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# GROUNDWATER CHEMISTRY RENDERING USING DUROV, PIPER AND ION BALANCE DIAGRAMS. STUDY CASE: THE NORTHERN PART OF SIBIU COUNTY

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**ABSTRACT.** The chemical behaviours of groundwater are dynamic fields of research. Variations and changes of groundwater, as drinking water source composition impress negative effects on human health. In Romania, groundwater represents free and common fresh water. Chemistry and quality of groundwater is changed due to natural and anthropogenic factors. The aim of this study is to determine and evaluate the chemical composition of groundwater from the northern part of Sibiu County using Piper, Durov, and ion balance diagrams. The graphical representations show the type of waters based on the ion content. As results, high concentrations of major anions ($SO_4^{2-}$, $Cl^-$, $NO_2^-$, $NO_3^-$) and cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$) were found and according to Piper and ion balance diagrams, the prominent types of waters are $Ca^{2+}$-$HCO_3^-$ type.

***Keywords:*** *groundwater, chemical composition, Durov diagram, Piper diagram, ion balanced diagram*

## INTRODUCTION

Water is a limited and vital resource for humans and nature. Water quality is significant, especially when it comes to anthropogenic and natural pollution. The importance of groundwater is given not only by its valuable mineral content, as drinking water, but also by its flow of pollutants.

Worldwide, countries face the same problems regarding the deterioration of groundwater quality. Natural pollution affects aquifers (China, India, European countries) composition with high concentrations of arsenic as natural enrichment

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of groundwater [1, 2]. Metal pollution and high concentrations of varied chemical compounds ($SO_4^{2-}$, $Cl^-$, $NO_2^-$, $NO_3^-$) impress negative influences on groundwater and soil quality [3-6].

In Romania, groundwater resources present significant concentrations of $NO_3^-$, $SO_4^{2-}$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ [7]. Dominant types of waters are $Mg^{2+}$-$Ca^{2+}$-$HCO_3^-$ and $Na^+$-$HCO_3^-$ types [8].

The objective of the current study is the determination of the physico-chemical composition of groundwater sources (water wells and streams) using Durov and Schoeller diagrams. The types of water are ascertained depending on the abundance of ions, using Piper and ion balanced diagrams.

## RESULTS AND DISCUSSION

Table 1 presents the summary statistics of the physicochemical indicators (pH, EC-electrical conductivity, TDS-total dissolved solids, $NO_2^-$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$) along with the environmental quality standards according to Romanian legislation [9], World Health Organisation Guidelines for drinking water [10] and U.S. EPA National Primary and Secondary Drinking Water Regulations [11].

**Table1.** Summary statistics of the physicochemical parameters

| Variable | | Minimum | Maximum | Water quality standards* | Guidelines values** | MCL*** |
|---|---|---|---|---|---|---|
| **pH (pH units)** | | 6.99 | 7.96 | 6.5-9.5 | - | 6.5-8.5 |
| **EC (µS/cm)** | | 637 | 1572 | 2500 | - | - |
| **TDS** | **(mg/l)** | 319 | 786 | - | - | 500 |
| **$NO_2^-$** | | 0.1 | 7.0 | 0.5 | 3.0 | 1.0 |
| **$NO_3^-$** | | 7.7 | 252 | 50 | 50 | 10 |
| **$SO_4^{2-}$** | | 30 | 252 | 250 | - | 250 |
| **$Cl^-$** | | 7.9 | 78 | 250 | - | 250 |
| **$Na^+$** | | 6.2 | 62 | 200 | - | - |
| **$Ca^{2+}$** | | 51 | 129 | 200 | - | - |
| **$Mg^{2+}$** | | 5.9 | 23 | 200 | - | - |
| **$K^+$** | | 0.65 | 13 | - | 20 | - |
| **$HCO_3^-$** | | 201 | 592 | - | - | - |

*According to Romanian Legislation [9], **according to the Guidelines for Drinking Water [10], ***according to U.S. EPA Legislation National Primary and Secondary Drinking Water Regulations [11].

The results show significant values for the indicators with higher values as the standards. Sample water S19 presents the higher value for the TDS (figure 1). Water wells samples S3, S4, S5, S6, S7, S17 and spring samples

S20, S21 present significant values for $NO_2^-$, while S7 is ten times higher as the MCL (maximum concentration level). Except samples S1, S6, S17, the rest of the water samples exceeds twice and more the $NO_3^-$ MCL. Sample S15 exceeds the $SO_4^{2-}$ MCL, while for the other samples the obtained values are lower as 250 mg/l (MCL).

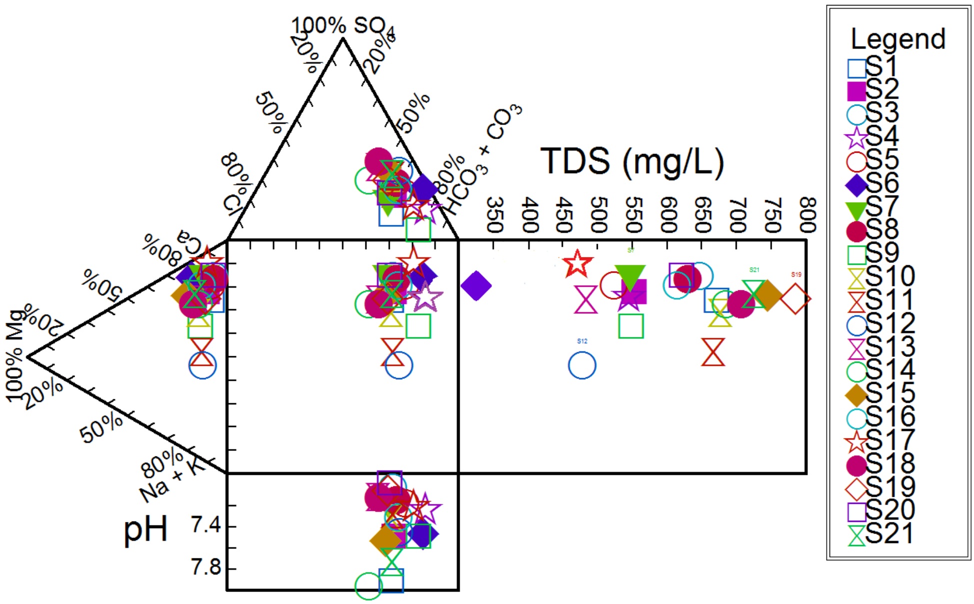


**Figure 1.** Chemical composition of water samples

The $HCO_3^-$ values are ranging from 201 mg/l (F1) to 592mg/l (F4), with a 444 mg/l mean. The Durov diagram is used to graphically illustrate cations and anions concentrations, related to pH and TDS values (figure 1).

The relative ion concentrations (after the charge balancing) are represented graphically by the ion balanced diagrams.

According to ion balance diagrams, all nineteen well water samples and both public spring samples are $Ca^{2+}$-$HCO_3^-$ type. Samples S1 and S6 present the lowest amount for the $NO_3^-$ and $SO_4^{2-}$ concentrations (figure 2).

Dispersion of ions is represented using Piper diagram. Largest anion dispersion is represented by $HCO_3^-$ concentration, and the $Ca^{2+}$ concentration has the largest cation dispersion. Pipere diagram shows the dominant water types, which is $Ca^{2+}$-$HCO_3^-$ type for all water samples, which indicates that the hydrochemistry of the groundwater samples is characterized by alkaline earths which exceed alkali metals [12] (figure 3).

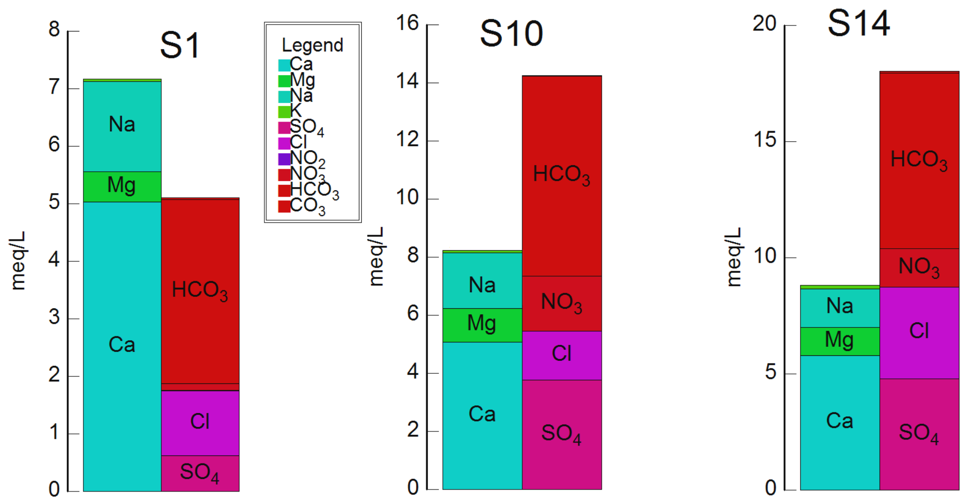


**Figure 2.** Ion charge balancing representation for samples S1, S10, S14

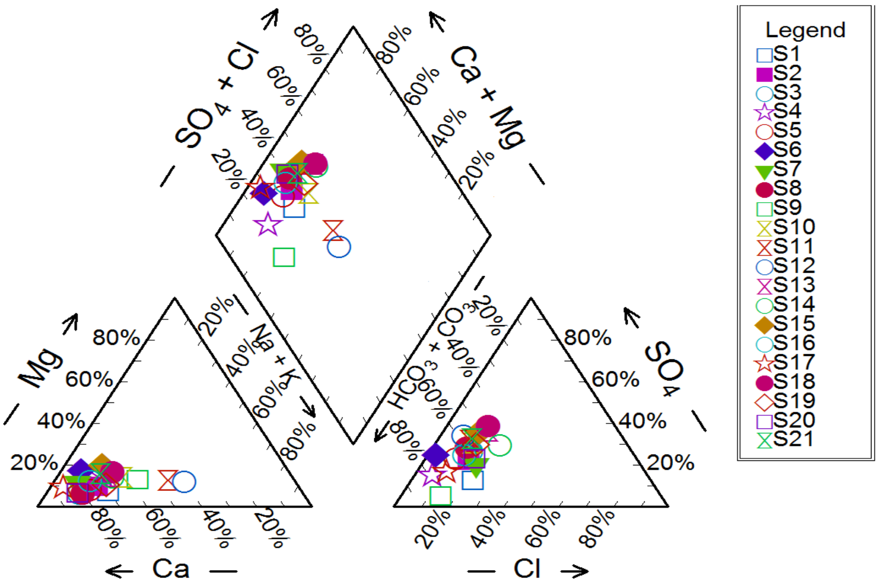


**Figure 3.** Classification of groundwater types after the ion charge

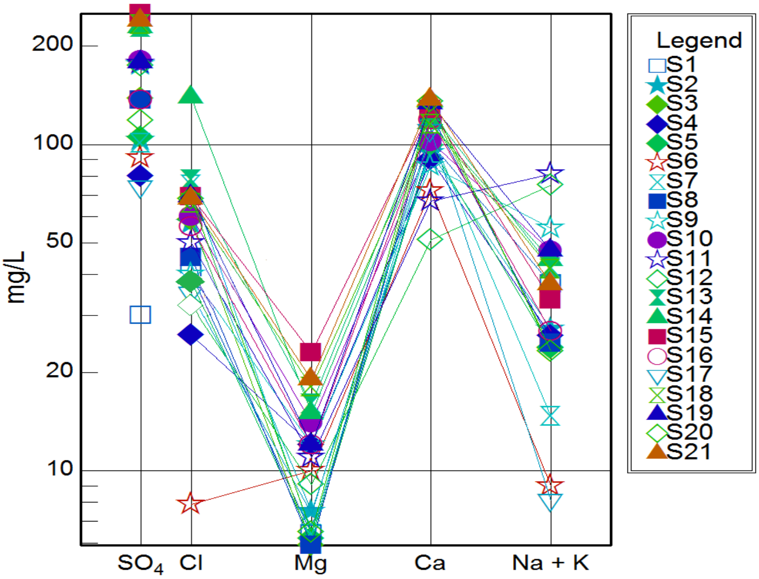


**Figure 4.** Ion concentrations and the ratio among ions

Variations of the chemical parameters concentrations ($SO_4^{2-}$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$) and the ratio among them are represented by Schoeller diagram in figure 4 [13, 14].

Higher concentrations for all water samples are $SO_4^{2-}$ concentrations, while $K^+$ concentrations are the lower ionic concentrations.

Samples S3, S13, S15, S21 have the highest $SO_4^{2-}$, $Cl^-$, $Mg^{2+}$ and $Ca^{2+}$ concentrations, while S4, S6, S7, S17, S19 present the lowest values for same parameters, as Schoeller diagram illustrates.

## CONCLUSIONS

The studied groundwater samples, from the northern part of Sibiu County, present significant chemical concentrations for major cations content ($Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$), main anions ($SO_4^{2-}$, $Cl^-$, $NO_2^-$, $NO_3^-$, $HCO_3^-$) and TDS values. Anions concentrations ($SO_4^{2-}$, $NO_2^-$, $NO_3^-$) exceed the MCLs from Romanian standards [8] and WHO Guidelines [9]. The TDS presents high values, while 50% of water samples show high concentrations of $SO_4^{2-}$ (>120mg/l) and all water samples are contaminated with $NO_3^-$ with concentrations among 50 mg/l and 150 mg/l (50 mg/l MCL).

According to Piper diagram and Ion balanced diagrams the water samples (water wells and streams) are classified as $Ca^{2+}$-$HCO_3^-$ type. Using Piper diagram, the ion dispersion is represented and it indicates that the largest anion dispersion is represented by the $HCO_3^-$ dispersions and the $Ca^{2+}$ concentration has the largest cation dispersion.

## EXPERIMENTAL SECTION

### Short description of the study area

Well water (S1-S19) and stream (S20, S21) samples were collected from the northern part of Sibiu County, which is situated in the Tarnavelor Plateau. The area is characterized with a temperate continental climate. The annual average air temperature ranges between 7-8 ºC. Annual precipitation ranges from 600 to 700 mm, with monthly and annual variations [15, 16].

Aquifers can be found from 0 to 0.5 m at the minor bed level and from 4 to 5 m in the major bed level and 10 m at the versant level [17]. Groundwater and streams constitute the fresh and free drinking water resources used by the Medias inhabitants.

The quality of groundwater is decay because of the near localized of the water wells from the anthropogenic sources (point sources). Point sources are collecting tanks, dry toilets, stables, waste water and storm drainage system. This situation occurs at national level and in the studied area.

### Sampling and sample preparation

Nineteen well water samples (S1-S19) and two spring samples (S20, S21) were collected in the rainy season of 2014 (March). The water samples were stored in 1000 ml pre-cleaned polyethylene-terephthalate (PET) bottles. Samples were kept in a freezer at 4 ºC. For major anions and cations measurements, water samples were filtered using plastic filter unit equipped with 0.45 µm disposable cellulose acetate filter membrane and for the cations samples were acidified using $HNO_3^-$(67%).

## MATERIALS AND METHODS

### Instrumentation

The physicochemical parameters (pH, TDS and EC) were measured using a multiparameter Multi 350i WTW (Germany). Using titration with HCl against methyl orange indicator, the $HCO_3^-$ content was analysed

For the anion content ($NO_2^-$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$), IC 761 Compact Methrom A.G. Switzerland ion chromatograph was used.

Mass spectrometry using a DRC II Perkin-Elmer Inductively Coupled Plasma-Mass Spectrometer (Perkin-Elmer, Canada), was used for the major cations ($Mg^{2+}$, $Ca^{2+}$, $K^+$ and $Na^+$) determination.

The graphical approaches represented by Piper, Durov, Schoeller and ion balanced diagrams were elaborated using AqQa 1.1 software.

## ACKNOWLEDGMENTS

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