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EVALUATION OF GEOCHEMICAL DATA OF SPRING WATER FROM PELOPONNES, GREECE

SUMMARY

Skayias (1978) presented in a report chemical analysis of water samples of 121 karstic springs from the Peloponnes together with a hydrogeological description of the spring sites. In this paper, we evaluate these hydrochemical data by means of statistical and graphical methods. The results are interpreted with respect to the hydrogeological origin and the hydrodynamics of the spring water.

The principles of the geological situation of the Peloponnes peninsula and of the groundwater bearing formations are described.

No special hydrogeological evaluation of the springs in detail is made, but attention is given to the overall phenomena which can be drawn out of the evaluation of the chemical data.

From the computerized hydrochemical data, various graphs were plotted automatically showing the data under different aspects.

As a result can be shown that a clearly defined group of samples with higher relative values of Mg and SO₄ is bound to a contact of the groundwater with metamorphic phyllites.

Roughly 80% to 85% of all springs at the Peloponnes located lower than about 10 m a. s. l. show more or less salt water intrusion from the sea.

No other major source of salt in the groundwater of this region seems to exist than the sea water. Only some springs related to phyllite formations show a special chemical composition which have, however, no practical consequence in terms of its aptitude as drinking water.

1. INTRODUCTION

SKAYIAS (1978) ⁽¹⁾ presented in a report chemical analysis of water samples of 121 karstic springs from the Peloponnes together with a hydrogeo-

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⁽¹⁾ SKAYIAS S. D.: *Inventory of Karstic Spring of Greece, I, Peloponnes-Zakynthos-Keffallinia*. Inst. Geology and Mining Research, Report. Athen 1978.

logical description of the spring sites. In this paper, we evaluate these hydrochemical data by means of statistical and graphical methods. The results are interpreted with respect to the hydrogeological origin and the hydrodynamics of the spring water. The work has been done in the frame of a scientific collaboration project dealing with Groundwater Technology in karstic aquifers.

1. 1. Geological background

The Neopaleozoic metamorphic basement of the Peloponnes is represented by two different lithologic series of rocks. The older one is consisting by holocrystalline rocks of high metamorphism (marbles, sipoines, gneisses) while the overlying is characterized by medium metamorphic rocks of epizonic character (phyllites, quartzites, etc.). These crystalline schists are found mainly in Parnon and Taigetos.

Mesozoic carbonate sedimentation lasted from the Triassic up to the Cretaceous - Eocene. These beds have a great extension all over the Peloponnes. The Mesozoic sediments lie on Neopaleozoic and cover it transgressively. Lying on the Permian phyllites, the beds of Triassic have been affected by a general metamorphism during the Alpic orogenesis. Lithologically the Mesozoic of the Peloponnes is mainly consisting of limestones, dolomites, cherts and clayey schists and ophiolites. The age of the ophiolitic complex characterizing the sub - Pelagonian zone is Jurassic.

During the Paleotertiary (Eocene - Oligocene), flysch sediments were deposited. The deposition of flysch in the various geotectonic zones differs in time.

During the Neotertiary, sediments of molasse type and of considerable thickness were deposited. They include marls, argiles, sandstones, conglomerates, marly limestones, etc.

The most important neogene basin of the Peloponnes is that of Megalopolis where thick beds of lignite occur. Other neogene basins of smaller extent are found in the departments of Korinthia, Ilia, etc.

The most recent Cenozoic sediments are of Quaternary age. They are characterized by the low grade or the complete lack of cohesiveness. These sediments are distinguished according to their composition and their origin in basin deposits, eluvial mantle, slope debris, cones of debris, fans, and terraces. Their existence is closely connected with the geomorphological evolution of the area and the cycles of geomorphogenesis.

The most important deposits of old and recent Quaternary in the Peloponnes are found in the coastal area from Korinthos to Patras and from Kyparissia to the basins of Kalamata, Skala, Argos, etc. The sediments of the Megalopolis basin, according to recent studies, have been formed from the Oligocene till the Pleistocene.

The quaternary deposits are of great hydrogeological interest because they constitute rich aquifers which can be developed by wells. However, naturally flowing springs usually originate from karstic aquifers built up by limestone or dolomite.

1. 2. General remarks on the hydrogeological situation of the springs

In his report, Skayias gives a complete description of each spring including a schematical hydrogeological cross-section. All springs are related to a karstic aquifer with different contacts to other formations like talus fans, phyllites and flysch. They differ mainly with respect to the topographical altitudes of the recharge areas and of the spring sites which both may influence the hydrological and chemical characteristics of a spring: the original chemical content of the infiltrating water varies with the topographical setting of the recharge area, and, the lower a spring site is located, the greater is the possibility of mixing the spring water with sea water. In this paper, no special hydrogeological evaluation of the springs in detail is made, but attention is given to the overall phenomena which can be drawn out of the evaluation of the chemical data. Also, we do not elaborate on discharge fluctuations, the hydrological balance and watershed analysis.

2. GRAPHICAL DISPLAY OF THE DATA

From the computerized hydrochemical data, various graphs were plotted automatically showing the data under different aspects (see figures No. 1 to 8).

All springs which are not identified with respect to their elevation or are located below 1 m above mean sea level are assigned to 1 m elevation. This manipulation was necessary to cope with the logarithmic scale used in the plots.

2. 1. Altitude versus concentration or quantity

The majority of the springs is located at altitudes between 100 and 1000 m above sea level (Fig. 1). Their discharge varies mainly between 20 and 200 m³/h. With decreasing altitude, the discharge seems to increase slightly.

The total dissolved solids (TDS in ppm) increase with decreasing altitude, also (Fig. 2). There is a limit at about 700 ppm which is not exceeded by springs located higher than 10 m (mostly 5 - 7 m) above sea level.

The distribution of the sodium (Na) cations shows in general the same relation to the elevation of the spring as TDS (Fig. 3). However, it is clearly visible that the content of Na starts to increase slowly already at greater altitudes, the reason of which will be discussed later. Fig. 4 shows that magnesium cations (Mg) split into two families:

- 1) one family shows a relation to the altitude similar to that of sodium,
- 2) the other family is a cluster called A. The springs of cluster A are identified and given in a list aside of the graph.

Calcium cations (Ca) show no clear relation to the altitude (Fig. 5). It is more or less constant at a value of about 100 ppm.

As Fig. 6 shows, bicarbonate (HCO₃-anion) varies very little, not exceeding a limit of about 300 ppm with dependency from altitude only in the uppermost elevations, where it increases with decreasing topographical levels.

Sulphate (SO₄-anion) and chloride (Cl-anion) show clear relations with the altitude (Fig. 7, 8), similar with sodium and magnesium. They start with a small increase of the ion content with decreasing altitude of the springs down to a level of about 5 m a. s. l., from which it raises strongly with further approach to the sea level.

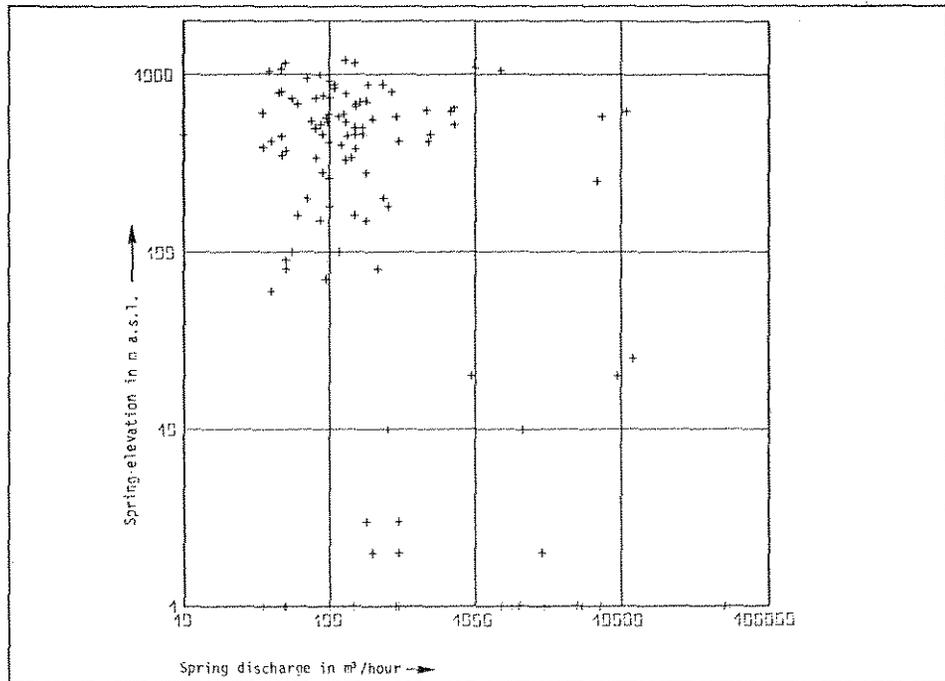


Fig. 1 - Spring elevation versus spring discharge

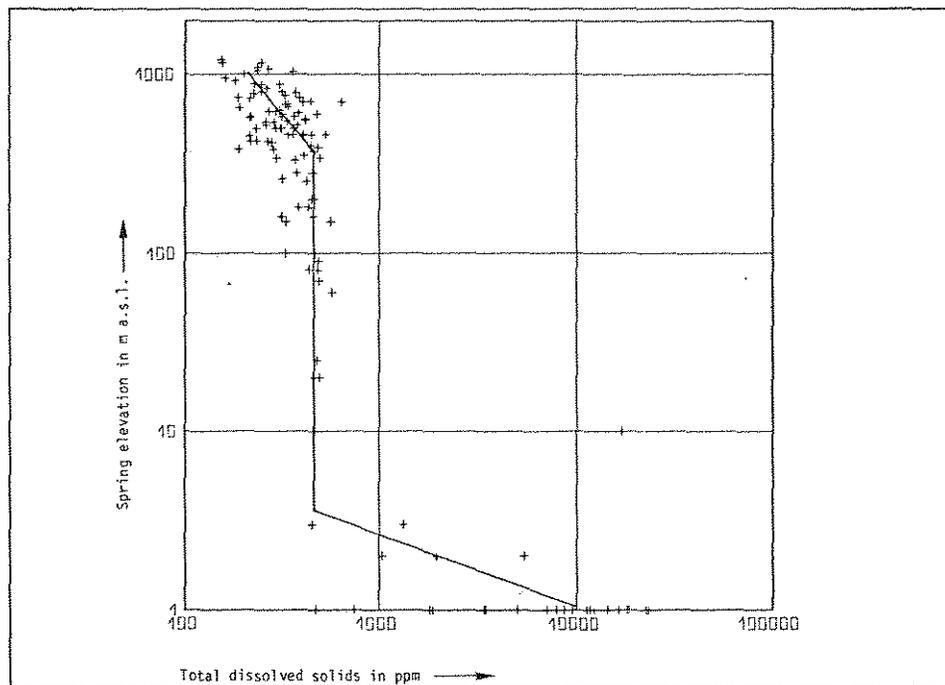


Fig. 2 - Spring elevation versus total dissolved solids

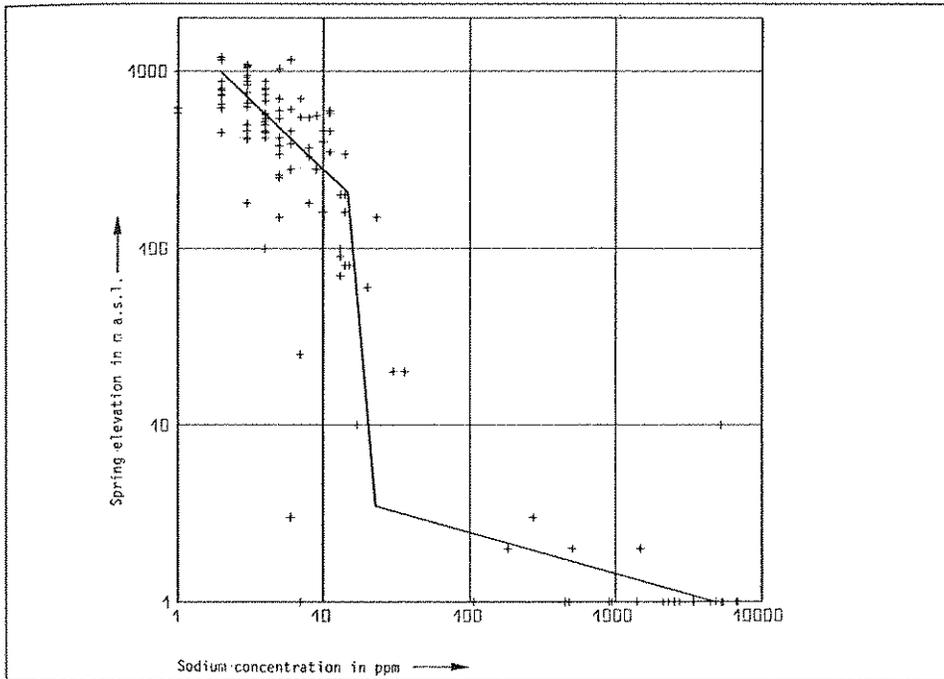


Fig. 3 - Spring elevation versus sodium concentration

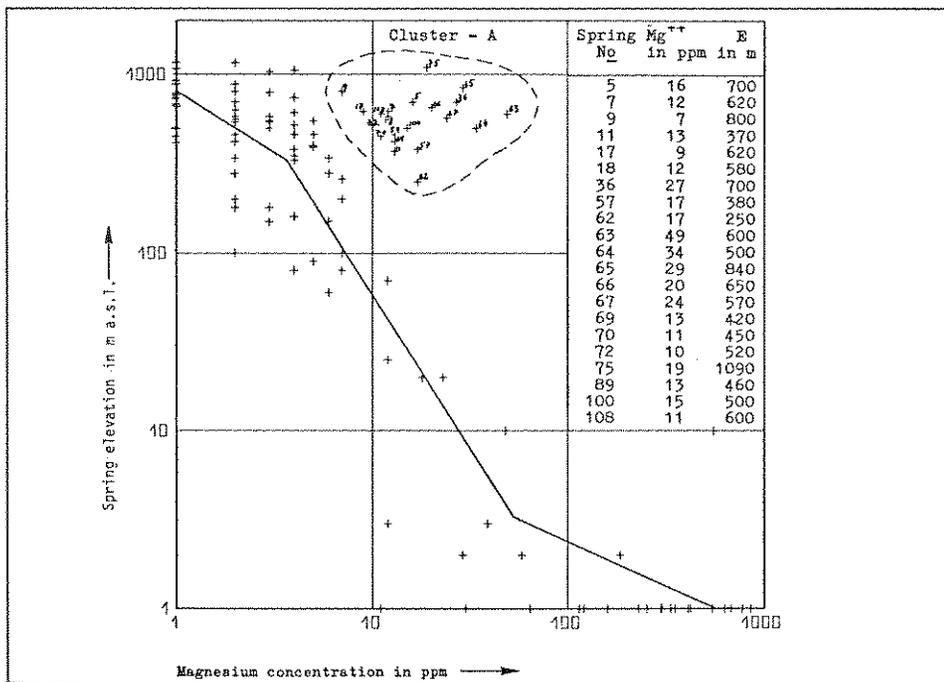


Fig. 4 - Spring elevation versus magnesium concentration

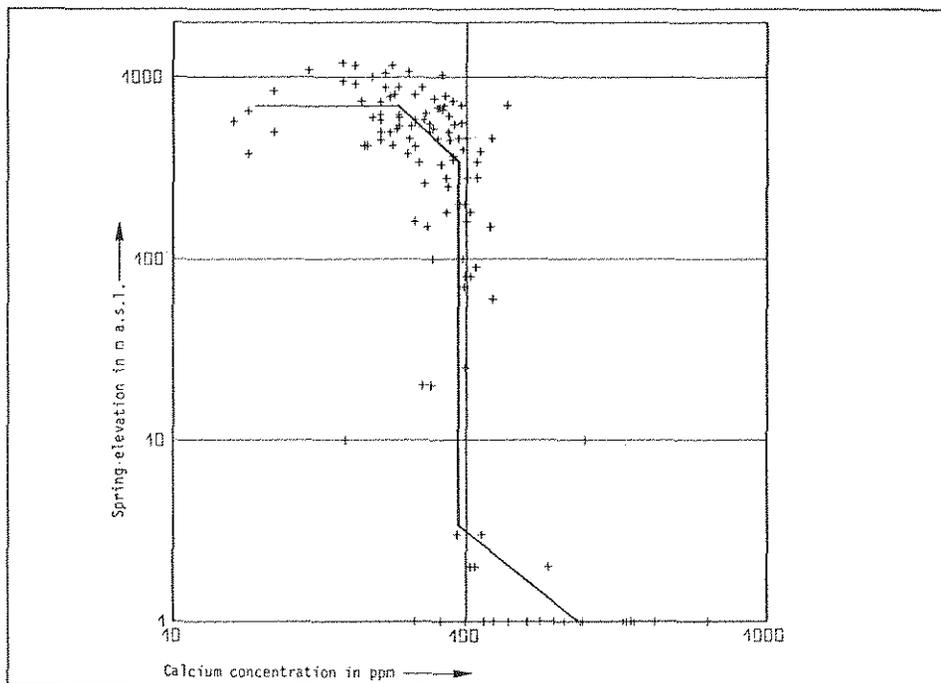


Fig. 5 - Spring elevation versus calcium concentration

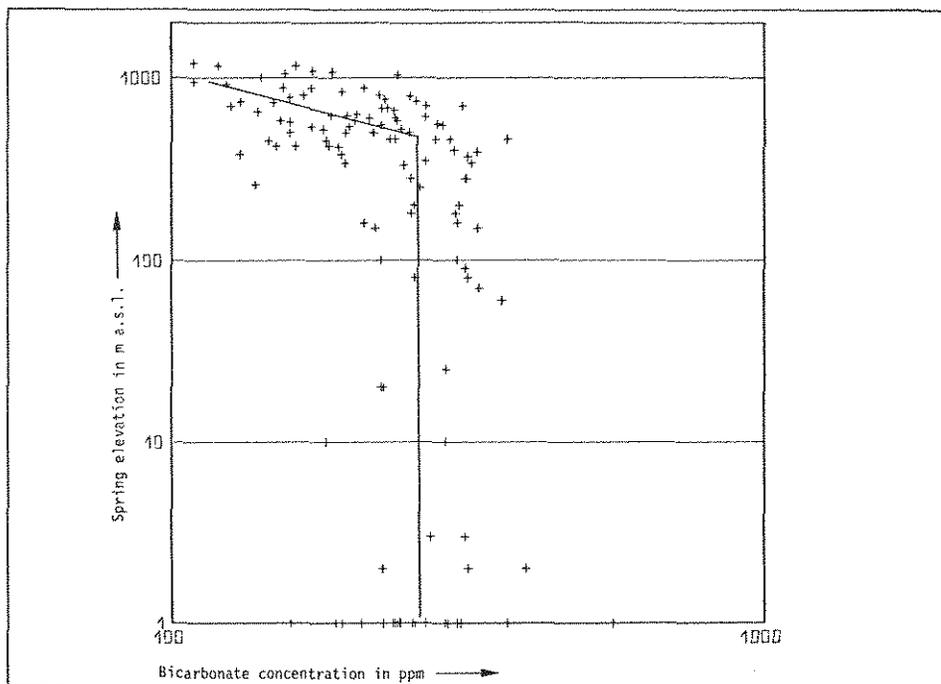


Fig. 6 - Spring elevation versus bicarbonate concentration

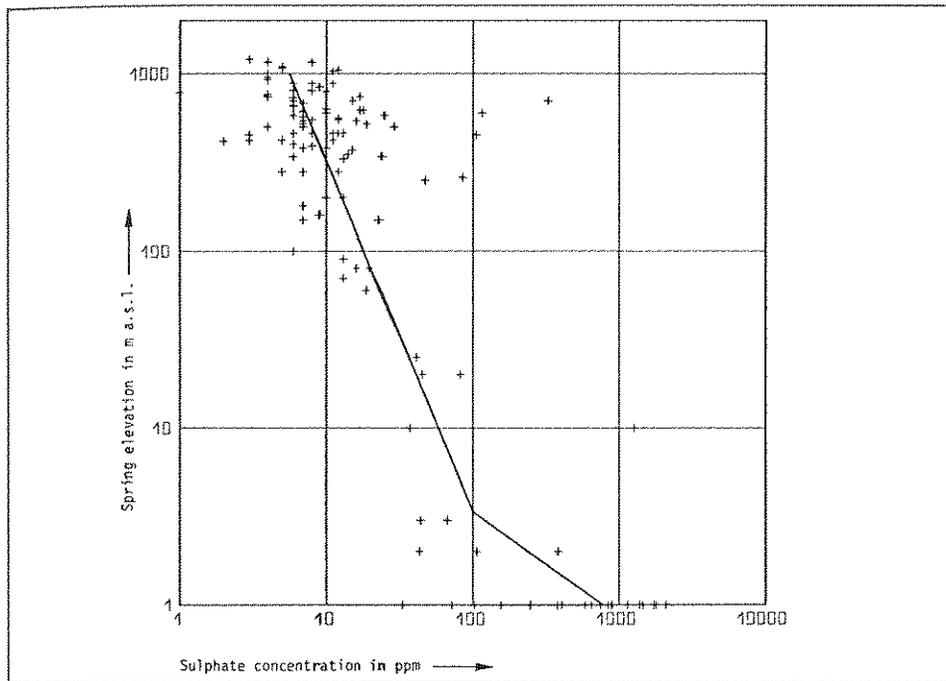


Fig. 7 - Spring elevation versus sulphate concentration

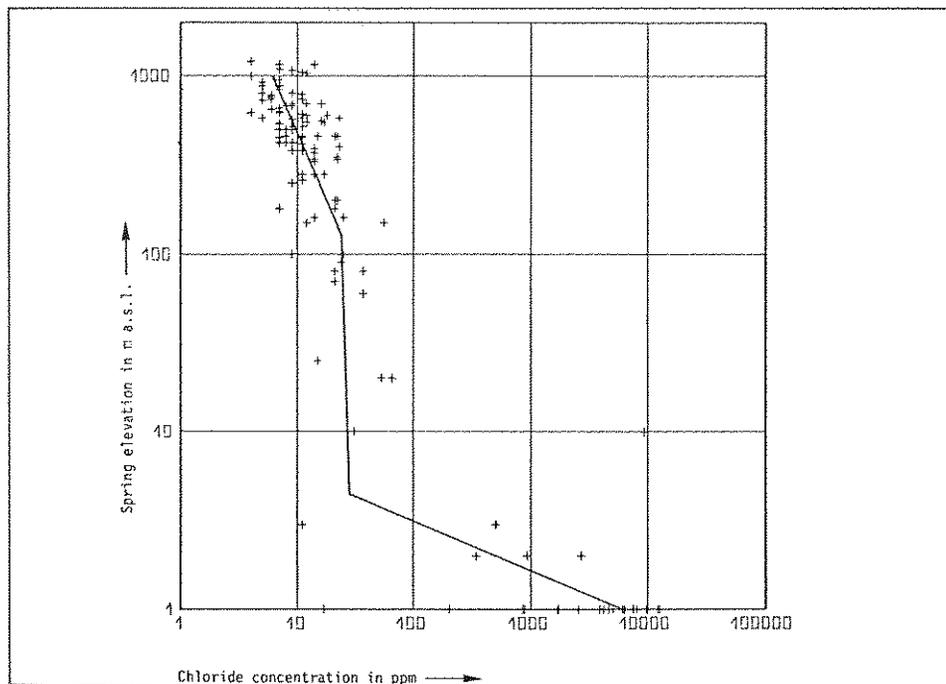


Fig. 8 - Spring elevation versus chloride concentration

2.2. Concentration versus total dissolved solids

The cation content of sodium (Fig 9) shows a very clear tendency. Two families are present:

- 1) a cloud with low sodium and TDS content and
- 2) nearly a straight-line function of increasing sodium and TDS content.

Magnesium concentration shows the similar trend as the sodium ions (Fig. 10); but in the case of low concentrations, three different families can be observed:

- 1) low magnesium content, representing most typical carbonatic karst waters,
- 2) medium magnesium content (dolomitic karst waters),
- 3) high magnesium content, which can be assigned to groundwater from phyllites.

Fig. 11 shows the calcium-ion (Ca) versus TDS. For low values of TDS, a clear upper boundary with a linear relationship between calcium content and TDS is shown. This is the chemical identification of karst groundwater. The chemical pattern of those springs plotted below this straight line probably is influenced by other hydrogeological formations.

The relation between hydrogencarbonate (bicarbonate) concentration and TDS (Fig. 12) is very similar compared with the relation between calcium and TDS; however, with increasing TDS starting from a TDS of about 600 ppm, the Ca-content increases slowly, while the HCO_3^- -anion keeps constant from that point.

Both sulphate (Fig 13) and chloride (Fig. 14) show a strong linear dependency from TDS like magnesium and the sodium ions at concentrations of more than 800 ppm TDS. At lower concentrations, sulphate tends to be over-represented while the chloride content is lower than it could be expected from the above mentioned relation.

2.3. Triangle diagrams

Two triangle diagrams (Type Piper) for the anions and the cations, respectively, are shown in Fig. 15.

The anions triangle pattern shows that the set of samples contains two families. One family with high HCO_3^- content belongs to those water samples coming from karst formations. A second family shows a high chloride concentration. These samples probably contain sea water.

The cation triangle pattern reflects the anion pattern; however, three groups of samples can be identified with relatively high concentration of magnesium cations. These three groups have been described already in Fig. 10.

3. INTERPRETATION

3.1. Remarks on the quality of the data

Since in Greece the hydrological year can clearly be divided into a dry and a wet season, it must be expected that the chemical composition of karst

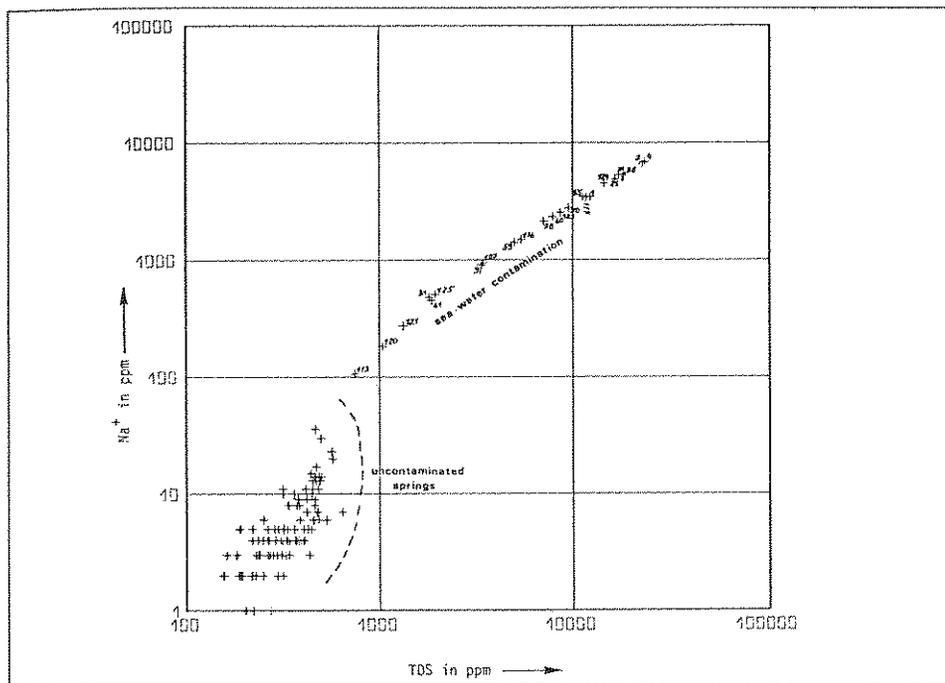


Fig. 9 - Sodium ion concentration versus TDS

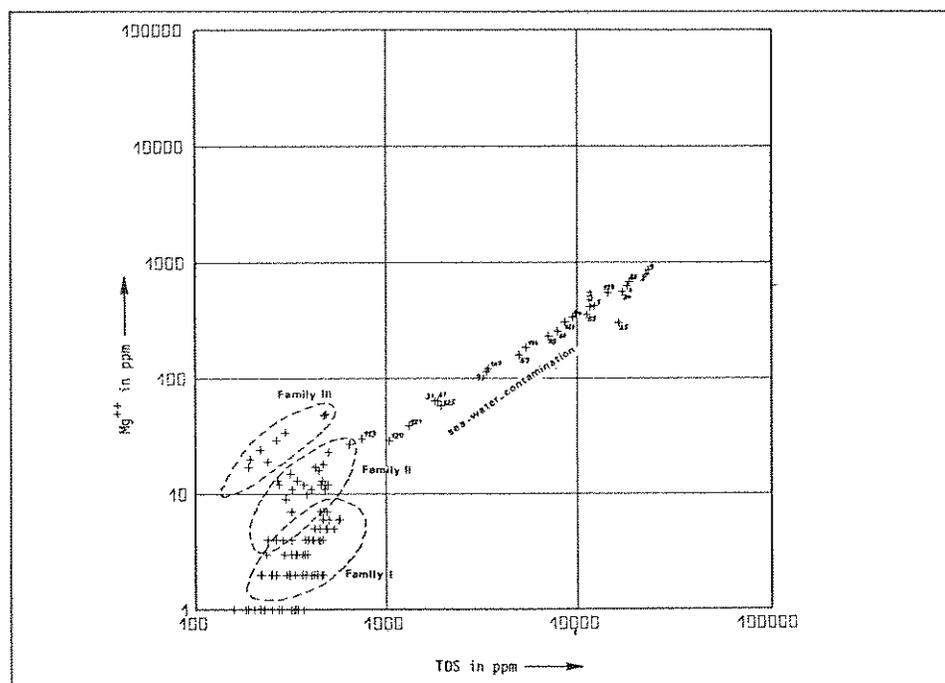


Fig. 10 - Magnesium ion concentration versus TDS

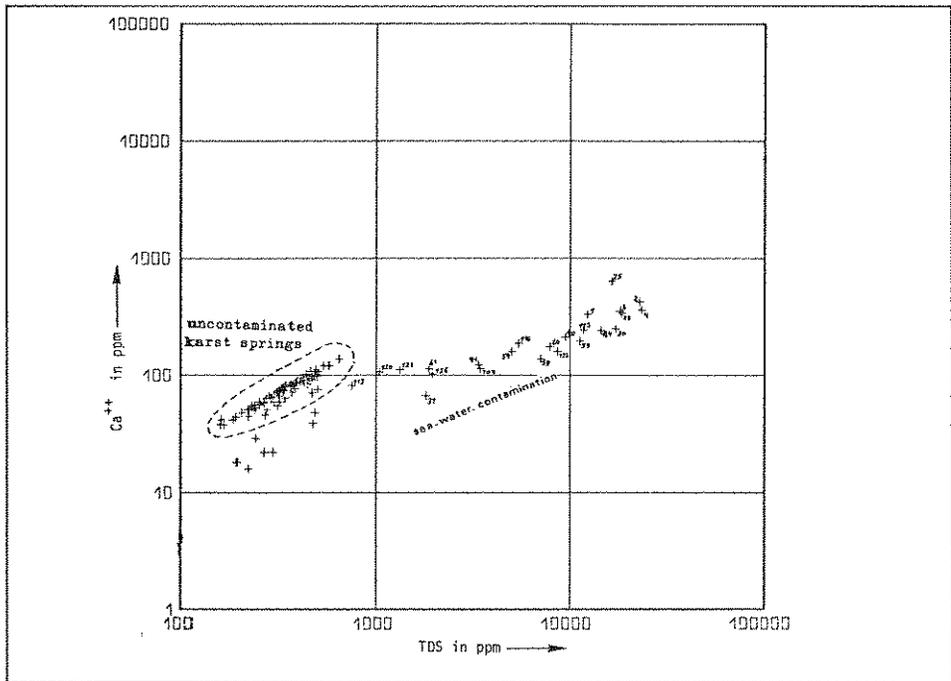


Fig. 11 - Calcium ion concentration versus TDS

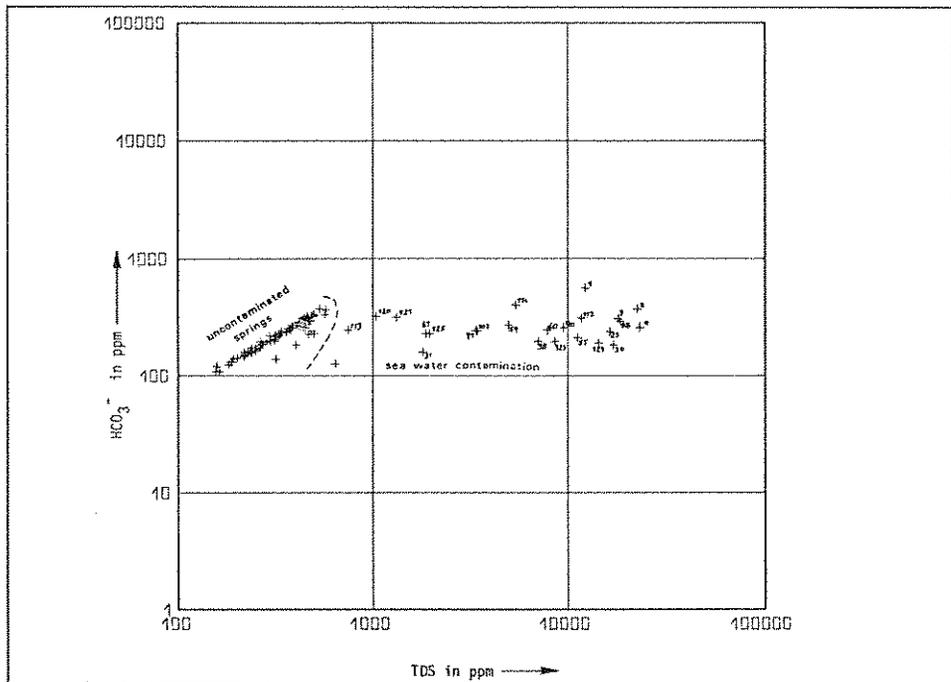


Fig. 12 - Hydrogencarbonate ion concentration versus TDS

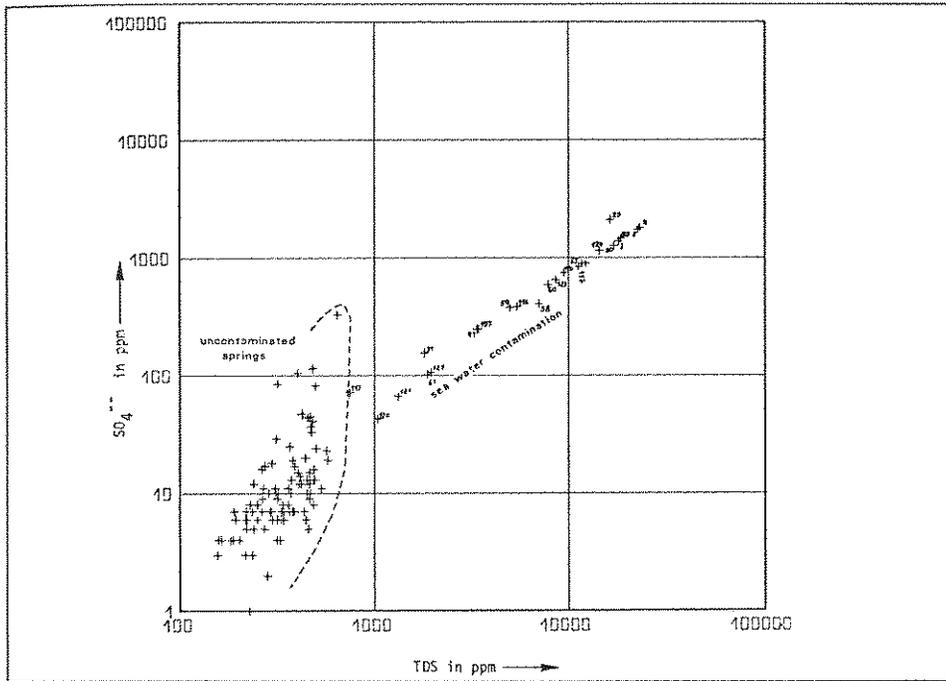


Fig. 13 - Sulphate ion concentration versus TDS

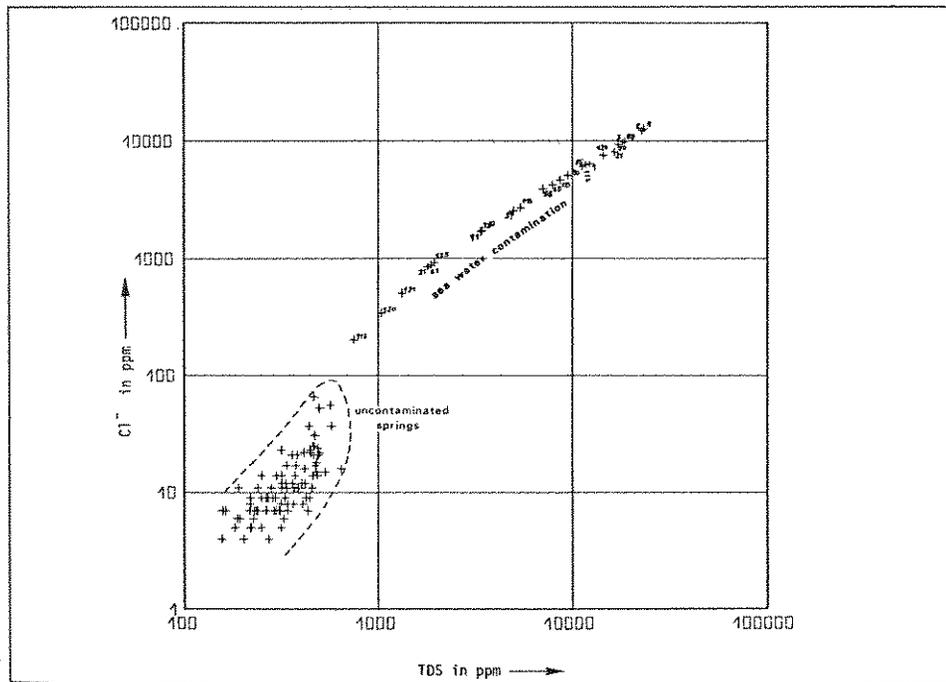


Fig. 14 - Chloride ion concentration versus TDS

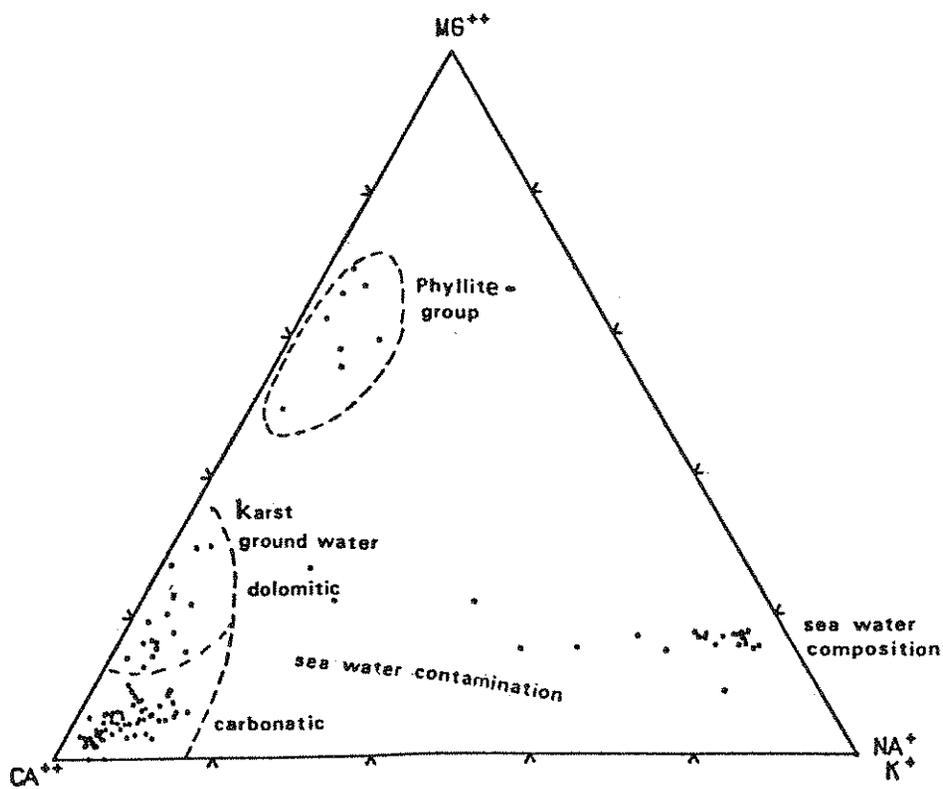
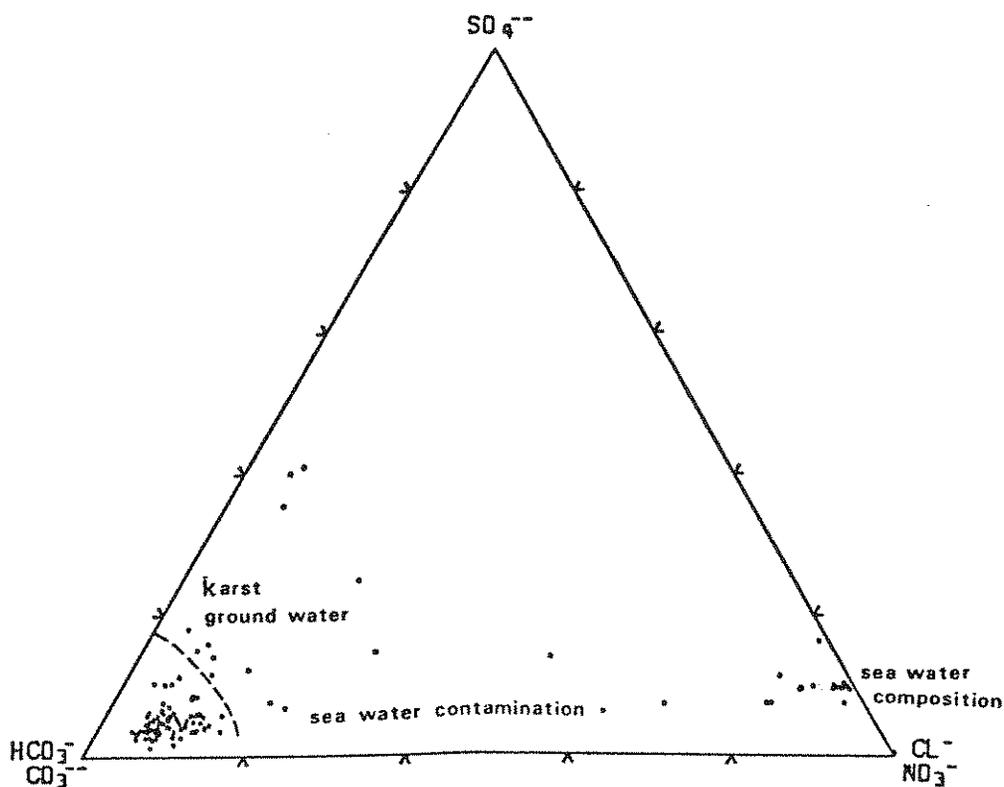


Fig. 15 - Triangle diagrams

TABLE I - Calculated contamination of spring water by sea water in %

No.	Spring No.	TDS		K		Mg		Ca		SO ₄		Cl		Na		Mean in %
		cor	%	cor	%	cor	%	cor	%	cor	%	cor	%	cor	%	
1	4	23000	58	425	97	836	63	291	36	1790	56	12680	58	6900	59	59
2	2	22400	57	384	87	758	57	355	44	1722	54	12250	56	6730	57	56
3	88	18200	46	259	59	659	50	271	34	1436	45	9962	45	5485	47	47
4	3	17700	45	308	70	607	46	283	35	1365	43	9732	44	5330	45	45
5	30	16800	42	190	43	534	40	179	22	1248	39	9341	42	5285	45	41
6	25	16000	40	140	32	280	21	566	71	2079	65	8065	37	4870	41	44
7	124	14100	36	230	52	525	40	170	21	1128	35	7533	34	4480	38	37
8	1	11950	30	228	52	403	31	263	33	881	28	6363	29	3445	29	31
9	117	11400	29	151	34	393	30	174	22	868	27	6256	28	3420	29	29
10	55	10900	28	118	27	333	25	126	16	820	26	6029	27	3445	29	26
11	90	9200	23	118	27	316	24	142	18	726	23	5033	23	2755	23	23
12	123	8300	21	132	30	284	22	90	11	630	20	4608	21	2530	22	21
13	60	7600	19	97	22	234	18	106	13	565	18	4182	19	2320	20	19
14	58	6800	17	87	20	210	16	68	8.5	386	12	3866	18	2120	18	16
15	116	5100	13	68	15	165	13	118	15	365	11	2675	12	1485	13	13
16	59	4700	12	55	13	139	11	89	11	358	11	2515	11	1400	12	11
17	107	3100	7.8	38	8.6	101	7.7	44	5.5	230	7.2	1703	7.7	935	8	7.7
18	91	3060	7.7	39	8.9	94	7.1	53	6.6	227	7.1	1668	7.6	900	7.7	7.4
19	125	1650	4.2	7	1.6	38	2.9	33	4.1	86	2.7	906	4.1	500	4.3	3.5
20	61	1550	3.9	17	3.9	44	3.3	44	5.5	84	2.6	859	3.9	442	3.8	3.7
21	31	1500	3.8	19	4.3	44	3.3			135	4.2	831	3.8	473	4	3.8
22	121	1000	2.5	7	1.6	19	1.4	42	5.5	47	1.5	485	2.2	266	2.3	1.9
Sea Water (Larnaka)		39620		440		1320		800		3192		22000		11760		
Uncontaminated Spring-Water		300		5		20		70		20		20		7		(estimated mean)

cor - By uncontaminated spring water concentration corrected value in ppm.

% - cor - value / sea water concentration.

Mean % - Arithmetic mean of %-value without TDS and largest and lowest value. (This figure is rounded).

water varies with the season in which the samples have been taken. However, the data evaluated in this paper have been collected all over the year. Due to the relatively small number of samples, it was not possible to differentiate them with regard to the collection date. In consequence, the interpretation does not reflect any seasonal effects on groundwater chemistry, but treats the variations statistically.

3. 2. Hydrogeological interpretation

There are three different sources of the chemical content of groundwater which can be observed in the spring samples of the Peloponnes:

- 1) the precipitation
- 2) the aquifer
- 3) the sea water.

From the aquifer, mainly the ions Ca, Mg, HCO_3 and SO_4 can be derived. It is quite clear, that the content of Ca and HCO_3 depends on the amount of limestone dissolved by the groundwater, and that the Ca/Mg ratio depends to great extent on the dolomitic parts of the aquifer (family II on Fig. 10).

As a result can be shown that a clearly defined group of samples with higher relative values of Mg and SO_4 (family III in Fig. 10, family A in Fig. 4 and in the triangle diagram) is bound to a contact of the groundwater, according to the hydrogeological cross-sections drawn by Skayias, with metamorphic phyllites.

The figures 1 to 8 show a clear increasing amount of the chemical components with decreasing altitudes of the spring sites. This may be due to the different travel times and ways of the groundwater from the recharge areas to the various spring sites: the longer the way, the more solids may be dissolved from the aquifer.

However, the slowly increasing chloride content with decreasing altitude is not necessarily connected with a dissolution of the rock dependent on the residence time, but may more likely depend on the altitude of the recharge area and / or on the distance from the sea, thus reflecting in the varying chloride content of the precipitation. This effect can be observed only at samples originating from spring sites located higher than about 10 m a. s. l.

Below this level, the spring water usually is, with varying degree, contaminated by sea water. Out of the samples collected on Peloponnes, 31 are from positions lower than 10 m above sea level. Four spring sites are below sea level, so that no water sample could be taken. 22 of remaining 27 are influenced by sea water of different quantity starting with 60% (spring site No. 4) down to about 2% (spring site No. 21; see table I). Nearly no salt water intrusion can be determined at the springs No. 68, 111, 112, 113 and 120, in spite of being situated lower than 10 m a. s. l.

4. CONCLUSIONS

Whether the springs are contaminated by sea water or not depends on the special hydrodynamic conditions (pressure drop near the spring mouth, pipe connection to the sea, etc.) which can not be worked out in detail in this interpretation. Since no deterministic relation can be given between sea water intrusion and the hydrologic parameters of a spring near the sea, no forecast can be done with regard to the quality of spring water for a special or newly found spring. No other major source of salt in the groundwater of this region seems to exist than the sea water. Only some springs related to phyllite formations show a special chemical composition which have, however, no practical consequence in terms of its aptitude as drinking water.

With the aim to better using the sea water contaminated springs by managing the discharge and the chemical quality, it would be necessary to study the variations in time of the discharge and water quality and the relation between them.

