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HYDROCHEMICAL CHARACTERISTICS AND GROUNDWATER QUALITY IN THE ISLAND OF LESVOS, GREECE

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ABSTRACT
The hydrochemical characteristics of groundwater in the island of Lesvos, Greece, were studied based on chemical analyses of groundwater samples collected from 30 locations covering all the island's major aquifers hosted in different lithological formations. The Plagioclase dissolution was found to be responsible for the observed high concentrations of Na and Ca in the majority of volcanic aquifers. Ultrabasic rocks enrich groundwater with magnesium while intense hydrothermal activity and extensive alteration zones, which exist locally as a result of a recent volcanic activity, are associated with the existence of sulphate type groundwater and acidic pH in some areas. Seawater intrusion was found to be associated with high Cl^- concentrations in three sampling locations. Based on sodium adsorption ratio, percent sodium, and the US salinity diagrams, the vast majority of groundwater samples were evaluated as suitable for irrigation purposes.

KEYWORDS: Groundwater, Hydrochemical, Lesvos island, SAR, USSL diagram.

INTRODUCTION

Lesvos is the largest island in the northeastern Aegean Sea and the third largest island in Greece after Crete and Euboea. Its area is 1,630 Km^2 with maximum length and width of about 75 Km and 40 Km, respectively.

The island is characterized by a complex geological setting and evolution, and it was subjected to a variety of geological processes resulted in a high geodiversity. It is expected that the present geological structure of Lesvos and all the processes which contributed to its geological evolution, have also a great influence to the hydrogeologic characteristics of the existing aquifers in the island and to their complex nature that cannot easily be categorized into specific hydrogeologic units. In general, however, several different types of the main aquifers may be identified based on the lithology of Lesvos, such as, for example the alluvial aquifers (areas of Gera, Evergetulas – Ippio, and Kalloni), the karstic aquifers (marbles, marble – schist sequences), the ophiolithic rock aquifers (central and east part of the island), the Neocene formation aquifers (conglomerate – sandstones), and the volcanic rock aquifers (north and western part of the island). Each of the above hydrogeologic systems exhibits unique hydrochemical characteristics that are a reflection of the specific geological, chemical and hydrological conditions that exist in the respective geological formation. The goals of the present study are: (i) to evaluate the groundwater chemistry in the different aquifers in the island of Lesvos, and assess groundwater quality and its suitability for irrigation, (ii) to identify the most important parameters and processes that affect the distribution of the major ions in groundwater, (iii) to explore the relationship between the geology and groundwater chemistry as well as the rock – water interaction (e.g. most of the mineral assemblages of volcanic rocks in Lesvos contain Na-feldspar, the role of which is very important to the water quality changes in the volcanic aquifers), and (iv) to explain the observed differences in groundwater hydrochemical characteristics in the different locations of the study area.

GEOLOGICAL SETTING

The geology of Lesvos has been described by Hecht (1971-1974), Katsikatsos *et al.* (1986) and Pe – Piper (1978, 1980, 1993). Hecht carried out the geological mapping of Lesvos and published the map on a 1:50.000 scale, Katsikatsos *et al.,* studied the geological structure of the oldest rocks (schists, marbles and ophiolites) while Pe-Piper presented in detail the petrology and mineralogy of the volcanic rocks.

The oldest rocks occur mainly in the eastern part of Lesvos (Figure 1) and are separated in two formations:

a. The autochthonous series (basement) consisting of metamorphic rocks dominated by schists and marbles. Their age is Early Carboniferous to Triassic.

b. The volcanosedimentary series (tectonic cover) consisting of different types of Lower – Medium Triassic low – grade metabasites and sedimentary rocks (crystalline limestones and schists).

In the central and eastern part of Lesvos, ultrabasic rocks with magnesite deposites (Agiassos and Gera's gulf area) also occur and are overthrust on the Triassic rocks.

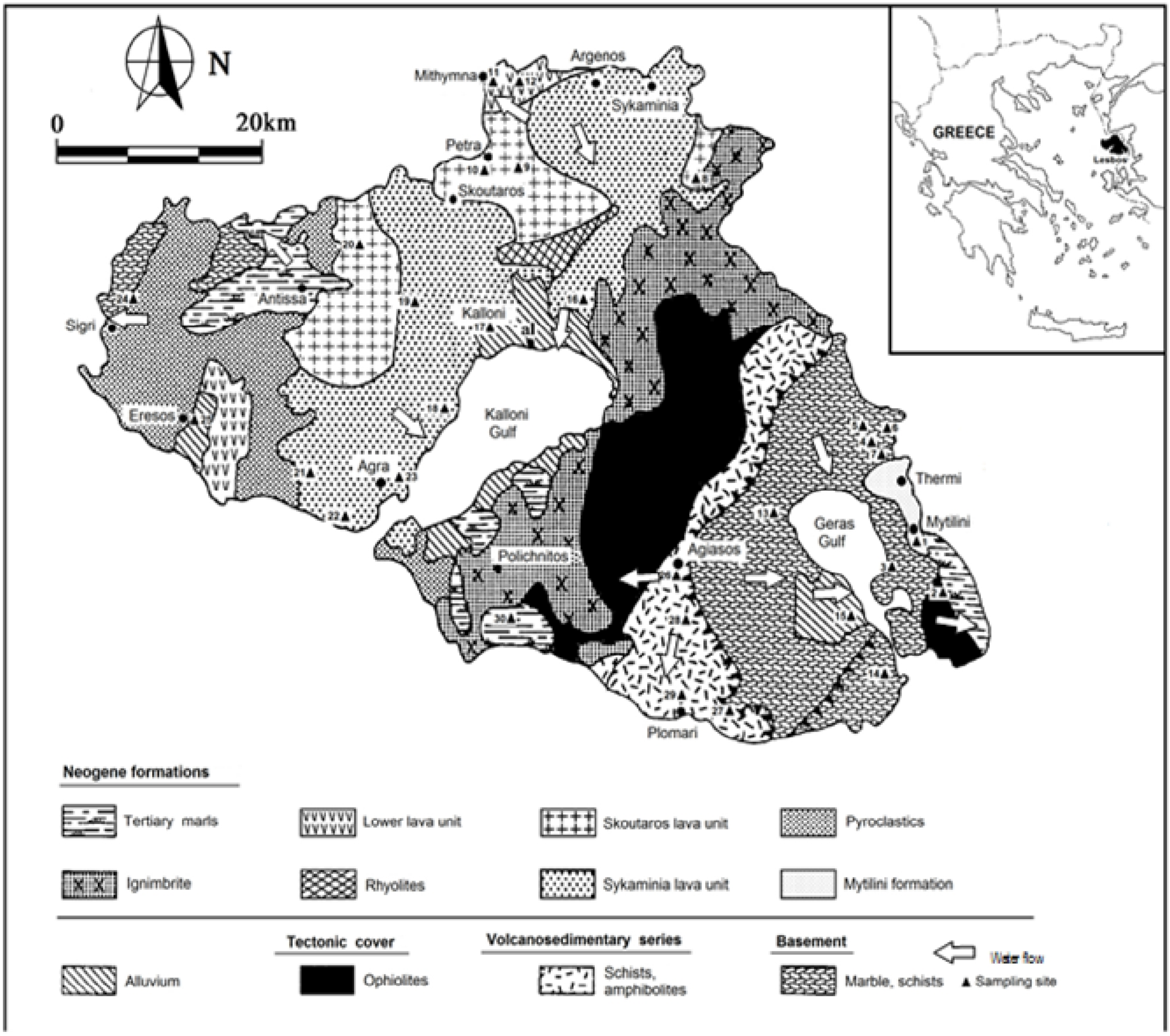

Figure 1. Geological map of the study area (based on Kontis, 1997) showing the sampling locations (triangles) and the main groundwater flow directions (arrows)

The major part of the island is covered by Neogene volcanic rocks, which were formed during a late Oligocene – middle Miocene calc-alkaline to shoshonitic volcanism, which took place in the northern and central Aegean Sea and western Anatolia (Fytikas *et al.,* 1984). The volcanic rocks include different types of lava, pyroclastic and epiclastic formations as well as ignimbrite covers. According to Pe – Piper (1980) and Pe-Piper & Piper (1993) the geology of the volcanics, from base to top, is as follows:

- Lower lava unit (andesites of Eressos, rhyodacites of Agra, volcanic rocks north of Petra).
- Skoutaros unit (andesites, basalts).
- Acidic volcanics (pyroclastics in western Lesvos, ignimbrites, rhyolites).
- Upper lava units (basalts, andesites).

According to K/Ar and Ar^{39} dating (Borsi *et al.*, 1972, Pe-Piper 1978, 1980) the age of the volcanic rocks ranges between 16.5 and 21.5 m.y. The existence of large zones of volcanic rock alteration (Tsoli-Katagas, 1979) and the presence of geothermal springs in different areas such as Polichnito, Lisvori, Argeno, Eftalou and Thermi indicate a recent volcanic and hydrothermal activity which took place in Lesvos.

A meta – alpine Neocene formation, including marls and marly limestones overlie the basement in the eastern and northwestern part of Lesvos.

SAMPLING AND ANALYTICAL PROCEDURE

Groundwater samples were collected from 30 locations throughout the Lesvos Island. In each location, one or more groundwater samples were collected from deep wells. The sample locations in the study area are shown in Figure 1. In order to explore the variation of Lesvos' groundwater quality, samples have been collected from all the island's major aquifers hosted in different lithological formations. Special care was taken to collect samples away from polluting human activities, which could affect the quality of the groundwater as well as to avoid the interaction between different lithological types of the aquifers, as a result of the "groundwater flow" (Figure 1).

The temperature of the samples collected was measured in situ and ranged from 18 to 22^{o}C.

The techniques and methods followed for collection, preservation, analysis and interpretation are those recommended by 20th edition of APHA (APHA, 1995). The collected samples were analyzed for major ions, such as F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{-2}, SO_4^{-2}, HCO_3^-, Na^+, K^+. Ca^{+2}, Mg^{+2} and NH_4^+. Unstable parameters such as pH and electrical conductivity (EC) were measured in the field . In addition, sample No 4 was analyzed for iron, which resulted in a value of 3470 mg L^{-1}. The ion concentration analysis data are shown in Table 1. The same table shows the type of the aquifer, from which the groundwater samples (e.g. volcanic, alluvial, karst) were collected.

RESULTS - DISCUSSION

pH

The pH values in most of the water samples of the study area range from 6.72 to 8.21, indicating a neutral or slightly alkaline nature. These values are within the limits (6.5–9.5) proposed by the Greek legislation for drinking water (O.G.G. 2001).

However, three of the analyzed groundwater samples (No 4, 19 and 21) show acidic pH values (6.44 5.22 and 4.58 respectively). These samples were collected from aquifers hosted within altered volcanic rocks in Pamfila, Anemotia and Mesotopos areas. In these cases, the acidic nature of groundwater may be due to the special geochemical conditions, which are related to a recent volcanic hydrothermal activity which took place in these areas. Thus for example, the low ph values of samples from Anemotia (No 19) and Mesotopos (No 21) in combination with their high sulfate concentrations, suggest that a sulfide salts oxidation to sulphate probably took place, according the following chemical reaction:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{-2} + 4H^+$$

Specific conductance (EC)

The specific conductance values are directly related to the amount and the nature of the soluble electrolytes. A high concentration of salts in irrigation water renders the soil saline. This also affects the salt intake capacity of the plants through the roots. On the other hand, it is known that human health is affected by the high concentrations of salts in drinking water. An indicative EC level in drinking water is about 400 μS cm^{-1}, while the maximum value is 2500 μS cm^{-1}.

The specific conductance of analysed groundwater samples range from 320 to 13700 μS cm^{-1}, while the average is 955 μS cm^{-1} and the standard deviation is 544 μS cm^{-1} The variation of EC in the different wells selected for the present study is mainly due to the various lithological types of aquifers as well as to other reasons such as sea intrusion or mixing of groundwater.

Hardness

Hardness results mainly due to the presence of divalent cations, of which calcium and magnesium are the most abundant in groundwater. It is known that water hardness is related to human health and, more particularly, some evidence indicates its role in heart disease (Schroeder, 1960).

According to Sawer & McCarty 's (1967) classification for hardness, 33% of the studied samples fall under the moderately hard class, 30% of the samples fall under the hard class and 66.7% fall under the very hard class (Table 2).The hardness of the water samples range from 105 to 6548 mg L^{-1}, with an average of 407 mg L^{-1} and standard deviation 200 mg L^{-1}. As expected, the lower hardness values are measured in aquifers hosted in volcanic rocks.

Table 2. Classification of groundwater based on total hardness

Total Hardness as $CaCO_3$ (mg L^{-1})	Water class	No of sampling site	Percentage (%)
0-75	Soft	-	
75-150	Moderate	20	3.3
150-300	Hard	8,12,16,17,19,21,23,24,28	30
>300	Very hard	1,2,3,4,5,6,7,9,10,11,13,14, 15,18,22,25,26,27,29,30	66.7

Percent sodium

Sodium concentration is important in classifying irrigation water because sodium reacts with soil and as a result a clogging of particles takes place, thereby reducing its permeability (Todd, 1980; Domenico and Schwartz, 1990). Percent sodium in water is a parameter computed to evaluate the suitability for irrigation and can be determined using the following formula:

$$Na(\%) = (Na^{+1} + K^{+1})x100/(Ca^{+2} + Mg^{+2} + Na^{+1} + K^{+1})$$

where the quantities of Ca^{+2} , Mg^{+2} , Na^{+1} , K^{+1} are expressed in milliequivalents per liter (meq L^{-1}).

The classification of groundwater samples with respect to percent sodium is shown in Table 3. The Na (%) values range from 5.6 to 48.6 and most of the samples fall under "Excellent" and "Good" classes.

The Na (%) is also used in order to classify the groundwater samples from the study area in relation with the electrical conductivity, according to the Wilcox diagram (Figure 2). From this figure, it is clear that most of the samples fall into the categories of "Excellent to Good" and "Good to Permissible", with the exception of samples from Lakerda (No 3) and Agra (No 22) sites, which fall into the category of "Doubtful to Unsuitable". These two sites are very close to the sea and their groundwater quality seems to be affected by partial water intrusion. It has to be mentioned here that the sample from the Pamfila site (No 4), despite the low Na (%) value, cannot be plotted into the above Wilcox diagram because of its extremely high EC value, which run to 13700 μS cm^{-1}.

Table 3. Classification of groundwater based on percent sodium (Na (%))

Na(%)	Water class	No of sampling site	Percentage (%)
<20	Excellent	2,4,9,10,11,13,18, 26,27,28, 29,30	40
20-40	Good	1,5,7,8,14,15,16,17, 19,20,21,23,24,25,	46.7
40-60	Permissible	3,6,12,22	13.3
60-80	Doubtful		
>80	Unsuitable		

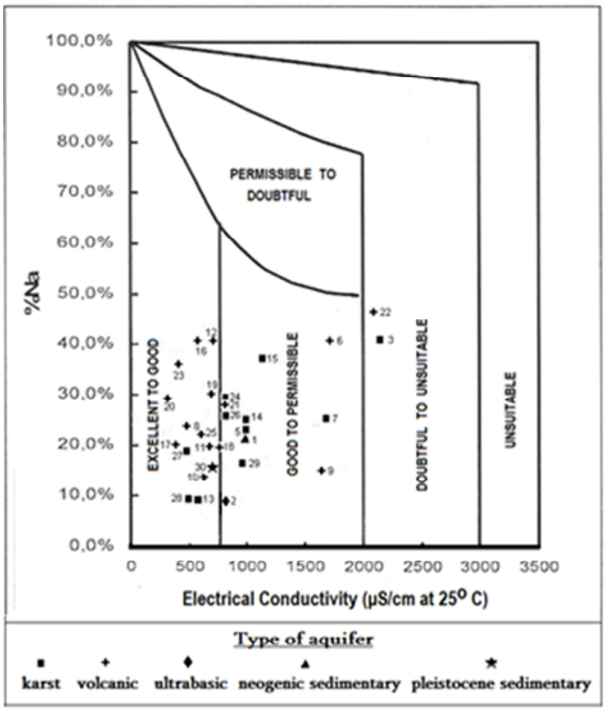

Figure 2. Plot of Sodium Percentage and Electrical Conductivity (based on Wilcox, 1955) for classification of groundwater for irrigation uses

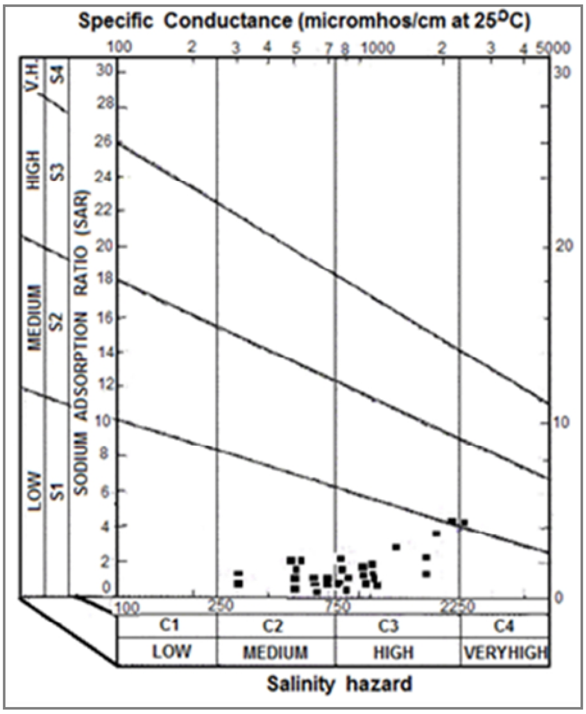

Figure 3. The quality of groundwater in relation to salinity and sodium hazard (after US Salinity Laboratory (1954)

Sodium Absorption Ratio (SAR)

SAR is an important parameter for the determination of the suitability of irrigation water because it is responsible for the sodium hazard. SAR is computed as

$$SAR = Na/\{(Ca+Mg)/2\}^{1/2}$$

where all ionic concentrations are expressed in meq L^{-1}.

SAR values of all the groundwater samples of the study area vary from 0.2 to 4.7 and are classified as excellent for irrigation. However, when the SAR and specific conductance of water are known, the classification of water for irrigation can also be evaluated by graphically plotting these on the US Salinity Laboratory (1954) diagram (Figure 3). From this figure, it is clear that 90% of the samples are grouped within C2S1 (medium salinity with low sodium) and C3S1 (high salinity with low sodium) classes. The groundwater samples from the Lakerda (No 3) and Agra (No 22) areas fall into C4S2 (very high salinity and medium sodium) and C3S2 (high salinity and medium sodium) classes, respectively, while sample No 3 (from Pamfila area) falls off the diagram, because of its very high EC value.

Major cations and anions

In order to study the chemical characteristics of groundwater in the Lesvos island, groundwater samples have been classified using the Na+K - Ca – Mg trilinear diagram for the cations (Figure 4) and the ionic SO_4^{-2}/Cl^- ratio for the anions (Table 4).

Figure. 4 shows that the majority of samples fall under the field of “No Dominant type” and “Calcium type”, and only two samples fall under the field of “Magnesium type”. The presence of magnesium type waters in Agia Marina (No 2) and Keramia (No 13) areas is mainly due to the geology of the above areas, which comprises rich in magnesium ultrabasic rocks and schist, respectively. On the other hand, the high values of Ca in the Agiasos aquifer is due to the dissolution of carbonate rocks (marbles) while smaller amounts of Ca occur in samples from the volcanic aquifers, as a result of plagioclase dissolution.

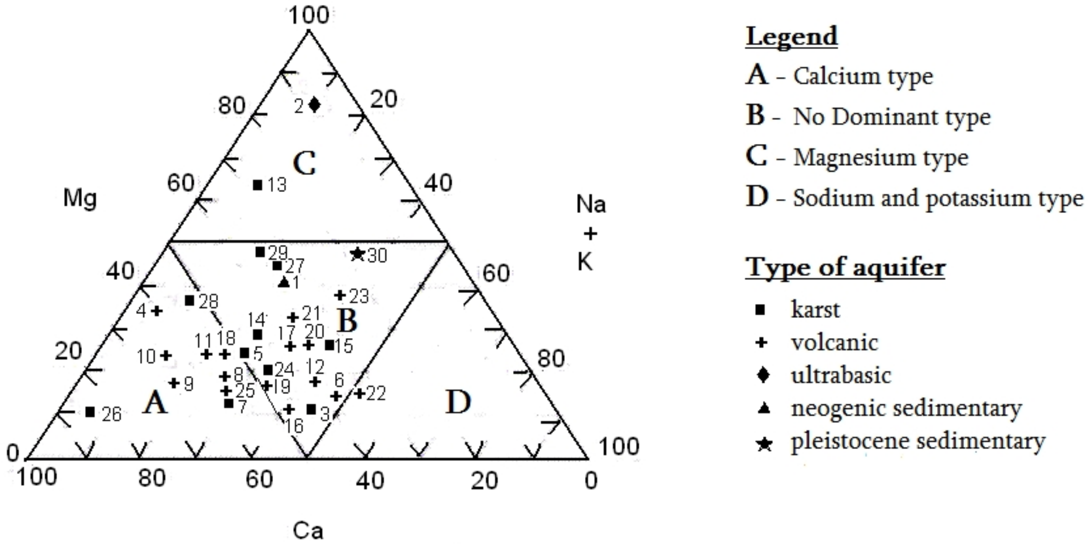

Figure 4. Groundwater samples plotted in Mg- Ca- Na+K diagram

Table 4. Classification of groundwater based on SO_4^{-2}/Cl^- ratio

SO_4^{-2}/Cl^-	Water class	No of sampling site	Percentage (%)
<0.2	chloride	1,2,3,4,8,16,17,20,23,30	33.3
0.2-1	chloride – sulphate	5,7,10,11,12,13,14,15,22, 24,25,26,27,28,29	50
1-5	Sulphate-chloride	6,9,18	10
>5	Sulphate	21,19	6.7

The relatively low HCO_3^- values (129-390 mg L^{-1}) indicate the absence of “Bicarbonate type” groundwater. As we can see in Table 1 the higher HCO_3^- concentrations appear at karst aquifers, which are hosted within carbonate rocks (marbles, limestones).

The classification of water samples based on SO_4^{-2}/Cl^- ratio shows that the majority of the studied samples belongs mainly to the “chloride – sulphate” and “chloride” types and less to the “sulphatechloride” and “sulphate” type (Table 4). The groundwater samples from Lakerda (No 3) and Pamfila (No 4) are characterized by very low values of SO_4^{-2}/Cl^- ratio. The low value of SO_4^{-2}/Cl^- ratio in the Lakerda area is due to the enrichment of the groundwater samples with chloride because of the saline water intrusion of the coastal aquifer. On the other hand, groundwater samples from the Pamfila area, besides the low SO_4^{-2}/Cl^- ratio value, are characterized by extremely high iron values (3470 mg L^{-1}) and acidic pH indicating that a probable dissolution of hypogene mineralization is taking place.

In contrast to the above areas, the groundwater samples collected from Anemotia (No 19), Mesotopos (No 21) and Stypsi (No 9) areas show very high values of SO_4^{-2}/Cl^- ratio (5.38, 5.02 και 3.63, respectively). As mentioned in the previous section, acidic pH values in Mesotopos and Anemotia have been measured, as well. The existence of this sulphate type groundwater could be associated with the intense hydrothermal activity and the extensive alteration zones, which exist in these areas as a result of a recent volcanic activity. The existence of the mineral alunite, $KAl_3(SO)_4(OH)_6$, within altered volcanic rocks in Stypsi and Mesotopos (Tsoli- Katagas, 1979; Kelepertsis and Esson, 1987), which is a characteristic mineral of kaolins formed under acid conditions and high SO_4^{-2} activity (Knight, 1977), it is also indicative. All the above indicate that the groundwater chemistry in these specific areas is greatly affected by the mixing of meteoric waters with deep seated acidic sulphur waters or/and dissolution of sulphate and sulphur minerals (e.g. see the previously described chemical reaction of FeS_2 oxidation).

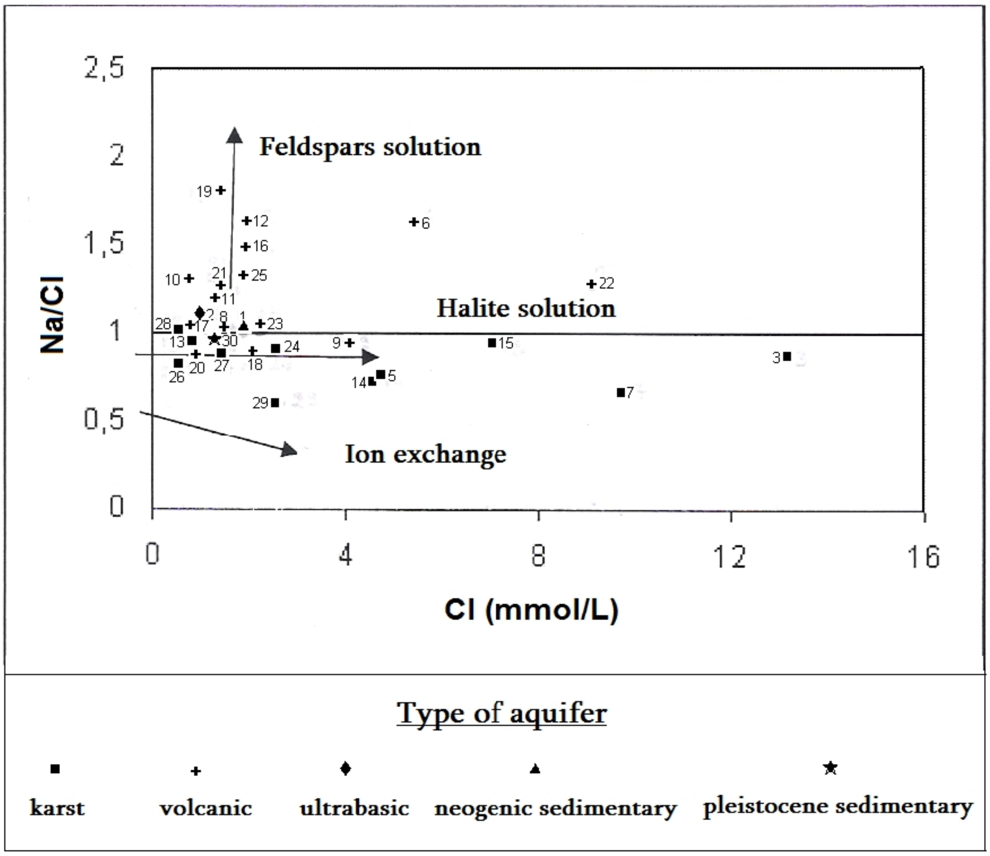

Figure 5. Correlation of Na^+/Cl^- ratio with Cl^-

Figure 5 shows the correlation between Na^+/Cl^- ratio and Cl^- concentration (expressed in mmol L^{-1}). From this figure it is obvious that the majority of volcanic aquifers are characterized by high values (>1) of Na^+/Cl^- ratio and low salinity, which are mainly due to the Na – feldspar (albite) weathering, according to the following reaction :

$$\underset{\text{(albite)}}{NaAlSi_3O_8} + H_2O + H_2CO_3 \rightarrow \underset{\text{(kaolin)}}{Al_2Si_2O_5(OH)_4} + 2Na^+ + 2HCO3^-$$

On the other hand, the low Na^+/Cl^- ratio values in combination with the high Cl^- concentrations in Lakerda (No 3) and Moria (No 7) areas, are indicators of sea water intrusion.

CONCLUSIONS

The groundwater chemistry of aquifers in the Lesvos Island is determined mainly by the specific geologic conditions. Thus, the ultrabasic rocks enrich the groundwater with magnesium (Agia Marina area) while the carbonate rocks and some types of volcanic rocks enrich the groundwater with calcium. On the other hand, the existence of high concentrations of Na in the majority of volcanic aquifers is attributed to the albite weathering.

The existence of sulphate type waters in Anemotia, Mesotopos and Stypsi is related to the ongoing hydrothermal activity in these areas, resulting from recent volcanic activity.

The special geochemical characteristics of the aquifer in the Pamfila area (high conductivity, extremely high concentrations of Cl^- and Fe) are probably due to the existence of a deep seated metalliferous source.

It is found that seawater intrusion is taking place in the Lakerda area and to a lesser degree in the Moria and Agra areas.

It is observed, based on the Wilcox and US Salinity Laboratory classification that most of the water samples fall in the suitable range for irrigation purposes, with the exception of the samples from the Lakerda and Agra areas.

Table 1. Chemical analyses of groundwater samples of the study area and the respective types of aquifers

No of samp. site	Aqui-fer type	pH	EC (μS cm^{-1})	F (mg L^{-1})	Cl^- (mg L^{-1})	NO_2^- (mg L^{-1})	Br^- (mg L^{-1})	NO_3^- (mg L^{-1})	PO_4^{-3} (mg L^{-1})	SO_4^{-2} (mg L^{-1})	(*) HCO_3^- (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Ca^{+2} (mg L^{-1})	Mg^{+2} (mg L^{-1})	NH_4^+ (mg L^{-1})	Total hardness (mg L^{-1} $CaCO_3$)
1	neog	7.12	970	0.30	82.30	0.02	0.00	7.75	0.00	15.80		56.50	2.55	73.10	50.40	0.01	390.08
2	oph	7.52	854	0.20	35.10	0.04	0.09	2.90	0.00	8.12		25.70	1.14	20.30	120.13	0.02	545.38
3	kar	7.07	2330	1.60	469.10	0.02	1.09	19.60	0.03	62.80		255.30	9.30	226.00	36.40	0.00	714.22
4	vol	6.44	13700	4.50	4897.00	0.00	2.80	4.70	0.00	11.00		209.50	37.90	1699.00	560.00	0.60	6548.48
5	kar	6.94	1068	0.88	174.50	0.24	0.00	6.10	0.00	117.90		86.20	5.30	151.20	43.80	0.30	557.91
6	vol	7.44	1884	1.40	195.30	0.22	0.00	0.90	0.00	312.50		210.40	57.00	165.00	42.30	0.10	586.20
7	kar	7.18	1764	0.7	348	0.04	1.16	2.4	0.00	164.8		141.1	20.1	255.7	42.5	0.10	813.5
8	vol	7.42	509	0.29	50.40	0.03	0.19	14.40	0.00	6.80		34.10	4.60	69.00	12.50	0.10	223.77
9	vol	7.37	1816	1.30	140.00	0.02	0.20	1.80	0.00	690.00	155.00	87.40	14.50	304.70	53.00	-	979.09
10	vol	7.32	594	0.28	27.60	0.04	0.00	4.90	0.00	12.20		23.70	1.70	90.60	18.20	0.09	301.18
11	vol	7.52	750	0.27	47.90	0.06	0.00	20.40	0.00	20.40	186.70	37.50	3.01	98.70	23.40	0.17	342.82
12	vol	7.38	777	0.59	77.70	0.15	-	9.03	0.00	27.70		84.60	6.40	71.40	17.40	0.00	249.94
13	kar	7.00	600	0.20	37.80	0.02	0.10	7.20	0.01	22.80	390.00	23.10	1.16	59.50	82.20	0.00	487.07
14	kar	6.63	1003	0.24	164.30	0.12	0.00	1.76	0.00	54.20		76.30	5.07	123.70	48.90	0.10	510.25
15	Kar	6.82	1250	-	250.60	0.04	0.00	2.40	0.00	95.00	338.10	165.60	-	129.60	61.02	0.09	574.89
16	vol	6.85	527	0.67	73.10	0.03	1.90	17.30	1.50	10.20		72.00	5.30	77.20	10.40	0.15	235.60
17	vol	7.02	320	1.04	31.30	0.20	-	5.90	0.20	5.60	170.00	22.00	6.30	38.50	15.70	0.00	160.79
18	vol	7.44	850	0.70	84.00	0.02	0.19	0.16	0.15	187.60		45.23	8.50	108.90	27.90	-	386.82
19	vol	5.22	814	0.16	52.10	0.50	0.14	0.10	0.00	>380		61.70	9.16	87.00	17.40	0.00	288.89
20	vol	6.93	305	0.21	39.03	0.31	-	6.61	0.00	4.80	129.00	21.80	5.51	25.20	10.26	0.00	105.18
21	vol	4.58	895	0.90	57.10	0.17	-	3.70	0.00	389.00		47.50	7.40	54.38	29.10	0.00	255.61
22	vol	7.00	2240	0.85	325.30	0.19	-	0.90	0.00	423.70		263.60	16.10	156.15	47.50	0.00	585.51
23	vol	7.21	495	-	90.90	0.04	-	16.90	0.00	15.00		58.90	-	36.00	32.00	0.10	221.67
24	kar-vol	6.72	862	0.29	98.50	0.01	-	9.05	0.00	47.50	272.10	58.40	5.60	79.35	20.14	0.00	281.07
25	vol	7.85	862	0.20	72.90	0.16	-	0.10	0.16	51.70		63.70	3.50	118.80	21.50	0.00	385.18
26	kar	7.25	637	0.06	20.90	0.04	0.05	22.10	0.00	19.80	317.30	10.50	0.70	136.00	10.70	0.00	383.65
27	kar	8.21	505	0.52	58.30	0.02	0.09	0.20	0.00	21.30	280.70	35.10	2.80	48.20	44.40	0.09	303.19
28	kar	7.24	518	0.02	20.00	0.00	-	1.30	0.00	21.00	159.00	13.00	0.89	63.00	25.65	0.10	262.94
29	kar	7.20	996	0.35	100.00	0.00	-	4.60	0.00	31.00	303.00	38.00	1.70	61.20	55.00	0.10	354.00
30	pleis	7.33	695	0.18	49.00	0.00	-	9.60	0.00	11.00		30.00	0.90	36.00	53.00	0.10	308.97

Type of aquifer: kar : karst, vol: volcanic, oph : ultrabasic (ophiolithic), neogen : neogenic sedimentary, pleis: pleistocene sedimentary

(*) : the HCO_3^- concentrations correspond to samples collected nearby the sampling areas at the same time period

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