

ORIGINAL ARTICLE

Evaluation of hydrogeochemical characteristics of Groundwater quality parameters through statistical analysis in Serres alluvial aquifer, East Macedonia (Greece)

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ABSTRACT

The present essay aimed to evaluate the hydrogeochemical analysis data in the heterogeneous alluvial aquifer in eastern Macedonia (Serres region) drained by Strymonas River in order to assess the groundwater quality characteristics and comprehend the hydrochemical-hydrogeological conditions occurring within the sedimentary formations of the study area. The accurate knowledge of the factors controlling the regional groundwater quality regime is important for planning sustainable water resources' use and management evaluating also the overall environmental regime. It has to be mentioned that domestic use and irrigation needs are mainly covered by groundwater abstraction from the aquifer through numerous boreholes. For that reason, data from the groundwater's physical and chemical analyses from two different sampling periods were collected (2005 – 2008, 2013 – 2015 with minor ions' variance between them $\pm 2-7\%$ and normal concentrate fluctuation between wet and dry periods $< 15\%$) and analyzed also studying thoroughly the nitrate pollution caused by manure, livestock and extensive use of fertilizers. The concentrations of major ions and trace elements of groundwater samples from approximately 115 site locations covering satisfactorily the alluvial aquifer were used to identify the hydrochemical characteristics as well as the hydrogeochemical origin. Hydrogeochemical methods such as descriptive statistics, ion ratios, binary diagrams, multicomponent plots, saturation indices supported by PHREEQC software as well as statistical techniques (Pearson correlation matrix, simple and multiple linear regression analysis) were combined to investigate the alluvial aquifer with respect to water quality, hydrogeochemical evolution and rock interactions between groundwater and surface water bodies. The results of saturation indices' calculation showed that nearly all of the water samples were saturated with respect to calcite and dolomite minerals supporting a long groundwater residence time hypothesis and under saturated with respect to sulfate ones. Calcite and dolomite dissolution determined the major ion chemistry but other processes, such as silicate weathering and cation exchange reactions, also contributed. Dissolution of carbonate minerals was the main source of major ions in the groundwater. Agricultural activities and urbanization cause locally an increase in the concentration of pollution-related ions i.e. sulphates and nitrates attributed to the occasionally excessive use of fertilizers and the absence of sewage systems. Moreover, the graphical interpretation was one of the methods used for summarizing and presenting different geochemical processes (Piper, Expanded Durov, Gibbs diagrams etc.). Combining the assessments' results, groundwater chemistry is mainly controlled by geogenic hydrogeochemical processes (geological structure, geothermal activity) but also, to a lesser extent, by human induced factors including intense agricultural activities and lack of sewage systems. Based on the analytical results, groundwater in the area is generally fresh while the abundance of the major ions is as follows: $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$ and $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$. The dominant hydrochemical facies of groundwater is Ca-HCO_3 and Ca-(Mg)-HCO_3 type correlated with the geological formations of the adjacent areas (carbonate, dolomite, ultrabasic rocks) and the residence time. Additionally, the concentration of trace elements were below the threshold values set by Directive 98/83/EC except for iron, manganese, zinc, aluminium and fluoride attributed to dissolution of basic-ultrabasic, volcanic, crystalline and metamorphic formations (gneiss, granite, schists etc.), bedrock's secondary alteration and reductive conditions (geogenic processes). Eventually, the integrated conceptual approach of different methodologies was successfully applied for the identification of hydrogeological and hydrogeochemical assessments within the study area.

Keywords: statistical – graphical methods, quality assessment, hydrogeochemical processes and origin, nitrate pollution, groundwater sustainability

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INTRODUCTION

In the present essay physico-chemical data were investigated with the aim at determining the main factors, mechanisms and variations controlling the groundwater's hydrogeochemistry within Serres alluvial aquifer. The purpose of most water quality studies is to point out the information and necessary knowledge to manage water resources as well as their use, control and development. The groundwater is commonly the most important source of water supply for the whole area. By using graphical and statistical techniques (correlation matrix, simple and multiple linear regression analysis, saturation indices), the relative importance of geological and hydrogeological aspects in controlling the groundwater flow and circulation as well as the geochemical effects influencing the hydrochemistry and aquifer susceptibility were addressed. Additionally, hydrochemical plots, binary diagrams and correlation between different elements can provide understanding of the environmental distribution of contaminants. The goals of the present study were the evaluation of groundwater chemistry in Serres aquifer, the assessment of groundwater quality and its suitability for different purposes (domestic, industrial and agricultural), the processes' identification affecting the distribution of the major ions and trace elements, the exploration of the relationship between the water-rock interaction and the explanation of the observed differences in groundwater hydrochemical characteristics. Therefore, the chemical composition of groundwater is influenced by some factors which include bedrock geology/hydrogeology, soil properties, extent of chemical weathering, water quality recharge and inputs (anthropogenic activities) from sources apart from water-rock interaction. For these reasons statistical methods such as variables' correlation, simple and multiple regression analysis, bi-elements scatter diagrams were used coupled with hydrochemical graphical methods (Piper, Expanded Durov, SAR, quadratic graphs etc.) for the analysis of groundwater composition. This paper provided simple procedures for the identification of the hydrogeological unit in which a groundwater sample was taken based on commonly available major ions geochemistry and various trace elements i.e. iron (Fe), manganese (Mn), aluminum (Al), zinc (Zn) and fluoride (F). The key processes that drive hydrogeochemistry and consequently water resources quality involve both geogenic and anthropogenic factors. The natural (geogenic) processes include redox transformations, ion exchange, dissolution and precipitation, water-rock interaction and intermixing of water bodies and others depending on the specific characteristics of the examined aquifer. The human-driven processes include point and diffuse pollution sources mainly related to agricultural practices and urbanization. The goals of the present study were to determine natural associations between groundwater samples and/or variables and to demonstrate the usefulness of the statistical analysis to improve the understanding of the groundwater composition. Attention was given to study the natural concentration of many ions and heavy metals in groundwater in order to establish the anthropogenic and geogenic sources affecting groundwater quality as well as the reactions that take place within the aquifer. Hence, hydrogeochemical investigation was carried out along the lowlands of Serres river basin, East Macedonia, to evaluate the groundwater chemistry, hydrogeochemical facies and assess the groundwater quality since the alluvial aquifer is of vital importance for the socio-economic development of the region supplying the needs of almost the entire domestic, irrigation and industrial demands.

REGIONAL SETTING

Site Location

The study area is located in the northern part of Greece of Central Macedonia Prefecture and East Macedonia River Basin District and lies between 22°52' and 23°53' N latitude and 40°40' and 41°25' E longitude. The complex geomorphology of Serres basin area (area of 2279 Km² and perimeter of 409.9 km) is consisted of smooth and almost flat surfaces with minor uplifts formed by the modern alluvial deposits of the river, that is, relief with gentle slopes, which become gradually steep towards the western and eastern outskirts in rocky formations. The study area is open to the sea at Southeast and is generally surrounded by higher or lower mountains and hilly areas (Menikio, Vrontous, Belles, Kroussia, Vertiskos, Paggaeo). Serres alluvial basin has a geomorphological characteristic of diverged drainage network (Strymonas River of 5th order, by Strahler, originated from Bulgaria and discharging into Strymonas Gulf) which has length of about several kilometers (120 km in the Greek territory), converges to the southeast and reaches the sea. The dendritic drainage network is mainly composed of intermittent small torrents flowing in an ENE-WNW direction mainly controlled by geological structural elements. The eastern and western mountainous areas show a sparse drainage network with very steep slopes and deep river bed, developed due to the presence of permeable formations (intensively tectonized rocks such as marbles, granites, schists etc.), while the valley areas in the middle form a relatively dense drainage network because of the less permeable alluvial deposits and the significant amount of infiltrated surface water. The

drainage network that runs Serres plain is rather extended due to the development of multiple artificial irrigation channels. The mean elevation reaches 118m above sea level (a.s.l.) ranging between the sea level (flat terrain) and approximately 1030m a.s.l. with the major and minor axis of 74.6Km (NW-SE) and 57.8Km (SW-NE), respectively. The region's climate belongs to the Csa type (by Köppen) which is representative of the Mediterranean climate with mild wet winters and mild hot and dry summers. According to the available hydrometeorological data, the mean annual precipitation and air temperature range between 400-580mm and 13.5-15.2°C, respectively with observed higher rainfall values in the mountains and lower ones in the valley [14].

Geology – Hydrogeology

As illustrated in the geological map (Figure 1, left), the wider area of interest is composed of several rock types including crystalline fractured rocks, highly weathered igneous and metamorphic rocks (e.g. granites, diorites, peridotites, gneisses, shales) comprising the bedrock of the local aquifers along the eastern and western outcrops of the alluvial plain and post-alpine unconsolidated sandy formations of Tertiary/Quaternary age along Strymonas River. The surrounding metamorphic rocks occupy almost the entire area consisted of gneiss, marbles (intensively tectonized) and lithological interchanges (schists, marbles and gneiss). The ophiolitic mélange consisting mainly of dakites and dolerites and locally of serpentinized mafic and ultramafic rocks is typical in the area. Generally, the ophiolitic sequence constitutes a poor aquifer or a practically impermeable formation. However, high capacity metamorphic aquifers occur where faulted and fractured zones due to secondary porosity prevail. The Neogene deposits of Miocene-Pliocene age include marls, sandy-marls, calcareous marls, marly limestones, conglomerates with sandstones intercalations, lignitic beds, lacustrine and deltaic deposits. Finally, recent deposits of Quaternary age composed of alluvial and elluvial fans, coastal sandy and clay-sandy sediments, debris cones mainly located in the coastal region and loose sediments of silts, sands and pebbles lie inside the regional basin acting as sufficient water storage which entirely depends on its variable thickness. The alluvial sediments (e.g. sands, clays) constitute the youngest formation covering the largest part of the tectonic graben whereas in the coastal areas sand dunes and coastal sediments (e.g. sands) prevail.

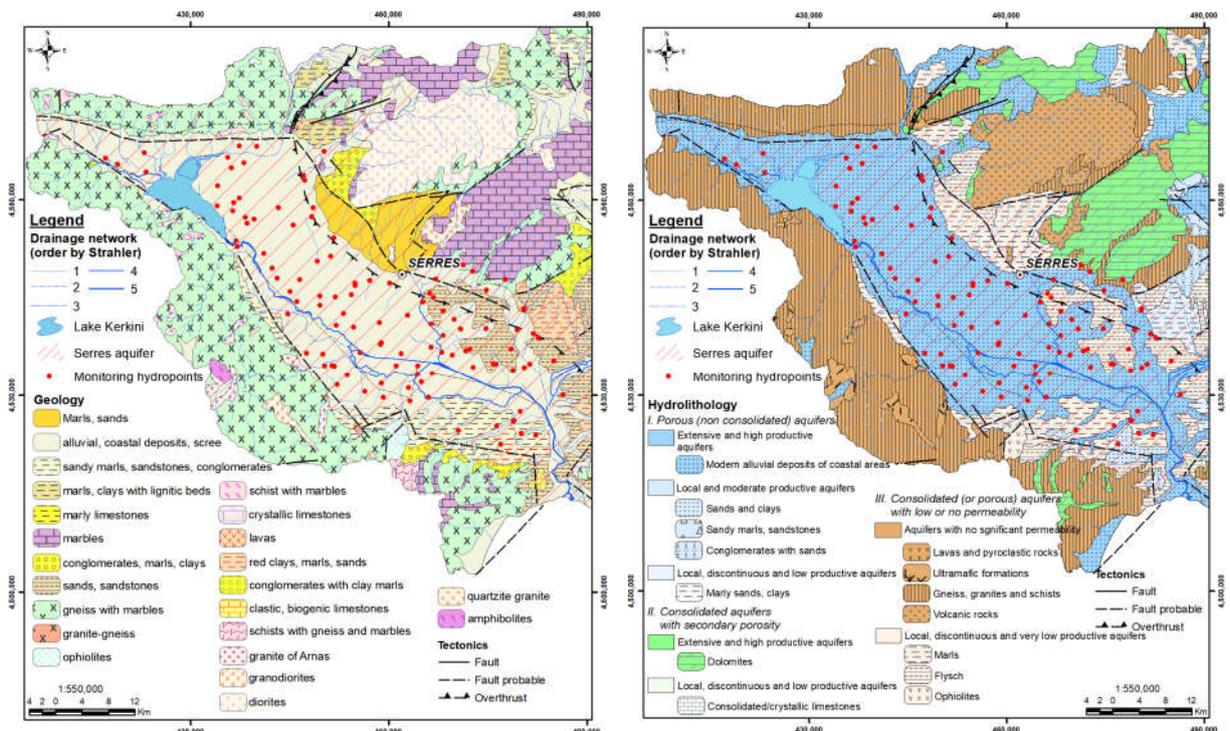


Figure 1: Geological (left) and hydrogeological (right) map of the study area with monitoring and sampling hydroponits.

From a hydrogeological aspect (Figure 1, right), groundwater resources occur in the alluvial sediments on both sides of Strymon as River. Recharge to such aquifers originates from direct rainfall infiltration, irrigation returns, perennial streams, canal percolation, torrent bed infiltration and laterally inflows from the adjacent metamorphic and karsticrocksas well as less permeable Neogene formations with the

groundwater flow to be from northwest to southeast. The basement complex rocks are generally considered as poor aquifers because of their low secondary porosity and permeability [14]. The groundwater occurrence in fractured igneous and metamorphic water bearing formations is controlled by the presence, width and direction of the joints, fractures, faults, dykes, karst pipes and other discontinuities that cross their mass. Hydrogeological observations have revealed that the majority of the water bearing geological formations show primary or/and secondary porosity. Therefore, the aquifers occurring in metamorphic and ultrabasic rocks are expected to have diffuse flow through small fractures and the granular matrix of the rock where the water seeps slowly through the aquifers. Quaternary formations have been deposited at the lower parts of the basin with materials derived from weathering of all previous formations which come across at higher topographic positions coming from the surrounding mountain range rocks. In the vertical direction, the pore spaces developed in the alluvium sediments act as a shallow granular aquifer (0.5-7m) and form potential water-bearing zones whereas the clay and silt intercalations decrease the overall permeability of the formation. As a result, a series of successive superimposed confined or unconfined aquifers of limited extent are expected to occur deeper inside the alluvial sequence. The confined aquifer consists of sands mixed with cobbles and pebbles situated below the Holocene unconfined aquifer. However, despite the described heterogeneity, on a regional scale a single unconfined aquifer may be considered where most of the boreholes have been drilled. The aquifer's thickness ranges from 10-120m with an average of 65m. Irrigational water is obtained by groundwater and river water extraction while potable water demand is met by groundwater pumped from shallow and deep boreholes.

MATERIAL AND METHODS

Dataset Sampling and Field Measurements

The groundwater samples were collected from 115 boreholes with variable depths ranging from 15 to 150m below ground level, along the river course and its tributaries (Neogene and Quaternary sediments) and were analysed for major ions and various heavy metals so as to evaluate the sensitivity of processes to environmental change induced by geochemical factors. The methods employed for this study are field measurements, sampling and laboratory analysis. The boreholes were pumped for some time before collecting groundwater samples so as to eliminate the residual water in the casing tube of the well (removal of stagnant water) and to obtain fresh water directly from the aquifer as well as to ensure stable conditions obtaining at the end representative uncontaminated groundwater samples. In order to investigate the groundwater quality parameters for different purposes, the groundwater was studied in two time periods (2005-2008, 2013-2015) with significantly very small variance ($\pm 2-7\%$) and limited concentrations' fluctuation between wet and dry periods. Sampling campaigns and field measurements were performed on a seasonal basis i.e. October (peak of dry period), January, April (peak of wet period) and July to evaluate and assess the seasonal variations in chemical compositions. Hence, sampling was intentionally carried out within these periods so as to deliver representative mean values for the entire hydrological years. The sample monitoring and analyses were made to obtain a selection as widely geographically and spatially distributed as possible (upstream, mid and downstream). All bottles were thoroughly prewashed with distilled water and then rinsed by sample groundwater before collecting to ensure the pollutants' elimination. After sampling, the bottle was capped immediately to minimize oxygen contamination and avoid the escape of dissolved gases. Physicochemical parameters (air-water temperature, pH, electrical conductivity, dissolved oxygen, oxygen reduction potential) were measured in-situ using portable instruments (WTW instrumentation) in order to acquire representative values of ambient aquifer conditions avoiding parameters' changes during transportation. Total Dissolved Solids, alkalinity and other ions (Ca, Mg, Na, K, HCO_3 , Cl, SO_4 , NO_3 , Fe, Mn, Zn, Al, F) were analyzed shortly after sampling in the accredited and certified Water Analysis laboratory of the Institution of Geology and Mineral Exploration (I.G.M.E.). For the major element analyses, the samples were field filtered on-site through 0.45- μm pore size filters and collected in acid-rinsed, sterilized and narrow-mouth polyethylene bottles with screw cap. The polythene bottles were completely filled without any air bubble before sealing the cap. Once the samples were taken, they were stored in a portable fridge (at 1-4°C temperature) prior to analysis in the laboratory to avoid high temperature and direct sunlight. Special care was taken into account to avoid contamination during sampling for dissolved trace elements. The measurement's analytical precision was determined by calculating the ionic balance error which was generally found to be within $\pm 5\%$. The locations from where groundwater samples were collected were also marked on the study area map by hand held portable GPS device.

Methodology Analysis

The hydrochemical analyses using standard laboratory procedures were carried out to improve our understanding of the principal hydrogeochemical processes taken place in the study area. The hydrogeochemical study of the groundwater was conducted using several methods (graphical illustration plots, statistical analysis, scatter-binary diagrams, ion exchange and saturation indices). Also, basic descriptive statistical parameters of the chemical analysis were calculated (Table 1), simple and multiple linear regression analysis tool was preferred to determine the correlation coefficient, if any, between the chemical compounds, PHREEQC hydrogeochemical equilibrium software was used for calculating saturation indices in order to detect the different mineral phases present in the aquifer. In addition, hydrochemical diagrams and graphs were used to identify the groundwater type and the hydrogeochemical facies and origin as well as to provide meaningful insight in the relationships between the variables studying their inter-elemental relationships.

Table 1: Descriptive statistical parameters of groundwaters' chemical data

Variables	N	Min	Max	Mean	Median	Std.Dev.	Range	Kurtosis	Skewness
pH (<i>dimensionless</i>)	107	7.29	8.21	7.74	7.75	0.21	0.91	-0.59	-0.01
EC ($\mu\text{S}/\text{cm}$)	107	281	3018	743	591	441	2737	7.26	2.34
TDS (mg/L)	107	164	1432	382	317	197	1267	7.23	2.21
TH ($\text{mg CaCO}_3/\text{L}$)	107	71	1158	262	224	180	1086	10.48	2.85
Alk. (mg/L)	107	123	620	251	228	99	497	3.01	1.70
Ca (mg/L)	107	18	319	65	53	47	301	12.22	3.23
Mg (mg/L)	107	2.2	114.2	24.3	19.2	20.4	112.0	4.38	1.95
Na (mg/L)	107	9.0	650.0	63.0	49.0	75.8	641.0	35.52	5.16
K (mg/L)	107	1.0	29.5	4.4	3.0	4.7	28.5	9.97	2.97
HCO ₃ (mg/L)	107	150.7	756.4	306.5	278.2	121.1	605.8	3.01	1.70
Cl (mg/L)	115	2.5	134.8	27.2	20.4	23.4	132.3	6.83	2.33
SO ₄ (mg/L)	115	2.5	473.6	52.7	35.7	71.7	471.1	19.74	4.06
NO ₃ (mg/L)	115	2.5	159.5	18.3	8.3	22.9	157.0	12.79	2.92
Fe ($\mu\text{g}/\text{L}$)	115	15.0	2913.3	132.3	15.0	399.8	2898.3	24.96	4.69
Mn ($\mu\text{g}/\text{L}$)	115	2.5	526.6	52.0	17.0	93.5	524.1	10.77	3.24
Zn ($\mu\text{g}/\text{L}$)	107	10.0	4633.3	171.5	64.3	497.5	4623.3	63.12	7.46
Al ($\mu\text{g}/\text{L}$)	28	8.5	297.4	77.8	55.4	72.5	288.9	2.47	1.71
F ($\mu\text{g}/\text{L}$)	52	25.0	1520.0	477.2	410.0	314.7	1495.0	2.73	1.55

The saturation index indicates the potential for chemical equilibrium between water and minerals and the tendency for water-rock interaction. For the identification of water types, the chemical analysis data of the groundwater samples were plotted and interpreted using different graphical representations such as Piper, Expanded Durov, Chebotarev, Sulin, Gibbs, quadratic etc. as effective tools to visualize and explore data properties as well as classify the water samples indifferent water-type categories. Quality assurance of all hydrochemical analyses was tested through electro-neutrality to be below $\pm 5\%$, thus results were within the acceptable margins for similar research assessments and considered reliable. For the purpose of constructing all plots and statistical calculation, data below analytical detection limits were set to a value of half of the detection limit. The parameters such as sodium adsorption ratio (SAR), soluble sodium percentage (%Na-Wilcox), Kelly's ratio (KR), residual sodium carbonate (RSC), magnesium hazard (MH) and permeability index (PI-Donen) were calculated to evaluate the suitability of the water quality for irrigation purposes [15, 16, 18, 20]. The accuracy and precision of analysis were tested through running duplicate analysis on selected samples revealing negligible systematic and random errors and the average results of all analyses were used to represent the data. Total dissolved solids (TDS) were used for Gibbs' diagrams to validate the significance of the hydrogeochemical characteristics and assess the sources of dissolved chemical constituents of groundwater. The results from the groundwater analysis were used as a tool to identify the process and mechanisms affecting the chemistry of groundwater from the study area. Finally, the spatial and temporal or seasonal variations of the observed water quality parameters were evaluated using the coefficient of variation (CV) to determine whether significant differences on the groundwater sources' concentrations at different sites and years exist.

RESULTS AND DISCUSSION

Descriptive statistics

Major anions and cations, pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), alkalinity (Alk.) as well as a limited number of trace elements were assessed on all samples collected. Based on the analyses performed the results showed that pH ranged between 7.30-8.20 indicating an alkaline groundwater type, electrical conductivity between 280-3000 $\mu\text{S}/\text{cm}$ (large variation was mainly attributed to geochemical process like ion exchange, reverse exchange, evaporation, silicate weathering, water-rock interaction, sulphate reduction and oxidation processes as well as human activities like application of agrochemicals polluting the groundwater), TDS between 160-1430 mg/L with higher observed concentration near the lower part of the river basin, bicarbonates between 150-760 mg/L mainly derived from the dissolution of silicate minerals and weathering of carbonate rocks, chloride concentration between 2.5-135 mg/L, nitrates between 2.5-160 mg/L and potassium between 1.0-29.5 mg/L mainly derived from the agricultural fertilizers and minerals like orthoclase, microcline and biotite present in igneous rock formations. The classification of groundwater based on TH [19] showed that a lot of the groundwater samples (~68%) fell in the hard category. The variation in total hardness values within the aquifer was due to fluctuation in calcium and magnesium concentrations due to the cation exchange reactions and water-rock interaction. Where nitrates exceeded the drinking water limits (50 mg/L) set by the EU Directive (98/83/EC) were due to the decaying organic matter, sewage and nitrogenous fertilizers from agricultural runoff. Nevertheless, nitrates were in general low (mean = 18.3 mg/L, median = 8.3 mg/L), indicating that despite the intensive agricultural activities there is limited contamination to groundwater. The higher values of calcium, magnesium and bicarbonate were recorded near the areas with carbonate formations, due to the dissolution of these rocks. Additionally, the cationic composition was also influenced by magnesium which was locally enriched as a result of the ultrabasic blocks and the dedolomitization process. Besides, water samples showed at some locations high sulphate content because of the low enthalpy geothermal field as well as high sodium one due to the weathering and subsequent dissolution of abundant Na-rich surface minerals, like Na-clays and Na-feldspars (granites, gneiss, schists etc.). Also, geothermal activity generally results in heavy metal enrichment. Moreover, the majority of trace elements' concentrations did not exceed the WHO threshold values for drinking water except locally for Fe, Mn, Zn, Al and F due to water-rock interaction with igneous, ultrabasic and metamorphic formations at the outskirts of the both sides of alluvial basin. The high values of standard deviations of some of the parameters showed that their concentration levels in the groundwater were fluctuating in a random manner indicating that chemical composition was affected by multiple mixing processes and thus, implying substantial difference in groundwater quality within the study area. However, the majority of the variables' standard deviation was lower than the average value indicating that the chemical properties of the groundwater were not widely dispersed. The concentrations of the analyzed chemical constituents are presented as box plots in Figure 2. The majority of the trace elements (e.g. Fe, Mn, Al, F and Zn) show the widest ranges between samples which most probably originated from natural weathering of such bearing minerals and rocks (igneous and metamorphic rocks including epidote, biotite, hornblende, iron oxides, topaz, apatite, mica and pyrite) whereas for the other heavy metals the values were either below the maximum acceptable values for drinking water or below the detection limit of the applied methodology analysis.

Graphical Methods

The graphical methods (Figure 2, 3) are useful to group the samples [9, 10], visually represent the dataset and provide valuable and rapidly accessible information regarding the chemical composition of water samples e.g. the relative proportion of the cations and anions (in meq/L). Chemical properties of groundwater in Serres alluvial aquifer are controlled both by natural geochemical processes such as bedrock geology, weathering, dissolution, precipitation, ion exchange and anthropogenic activities. Piper trilinear diagram was applied for the purpose of characterizing groundwater types using hydrochemical data. From the analysis of this diagram, HCO_3^- is the dominant anion whereas Ca, Mg and in a lesser extent Na were the most dominant cations. On the right triangle, the majority of the samples plotted in the left corner suggesting a significant content in HCO_3^- . Molar cation and anion concentrations followed the order $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$, respectively. In the study area, the dominant hydrochemical facies of groundwater is Ca- HCO_3^- , Ca-Mg- HCO_3^- in recharge areas and Na- HCO_3^- in transition zone where mixing processes prevail during aquifer's freshening. The Ca- HCO_3^- water type indicated dissolution of calcite which corresponded to fresh water not affected by seawater intrusion phenomena whereas Ca-Mg- HCO_3^- water type attributed to Mg-bearing minerals found in several geological formations (e.g., ophiolites, dolomites, gneiss, granites etc.). The aforementioned two types were plotted on the diamond-shaped field parallel to the left side, indicating groundwater from recharge areas not

affected by seawater intrusion. The results of plotted chemical data on expanded Durov's diagram were used to identify the geochemical evolution of groundwaters where the groundwater are initially recharged by Ca-HCO₃ water (fresh water) and undergo water-rock interactions (dissolution) and mixing. Therefore, expanded Durov plot agrees with the Piper one suggesting that Mg-HCO₃ water type (fresh water-recharge) is associated with dolomitic limestones and ultrabasic rocks of bedrock as well as sediments derived from erosion which have been deposited across the basin. Ca-HCO₃ water type was also met indicating recharge waters from karst aquifers.

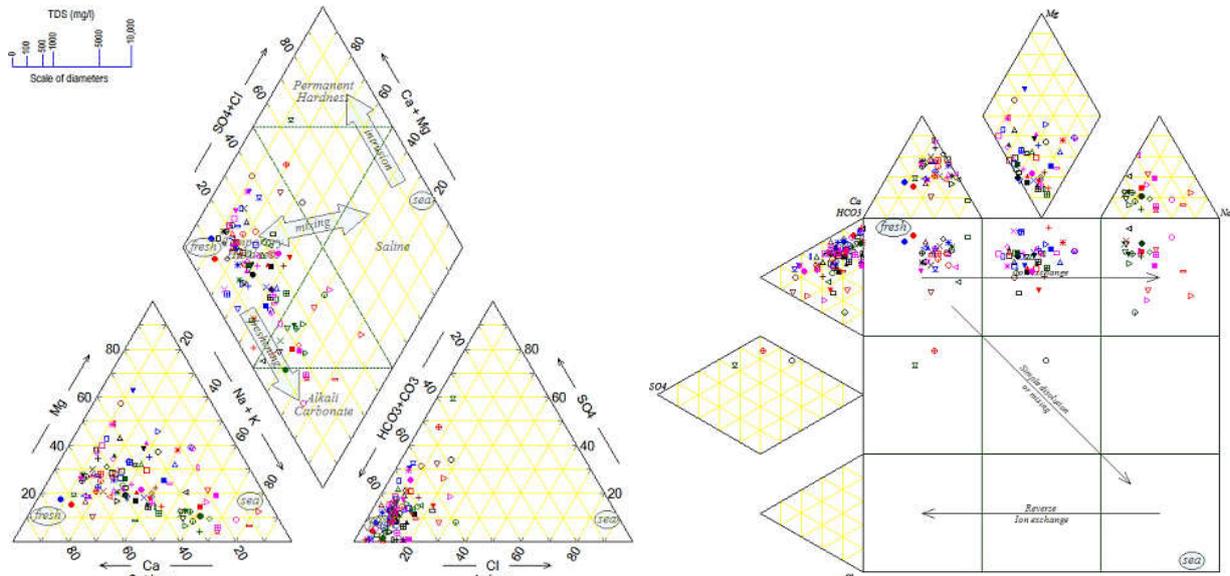
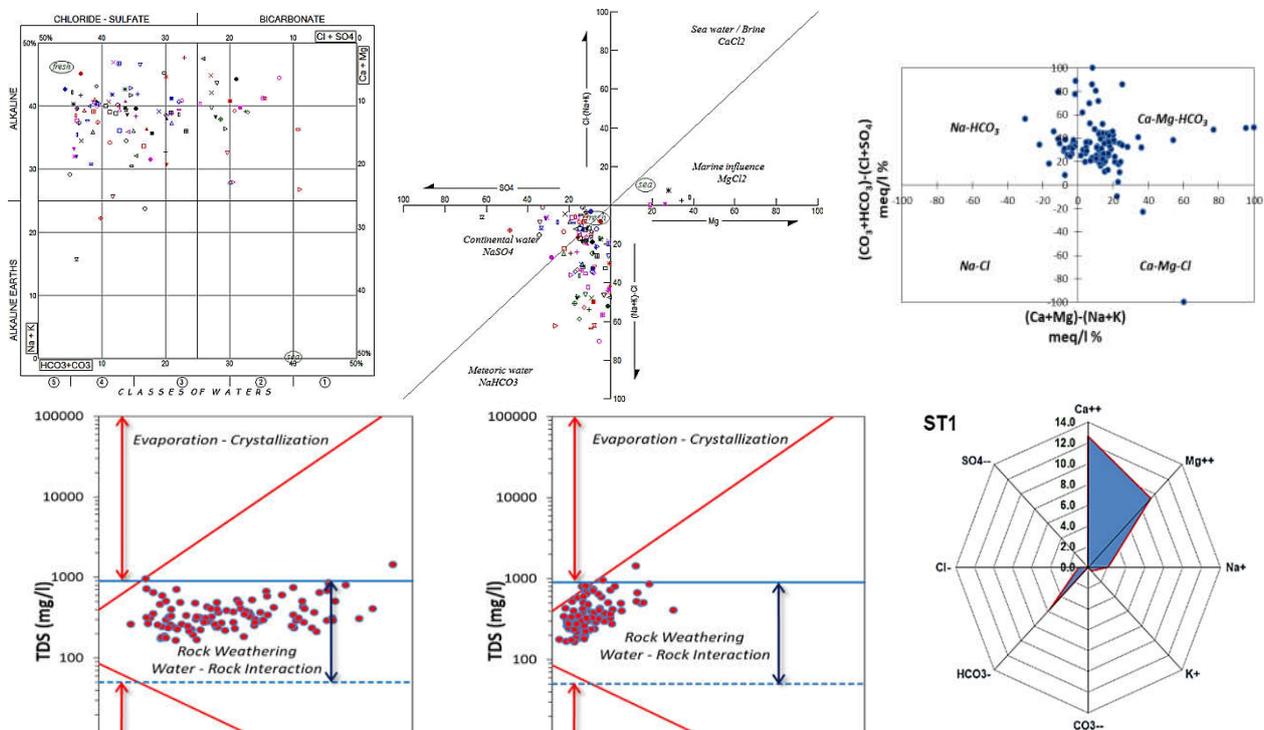


Figure 2: Hydrochemical facies of groundwater (from left to right: Piper, expanded Durov) showing the groundwater type and origin.



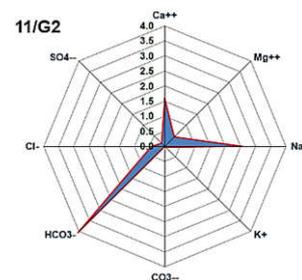


Figure 3: Chebotarev and Sulina diagrams showing the groundwater type and origin. Gibbs' diagrams and spider type hydrogeochemical graphs derived from the ion ratios and major ions' correlation.

The same conclusion was derived from Chebotarev and Sulina diagrams (quadratic and spider type graphs, Figure 3) showing the alkaline origin and the dominant ions as well as the water type of the groundwater samples. Plotting of values of specific water quality parameters over the Gibbs' diagrams gives us an insight as to which particular factor—evaporation, precipitation or rock–water interaction plays the dominant role in controlling the hydrogeochemistry of an area. Gibbs' diagrams (Figure 3) were prepared using TDS, sodium, potassium, calcium, chloride and bicarbonate concentrations in groundwater. Almost all the samples fell in rock-water interaction dominant zone in both diagrams indicating chemical weathering of rock-forming minerals as the prime factor influencing the groundwater quality suggesting dissolution and displacement of minerals constituting the aquifer materials, whereby water-rock interactions gradually increased due to rock-forming minerals and partially inclined towards evaporation dominance. This is expected due to the increasing rock–water interactions, the weathering of host rocks and chemical weathering of rock forming minerals, which cause mineral dissolution [1, 2, 6].

Ion Ratio Analysis

In order to assess the groundwater suitability to irrigation (Figure 4), several ionic relationships were calculated based on sodium adsorption ratio (SAR), Wilcox's diagram (%Na), permeability index (PI), Kelly's ratio (KR), residual sodium carbonate (RSC) and magnesium hazard (MH) as derived parameters. The suitability of groundwater for irrigation purposes depends upon the effect of mineral constituents of water on both plants and soils. SAR is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops as sodium concentration can decrease the soil permeability and soil structure. Chemical parameters when plotted in the SAR diagram indicated that ground waters were of C₂-S₁ and C₃-S₁ types showing medium to high salinity hazard and low alkalinity one which is good and safe for long-term irrigation with some caution required with regards to sensitive crops and heavy soils while those samples lying beyond this area indicated salt enrichment and hence could not be used directly on soils without special salinity and sodium controlling treatments (adequate drainage). Wilcox uses % sodium and specific conductance in evaluating the suitability of groundwater to irrigation. Classifying groundwater based on that the 70% of the groundwater samples fell in the field of excellent to good, 24% fell in the field of good to permissible and only 6% fell in the field of permissible to doubtful. The Permeability index (PI) of the groundwater samples is classified under class I (>75%), class II (25-75%) and class III (<75%) orders; class I and II waters are categorized as good for irrigation with 75% or more of maximum permeability while class III waters are unsuitable with 25% of maximum permeability. Based on Permeability Index values the majority of groundwater was designated as class I and II (0-75%) indicating the suitability for irrigation purpose.

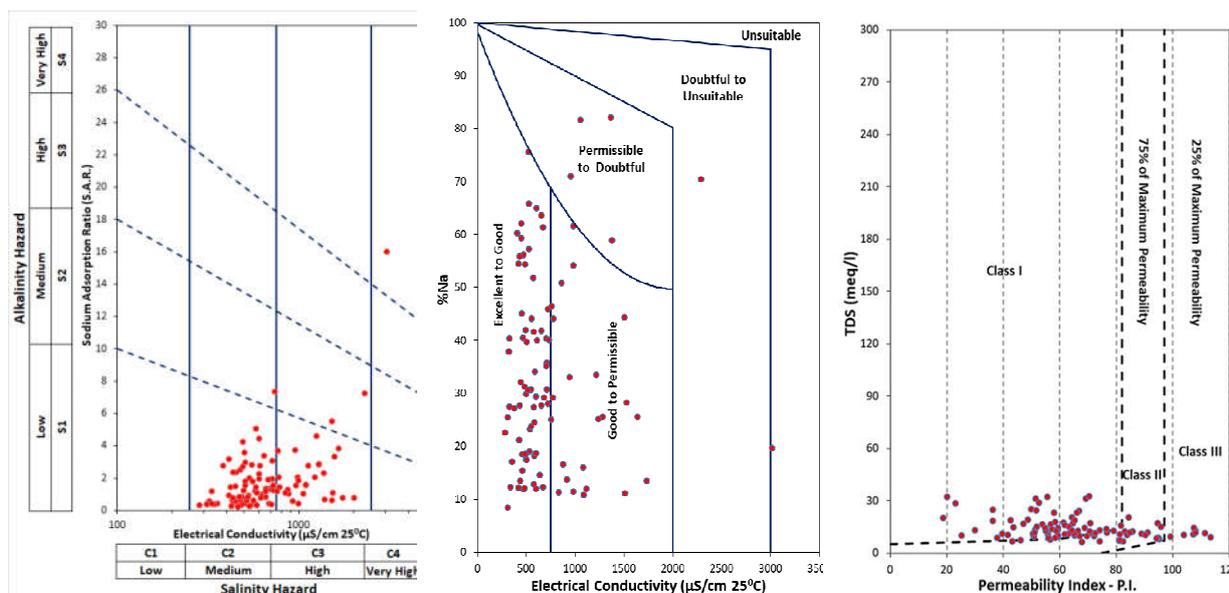


Figure 4: Richards (SAR), Wilcox (%Na) and Doneen (PI) diagrams (from left to right) for groundwater suitability classification for irrigation purpose.

Sodium measured against calcium and magnesium was considered by Kelly. Kelly's ratio (KR) values in the groundwater samples by 79% had KR value below 1, suggesting that water is suitable for irrigation while 21% of the samples are found to be higher than 1 signifying their adverse effects on irrigation utility. RSC has been calculated to determine the detrimental effect of carbonate and bi-carbonate on the quality of groundwater for agricultural purpose. When the RSC values are less than 1.25meq/L, the groundwater is considered to be safe for irrigation. If the value is between 1.25meq/L and 2.5meq/L the water is marginally suitable, while values above 2.5meq/L indicate the groundwater unsuitability for irrigation leading to an increase in the adsorption of sodium (alkaline nature in soil) and that such alkaline soil becomes infertile. About 74% of groundwater samples had values < 1.25meq/L, thus being suitable for irrigation, 14% between 1.25meq/L and 2.5meq/L while 12% had values > 2.5meq/L and thus being unsuitable for irrigation. The majority of the groundwater samples fell in safe category. Negative values of RSC indicate high concentrations of calcium and magnesium in the groundwater. Thus, magnesium and calcium concentrations are also vital in evaluating the groundwater quality. Magnesium can give more adverse effects on soils than calcium. Hence, it is essential to assess the magnesium hazard ratio (MH). The samples having MH values above the permissible limit of 0.5 indicate the unfavorable effect on crop yield and increase in the soil alkalinity. Those samples would adversely affect the crop yield by making it more alkaline. According to magnesium hazard ratio classification, about 83% of groundwater samples were found to be < 0.5 making the groundwater suitable for irrigation while 17% of groundwater samples were found to be > 0.5, thus making them unsuitable for irrigation.

According to $(Ca+Mg)/(SO_4+HCO_3)$ ratio, the samples lying above the line 1:1 showed that calcite minerals dissolution prevailed (carbonate formations) while those lying below the line 1:1 indicate that silica minerals dissolution process prevailed (igneous, ultrabasic and metamorphic rocks). As illustrated in Figure 5, most of the groundwater samples were allocated below the line 1:1, indicating that there were sites where silicate dissolution prevailed against carbonate dissolution. This was attributed to the composition of the alluvial sediments where silicate mineral categories were included. However, some samples deviated significantly from the aforementioned line and clearly reflected the predominance of either silicate or carbonate weathering without any specific spatial pattern. In respect to Cl versus Na diagram, it is evident that does not follow a linear (1:1) approach, at least for the majority of samples, suggesting that groundwater exploitation is induced by intermixing of multiple-sourced groundwaters of variable salinities along specific flow paths (poorly treated waste waters can contribute to the input of Cl in the groundwater). This scatter diagram revealed that the ionic concentrations fell below the 1:1 equiline indicating that the groundwater composition resulted from the silicate weathering which was the dominant hydrogeochemical process, while those falling along the equiline were due to both carbonate weathering and silicate weathering. In absence of any Cl-bearing mineral in the substrate, elevated Cl levels in groundwater may be additionally attributed to leaching of surface/subsurface salts and irrigation water return flow. Finally, in respect to Na/Cl vs Cl diagram the majority of groundwater

samples fell above the red line indicating both Na-feldspars and halite dissolution recharging the groundwater with such minerals developed inside the crystalline rocks of the basement.

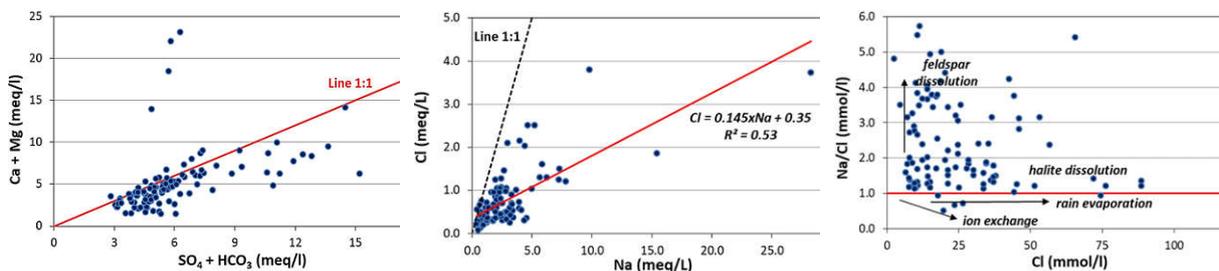


Figure 5: Various ionic ratio graphical presentations showing geochemical classification and hydrochemical parameters of groundwater.

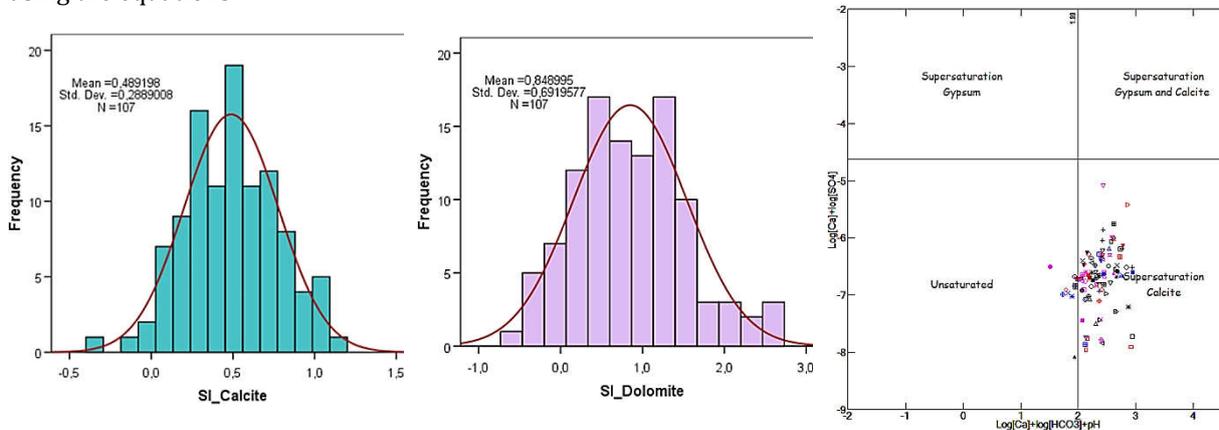
Saturation Indices

Saturation index (SI) calculations of some common minerals using the PHREEQC geochemical code were employed to determine whether a mineral species is likely to dissolve or precipitate in the groundwater flow system. The saturation index approach allows predicting the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy. Saturation index is defined as the logarithm of the ratio of ion activity product (IAP) to the mineral equilibrium constant at a given temperature and expressed as [7, 8, 11]:

$$SI = \log(IAP \times K_{sp}^{-1})$$

where *IAP* is ion activity product of the species that compose the mineralization and *K_{sp}* is solubility product of the associated mineral. Mineral phases that are clearly undersaturated (less than zero) will tend to be dissolved, whilst mineral phases that are clearly supersaturated (more than zero) will precipitate these mineral phases with the groundwater being incapable of dissolving more of the mineral; equilibrium is achieved for SI values between -0.1 and +0.1 (Figure 6). The higher SI values are related to aquifers, where diffuse flow dominates and hence, a longer groundwater residence time is expected. Groundwater samples of Serres alluvial aquifer were strongly saturated with respect to carbonate mineral phases, mainly dolomite (-0.08<SI<+2.80) and slightly saturated with respect to aragonite whereas all groundwater samples are under saturated with respect to gypsum and anhydrite (insufficient amount of minerals for solution or short residence time). These minerals are hosted in rock formations (limestones and dolomites) observed in the study area. The SI results indicate that the dissolution of carbonate rocks is taking place within the aquifer, with the highest values being related mainly to the precipitation of the calcite mineral. The hydrochemical processes that mostly influence the species of groundwater chemistry are leaching and dissolution of surface and subsurface weathered rocks with the effect of reverse and normal ion exchange throughout water-rock interaction. Carbonate mineral dissolution with ion exchange reactions of groundwater samples within Serres alluvial aquifer are the major hydrogeochemical processes responsible for the concentration of major ions in groundwater.

Additionally, the Chloro-Alkaline Indices (CAI_{1,2}) define the ionic exchanges between groundwater and the aquifer rocks. The Chloro-Alkaline Indices 1,2 used in the evaluation of Base Exchange were calculated using the equations:



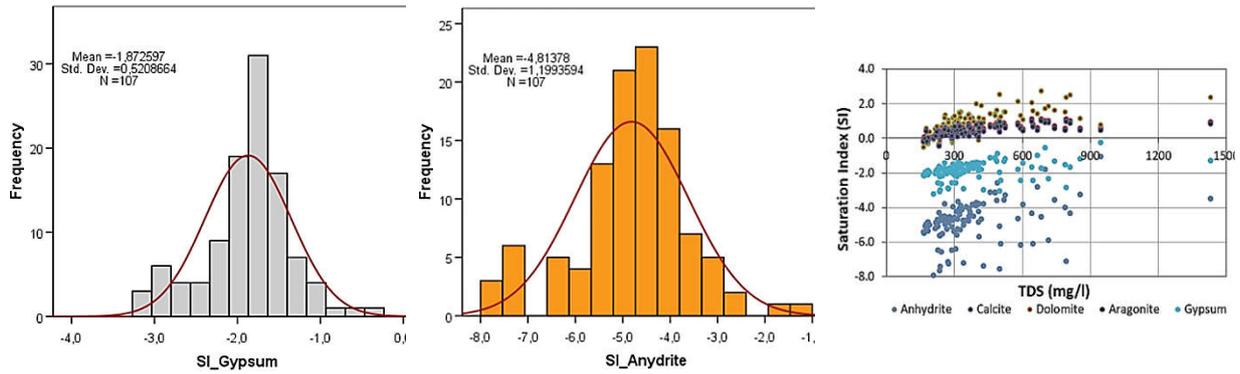


Figure 6: Histograms with saturation indices graphical presentation of the main mineral facies, Calcite-Gypsum dissolution graph and TDS values for groundwater samples with respect to S.I.

$$CAI_1 = [Cl - (Na + K)] / Cl$$

$$CAI_2 = [Cl - (Na + K)] / (SO_4 + HCO_3 + CO_3 + NO_3).$$

These ratios are positive when the sodium and potassium contents are low i.e. when groundwater has been slightly in contact with minerals able to release these interchangeable cations easily. These ratios are negative when the sodium and potassium contents are high, i.e. when groundwater has been strongly in contact with minerals able to yield these interchangeable cations easily. In the case of the Serres alluvial aquifer, the Base Exchange index is negative in 100% of the samples. This indicates that the groundwater exchanged alkaline earths Ca and Mg against the alkalis Na and K of clays contained in the bedrock environment [10].

Statistical Analysis

Statistical analysis has been widely used with the aim to simplify, compile and evaluate/classify large datasets in order to statistically examine the correlations among the physical-chemical parameters of the local aquifers which is of vital source for domestic and agricultural activity in the regional area. In most of the cases this technique is applied to the water quality of the whole area in order to assess trend detection, pollution source identification, optimization of water quality parameters and water quality monitoring stations. Statistical methods including Pearson correlation matrix, simple and multiple linear regression analysis were used to evaluate the interpretation of a complex groundwater quality dataset [3-5, 12, 13, 17].

Correlation Coefficient Matrix

The correlation matrix (Pearson's) is useful because it can point out associations between variables that can show the overall coherence of the dataset and indicate the participation of the individual chemical parameters in several influencing factors (Table 2). The Pearson correlation coefficient simplifies the complexity of hydrochemical data and show the extent of dependence of one variable on the other. This implies whether the relation between the variables is positive or negative. Thus, the correlation measures the observed co-variation. The data were statistically computed using correlation coefficient in order to indicate the sufficiency of one variable to predict the other. The major factors were dissolution and chemical weathering. In general, the variation in relationship shows the complexity in the groundwater quality and the effect of the water-rock interaction. The correlation matrix of eighteen (18) variables is presented in Table 2. From the correlation analysis, competitive and non-competitive ion relationship between the major ions was demonstrated. In general, the geochemical parameters showing correlation coefficient >0.7 are considered to be strongly correlated whereas value between 0.5 and 0.7 shows moderate correlation. Correlation analysis within the study area showed that the relationship between the parameters with high ion character was higher than those parameters with less ion character and that the variation in relationship showed the complexity in groundwater quality and the effect of the water-rock interactions. In the present study, there was an almost perfect correlation between EC and TDS and furthermore, TH had a strong positive correlation with Ca and Mg suggesting that the aquifer chemistry is mainly controlled by these ions. The EC values exhibit high positive correlation with Ca, Mg, Na, K, HCO_3 , Cl, SO_4 , F, TDS, Alkalinity and TH showing that these parameters have similar hydrochemical characteristics in the study area.

Table 2: Correlation coefficient matrix (by Pearson) among groundwater quality parameters

VARIABLES	pH	E.C.	T.D.S.	T.H.	Alk.	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	NO ₃	Fe	Mn	Al	Zn	F	
pH	1.00																		
E.C.	-0.01	1.00																	
T.D.S.	-0.01	0.94	1.00																
T.H.	-0.32	0.70	0.61	1.00															
Alk.	0.06	0.72	0.79	0.40	1.00														
Ca	-0.39	0.55	0.46	0.93	0.18	1.00													
Mg	-0.15	0.73	0.68	0.86	0.62	0.61	1.00												
Na	0.24	0.77	0.78	0.12	0.62	-0.02	0.29	1.00											
K	0.02	0.52	0.50	0.45	0.61	0.20	0.69	0.34	1.00										
HCO ₃	0.06	0.72	0.79	0.40	1.00	0.18	0.62	0.62	0.61	1.00									
Cl	0.02	0.76	0.78	0.34	0.56	0.24	0.39	0.73	0.30	0.56	1.00								
SO ₄	-0.06	0.40	0.60	0.28	0.20	0.28	0.22	0.28	0.03	0.20	0.34	1.00							
NO ₃	-0.26	0.23	0.20	0.35	0.07	0.41	0.19	-0.06	-0.09	0.07	0.31	0.27	1.00						
Fe	0.08	0.19	0.18	0.01	0.10	-0.04	0.07	0.27	0.06	0.10	0.09	0.20	0.09	1.00					
Mn	0.11	-0.07	-0.09	0.00	-0.02	0.01	-0.02	-0.07	-0.02	-0.02	-0.14	-0.12	-0.17	0.50	1.00				
Al	-0.22	0.25	0.25	0.35	0.22	0.39	0.23	0.13	0.11	0.22	0.01	-0.11	0.07	0.28	-0.11	1.00			
Zn	-0.11	0.04	0.08	0.11	0.02	0.14	0.03	-0.04	-0.07	0.02	0.00	0.17	0.02	-0.03	-0.02	0.55	1.00		
F	-0.26	0.54	0.48	0.51	0.20	0.48	0.47	0.32	0.41	0.20	0.52	0.05	0.15	0.19	-0.05	0.40	-0.02	1.00	

(Coefficient value greater than 0.7 is considered to be strongly correlated whereas value between 0.5 and 0.7 implies moderate correlation)

The Ca and Mg concentrations presented a positive correlation ($r=0.61$) indicating a common source due to formations rich in Ca-Mg minerals (limestones, dolomites). Also, the same conclusions can be derived by the positive correlation ($0.62 < r < 0.69$) between Mg, K and HCO₃. Moreover, Cl and Na, K contents were strongly related ($r > 0.73$) suggesting the chloride salts' dissolution. Correlations between ions and TDS suggested that TDS was mainly derived from Mg, Na, K HCO₃, Cl and SO₄. The positive correlation of silicates with Ca and Na revealed that the long residence time of the stagnant river water facilitated the rock-water interaction and hence the silicate weathering. Furthermore, there was a strong correlation between Zn-Al and Fe-Mn suggesting precipitation of salts and minerals as well as ion exchange between soil minerals and water. The result of the correlation analysis also revealed that Na was positively related to F suggesting an increase in F concentration with increased Na concentration. There was as well a positive correlation between F, Mg and Ca which confirmed that fluoride-rich groundwater was often associated with high calcium-magnesium concentrations. Also, F was significantly positively correlated with EC, TH and Cl.

Single and Multiple Linear Regression Analysis

Simple linear regression analysis (Figure 7) was used to describe the co-variation between some variable of interest and one or more other variables. Regression analysis was performed to estimate or predict values of one variable based on knowledge of another variable for which more data are available and was subjected to ascertain the groundwater quality characterization. The model for simple linear regression is as follows:

$$Y = b_0 + b_1 X$$

where Y is the dependent variable, X is the independent variable, b_0 is the intercept which is the coefficient of regression and b_1 is the slope. The results of the regression analysis revealed that by measuring the value of EC, TH, TDS, Ca, Mg, Na and Cl (strong positive correlation) can be respectively calculated. Na and Cl can also be calculated by measuring the value of TDS. Moreover, Alkalinity can be directly calculated by measuring HCO₃. Finally, TH can be easily calculated by measuring only Ca and Mg. Below, binary diagrams between chemical elements were drawn to better understand the processes and specify the origin of the major elements participating to the groundwater mineralization showing also the related equations.

Multiple linear regression analysis is a statistical tool that allows examining how multiple independent variables (X_1, X_2, \dots, X_n) are related to a dependent variable (Y). Once identified how these multiple variables relate to a dependent variable, one can take information about all of the independent variables and use it to make much more powerful and accurate predictions. Adjust criteria for the multiple regression equation to the observed data are the correlation coefficient R , the determination coefficient R^2 and the adjusted R^2 . The aforementioned analysis took into account that EC as dependent variable was a linear function of the rest hydrochemical independent variables (Ca, Mg, Na, K, HCO₃, Cl, SO₄ in mg/L) based on Pearson's correlation matrix (Table 2) expressed as (Davis 1986):

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_5 X_5 + b_6 X_6 + b_7 X_7 + b_8 X_8 + \varepsilon$$

$$EC = b_0 + b_1 Ca + b_2 Mg + b_3 Na + b_4 K + b_5 HCO_3 + b_6 Cl + b_7 SO_4 + \varepsilon$$

where ε is the error, namely, the difference between the measured and predicted value of the dependent variable, b_0 is the constant, namely, the intercept and $b_1...7$ are the multiple regression coefficients which describe the independent variables' influence. According to the analysis, the equation which describes the relationship between the EC and the above ions for the alluvial aquifer's ground water based on the mean over annual concentration (no significant concentration difference during the sampling periods) is:

$$EC = 11.81 + 3.53 \times Ca + 5.04 \times Mg + 3.31 \times Na - 0.34 \times K + 0.37 \times HCO_3 + 1.82 \times Cl + 0.21 \times SO_4$$

The correlation coefficient R is 0.986, the determination coefficient R^2 equals to 0.972 which means that the model explained the 97.2% of the variance and the adjusted R^2 is 0.970 meaning that the use of these ions as independent variables could accurately predict the dependent variable, that is, EC. The usefulness of the above relationship is very crucial as it is possible through values from a representative sample to determine the proportions (%) with which each ion participates in the value of electrical conductivity (EC), namely, the groundwater's hydrochemistry.

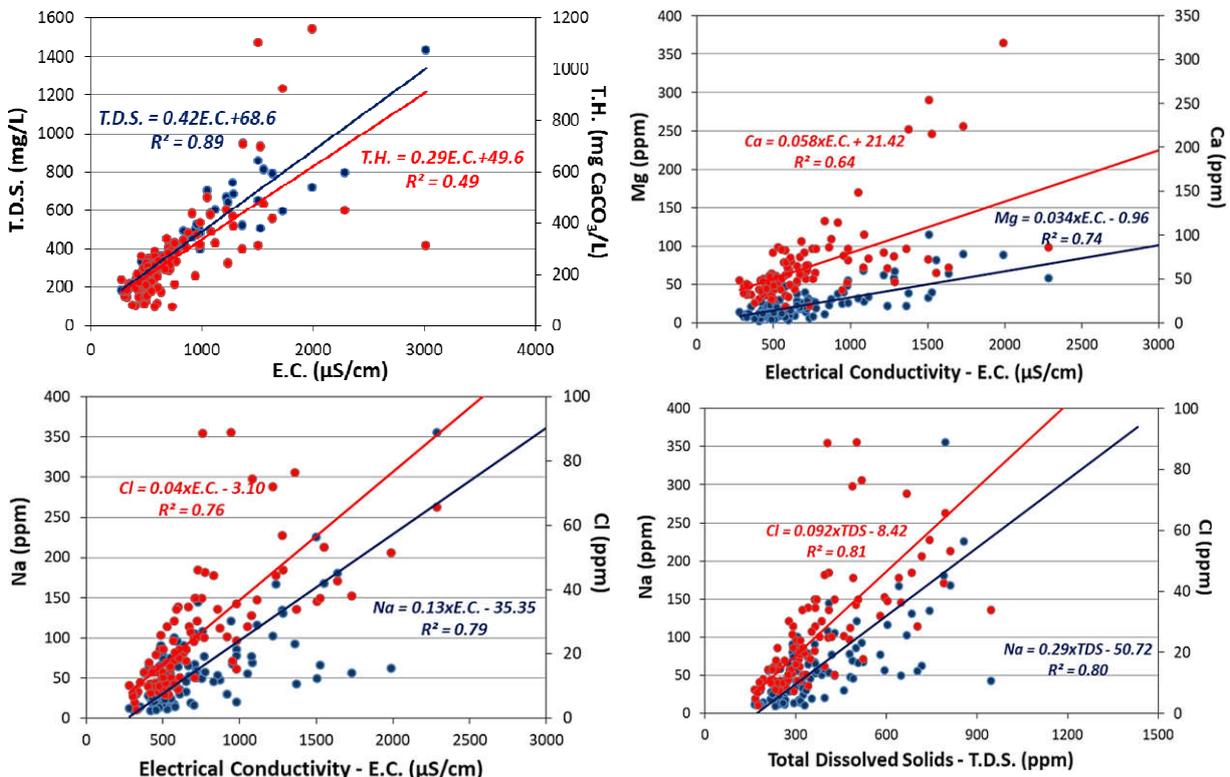


Figure 7: Linear regression graphs and equations for various binary diagrams showing geochemical classification and hydrochemical groundwater quality parameters.

Nitrate pollution

The major anthropogenic driving forces that affect the study area are urbanization, intensive agriculture and industrial activities; however, agriculture is the dominant economic activity in the region, as illustrated in Figure 8 (left).

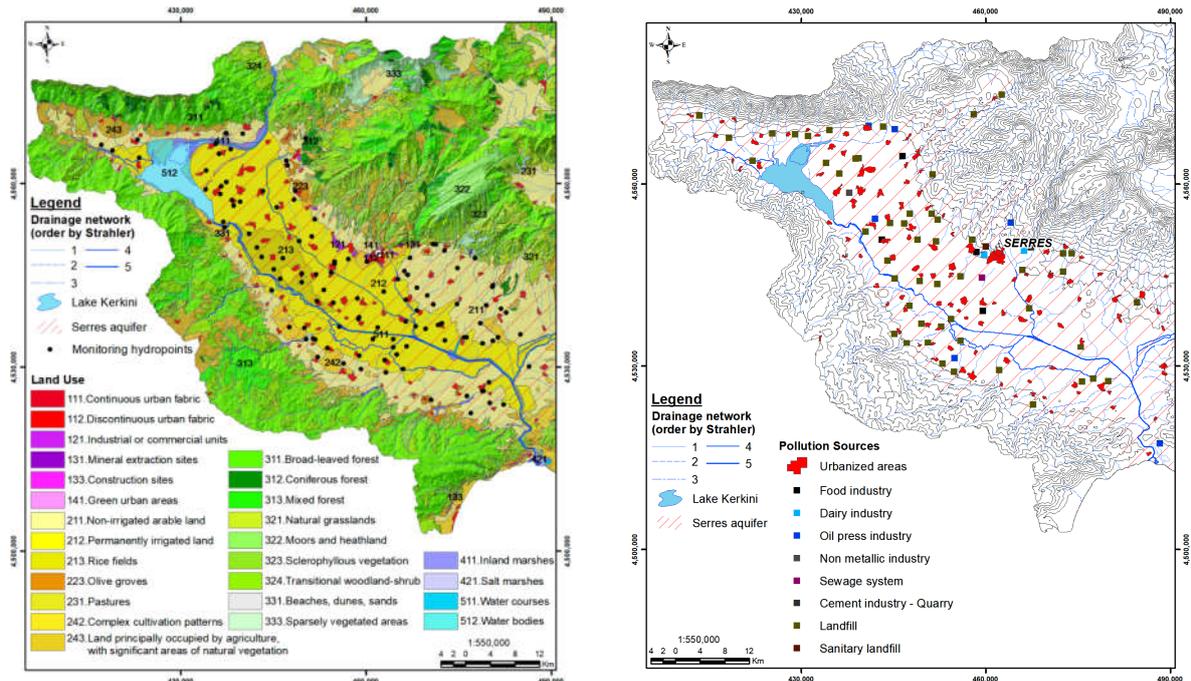


Figure 8: Land use map based on CORINE 2012 (left) and distribution of pollution point sources within Serres aquifer (right).

According to the land use (CORINE 2012) within Serres plain, the dominant use remains the arable, permanent irrigated lands, rice fields and lands with complex cultivation patterns. High nitrate concentrations are related to the agricultural activities, the untreated disposal of domestic waste as well as livestock and manure production [1, 21, 22]. Also, point sources of contamination such as the discharge of untreated domestic effluent, mainly from septic tanks, as a result of a sewage network absence in the small settlements within the study area, may contribute to nitrate pollution (Figure 8, right). The city of Serres is equipped with sewage treatment plants; however, small villages, farms and isolated houses are equipped with individual wastewater treatment systems. The results showed that at the east and southwest of the river's upstream, the groundwater is affected by the agricultural activities and in the downstream both anthropogenic (septic tanks, lack of modern sewage systems) and chemical weathering factors were found to be significant. The use of nitrogenous fertilizers in the intensively cultivated area contributes to the increase of nitrates concentration at some locations within the aquifer. Nitrates range from 0 to 160mg/L though should be noted that the threshold of 50mg/L set by Directive 98/83/EC was only exceeded by 10 groundwater samples out of 115 (~9%). It should also be pointed out that NO_3 concentrations are abruptly decreased locally, even between adjacent boreholes, which is probably attributed to the locally developed anoxic conditions that favor the depletion of potential reductants like nitrates, a fact that explains sufficiently the anomalies in NO_3 spatial distribution (Figure 9, left). For this reason, a monitoring program on groundwater quality should be established in boreholes close to nitrate polluted areas in order to avoid further nitrate pollution phenomena on a larger scale. In addition, integrated treatment plants must be constructed and operate so as to eliminate the use of septic tanks replacing the obsolete sewage systems. Finally, as illustrated in Figure 9 (right), the pie charts give an overall image of the groundwater's hydrochemical characteristics indicating that towards southeast the pies become larger due to the increase of TDS as a result of mineral enrichment through surface water movement and groundwater flow.

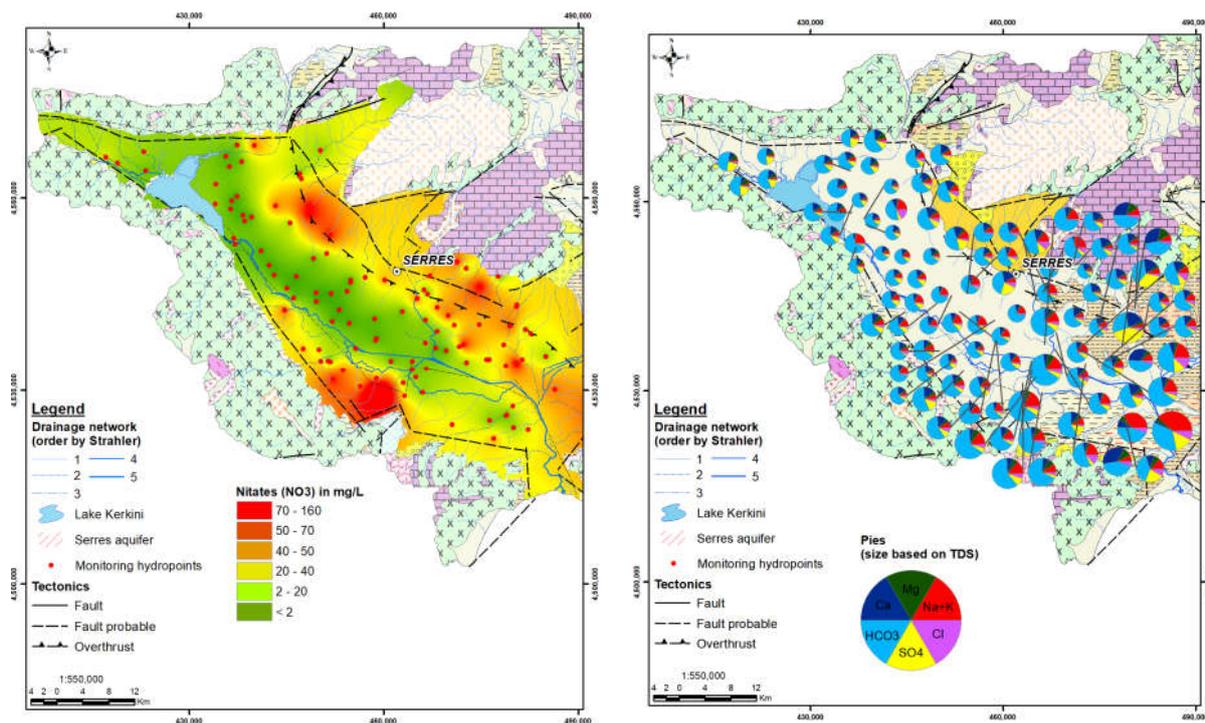


Figure 9: Nitrate concentration distribution map through Kriging geostatistical processing (left) and hydrochemical map (pie charts) (right) of the study area.

CONCLUSIONS

The study is concerned with the impact of hydrochemical processes on the groundwater quality within the aquifer. Statistical (correlation analysis, simple and multiple regression analysis) and graphical analyses are multivariate techniques that were found useful for identifying groundwater on the basis of hydrochemistry and assessing the main hydrogeochemical processes and anthropogenic activities through the analysis of hydrochemical data from 115 groundwater samples. The linear regression analysis confirmed the positive relation of EC with Ca, Mg, Cl, Na and TDS in the study area. Also, the ion ratio technique explained the hydrochemical processes taken place within the aquifer as well as the groundwater's hydrogeochemical origin. Various hydrogeochemical processes including dissolution, adsorption and ion exchange along with the weathering of carbonate minerals were found to take place in the study area. The majority of the sampling sites showed a (Ca or Mg)-HCO₃ water type in recharge areas leading to the conclusion that weathering of carbonate minerals is the main hydrogeochemical process controlling the hydrochemical composition and Na-HCO₃ water type from mixing processes in transition zone. Computer simulation, on the other hand (PHREEQC), indicated that a considerable number of samples were saturated in respect to minerals calcite, dolomite and aragonite and unsaturated in respect to anhydrite and gypsum indicating a long residence time. Sulphates and nitrates concentration suggested the human induced sources dominated by the application of septic tanks, fertilizers and manures in agricultural areas as well as geothermal activity (SO₄). Additionally, the concentrations of the trace elements were lower than the standard limits except for iron, manganese, zinc, aluminum and fluoride due to natural procedures (geogenic) attributed to local rock formations' dissolution of the trace element bearing minerals inside the alluvial sediments. Hence, this study showed the efficacy of both graphical plots and multivariate statistical methods as an efficient exploratory tool for the interpretation of complex water quality datasets and established the main factors and mechanisms that control the chemical composition of groundwater in the study area which are important and effective for the management of water quality. Rational management should be applied, aiming at sustainability of groundwater resources in the study area including limitation of fertilizing process and construction of modern sewage systems. The results of this study helped to significantly improve the understanding of the aquifer which is an important resource for the development of this region and may contribute as well for a better management of this vital resource. Finally, it is recommended that a long term groundwater monitoring and quality assessment be acquired to sustainably address the environmental management aspects as well as to avoid groundwater quality degradation providing sustainable development.

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