CHEMICAL CHARACTERIZATION OF SOME GROUND WATER BASINS TO ESTIMATE TDS-EC RELATIONSHIP DEPENDING ON IONS SPECIES AND CONCENTRATION

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Abstract- Two primary concerns associated with natural resources revolve around the conservation of water quality and quantity. Groundwater represents a crucial asset for a country, but its extensive and intensive use has led to global challenges related to both scarcity and pollution. This study focuses on 24 groundwater samples collected from three distinct water basins in Albania. The samples underwent analysis for parameters such as *pH*, *EC*, *TDS*, cations, and anions. The results are used to explore the correlation between *TDS* and *EC* based on major ionic species and their concentration ranges. Typically recommended within a range of 0.55-0.8, the conversion factor is influenced by the specific ions present, their concentrations, and their mobility, which induces competition and affects their contribution to the measured *EC*. This research contributes additional evidence regarding the significant impact of ions and their concentration on this relationship influencing the conversion factor. The results obtained show that *TDS-EC* relationship is perfect linear for a specific *EC* range. The conversion factor resulted in different values for three groundwater basins studied strongly influenced by the groundwater composition. *EC* resulted mostly correlated to anions than cations. This fact was confirmed by the multi parameter regression analysis. The wide ranges of conversion factors calculated for three groundwater basins suggest that using *TDS/EC* relationship for *TDS* calculating should be carefully used especially when accurate results are required. Continuous monitoring of groundwater conductivity should be carried out as an important quality indicator of any seawater intrusion or eventual pollution.

Keywords: *TDS*, *EC*, Relationship, Conversion Factor, Concentration Range, ION Mobility.

1. INTRODUCTION

Freshwater, a global wealth, is subject to anthropogenic pollution, asking for continuous quality and quantity management. Groundwater, comprising 30% of global freshwater, faces escalating demand driven by human needs, leading to rapid quality deterioration from industrialization, urbanization, and agriculture, [1]. Preserving water sources is a top-priority global concern, demanding continuous monitoring and precise evaluation.

Albania's rugged terrain and diverse geological formations, especially carbonates, provide abundant natural water sources, including rivers, streams, groundwater, lakes, seas, and lagoons. Situated in the eastern Mediterranean region, Albania has a narrow territory with an extensive coastline along the Adriatic and Ionian Seas. Despite their short length, Albania's numerous rivers form a widespread network of hydrographic ponds across the country. Various studies have been conducted to characterize these water bodies [2, 3]. Shallow groundwater often contains calcium and/or magnesia bicarbonate, with higher mineralization observed in coastal areas like Durres, Terbuf, and Divjaka. Conversely, Korca, Lezha, and Lushnja water basins harbor substantial artesian or deep groundwater sources.

Furthermore, numerous karstic regions, linked with carbonate and sulphatic rocks like lime, dolomite, gypsum, and anhydrite, serve as vital sources of potable water for local communities and irrigation. Prominent examples include Bistrica, Viroi in Gjirokastra, Cold Water in Tepelena, and Selita in Tirana. These water sources, regarded as national wealth, have undergone thorough physical, chemical, and biological characterization.

Groundwater quality is influenced by natural factors like climate, lithology, mineral weathering, and salt solubility, along with anthropogenic activities such as mine acid drainage, agricultural runoff, and industrial or domestic wastewater leakage. Over-pumping and reduced groundwater recharge contribute to salinization and seawater intrusion, especially problematic in coastal aquifers [4, 5]. Water's chemical composition is shaped by the rocks and soils it encounters, revealing insights into weathering processes and natural or human-induced activities [6]. Significant geological variations can lead to differing conductivity values in adjacent water bodies.

For instance, freshwater flowing through granite rocks typically exhibits low conductivity, while clay and limestone soil layers contribute to higher conductivity levels [7]. To comprehensively assess water ionic strength, measurements of electrical conductivity (*EC*), salinity, and total dissolved solids (*TDS*) are widely used. *EC* and *TDS* are particularly important parameters, especially in coastal regions, as they increase with rising ion content, indicating water salinity levels. Thus, they are valuable tools for studying seawater intrusion [10].

1.1. Salinity

Salinity, linked to water's salt content, is crucial for characterizing seawater or brackish water and strongly influences conductivity [7]. However, it's often conflated with *TDS*, despite representing slightly different concepts [9]. Estimating groundwater salinity is vital for anticipating seawater intrusion and addressing water quality and scarcity issues, especially as 70% of the global population faces water scarcity. Salinity is commonly derived from conductivity measurements due to the well-established relationship between salinity and *EC*, particularly in seawater. Though the relationship between *TDS* and *EC* in groundwater is more complex, it's worth exploring [9].

1.2. Total Dissolved Solids

The *TDS* measure all inorganic and organic matter dissolved in water, including minerals, salts, and metals, but it's a rough estimate [10], [9]. The inorganic fraction mainly comprises major ions like calcium, magnesium, sodium, bicarbonate, chlorides, and sulfates, considered natural constituents of water bodies [11]. *TDS* can be measured using various chemical methods like titration or spectrometry. *EC* is a useful metric for freshwater quality, representing the sum of ions in water. The Albanian National Standard sets *TDS*<1000 mg/L for drinkable water, aligning with WHO guidelines [12].

Table 1. TDS levels for groundwater [13]

TDS levels	Water type
<500 ppm	Desirable for drinking
500-1000 ppm	Permissible for drinking
1000-3000 ppm	Not recommended for domestic use, useful for irrigation
>3000	A higher than 3000 ppm *TDS* level is considered unsuitable for drinking and irrigation. Even the filters cannot support these high *TDS* levels

A high *TDS* value may indicate hard or saline water, possibly with a high nutrient load, and these characteristics can have a direct impact on various water uses. *TDS* analysis is crucial for understanding groundwater quality, especially in assessing the impact of seawater intrusion, and it provides more insights than *EC* analysis alone [10]. Low *TDS* levels make the drinking water tasteless while high *TDS* of a pretended freshwater is considered as a signal that the water should be checked for other external intrusions, making it unsafe for human even for irrigation.

There are several methods available to reduce high *TDS* in water treatment plants, including water distillation, reverse osmosis, water deionization, dissolved air flotation, etc. Each method has its own set of advantages and disadvantages, and the choice depends on the intended use of the water after treatment [14-17]. Accurate measurement is essential for designing effective methods to reduce *TDS* or monitor desalinization processes. Various techniques, such as gravimetric analysis, elemental chemical analysis, or *EC* measurement, can be employed. Gravimetric analysis involves evaporating a water volume filtered through a 0.45 μ membrane fiber to dryness at a specific temperature and duration, with the difference in container weight providing *TDS* content [10, 16, 18].

However, variations in temperature and duration may occur based on water composition, leading to potential errors and interferences [18], [19]. Factors influencing this method include sample volume, nature of dissolved species, drying time, temperature, container material, and drying oven type. Elementary chemical analysis involves analyzing all present ionic concentrations, with the sum providing *TDS* calculation. However, this method is cumbersome and prone to inaccuracies due to potential presence of minor ions. Electrical conductivity method estimates *TDS* by assuming dissolved solids are predominantly ionic species, with a linear *TDS-EC* relationship. It requires measuring only *EC* and employs a conversion factor to estimate *TDS*, offering quick results without sophisticated equipment or lengthy drying time. This method can be employed in-situ for immediate results [10], [18].

1.3. Electrical Conductivity

The *EC* serves as a crucial water quality parameter, determining its suitability for various purposes including drinking, domestic, agricultural, livestock, and industrial uses [4]. It quantifies water's ability to conduct electric charge [10], [20-22], which is vital because salts and other substances can influence its quality for intended applications [20]. Although no universal standard for water conductivity exists due to environmental variations, generalized conductivity ranges are recommended for categorizing water sources based on their intended use. The Albanian National Standard sets an acceptable maximum limit of *EC* < 2500μS/cm for drinkable water [12]. Table 2 provides a classification of water use based on *EC* levels.

Table 2. Classification of water use according to EC [23]

0-800 μS/cm	Low *EC* range: drinking water supplies, irrigation, and all livestock
800-2500 μS/cm	Medium *EC* range: irrigation, all livestock and sometimes drinking water at lower values preferred
2500-10,000 μS/cm	High *EC* range, not recommended as drinking water, but up to 3000μS/cm is still considered safe. It is used for irrigation up to 6000 μs/cm on very salt tolerant crops
>10,000 μS/cm	A higher than 10,000μS/cm is considered unsafe for drinking water or irrigation

Electrical conductivity is influenced by dissolved salts, acids, and bases, reflecting overall ion concentration in water [24]. Higher ion concentration correlates with

increased electrical conductivity [24]. *EC* measurement is simple, fast, and cost-effective compared to the lengthy gravimetric *TDS* analysis, which can yield inaccurate and irreproducible results. It can be employed in-field, serving as an indirect method to estimate total dissolved solids [11]. As a routine and rapid characterization tool, *EC* measurement can effectively serve as an indirect indicator for *TDS* measurement.

Among the factors influencing solution conductivity - ions concentration, type of ions, and temperature - the concentration of ions is the most significant and easily comprehended [25]. However, the influence of ion type can be complex, considering factors such as mass, size, electrical charge, and interaction with water molecules. This complexity presents challenges in interpreting *EC* values solely based on individual ion concentrations. The chemistry of water systems is both simple and intricate, particularly when interactions between dissolved ions and water ions affect predicted *EC* values. Tikhonov (2019) extensively investigated how ion concentration affects mobility, finding that higher molar mass and ion valence lead to decreased mobility as ion concentration increases. Therefore, the overall influence on electrical conductivity is a complex relationship involving two opposing factors: ion mobility and concentration.

Temperature of sample during measurement is another factor to be considered. Its direct influence on *EC* readings is scientifically explained and no exceptional rule exists. It does not have a strong contribution in *EC* readings, but it is consistent and always present. Studies have reported that conductivity will increase by 2%-3% for each 1°C increase in temperature [25], [7]. To minimize this factor, the existing conductometers are equipped with temperature probes to compensate the difference of temperature against the reference one, ensuring complete comparison of the *EC* measurements across various samples.

The abovementioned factors have a direct impact on measured *EC* values. Environmental pollution and climatic changes may also cause a significant decrease or increase in normal *EC* values, depending on the pollution origin [26]. Changes in conductivity may not always indicate all sources of water pollution. For instance, the presence of oil or addition of organic compounds may decrease conductivity, as these substances do not ionize but contribute to dissolved solids. In such cases, pollution may go undetected through conductivity measurements [23]. Therefore, interpreting data from direct *EC* measurements requires caution.

1.4. Correlation between *TDS* and *EC* in Groundwater

The conductivity of water is predominantly influenced by dissolved ions, resulting in a direct relationship between *TDS* and *EC* [8, 9, 11, 24]. However, the correlation between *TDS* and *EC* may not always be strictly linear due to variations in the conductive mobility of ionic species [11, 19]. Ion mobility, determined by interactions with water molecules, further impacts *EC* measurements and consequently influences derived *TDS* values [24]. The equation between *TDS* and *EC* can be expressed in the general form [8, 9, 18, 25]:

$$TDS = k \times EC \tag{1}$$

The slope of the relationship between *TDS* and *EC*, represented by the conversion factor (k), is typically dimensionless. However, for accuracy and comparability, *TDS* should be expressed in mg/L and *EC* in µS/cm. The value of k is influenced by the same variables that affect *EC*. Some scientists [9, 11] prefer to use a regression between *TDS* and *EC* without intersecting the origin, as stated in [9]. In this case, Equation (1) is expressed as follows [9], [11]:

$$TDS = k \times EC + c \tag{2}$$

where, c is the intercept value is a consequence of other nonionic species present in water. Previous studies to accurately determine mathematical relationship between *EC* and *TDS* were done decades ago, [10]. The conversion factor varies between 0.55-0.85/0.9 (some authors) or 0.5-0.7 (others), with an average value of 0.7/0.64 considered typical. This variation depends on factors such as the nature of soluble ionic components, their individual activity, ions activity, ionic strength, and water temperature [9-11], [18], [23, 24].

When NaCl is the dominant salt, there is an adjustment in the conversion factor. In this scenario, the conversion factor typically falls within the range of 0.5-0.67, with a commonly used factor of 0.64 [19]. However, [9], citing other authors, provide a broader range of 0.48-0.86 for fresh mountain water streams dominated by NaCl, where lower values are associated with NaCl-dominated waters and higher values with Ca $(HCO_3)_2$ dominated waters. Meanwhile, for sulphatic waters, the recommended value is 0.7 [9]. A *TDS* conversion factor ranging from 0.55-0.7 is generally recommended in standards methods [21]. However, when measuring mixed water or saline water (with a conductivity value exceeding 5000µS/cm), the *TDS* constant should be higher, approximately around 0.735-0.8. In instances where extreme values of k are obtained, further in-depth investigation or measurements should be conducted to identify any external factors influencing this value.

When the concentration of dissolved solids reaches a certain high level (10-500 mmol /L), ion pairs weaken each other's charge, and the relationship between *TDS* and *EC* is no longer linear. It is best fit with a third-order polynomial or an exponential equation [19, 23]. These findings indicate that determining the exact value of this conversion factor is not straightforward; moreover, it is strongly linked to the nature of the water. Thus, investigations persist with diverse modifications to research methods [8]. This paper represents an additional study in the current research literature of this topic estimating the relationship for some typical groundwater and the contribution of specific ions in this relationship. Moreover, the contribution of the most important ions present in water across different concentration ranges is also studied, illustrating their impact on the conversion factor.

2. MATERIALS AND METHODS

2.1. Water Sampling

A total of 24 water samples were obtained from groundwater sources situated in three Albanian hydrologic basins: Ionian, Shkumbin, and Mat water basin. The collection sites were strategically identified at pumping stations, the locations of which are illustrated in respective dots in Figure1.
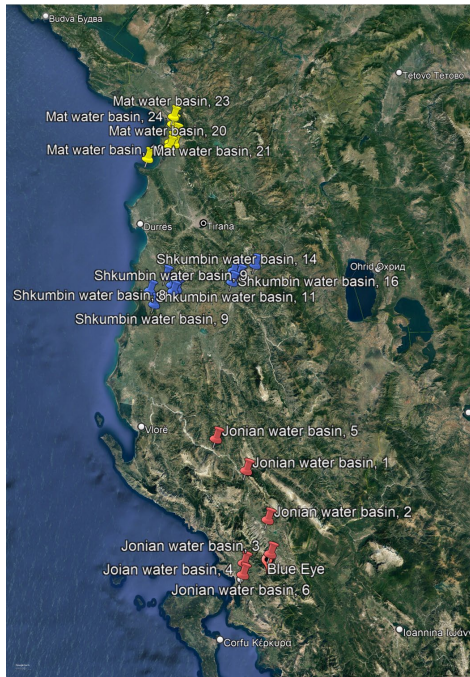

Figure 1. Geographic distribution of ground water sampling sites

The primary usage of this water encompasses domestic, irrigation, and technological applications as a potable water supply. The sampling period was May 2023. To ensure integrity during transportation, the samples were meticulously placed in *PET* bottles, securely sealed within cooling bags, and appropriately labeled based on their respective groundwater sources. Sample temperature was recorded. The samples were stored in the refrigerator at 4°C until analysis to inhibit any microbial activity. Three samples were collected from each sampling site.

2.2. Physicochemical Analysis of Groundwater Samples

The main water parameters, including *pH*, *EC*, *TDS*, and ionic composition (SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Fe^{2+}) were measured. In addition to the commonly found major cations and anions in groundwater, various minor water species were also analyzed, including: NH_4^+, PO_4^{3-}, NO_2^-, NO_3^-, total organic carbon (*TC*) and total nitrogen (*TN*). Official standard methods [21] have been used for the analysis of cations and anions. *TDS* was measured by evaporation to dryness maintaining for 3h at 180 °C, *EC/pH* were measured by using a pH/conductometer, *TC*, *TN* was measured by C/N multi parametric equipment. All the results reported show the average value of three replicates.

2.3. Data Analysis

To assess the relationship between *TDS/EC* related to ions composition in groundwater, descriptive analysis, and multiple regression techniques, using Minitab 21 and SPSS software, were used. The specifics are outlined within the experimental findings. All graphical representations have been generated using Origin software.

3. RESULTS AND DISCUSSION

3.1. Water Characterization

The data set distributions for all physicochemical characteristics of considered water samples are summarized in Figure 2. According to the findings all the groundwater samples are of an alkaline nature with a *pH* range from 7.38-9. The temperature ranges between 8.5 °C to 11°C. Meanwhile, *EC* ranges between 250-2100μS/cm being characteristic for natural unpolluted groundwater. According to VKM 379/2016 [12], potable water should have an acceptable *EC* value less than 2500μS/cm and *TDS* in 140-1200mg/L ranges. Only two samples belonging to Mat water basin show *TDS* value higher than 1000mg/L. These samples are the most saline ones, with the highest sodium and chlorine content. This may be a result of seawater intrusion or salt leaching from the surrounding soil [1]. This type of water, according to the groundwater classification given in Table 1, is not permissible for drinking but may be used for irrigation. Control of the data obtained between six dominant cations and anions was made based on the ions balance calculation [4, 6, 30], as Equation (3):
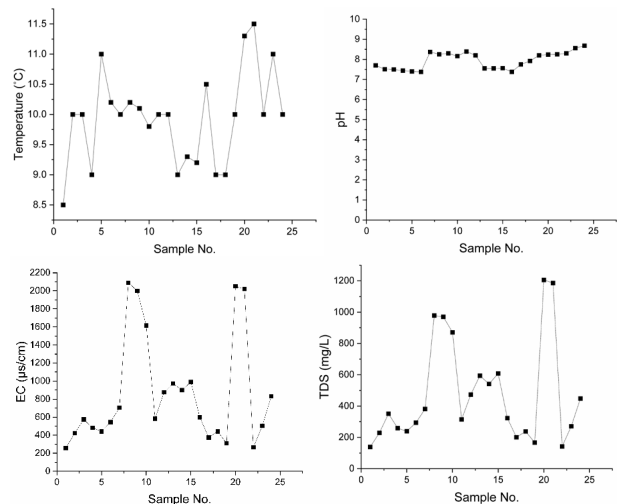
Balance error (%) =

$$= \frac{\sum Cations\ (\frac{meqv}{L}) - \sum Anions\ (\frac{meqv}{L})}{\sum Cations\ (\frac{meqv}{L}) + \sum Anions\ (\frac{meqv}{L})} \times 100 \quad (3)$$

where,
$\sum Cations$ (Ca^{2+}, Mg^{2+}, Na^+) = 223 meqv/l
$\sum Anions$ (Cl^-, HCO_3^-, SO_4^{2-}) = 220 meqv/l

Cation anion balance *error*=0.7% (standard limit of ±5%) showing high accuracy in ions measured [4, 6, 30].
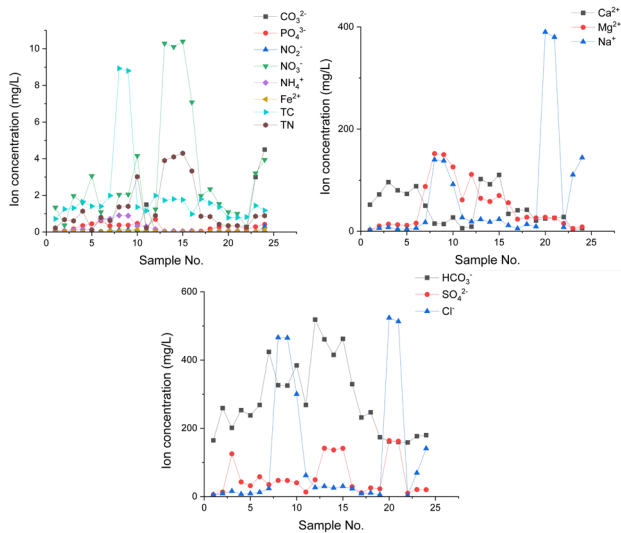
Figure 2. Parameter Distribution

Sodium is the cation with the highest concentration in total for all the samples followed by Ca^{2+} and Mg^{2+}, which resulted approximately at equal amount. Seven samples belonging to Shkumbin groundwater basin show a quite different trend of Ca^{2+} against Mg^{2+}. Magnesium is apparently at a higher amount than calcium in these samples, being sodium and magnesium the major contributing cations for these samples. Apparently, this variability of Mg^{2+} concentration is related to Ca^{2+} and Mg^{2+} exchange during dolomitization in deep reservoir rock [18], [20]. The bicarbonate ion is the most dominant anion present in water, followed by chloride and sulphate, depending on the specific water sources.

To summarize and describe the main features of our water characteristics dataset, descriptive statistical analysis is conducted. Least square regression was completed at a 95% significance level (α=0.05) to obtain a best fit curve of the data. The results are summarized in Table 3. They are important to understand the tendency, variability, and shape of the experimental data. The 24 samples tested show a normal range of EC at the highest value 2090 µS/cm (<2500 µS/cm), showing that the three water basins present characteristic values of fresh groundwater, while TDS shows a maximum value at 1206mg/L higher than the permissible limit for drinking water (>1000 mg/L) (Table 1).

Table 3. Statistical data for all the water characteristics

	pH	EC (µs/cm)	TDS (mg/L)	TDS/EC k	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	Cl^-	HCO_3^-
Mean	7.9	747	406	0.547	44	43	52	45	88	271
Standard Error	0.097	122	65	0.00735	7.1	10	21	10	35	24
Median	8.0	559	305	0.5394	37.6	24.9	12.6	30	20	250
Standard Dev.	0.436	547	292	0.036	32	44	92	45	156	105
CV%	5	73	72	6.55	73	103	177	100	178	39
Kurtosis	-1.52	2.06	2.23	0.548	-1.01	0.75	9.70	2.26	3.75	0.24
Skewness	0.029	1.717	1.694	0.139	0.482	1.326	2.925	1.780	2.187	1.015
Range	1.3	1833	1067	0.15	100	150	387	158	520	360
Minimum	7.38	257	139	0.47	2.00	2.43	2.64	5.35	3.55	158.60
Maximum	9	2090	1206	0.61	102	152	390	164	524	519
Count	24	24	24	24	24	24	24	24	24	24
Conf. Level (95.0%)	0.204	256	137	0.56	15	21	43	21	73	49
	T(°C)	K^-	Fe^{2+}	CO_3^{2-}	PO_4^{3-}	NO_2^-	NO_3^-	NH_4^+	TC	TN
Mean	9.9	2	747	406	0.282	0.030	2.431	0.193	1.742	1.070
Standard Error	0.164	0.433	122	65	0.043	0.015	0.559	0.061	0.387	0.240
Median	10.0	1.085	559	305	0.285	0.004	1.790	0.070	1.380	0.820
Standard Dev.	0.733	1.9	547	292	0.193	0.068	2.498	0.271	1.731	1.072
CV%	7	101	73	72	68	225	103	140	99	100
Kurtosis	-0.17	3.44	2.06	2.23	-0.41	12.00	4.65	2.12	17.97	2.36
Skewness	0.110	1.999	1.717	1.694	0.417	3.302	2.020	1.780	4.144	1.809
Range	2.8	7	1833	1067	0.685	0.290	10.3	0.910	8.210	3.790
Minimum	8.50	0.330	257	139	0.005	0.000	0.000	0.000	0.720	0.110
Maximum	11	8	2090	1206	0.690	0.290	10.290	0.910	8.930	3.900
Count	24	24	24	24	24	24	24	24	24	24
Conf. Level (95.0%)	0.343	1	256	137	0.090	0.032	1.169	0.127	0.810	0.502

Average and median values are quite near to each other for T, pH and HCO_3^-. This is reflected in the values of Coefficient of Variance (CV %) which resulted <10% for temperature and pH and 39% for HCO_3^-. The other parameters showing narrow variability are Ca, EC and TDS (CV<75%). The high variability shows Na^+, and Cl^- with a similar CV% (respectively 177% and 178%) followed by Mg^{2+} with 103%. In fact, these three ions will be present at abnormal amounts in the highest deviating samples from the TDS-EC linear relationship (Figure 4). These samples belong to high saline water. The excess of chloride in the groundwater is usually considered as a pollution indicator or intrusion of waters of different composition or for water mass movement traceability [22].

Table 3 also reveals that the conversion factor range between TDS and EC (k) is 0.47-0.61 for each sample individually, with an average of 0.54 across all samples. This average value falls within the lower end of the range reported in the literature, [8, 10, 18, 24]. This phenomenon may be ascribed to the relatively low concentration of ions present in the tested groundwater, which creates favorable conditions for the mobility of ions without hindrance, blockage, or complexation with each other. According to [9], the low k may be attributed to the loss of volatile or

organic constituents during the drying process when measuring *TDS*. However, this explanation does not apply to this case, as the underground water tested for organic compounds, estimated by their *TC*, exhibited normal *TC* values for groundwater. All *TC* values were lower than 2mg/L, except for two samples with an exceptional *TC* value of 8 mg/L being also the highest deviated samples from overall linearity. The reason probably is the bicarbonate decomposition during *TDS* analysis, as bicarbonate is the most abundant anion compared to sulphate and chloride ions.

3.2. TDS - EC Relationship

To determine the *TDS-EC* relationship, linear regression is utilized by fitting a linear equation to the *TDS-EC* parameters measured across all samples, regardless of their varying ionic concentration ranges. The *EC* (independent variable) values range between 200 µS/cm- 2090 µS/cm, being characteristic for groundwater. The regression parameters obtained are shown in Figure 3.
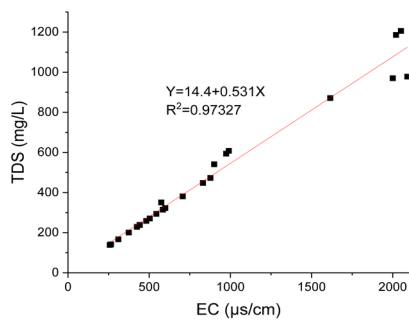

Figure 3. Relationship between *TDS* and *EC* for all the groundwater samples

A linear *TDS-EC* relationship is noticed. The overall coefficient of correlation is R^2=0.973 showing a high correlation between the two parameters. Some deviations are noticed in higher *EC* values, particularly those exceeding 2000 µS/cm. Specifically, seven samples display marked deviations from the overall linear relationship. Among these, four samples - two from the Shkumbin water basin and two from the Mat water basin - exhibit the highest levels of sodium and magnesium compared to all other samples, resulting in distinct behavior. These two samples demonstrate higher EC values, averaging 2060 µS/cm with a *TDS* of 975mg/L. Furthermore, both samples exhibit chloride ion levels among the highest observed, indicating elevated salinity compared to others. The conversion factor for these two exceptional samples resulted in the lowest value of *k*=0.47. Such values have also been reported by [9]. This was expected and explained by the high content of both mobile sodium and chloride ion compared to all other samples. On the other side, sodium, and magnesium, both present in approximate high concentrations, have relatively small atomic weight though being mono and bivalent ions. Because of their apparent mobility they have a strong influence on *EC* values, influencing the water conductivity. However, this influence is different for the two ions.

After literature [23], in cases where magnesium (Mg) is the dominant cation, *EC* values tend to be lower than anticipated. This phenomenon occurs because magnesium, being a larger ion compared to sodium, is more strongly attracted to water ions, leading to the formation of hydrated compounds. Magnesium carries two positive charges, making it theoretically more conductive compared to sodium. However, it is less mobile than sodium and chloride ions. The authors of [24] have also presented in his work the ion mobility drop order with increasing concentration in water, with magnesium identified as the least mobile ion, particularly at higher concentrations. In these samples, the significant presence of magnesium, alongside the mobile sodium and chloride ions, creates an overlapping effect.

Two other deviating samples present similar ionic scenario as two previous ones, but they belong to Mat water basin. Both have the highest level of sodium and chloride of all the samples. The only difference is the low level of magnesium compared with the previous ones, but with the highest sulphate presence. Their *EC* is respectively 2050 µS/cm and 2022 µS/cm (comparable to both Shkumbin samples) with *TDS* 1206mg/L and 1185 mg/L respectively. Their *TDS/EC* ratio is almost the same for both these samples at 0.58. This value is within the reported range (0.5-0.67) by [19], but lower than the average factor commonly proposed (0.64) to be used for this type of saline water [19]. The elevated concentrations of the high mobile chloride and sodium influence in higher *EC*. According to [24] the bulky sulphate ion in high concentration shows a greater mobility drop compared to all the other prevailing ions, the same situation as with magnesium for the previously discussed samples. Its influence is again hidden by the most mobile ions: sodium and chloride.

Although these samples have the highest level of *EC* because of the high ionic mobility, their *TDS* do not follow the same relationship as the other samples in low and medium ionic concentrations. *EC* is mostly dependent on electronic charges and mobility, while *TDS* is dependent on ionic concentration. Electronic charge does not follow the same *TDS* trend. As a result, even though the *EC* values for four deviating samples fall within a narrow range of 2020-2090µS/cm, their *TDS* range is wide enough (975-1206mg/L) to draw attention for further analysis and discussion.

These four samples with *k*=0.47 (two Shkumbin water samples with high magnesium presence, except for sodium and chloride) and *k*=0.58 (two Mat water samples with high sulphate presence, except for sodium and chloride) are the causes of linearity deviation and much lower *k* values than literature recommendations. Three other remaining samples of Shkumbin water basin showing a slight deviation even in somewhat medium *EC* level at an average *EC* of 955 µS/cm, have the highest level of calcium and bicarbonate. This higher amount of calcium influences the *TDS* value but contributing to a lower respective *EC* than expected. Although carrying two positive charges its conductivity is decreased because of its high concentration in water, limiting its mobility.

The conversion factor for these samples is higher than average and for each of them individually equal to 0.61 confirming the argument. The bicarbonate content is also the highest, contributing to a decreased mobility. These samples are indicative of typical fresh groundwater, with their conversion factor falling within the commonly recommended range of 0.55-0.7.

3.3. EC-TDS Ionic Composition Relationship

A comprehensive analysis involving correlation matrices and linear regression has been undertaken to explore the relationship among all measured parameters, with a specific focus on the TDS/EC ratio, at a significance level of 5%. Additionally, cluster analysis (CA) has been employed to identify similarities among the measured parameters and ionic composition. The correlation matrix displayed in Figure 4 illustrates the strongest associations among ions, as well as their links with EC and TDS. A correlation coefficient (r) exceeding 0.7 indicates a strong correlation, while values between 0.5 and 0.7 suggest a moderate correlation [1].
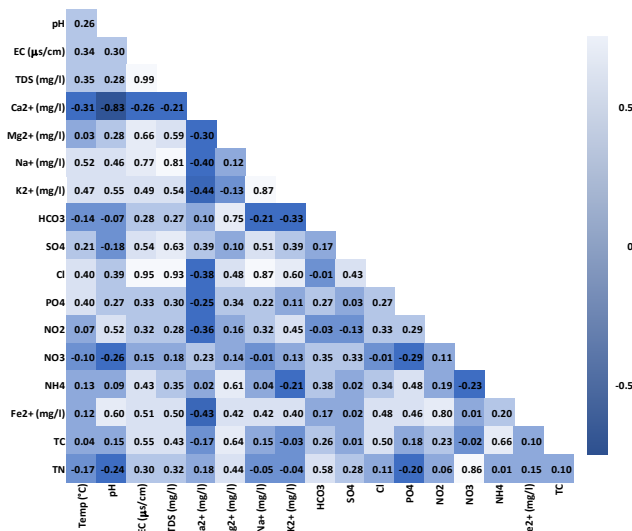

Figure 4. Pearson's correlation matrix for all parameters

As depicted, the ions exhibiting the strongest correlations are Na^+ with Cl^- ($r=0.87$) and Mg^{2+} with HCO_3^- ($r=0.75$). The correlation between Na^+ and Cl^- is often utilized to discern the origin of salinity, whether it stems from water evaporation or saline water intrusion [4]. However, these discussions fall outside the scope of this paper. Furthermore, Na^+ demonstrates a moderate correlation with SO_4^{2-} ($r=0.51$), hinting at the potential derivation of these ions from sulfate-bearing rocks. Mg exhibits a strong correlation with HCO_3^- ($r=0.75$) but displays a negative correlation with Ca^{2+}. In general, there exists an equilibrium between Ca and Mg, associated with the exchange of Ca^{2+} and Mg^{2+} during dolomitization in deep reservoir rocks, as proposed by previous researchers [18, 20]. The arguments presented and previously discussed regarding the deviations observed in some samples corroborate these findings. Ca^{2+} emerges as a significant ion only in low concentrations within the samples from the Ionian water basin.

As for EC, it is strongly correlated to TDS ($r=0.99$) followed by Cl^- (0.95) and Na^+ (0.77) and moderately correlated to Mg^{2+} (0.66) and SO_4^{2-} (0.54) but negatively correlated to Ca^{2+} (-0.26). Regarding the Ca^{2+} ion, dependence of EC against its concentration exhibited a particularly interesting behavior. All the values showed a wide distribution without any relationship prediction. Figure 5 illustrates this fact. The overall EC-Ca relationship can be better explained by considering some segmented linearity depending on the Ca^{2+} concentration range. The figure shows that Ca^{2+} is correlated to EC at low concentration range. This can be explained because Ca^{2+}, with two positive charges shows its full mobility as free ion in dilute water solution. Being a relatively large ion, Ca^{2+} decreases its mobility in a concentrated solution, posing difficulties to find its way. This is also reported by [24].
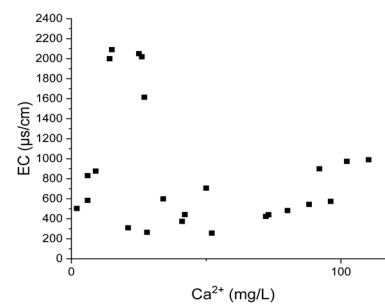

Figure 5. EC-Ca^{2+} relationship

Moreover, the data for all the samples show there exist a negative correlation between Ca-EC (-0.26) and Ca-Na (-0.4). This negative correlation in high Ca^{2+} concentration is also shown by [27]. Ca-Na negative correlation (-0.4) verifies that in the ion exchange process, the sodium increase can restrain the calcium ion content. This is also reported from another researcher [28]. Regarding the impact of total cations and anions on EC, the experimental data presented in the graphs in Figure 6 suggests a more pronounced correlation between EC and anions compared to cations. This observation is consistent with the conclusions drawn by [24], who similarly acknowledged this trend. Conversely, [6] have reported a stronger EC correlation with cations.
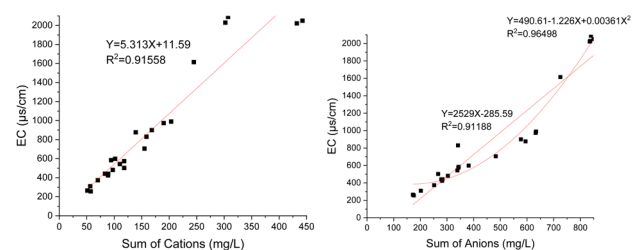

Figure 6. The impact of total cations and anions on EC

The relationship between EC and sum of cations is best described by a linear fit, whereas for anions, a second-order polynomial equation provides a better fit. Examining the correlation matrix, the formation of three distinct clusters among the parameters is obvious, with the most

notable, in terms of similarity, the *TDS-EC* cluster. Dendrogram presented in the Figure 7 illustrates this fact. This implies that electric conductivity and total dissolved solids exhibit the most significant correlation. Furthermore, both are intricately associated with Cl^-, suggesting a robust correlation between them. In contrast, the relationship of *EC* with the other ions seems to be comparatively weaker.
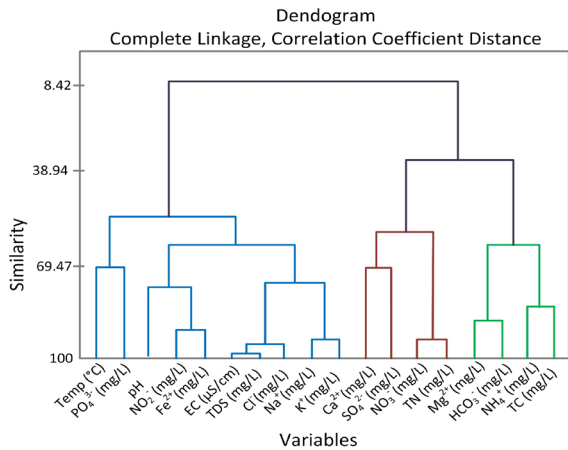

Figure 7. Dendrogram of hierarchical cluster analysis of groundwater samples

3.4. Predictive Groundwater *EC* Values Based on Dominant Ion Types and Concentration

In order to statistically model the relationship between the electrical conductivity and the ions present in water, a multiple linear regression was executed using the SPSS software. Multivariate statistical analysis is a numerical and independent method for groundwater classification permitting the creation of correlations between chemical parameters and groundwater samples [1]. The considered

ion species encompassed Ca^{2+}, Mg^{2+}, Na^+, Cl^-, HCO_3^-, and SO_4^{2-}, as the predominant constituents in the examined water samples. The analysis covered a spectrum of *EC* values ranging from 257 to 1000 μs/cm. Three mathematical methodologies were explored: stepwise, backward, and forward. The selection of the stepwise method was based on a comparison of the mathematical regression parameter results (not included in this paper). The findings of the regression analysis are summarized in Table 4.

In examining the results of the multiple regression analysis, several key metrics provide valuable insights into the effectiveness and reliability of the model. The Multiple Correlation Coefficient (*R*) of 0.997 indicates an exceptionally high correlation between the observed and predicted values. This suggests that the model is adept at capturing the relationship between the predictors and the dependent variable. The Coefficient of Determination (R^2) is an impressive 0.994, implying that approximately 99.4% of the variability in the dependent variable is accounted for by the model. The Adjusted R^2, slightly lower at 0.993, considers the number of predictors, providing a more conservative estimate of the explained variance. The Standard Error of the Estimate (19.54418) serves as a measure of the typical distance between observed and predicted values. This value indicates the precision of the model's predictions, with lower values being preferable. The Durbin-Watson statistic, standing at 2.379, suggesting that there is not a strong indication of autocorrelation in the residuals. This is crucial as it ensures the independence of the model's error terms. Moving to the ANOVA results, the extremely low significance value (5.2902E-17) underscores the overall significance of the regression model. This implies that the model is highly effective in explaining the variance in the dependent variable.

Table 4. The multiple regression results

Model Summary				
R	R^2	Adjusted R^2	Std. Error of the Estimate	Durbin-Watson
0.997	0.994	0.993	19.54418	2.379
ANOVA				
Significance = 5.2902E-17				
Coefficients				
Variable	Status	Coeff.	Sig. (p)	Collinearity statistics
				Tolerance	VIF
Constant	-	35.67	0.017813	-	-
Cl^-	Included	3.546	1.021E-13	0.996	1.004
HCO_3^-	Included	1.255	1.203E-13	0.643	1.556
SO_4^{2-}	Included	1.871	9.9443E-11	0.643	1.554
Na^+	Excluded	-	0.637	0.114	8.747
$Ca^{2+}+Mg^{2+}$	Excluded	-	0.326	0.065	15.327
Collinearity diagnostics				
Eigenvalue	Condition index	Variance Proportions		
		Constant	HCO_3^-	Cl^-	SO_4^{2-}
0.051	7.820	0.84	0.96	0.03	0.26
Residuals Statistics				
	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	265.8005	987.5833	583.0000	234.01738	19
Residual	-38.69049	31.66299	0.00000	17.84131	19
Std. Predicted Value	-1.355	1.729	0.000	1.000	19
Std. Residual	-1.980	1.620	0.000	0.913	19

4. CONCLUSIONS

This paper presents experimental findings on the characterization of three Albanian groundwater basins. The primary objective is to assess the correlation between electrical conductivity and total dissolved solids, as well as the ionic composition of water. The correlation relationship *TDS-EC* for the groundwater samples is perfect linear for the range 250-1600 µS/cm showing a strong correlation between them. Some slight deviations from the overall linearity are presented for samples with *EC* > 1600 µS/cm. The overall conversion factors for all the samples range between 0.47-0.61 with an average value of 0.54 being at the lowest side of the widely recommended range 0.55-0.8. In conformity with these ranges are the Ionian water basin samples showing a conversion factor of an average value *k*=0.55. These samples show a typical ionic system predominating by Ca^{2+} and HCO_3^- without any deviation in *TDS-EC* relationship.

The samples belonging to Shkumbin water basin demonstrate different scenarios. They are separated in two subgroups: Ca^{2+}-HCO_3^--SO_4^{2-} with *k*=0.61 and Na^+-Cl^--Mg^{2+} with *k*=0.47. The first subgroup does not show any deviation from the overall linearity. The second subgroup belongs to the most saline ones, with a high contribution of mobile ions sodium and chlorine leading to an elevated *EC*. The abnormal high sodium and chlorine ions present in these sampling wells may show some seawater intrusion affecting the quality. The *EC* higher than excepted from *TDS* may also show some pollution as these samples show presence of organic matter expresses as *TC*. These carbonic compounds may have been degraded during sample drying leading to a low *TDS* level. These facts need to be monitored and analyzed in detail. The samples belonging to Mat water basin show a conversion factor *k*=0.54 same as Ionian ionic system Ca^{2+}-HCO_3^-. Only two samples deviate from the linearity which present different chemical composition scenario: Na^+-Cl^--SO_4^{2-} with an average conversion factor *k*=0.59.

EC has been shown to be mostly correlated to anions than cations. The most correlating ion to *EC* is Cl^- followed by Na^+. A second order polynomial equation best fits for the EC-anions relationship, while a linear equation is better fit for EC-cations relationship. A multi parameter regression analysis generated an equation to calculate *EC* from the dominant anions for all the samples in total, excluding the deviating samples. Continuous monitoring of groundwater conductivity should be carried out as an indicator of seawater intrusion or eventual pollution. The wide ranges of conversion factors calculated for three groundwater basins suggest that using *TDS/EC* relationship for *TDS* calculating should be carefully used especially when accurate results are required.

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