.67** (12.0) (1)	3.67 – 41.33 (22.50)	–	0.33 – 16.33 (2.47)	60 (2) / 70 (3)	1.5
NO_3^-	0.13 – **14.90**·10^3 (2.47·10^3)	0.22 – **4.75**·10^3 (2.02·10^3)	1.59 – 2.45·10^3 (1.84·10^3)	0.006 – **4.25**·10^3 (1.62·10^3)	*3.7·10^3* (3)	10.3
Cd	0.06 – 0.18 (0.09)	0.06 – 0.17 (0.10)	0.07 – 0.21 (0.13)	0.06 – 0.14 (0.10)	0.83 (4)	0
Pb	0.10 – 0.41 (0.22)	0.11 – 0.37 (0.23)	0.06 – 0.21 (0.16)	0.08 – 0.43 (0.23)	3.57 (5)	0
Ni	0.06 – 0.71 (0.36)	0.08 – 0.32 (0.16)	0.11 – 0.73 (0.51)	0.04 – 0.79 (0.49)	11(6) / 2.8 (7)	0
Cu	0.10 – 1.27 (0.53)	0.73 – 2.18 (1.06)	0.77 – 2.17 (1.03)	0.07 – 3.27 (0.86)	500 (8)	0
Fe	0.08 – 9.05 (2.07)	3.93 – 16.42 (6.57)	2.35 – 16.30 (4.98)	0.93 – 18.57 (5.79)	800 (8)	0
Zn	0.10 – 61.33 (9.75)	0.20 – 1.79 (0.77)	1.15 – 6.09 (3.01)	1.37 – 136.00 (23.46)	300 – 1,000 (8)	0

(1) min – max (mean); (2) *acceptable daily intake (ADI) recommended by the European Commission's Scientific Committee on Food (SCF) (EC 1992; EC 1997);* (3) *acceptable daily intake (ADI) recommended by the Joint Expert Committee of the Food and Agriculture (JEFCA) of the United Nations/World Health Organization (WHO) (EFSA 2008; FAO/WHO 2003);* (4) *provisional tolerable daily intake based on the provisional tolerable monthly intake of 25 μg/kg bw (FAO-WHO, 2018);* (5) *TDI (FAO-WHO, 2001);* (6) *TDI (Tolerable Daily Intake) (WHO, 2007);* (7) *TDI (EFSA, 2015);* (8) *PMTDI (Provisional Maximum Tolerable Daily Intake) (FAO-WHO, 2018);*

Table 3. Evaluation of water suitability for agricultural purposes, based on specific indices

Wells location	*SAR*	*Na (%)*	*RSC*
Cluj County	0.1 – 3.6 (1.2) (1)	1.9 – 36.8 (23.7)	-17.9 – 0.1 (-4.6)
Sălaj County	0.3 – 2.5 (0.9)	5.5 – 32.9 (16.3)	-18.6 – -2.2 (-5.9)
Satu Mare County	1.4 – 2.2 (1.8)	24.2 – 29.1 (26.0)	-10.4 – -1.4 (-5.4)
Alba County	0.3 – 2.1 (1.1)	5.3 – 58.4 (27.6)	-7.2 – 2.3 (-2.2)
Suitability	**excellent** (< 10) (Richards, 1954; Singh, 2019)	**excellent** (< 20), **good** (20 – 40), **permissible** (40 – 60) (Wilcox, 1955; Singh, 2019)	**suitable** (< 1.25), **marginally suitable** (1.25 – 2.5) ; (Lloyd and Heathcote, 1985; Singh, 2019)

5. Conclusions

The analysed physico-chemical parameters indicated some specific problems for the investigated wells, due to the high content of NO_3^-, Ca^{2+}, Pb, Ni, Cl^-, Fe, SO_4^{2-}, NO_2^-, Cd, Mg^{2+} and Na^+. The WQI provided a clear understanding of the overall water quality. Based on WQI, a total of 40% of the private wells are suitable for drinking, while 60% are not recommended to be used for drinking in high quantities and for a long time.

The calculated ingested dose indicated that the continuous consumption of water from some of the investigated private wells represent a significant risk for human health, because of the high content of nitrite and nitrate.

Most of the wells correspond to Ca-HCO_3 and Ca-Mg-Cl type. The Gibbs diagrams showed that the rock weathering and water–rock interaction are the main processes, which control the hydrogeochemical evolution of the analyzed groundwater. The CAI indices reflect the impact of the indirect base-exchange reaction on the groundwater chemistry, indicating a chloro-alkaline disequilibrium.

The calculated indices showed that all the investigated wells can be safely used for irrigation purposes, having a suitable quality for this type of usage.

The present study emphasized the necessity of groundwater quality assessment in rural areas. The obtained results are useful both for the consumers and for the policymakers.

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