INVESTIGATION OF THE MANISA KARST SPRINGS BY MEANS OF WATER CHEMISTRY AND ISOTOPE HYDROLOGY

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SUMMARY: Water chemistry and environmental isotope analyses of the Manisa karst springs have been carried out in order to determine the origins, and reservoir capacities of these springs. Studies have also been directed towards incrustation and corrosion properties of the waters.

As a result of the water chemistry analyses, the general properties of the water samples are suitable for drinking from the standpoint of chemical and biological aspects. The hydrogen ion concentration of the waters is higher than 7. EC is generally lower than 650 micromho/cm. Chlorine and sulphate concentrations are much lower than the acceptable limits. The dominant salts are $CaCO_3$ *and* $MgCO_3$*. The hardness of the waters is about 30°FH. In general, the spring waters tend to cause incrustation in pipes.*

With the help of the stable isotopes (^{18}O *and D) and Tritium analyses, the recharge areas of the springs and the relation between them has been investigated and water points have been classified under three groups: 1st Group: G1, G2, G3 Ilica group; 2nd. Group: G4, G5, G6 Sarikiz group, 3rd Group: G9, G10, G11, G13, G14, Göksu group.*

Key Words: Isotope Hydrology, Water Chemistry, Karst Springs.

INTRODUCTION

Along with the hydrogeological investigations of the Manisa springs which were proposed as a first stage of the Potable Water Supply Project for the city of Izmir, water chemistry and isotopic studies have also been carried out. These were intended to gain information about the origins, and reservoir capacities of the springs and to find out whether they will cause incrustation or corrosion in the pipes.

The general properties of the spring waters followed by detailed analyses and an interpretation of these properties are given at the beginning of the paper. The results of the chemical and isotopic analyses of these springs can be readily checked from the Tables 1, 2 and 3.

Springs of great discharges have been named by project codes (G1, G2, etc.) which were also marked at the sampling locations. Thus, sampling from different points and elevations in each sampling process has been avoided.

In situ measurements of pH, EC and CO_2 were made in the sampling processes.

Apart from the sample of 1 litre for water chemistry analysis, two samples one of one litre the other of 100 cm^3 (using standard bottles) were taken for Tritium and 0-18 and Deuterium analyses respectively.

Chemical analyses and natural tritium analyses of the waters have been made at the DSI laboratories whereas the 0-18 and deuterium contents have been determined at the Heidelberg University. Apart from the routine measurements and analyses, phosphorus fluorine and boron analyses have also been carried out. Most water chemistry evaluations were based upon samples taken in April, July and November 1972.

GENERAL HYDROGEOLOGY

The permanent and larger of the Manisa springs are the Göksu, Göldegirmeni and Palamut springs which are fed by Mesozoic limestones and the Srikiz springs which

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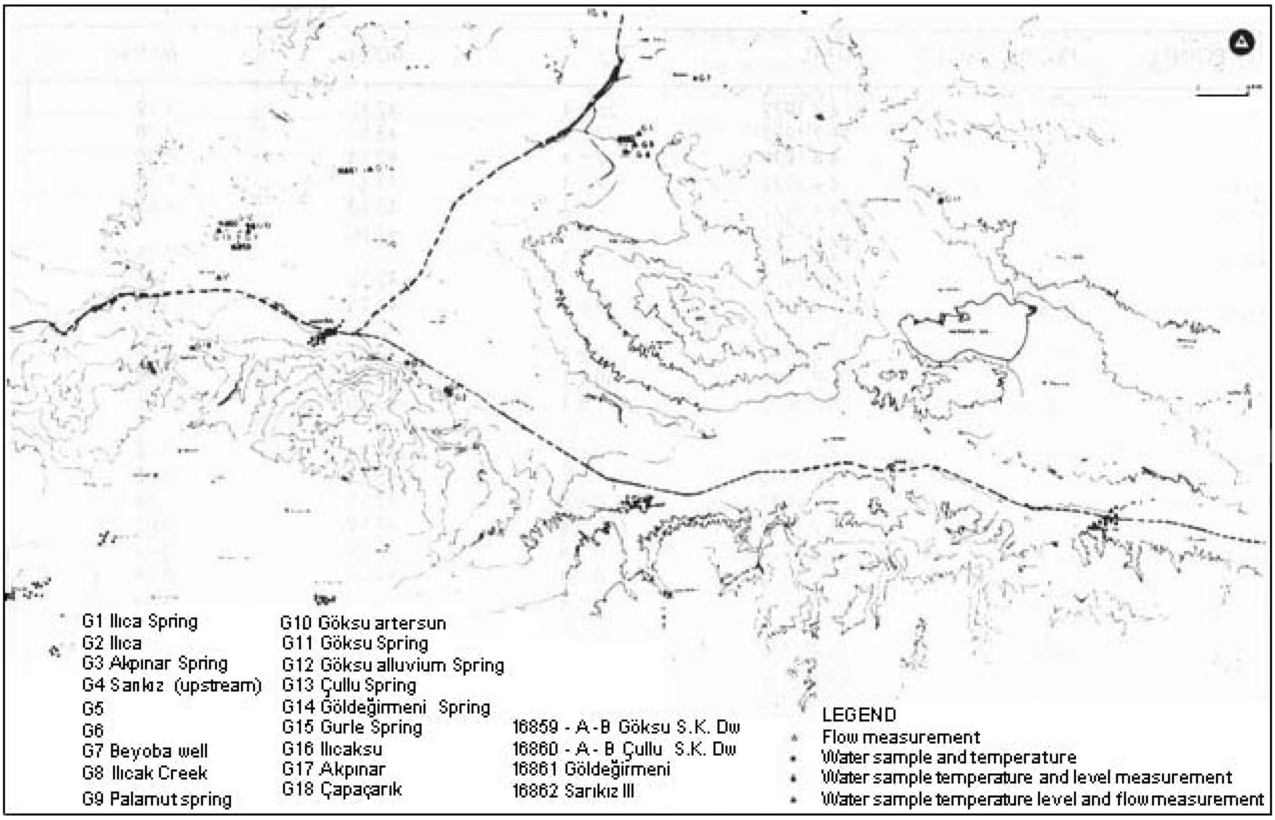

Figure 1: Map of the Study Area and Water Points.

are fed by Neogene limestones and thought to be related to the Mesozoic limestone aquifer as well.

Mesozoic limestones are karstic and constitute the biggest groundwater reservoir in the area. Apart from that there are the Neogene limestones which comprise groundwater reservoir of secondary importance in the area. Thus, hydrogeological investigations have been made with a view to determining the hydrogeological properties of the Mesozoic and Neogene aquifers.

WATER CHEMISTRY

All of the water samples taken from the springs and drilling wells in the area are suitable for drinking as far as chemical and biological aspects are concerned.

As regards the water chemistry, the general properties of the water points are as follows:

The hydrogen ion concentration (pH) of the water is higher than 7. Despite seasonal variations, specific conductance (EC) is generally lower than 650 micromho/cm (Figure 4). Chlorine and sulphate concentrations are much lower than the acceptable limits, being less than 0,50 meq/l. The dominant salts are $CaCO_3$ and MCO_3. The hardness of the waters is about 30°FH, but there are seasonal variations (Figure 7). In general, the spring waters tend to cause incrustations in piper.

Boron: The boron content of the water is lower than 0,60 mg/l (Table 2). It is usually significant in the waters fed by igneous rocks and especially in the case of thermal springs. Deposits in closed basins contain a considerable amount of boron and boron salts as well. In the study area, it was found that the ratio of recharge from igneous rocks is lower than that from sediments.

Fluorine: The fluorine content of the spring waters is much below the acceptable limit for potable waters, varying between 0-0.57 mg/l (Figure 5). Fluorine occurs in solutions as F ions. The most important fluorine source is the mineral fluorite (CaF_2). Apart from that, minerals such as apatite, amphibole, hornblende and some mica in the sedimentary and igneous rocks contain fluorine. Fluorine concentration is below 1.0 mg/l in the waters where the total of dissolved salts is less than 1000 mg/l.

Phosphorus: Phosphorus has been detected in negligible concentrations lower than 0,05 mg/l (Figure 5). The source mineral is apatite. Apatite also contains fluorine, chlorine, and hydroxide ions. Minerals containing phosphorus are widespread in the igneous and marine sediments.

Table 1: Manisa Springs Environmental Isotope Analyses.

WATER POINTS	PROJECT CODE	DATE	T	δD%o	δO^{18}%o
Ilica I	G 1	4.4.1972	26 ± 4	-42.12	-7.19
		26.7.1972	27 ± 4	-43.51	-7.28
Ilica II	G 2	4.4.1972	22 ± 4	-42.14	-7.20
Akpinar	G 3	4.4.1972	24 ± 4	-43.41	-7.54
Sarikiz I	G 4	4.4.1972	7 ± 4	-40.63	-6.65
		25.7.1972	7 ± 4	-41.60	
Sarikiz II	G 5	4.4.1972	8 ± 4		-6.59
		25.7.1972		-42.25	-6.75
Sarikiz III	G 6	4.4.1972	2 ± 4	-41.25	-6.62
		25.7.1972		-40.99	-6.64
Beyoba	G 7	4.4.1972	157 ± 16	-42.61	-6.98
		25.7.1972	149 ± 15	-42.82	-6.86
Ilica	G 8	4.4.1972	12 ± 4	-43.23	-6.96
		-		-	-
Palamut	G 9	4.4.1972	0 ± 4	-44.44	-7.68
		25.7.1972	0 ± 4	-45.53	-7.56
Göksu	G 10	5.4.1972	0 ± 4	-42.12	-6.96
		23.7.1972	0 ± 4	-41.99	-7.01
Göksu Lake	G 11	5.4.1972	0 ± 4	-42.97	-6.94
		23.7.1972	0 ± 4	-40.28	-6.94
Göksu Spr.	G 12	5.4.1972	10 ± 4	-	-6.64
		-		-	-
Çullu Spr.	G 13	5.4.1972	0 ± 4	-40.34	-6.91
		23.7.1972	0.3 ± 4	-40.65	-6.97
Göldegirmeni Spr.	G 14	5.4.1972	0 ± 4	-42.52	-6.94
		23.7.1972		-41.43	-6.97

Phosphorus which is released in case apatite is treated with water may associate with the other minerals. Floods and agricultural chemicals are chiefly responsible for the increase of phosphorus concentration in surface waters and shallow aquifers.

The Sarikiz (G4, G5, G6) and Palamut (G9) springs originate in hard crystalline limestones whereas waters of the other springs and drilling wells represent waters from limestones locally influenced by clays.

The Göksu (G11), Göldegirmeni (G14) and Çullu

Table 2: Manisa Springs Analyses.

PROJECT CODE	Water Point	21.11.1972 B(ppm)	21.11.1972 F (ppm)	21.11.1972 P (ppm)	21.12.1972 Carbondioxide (ppm)	25.7.1972 Free (CO_2 ppm)
G1	Ilica I	0,32	0,04	0,010	50	53,0
G4	Sarikiz I	0,20	0,54	0,030	34	13,0
G5	Sarikiz II	0,42	0,38	0,020	30	15,0
G6	Sarikiz III	0,47	0,57	0,030	20	18,0
G9	Palamut	0,12	0,00	0,06	24	1,0
G10 (14519-A)	Göksu (Artesian)	0,30	0,29	0,030	34	27,0
G13	Çullu Lake	0,42	0,04	0,050	38	17,0
G14	Göl Degirmeni	0,42	0,18	0,040	34	27,0
16861	Göl Degirmeni artesian	0,59	0,08	0,050	18	
16859-A	Göksu Artesian	0,52	0,29	0,020	34	
16859-B	Göksu Artesian	0,44	0,08	0,030	42	
16860-A	Çullu Artesian	0,38	0,29	0,050	38	
16860-B	Çullu Artesian	0,36	0,29	0,040	38	

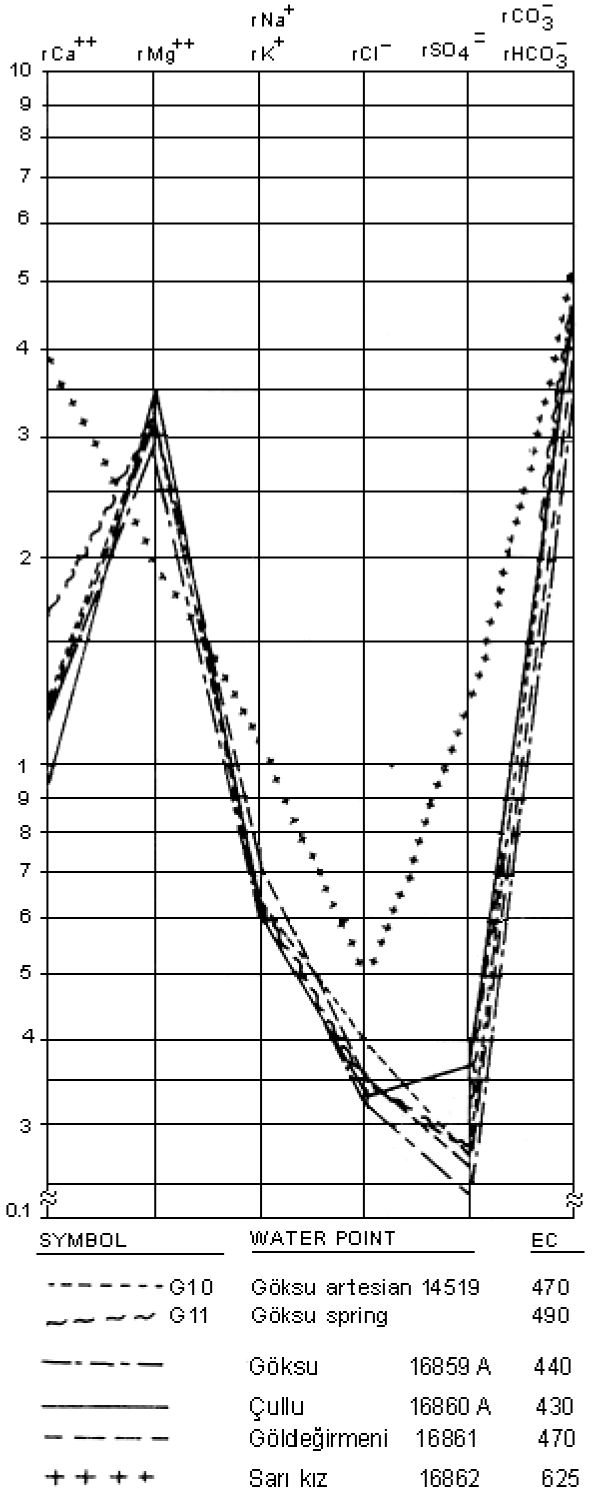

Figure 2: Comparison of Waters from Spring and Drilling wells (Based upon the analyses November 1972).

springs appear to be the three close discharge points of waters coming from clayey formations and dolomites.

According to the results of the chemical analyses of the Göksu (G11) and Çullu (G13) springs, the Ca/Mg ratios show seasonal variations. For instance, in the April and May samples, Ca/Mg ratio equals 1 wherease it is lower than 1 in November, thus, implying that the dolomites are of great importance in the spring recharges.

Chemical analyses of the Göksu (G11) and Çullu (G13) springs for April, July and November have been plotted on semi-log diagrams (Figure 10) so that the variations in Ca and Mg content in November can be clearly seen. As to the other chemical ions in the spring waters, no variation has been observed.

Waters affected by dolomites reach the springs Palamut (G9) and Göldegirmeni (G14) much sooner than Göksu (G11) and Çullu (G13) (in July) and increase with time in November.

It is possible to observe the chemical variations in the Palamut spring water in April, July and November on semi-log diagrams.

As a result of the chemical analysis of the Ilica (G1 and G2) springs in April, it has been found that recharge of groundwater takes place only from Mesozoic limestones, whereas in July and November some indications of the waters being in contact with dolomites were observed. Waters from the drilling wells numbered 16859, 16860 and 16861, show similarities in chemical characteristics and are in accordance with the results of the November analyses of the springs near them. However, the water of Sarikiz drilling well numbered 16862 bears characteristics of pure limestone water. Some water previously in contact with magnesian rocks mixes with the Sarikiz spring waters in November, however, the drilling well numbered 16861, which was drilled in the same formation receives its water from pure limestone, as can readily be inferred from Figure 10. Results of chemical analyses of Karayenice spring reflecting the properties of Neogene limestone were plotted on the semi-log diagram of Figure 9.

As is revealed in the graphs of seasonal saturation index variations (Figure 8), in general, waters are saturated with respect to calcite. These characteristics of the waters tend to be more marked after September, becoming neutral in April and August or aggressive as is encountered in G1 and G6.

As regards the karst hydrogeology, springs in the study area represent the diffuse flow system.

From the interpretation of Figures 6, 7 and 8 the following points can be concluded:

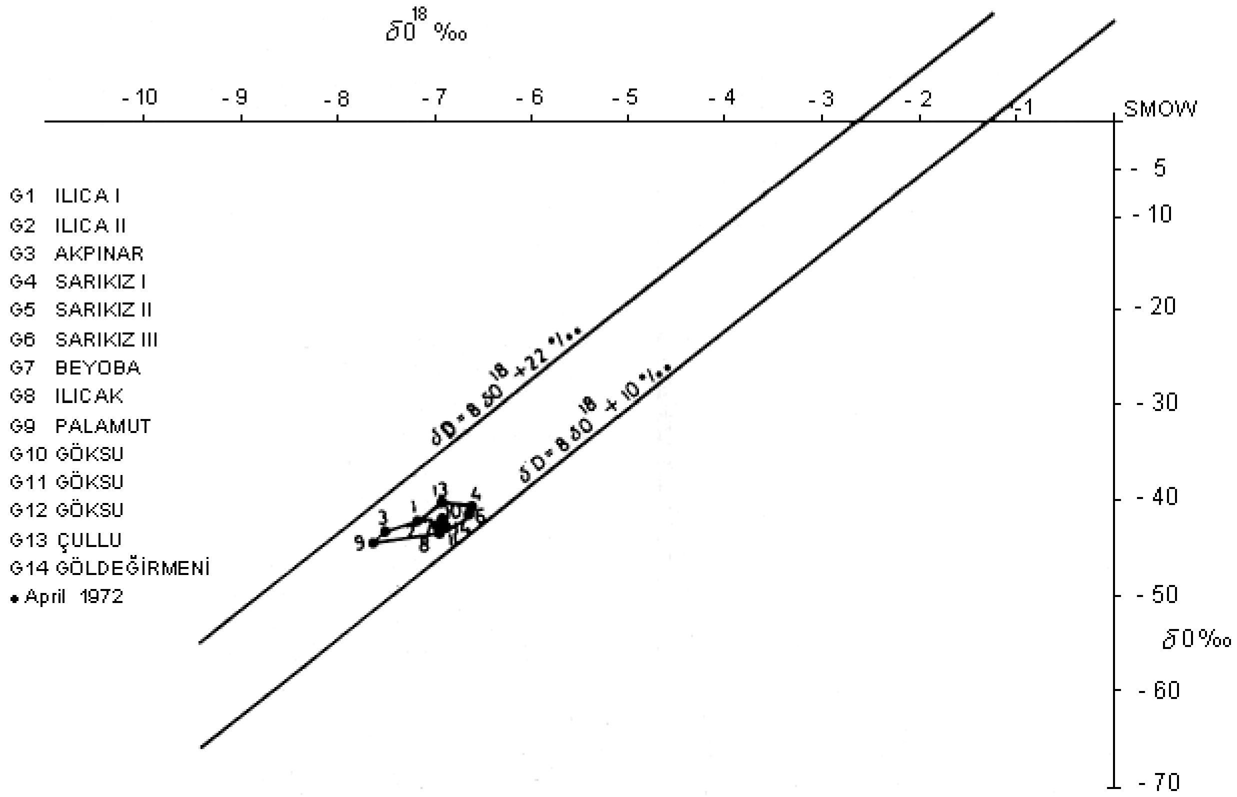

Figure 3-A: Results of Environmental Isotope Analyses.

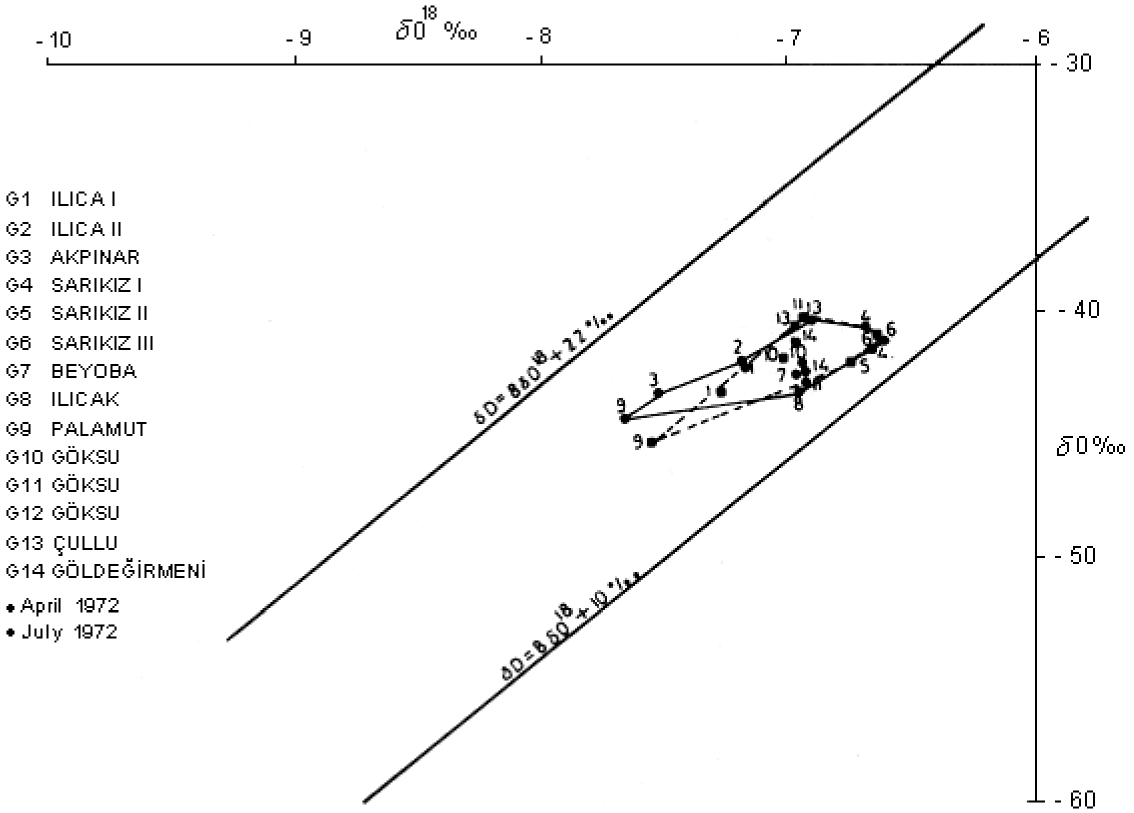

Figure 3-B: Results of Environmental Isotope Analysis.

Waters of diffuse flow system are saturated with respect to $CaCO_3$. For a whole year, only small variations in temperature and in results of chemical analysis (especially in carbonate hardness) take place; whereas variations in CO_2 partial pressure are quite high. This kind of springs contains much more CO_2 than those of conduit flow system. However, this difference is not as much as that for saturation indexes.

As is well known, in general, all spring waters contain more CO_2 than the average atmospheric CO_2 value ($pCO_2=10^{-3.5}$ atm). Waters in these systems are saturated with respect to dolomites and generally undersaturated with respect to calcite.

Waters in contact with calcite are aggressive in spring and summer, and over saturated in winter.

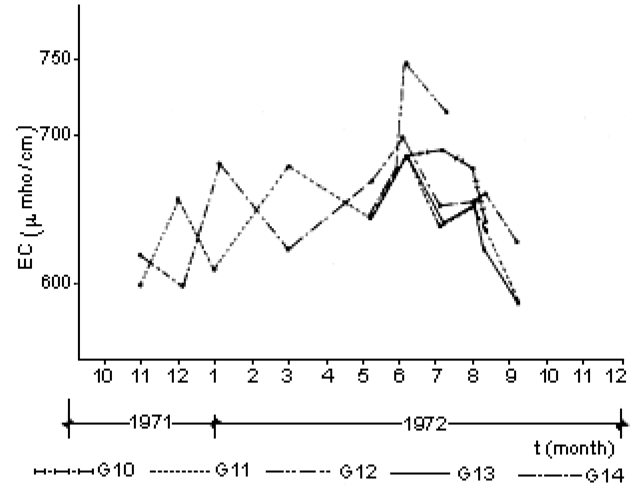

Figure 4: Seasonal Variations in Electrical Conductivity.

The above mentioned features imply that the springs under study could represent diffuse flow system.

In the conduit flow system, spring waters are undersaturated due to their relatively short travel times during which they are in contact with rock surfaces since they have a rapid flow through conduits and large caverns. Thus, the water is unable to dissolve much $CaCO_3$ and cannot be saturated easily.

In this system, large variations in temperature and carbonate hardness are usual. The amount of CO_2 shows a tendency to remain constant through the seasons. These waters are always aggressive in chemical character, showing no seasonal variations with regard to calcite and dolomite.

ISOTOPE HYDROLOGY

Stable Isotopes

Within the framework of this study, water samples have been taken twice a year (in April and July) from Manisa springs and all other water points in the area (all G stations) for 0-18 and Deuterium analysis.

Analyses of 0-18 and D have been made by Prof. Dr. K. Münich and Dr. Zimmerman at Heidelberg University, Germany. The values of the environmental isotopes are given in Table 1.

The results of the analyses have been plotted on the 0-18-D graph of Figure 3, so that interperations can be made with respect to this graph.

According to this: All of the waters collected from the Manisa springs and the surrounding water points occur between the Eastern Mediterranean line and the Craig Meteoric line with the intersection points 22 and 10

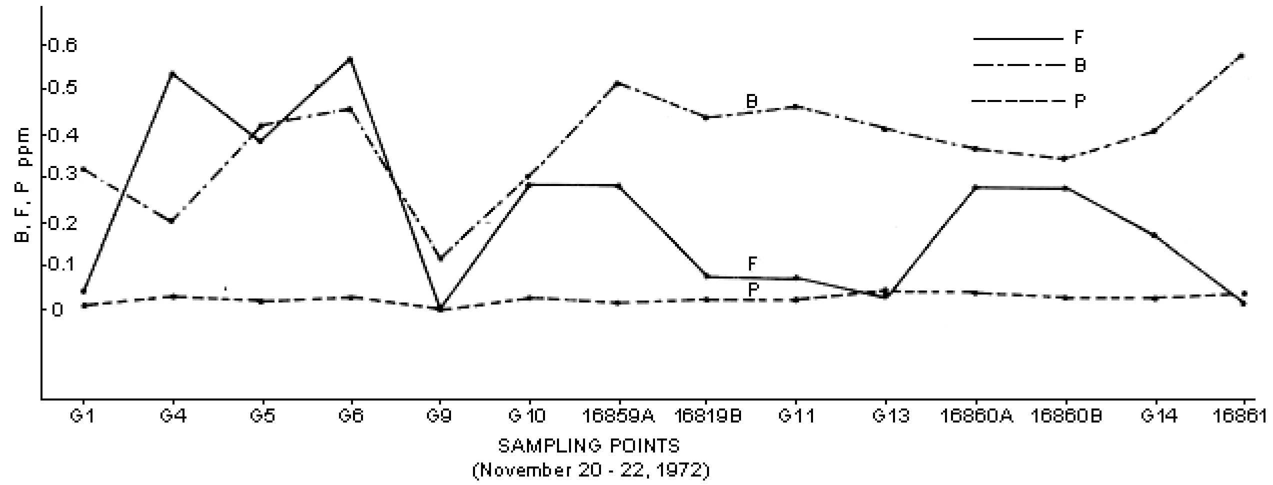

Figure 5: Spatial Variations in B.F.P. Concentrations.

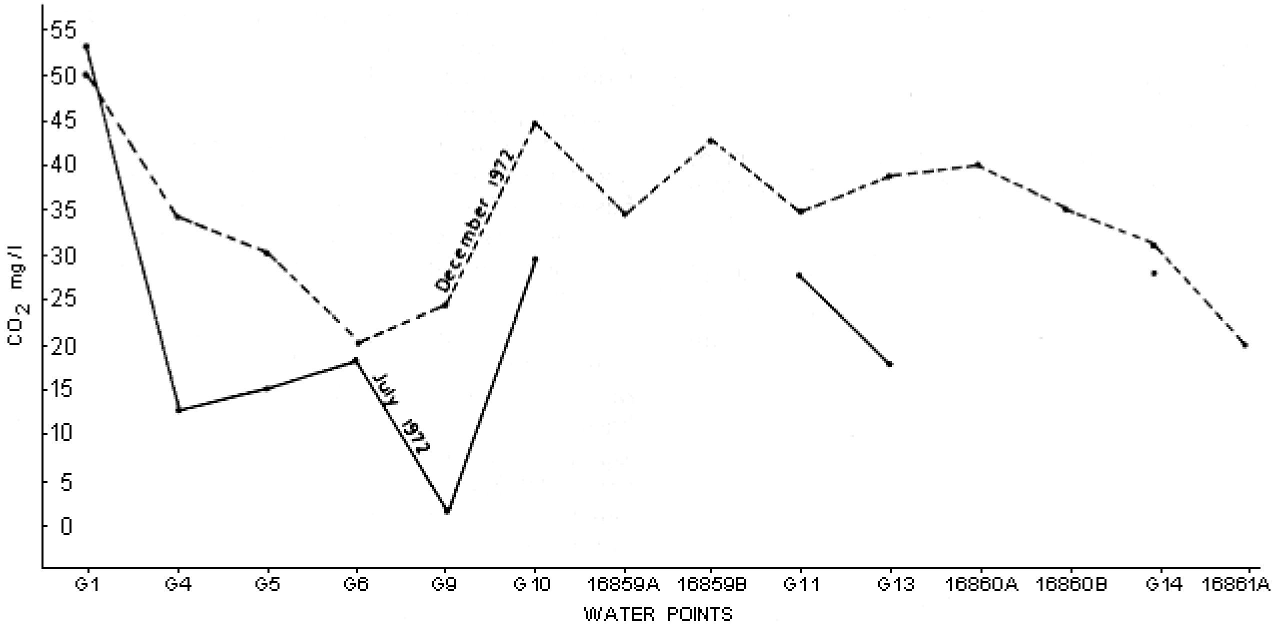

Figure 6: Spatial Variations in CO_2 Concentrations

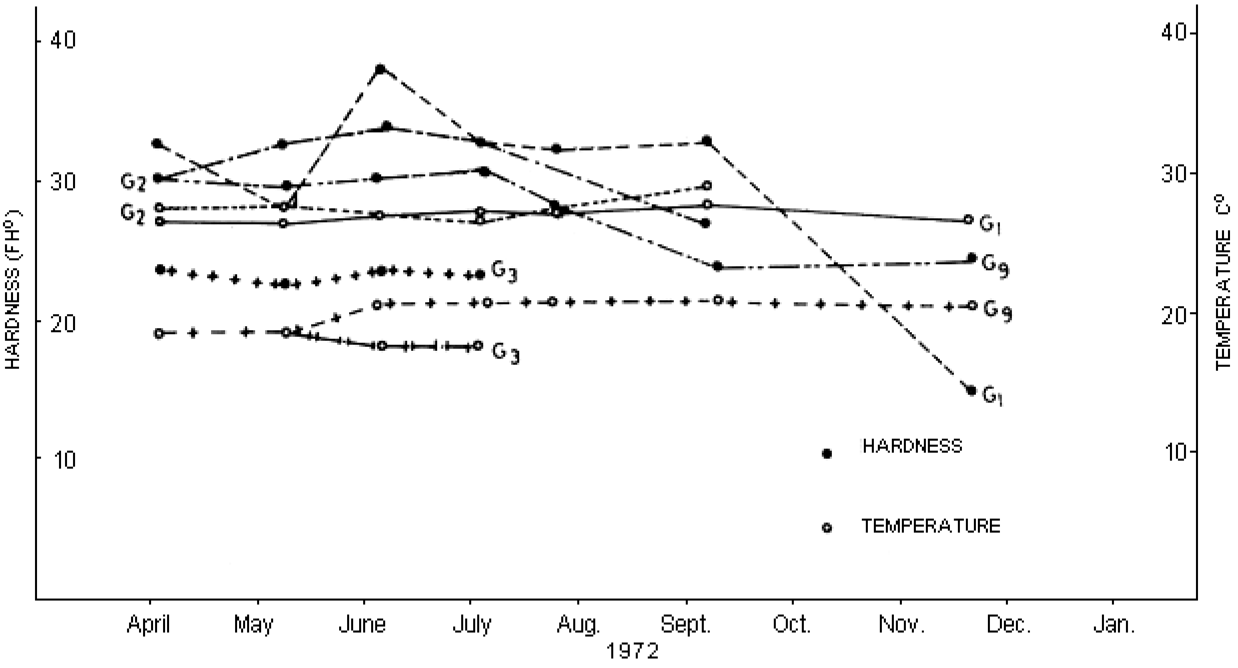

Figure 7A: Graph of Seasonal Variation in Temperature and Hardness.

respectively with an average slope of 8°. In general, they are below the value of 0-18-6.5% 0 and D = - 40 %0.

The following conclusions can be stated in this case:

All water points are under the effect of precipitation occurring in the surroundings. Waters of different origin have not been encountered, and there is no hydrogeological relation with the adjacent basins. However, stations G9, G3, G1, G8, G11, G13, G14, and G6 have different isotopic compositions and G9 is the closest station to the recharge area, having the lightest water in the group. Thus, its recharge area is higher than that of the others.

G stations can simply be divided into groups as follows; Springs of Ilica I (G1), Ilica II (G2) and Akpinar spring (G3) belong to the same recharge area i.e., Manisa Mountain.

Table 3: Table of Chemical Analyses.

Project	Water Point	Date	T°C	PH	EC	Na	K	Ca	Mg	CO_3	HCO_3	Cl	SO_4	Σcat.	Ca/Mg
G.1	Ilica I Spr.	4.4.1972	27	6.9	650	0.40	0.1	4.5	0.80	0.0	6.47	0.34	0.41	5.80	5.62
G.4	Sarikiz I.Spr	4.4.1972	23	7.1	625	0.81	0.18	3.6	2.30	0.0	5.25	0.70	0.78	6.89	1.56
G.5	Sarikiz II.Spr	4.4.1972	23	7.2	625	0.62	0.08	3.7	2.8	0.0	6.20	0.36	0.46	7.20	1.32
G.6	Sarikiz Spr.	4.4.1972	23	7.3	625	0.75	0.09	4.09	2.0	0.0	5.20	0.60	0.83	6.93	2.00
G.9	Palamut Spr.	4.4.1972	19	7.3	525	0.25	0.05	3.0	2.19	0.0	5.70	0.28	0.17	5.49	1.30
G.11	Göksu Spr.	4.4.1972	25	7.3	620	0.68	0.08	3.49	3.09	0.0	6.35	0.36	0.48	7.34	1.12
G.13	Çullu Spr.	4.4.1972	25	7.4	610	0.56	0.08	3.10	3.0	0.0	6.0	0.34	0.33	6.74	1.03
G.14	Göldegirmeni Spr.	4.4.1972	23	7.4	650	0.55	0.07	3.40	2.46	0.0	6.65	0.36	0.46	6.48	1.38
G.2	Ilica II Spr.	9.5.1972	28	7.0	700	0.71	0.22	5.40	1.10	0.0	6.55	0.40	0.48	7.43	4.91
G.3	Akpinar Spr.	9.5.1972	19	7.4	488	0.20	0.19	3.40	1.10	0.0	4.42	0.30	0.17	4.89	3.09
G.7	Beyoba Well	9.5.1972	21	7.6	486	0.54	0.19	2.00	2.60	0.0	3.80	0.40	1.13	5.33	0.77
G.8	Beyoba-Ilick Str.	9.5.1972	17	8.0	515	0.42	0.19	3.00	2.10	0.0	4.90	0.40	0.41	5.71	1.43
G.10	Göksu Artesian	9.5.1972	23	7.3	646	0.66	0.19	3.60	2.70	0.0	6.45	0.40	0.30	7.15	1.33
G.12	Göksu Alluvium Spr.	9.5.1972	20	7.3	680	1.15	0.32	3.30	3.20	0.0	6.78	0.60	0.59	7.97	1.03
G.15	Gürle Spr.	18.12.1972	15	7.2	530	0.74	0.10	3.09	1.90	0.0	4.90	0.40	0.17	5.83	1.62
	Karayenice Sp.	24.7.1972	-	7.4	720	0.82	0.31	2.79	4.01	0.0	6.18	0.60	0.63	7.93	0.69

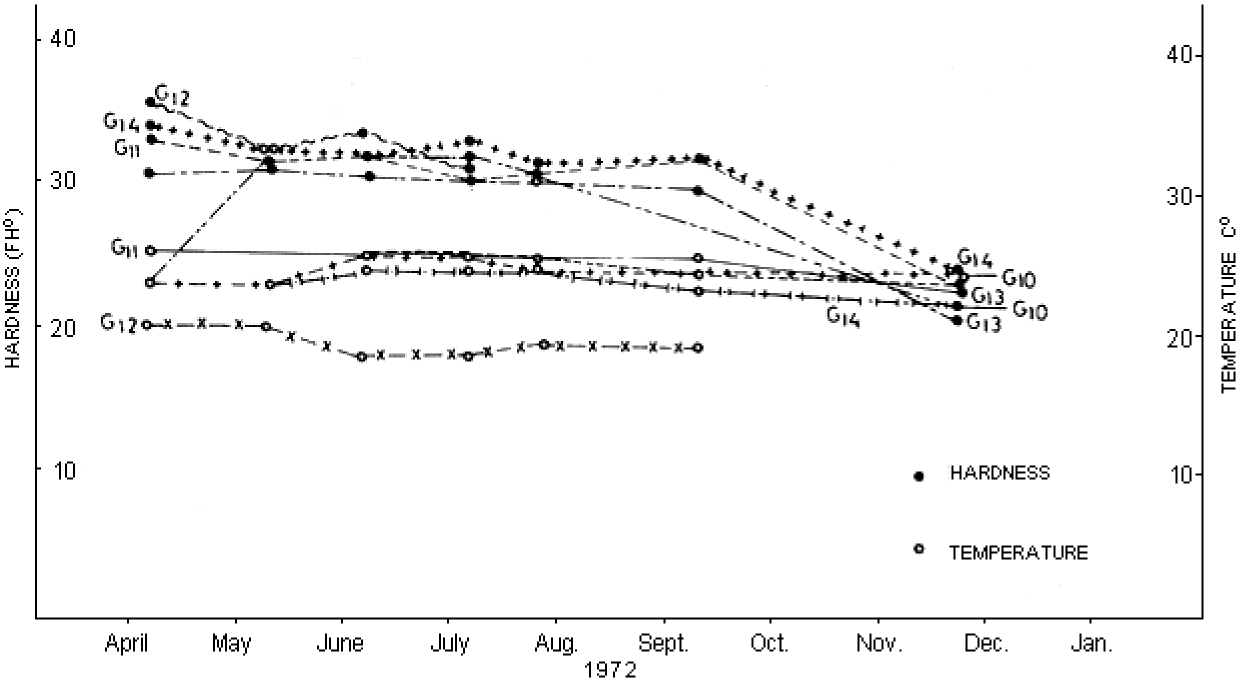

Figure 7 B: Graph of Seasonal Variation in Temperature and Hardness.

Constituting a different group, waters from the springs of the Sarikiz I (G4), Sarikiz II (G5) and Sarikiz III (G6) are relatively heavier with respect to stable isotopes, indicating that their recharge area is not significantly high or is under the effect of shallow aquifer water.

The Beyoba shallow well (G7) and the Ilicak stream waters are different in origin but effected by the same recharge area.

Water from the Palamut (GG9) spring is near high recharge areas, containing light stable isotopes.

Waters of the Göksu drilling well (G10) (14519-A), Göksu spring (G11), Çullu spring (G13) Göldegirmeni spring (G14) belong to the same recharge area, representing the same aquifer. Their recharge area is the same

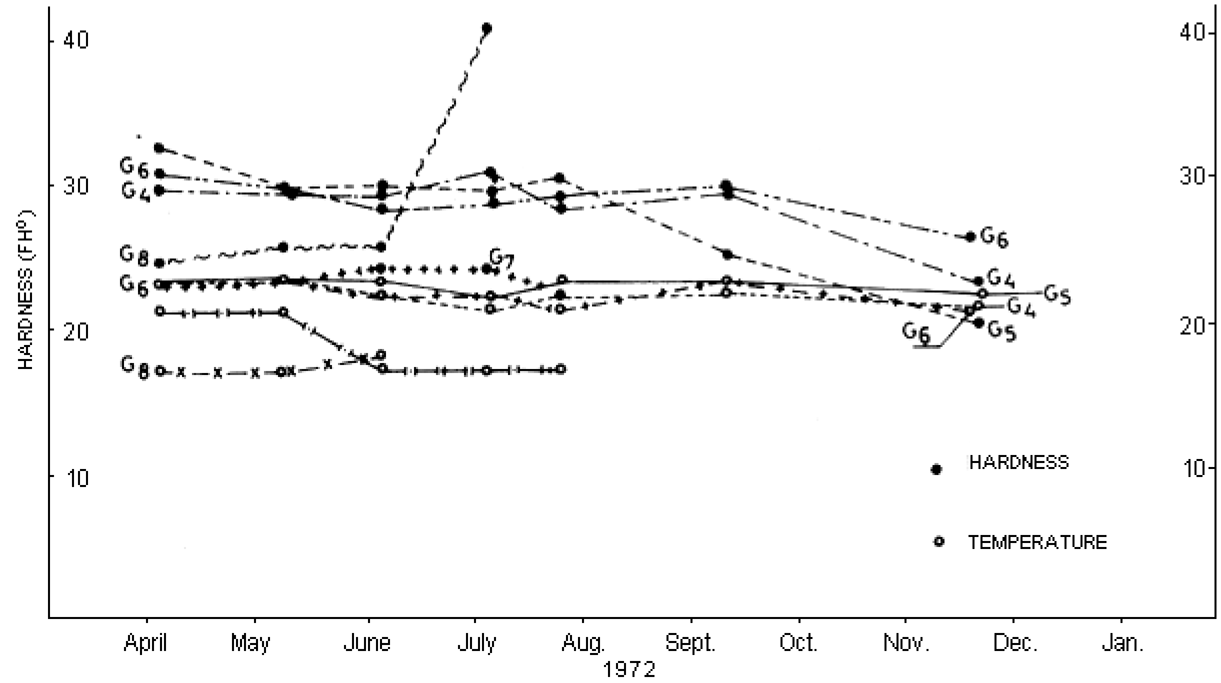

Figure 7-C: Seasonal Variations in Hardness and Temperature.

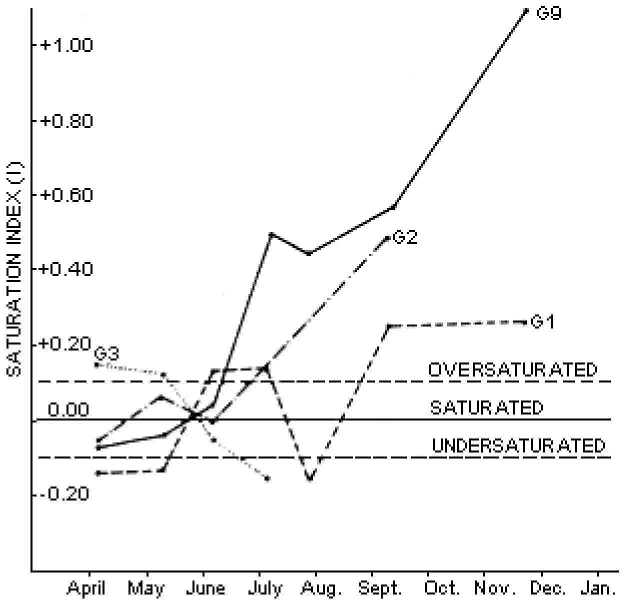

Figure 8-A:Seasonal Variations in Saturation Index.

as that of G9. However, G9 is different in origin, thus revealing that Göksu springs are effected by the precipitation of lower elevations as well.

Stable isotope analyses of the Göksu shallow spring (G1) have not been carried out.

There is not much difference between the April and July values for springs whose stable isotope analyses were performed.

Stable isotope values of G stations are considered to yield the line D=8.0 18 + 16% 0 representing Antalya precipitations, thus pointing out that precipitation falling onto recharge areas may be of Mediterranean origin.

Tritium: Water samples taken from G stations in April and July have been sent to DSI Tritium Laboratory for the analyses and the results of the April samples have been received (Table 1).

Tritium values, in general, verify the results from stable isotopes. That is:

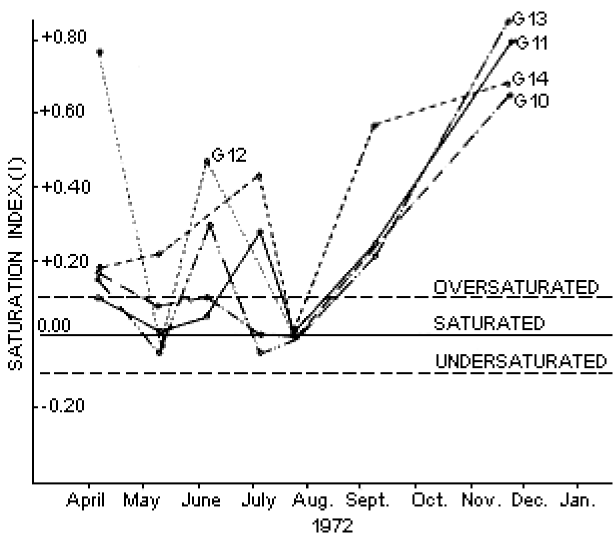

Figure 8-B:Seasonal Variations in Saturation Index.

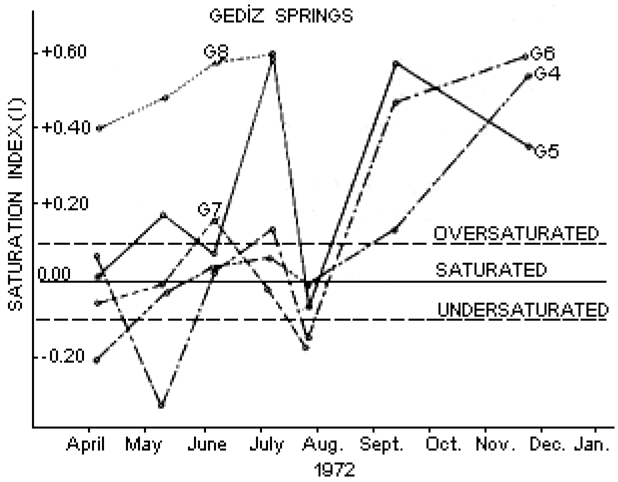

Figure 8-C: Seasonal Variations in Saturation Index.

Spring of Manisa mountain G1, G2, and G3 contains tritium values affected by nuclear experiments and their waters have several years as turnover time.

Sarikiz spring G4, G5, G6 contain tritium in small amounts. G6 can be considered to be tritium free. Mean while, waters of G4 and G5 can be thought to be effected by shallow aquifer water. Water from G7 Beyoba shallow well is a very recent water, having no relation with the Sarikiz springs. The Tritium concentration of G8 Ilicak stream is very close to those of the Sarikiz spring waters (G4, G5). This may imply that Sarikiz G4 and G5 springs are influenced by Ilicak stream. However, this view needs to be justified by further studies.

Waters from G9 Palamut spring, G11 Göksu spring, G13 Çullu spring G14 Göldegirmeni spring do not contain tritium. In a general approximation they must have reached underground before 1952.

Tritium value of G12 Göksu shallow spring water is higher than that of Göksu spring water.

According to an evaluation from the isotope values, the following can be stated:

Working from the stable isotope and tritium values, the recharge areas of the springs and the relation between them have been investigated and 3 groups have been distinguished as follows; 1st group: G1, G2, G3 ýllica group, 2nd group: G4, G5, G6 Sarikiz group, 3rd group: G9, G10, G11, G13, G14 Göksu group.

Waters classified under the above three groups are different from each other in origin. The Göksu group waters especially are under the influence of high recharge areas, and contain no tritium, which implies a groundwater age of at least 25-30 years.

Seasonal variations in the discharges of these springs are not significant either, because waters coming from precipitation do not contributes appreciable amounts to such a big resevoir.

Sarikiz spring waters represent a long travel time as well, but the biggest discharge takes place from G6 water point. Shallow aquifer waters are effective at G4 and G5 points.

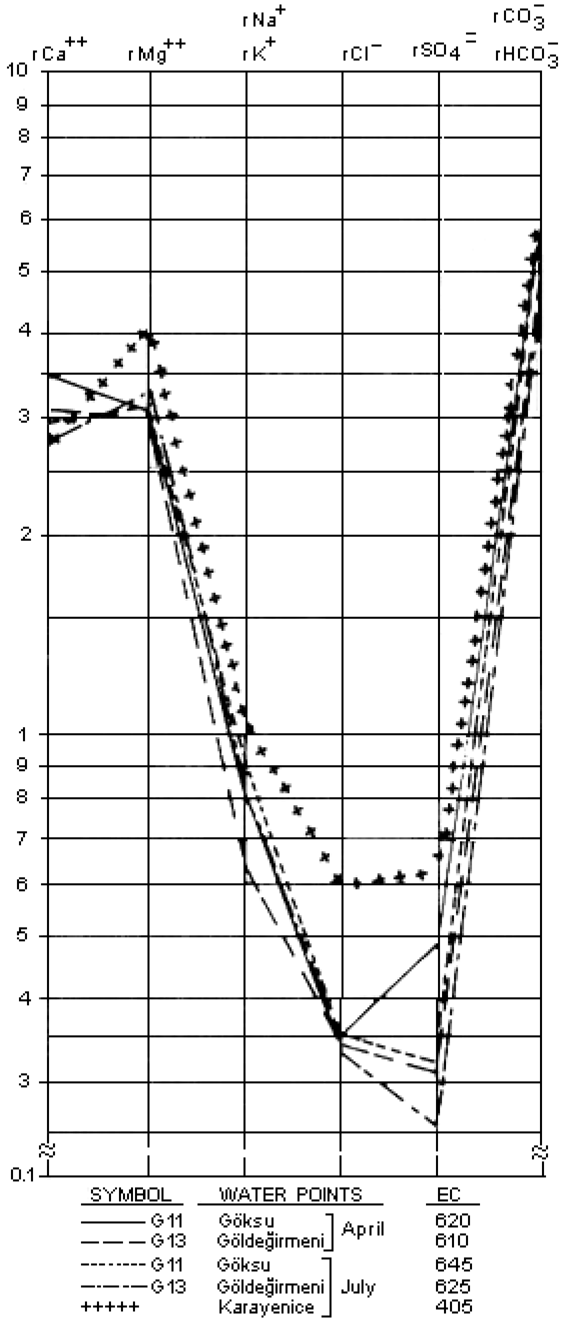

Figure 9: Comparison of Spring Waters (based upon the Analyses April-July 1972).

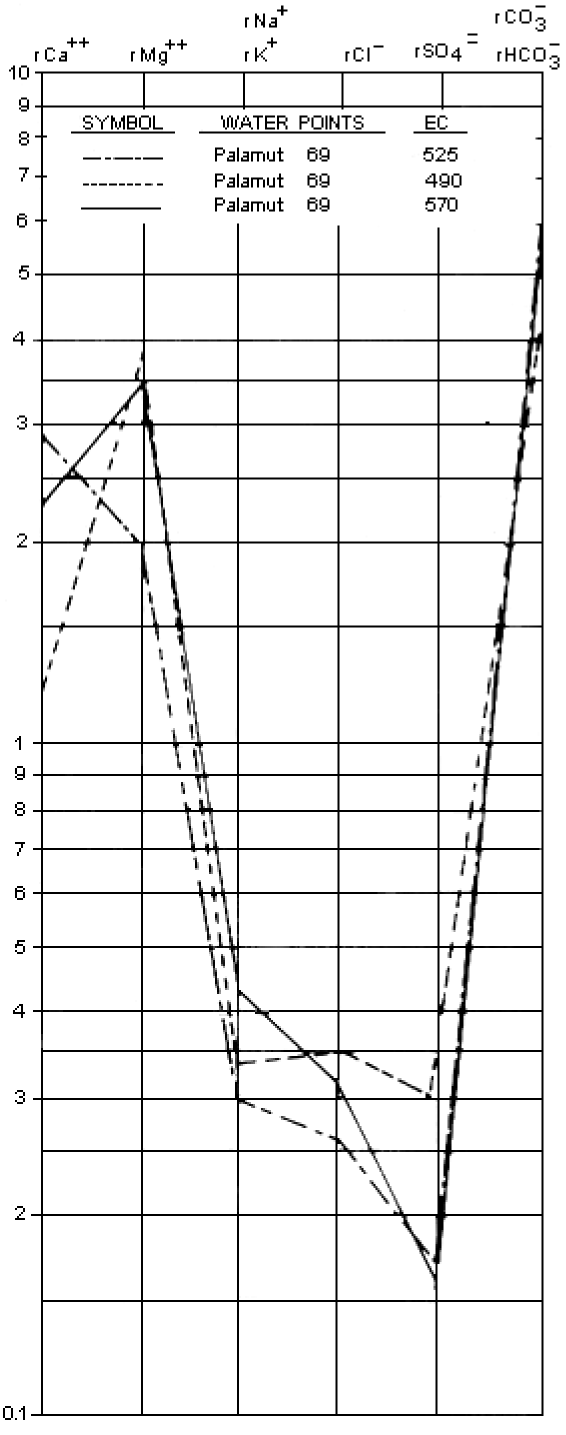

Figure 10: Comparison of Spring Waters (based upon the Analyses April-July and November 1972).

As for the Ilica group springs a definite interpretation is not possible since isotope values of previous years are not available. However, based on the tritium value of the Beyoba shallow pell (157T.U.) it may be suggested that waters of the Ilica group springs have turnover time of several years.

The interperations made so far are based upon the available isotope values. It is believed that isotope studies covering longer time intervals would not significantly change the above interperations.

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