

Geochemical exploration of a volcano-sedimentary aquifer system in northern Greece

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ABSTRACT: In this note, hydrochemical data from a volcano-sedimentary aquifer of the Skydra region, Northern Greece, are analysed following an integrated approach, where results obtained with classical hydrochemical methods (saturation index, mixing diagram, characteristic relationships) are compared with those obtained from multivariate statistical technique correspondence analysis (R-mode factor analysis). From several groundwater samples collected from bore-wells the pH, the total dissolved solid, the electrical conductivity, the temperature and the major ions (Ca, Mg, Na, K, SO₄, NO₃, HCO₃, Cl and SiO₂) were measured. Within the investigated area, different hydrochemical facies have been recognised, basically generated by different geological formations but also induced by human activities. In order to characterise the different facies and to infer the relationships among them, thirteen parameters are chosen and elaborated by applying multivariate analyses. Accordingly, the chemical data of the aquifers can be grouped following five major factors which best fit the total variance of the data. These factors indicate the alimentation area and the influence of the regional geology for the hydrochemical characteristics of the principal aquifer systems.

Key terms: hydrochemistry, volcano-sedimentary aquifer, factor analysis, ground water pollution, northern Greece

Introduction

The area corresponds to the northwestern sector of the wider Thessaloniki-Gianitsa plain (Fig. 1) and has an almost flat morphology with altitudes ranging from 30 to 100 m a.s.l. The major strands of the hydrographic system are represented by the southwards flowing Almopeos River, which also represents the eastern limit of the investigated area, the Edeseos River, to the north, and the Arapitsa River, to the south, both flowing eastwards (Fig 2).

During the last decade, due to the increase of farmed areas and especially due to the increased need of irrigation water, numerous wells have been drilled and large amounts of groundwater resources from the confined volcano-sedimentary multiaquifer system have been pumped out. The depth of the drillings relative to the surface varies between 70 to 180 m and the water supply varies from 55 to 200 m³/h.

In order to i) determine the alimentation zones of the volcano-sedimentary aquifer system, ii) distinguish the different hydrochemical facies, iii) understand the relationships between the regional geology and the hydrochemical characteristics and iv) evaluate the influence of the human activities on the quality of the water resources, numerous groundwater samples from bore-wells have been collected, the chemical-physical parameters have been measured and major ions analyses have been performed.

The hydrochemical results of the analyses have been interpreted, firstly, according to nowadays classical hydrochemical methods, such as the space distribution of

the chemical species, the diagrams of correlation between the different ions and the triangular diagram of Piper (1944), secondly, by applying multivariate statistical techniques. Thirdly, the two sets of results, classifications and interpretations have been compared.

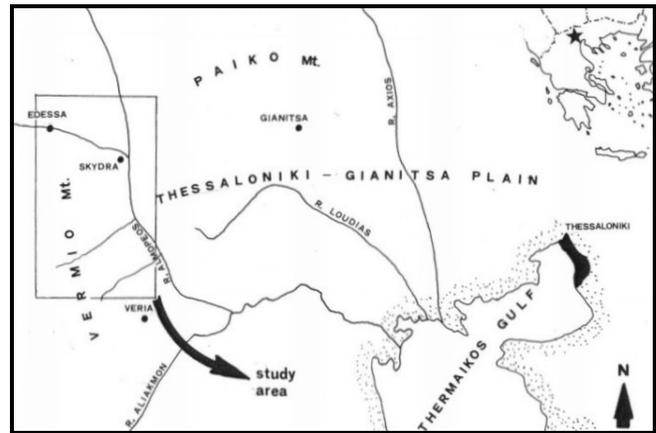


Figure 1: Location map of the investigated area.

Geology

From a geological point of view, the study area belongs to the Almopia Zone, representing one of the several geotectonic and palaeogeographic zones of the Internal Hellenides. According to Mercier (1966) and Mercier and Vergely (1971), the principal outcropping lithologies (Fig 2) are marbles and other

carbonate rocks of various ages, ophiolites and associated materials (Upper Jurassic-Cretaceous), flysch (Upper Cretaceous-Palaeocene), volcanic and volcanoclastic materials and local travertine deposits (Pliocene-Pleistocene).

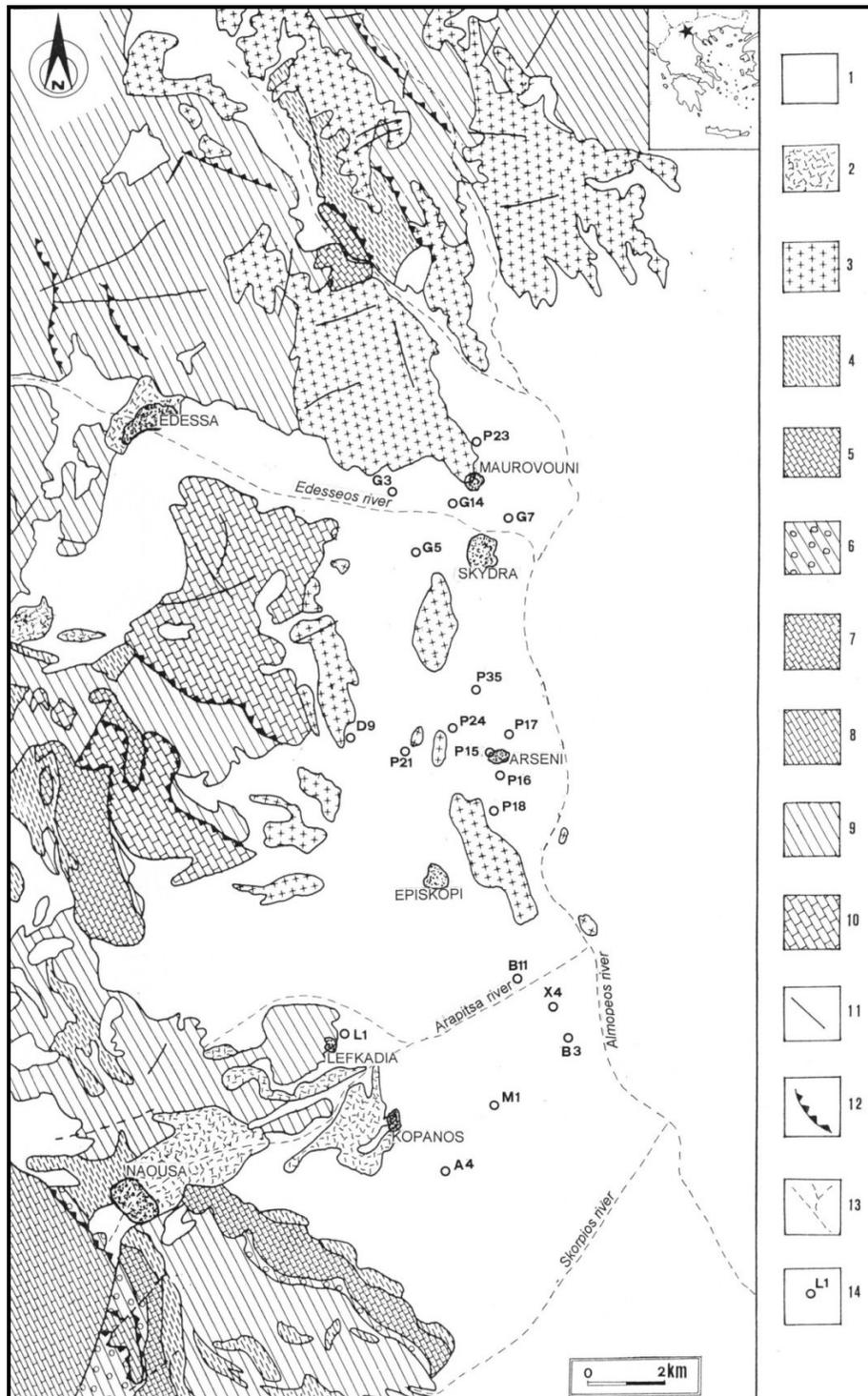


Figure 2: Geological map of the broader area of Skydra. 1: Quaternary alluvial deposits; 2: travertine deposits (Pliocene-Pleistocene); 3: volcanic formations and tuffs (Pliocene-Quaternary); 4: flysch (Upper Cretaceous-Palaeocene); 5: limestone with alternating calcschists; 6: conglomerate schists and calcschists; 7: undifferentiated carbonate rocks (Stenimachos and Grameni Vrisi units); 8: undifferentiated carbonate with alternating conglomerates (Upper Vermio unit); 9: marbles; 10: ophiolites, ophiolitic m \acute{e} langes and associated materials; 11: faults; 12: major thrusts; 13: hydrographic network; 14: bore-wells.

Except tuffs, none of these rocks crop out within the investigated area, which is mainly covered by Quaternary alluvial deposits. The tuffs are Pliocene-Early Pleistocene in age (Kolios *et al.*, 1980), showing a latitic latito-andesitic composition (Elefteriadis 1977) and are supposed to have been deposited by gravity mud-flow mechanisms coming from the near volcanic centre of Vora.

As concerns tectonics, a system of normal faults, mainly trending NW-SE and ESE-WNW, affected the area during Pliocene-Quaternary times (Mountrakis, 1985; Lalechos, 1986).

Hydrogeology

Based on the underground lithological data, as obtained from numerous bore-wells, and according to several geo-electrical logs, three principal hydrogeological units have been recognised (Rapti *et al.*, 1993; Rapti, 1995). From top to bottom, these units are i) Quaternary alluvial sediments, ii) volcano-sedimentary materials and iii) argillaceous-rich deposits.

The Quaternary alluvial sediments consist of alternating mud, sands and pebbly sands. They show both lateral and vertical granulometric variations, while their total thickness ranges between 0 and 30 m. The amount of water within this unit is mainly contained in the sandy layers and it has been recently strongly decreased due to the drastic down drop of the water table.

The volcano-sedimentary materials of the second unit mainly consist of tuffs, whether compacted or fractured, alternating with muddy, sandy and conglomerate layers of alluvial origin. Also this unit shows strong vertical and horizontal lithological heterogeneity at the local scale, which is superimposed to a regional decrease of the volcanogenic component toward the south, as a direct consequence of the northern origin of these materials. For example, in well P23 near Mavrovouni (Fig 2) the tuffaceous component represents the 95% of the unit, while in well A4 near Kopanos this component is reduced to only 5%.

The principal aquifers of the study area are located within the volcano-sedimentary formations. On the contrary, the Quaternary alluvial sediments do not, or slightly, contribute to the water supply of the wells that varies from 55 to 200 m³/h. The thickness of this unit presents important variations, ranging between 25 m, to the west, and 270 m, to the east. Following several pumping tests carried out in different wells, we can infer that the aquifers are of artesian type, with storage coefficients varying between $1.5 \cdot 10^{-3}$ and $1.36 \cdot 10^{-4}$, the transmissivity between $1.17 \cdot 10^{-2}$ and $2.4 \cdot 10^{-4}$ m²/s the permeability from $1.1 \cdot 10^{-3}$ and $2.7 \cdot 10^{-6}$ m/s. The higher values of transmissivity are found in wells where the volcano-sedimentary formations is interbedded with thick and frequent conglomerates and sands and few argillaceous layers. In contrast, the lower values are found where tuffs are more lithified and alternating with frequent argillaceous layers.

The strong increase at depth of layers with a mainly

argillaceous component represents the limit between the second and third hydrogeological units. Within the investigated area, the top of the lowermost unit has been found at a variable depth of 70-290 m from the surface. It is noteworthy to say that these deposits form the impermeable base of the volcano-sedimentary aquifer system.

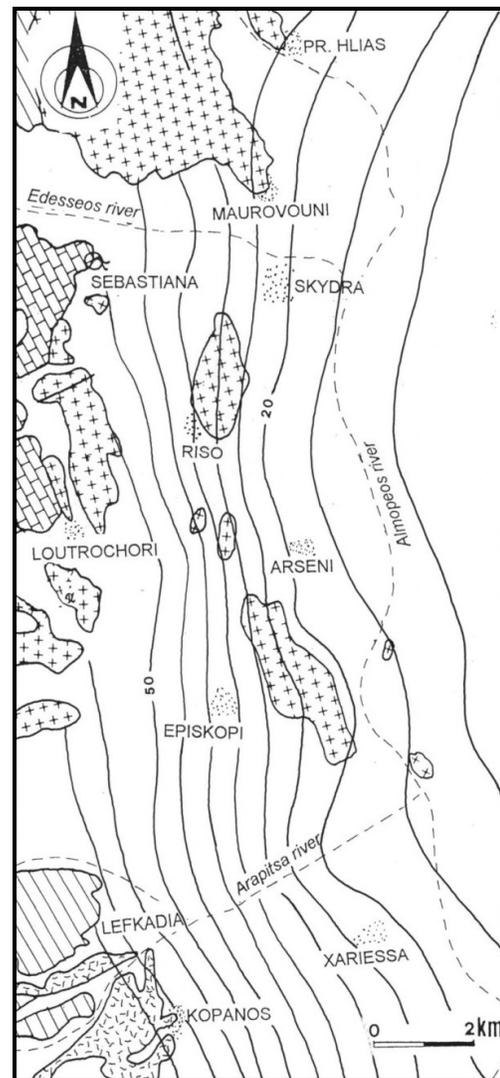


Figure 3: Piezometric map, relative to the month of May 1993 (in meters a.s.l.).

From the measurements of the water level and the consequently obtained piezometric map (Fig. 3), it is clear that the principal water supply of this multiaquifer comes from the west and flows to the east. Therefore, also according to the geological map (Fig 2), the aquifers are fed mainly from the carbonates formations of Sevastiana, the fracture zones within the ophiolitic series (Lefkadia zone) and partially from the volcanic formations outcropping in the north-western sector of Mavrovouni.

Hydrogeochemistry

Groundwater samples from 19 wells (Fig 2), with a homogeneous distribution in the study area, were collected during the month of May 1993 to examine the hydrochemical characteristics of the volcano-sedimentary aquifer. In order to obtain representative samples of the aquifer systems, at each site, sampling was performed after at least 20 minutes pumping.

Electrical conductivity (E.C.), pH, temperature of the water, were directly measured in the field. Subsequently, in the laboratory, the samples were analysed for the determination of major ions such as Ca, Mg, K, Na, SO₄, Cl,

NO₃, HCO₃ and SiO₂, using the standard procedure proposed by the U.S. Environmental Protection Agency (1974). The results of the major element concentrations of the groundwater samples are listed in table 1.

Based on the element concentrations (Tab. 1), the prevailing cation is represented by calcium with percentages between 26.6% and 74.2% of total cation concentrations, while the major anion is the bicarbonate, with percentages in the range of 70-92% of total anion concentrations. Moreover, the silica concentration varies from a minimum of 9.1 mg/l in well A4, to a maximum value of 59.8 mg/l in well P16 (Fig 2).

Table 1: Major concentrations in groundwater of Skydras area (concentrations are in mg/land the electrical conductivity (E.C.) in microS/cm a 20°C). For sample location, see Fig 2.

well	pH	E.C.	TDS	Ca	Mg	K	Na	HCO3	SO4	Cl	NO ₃	SIO2	Mg/Ca	SiO ₂ /Ca	hydrochemical type
A4	7,25	581,2	333	82,6	29,43	0,8	7,6	375	15	5,1	6,16	9,24	0,36	0,11	(Ca-Mg)-HCO3
B11	7,17	761	427	90,4	33,45	1,5	8,7	391,3	49	8,9	15,4	11,1	0,37	0,12	(Ca-Mg)-HCO3
B3	7,31	794,4	455	100,4	34,2	1,6	7,4	421	20	7,9	1,32	11,5	0,34	0,11	(Ca-Mg)-HCO3
D9	7,37	589,7	347	98	25,6	0,9	8,5	447,2	1	9,8	1,76	10	0,26	0,1	Ca-HCO3
G3	7,19	673,4	380	88	36,4	2,4	13,6	411	50	9,3	7,04	11	0,41	0,13	(Ca-Mg)-HCO3
G14	7,3	738	424	93,2	37,6	2,9	13,5	440	58	13	9,68	29,8	0,40	0,32	(Ca-Mg)-HCO3
G5	7,1	807,9	458	84	37,1	2,6	14,3	316	100	13,6	11	24,4	0,44	0,29	(Ca-Mg)-HCO3
G7	7,13	829,3	475	112	43,22	4,7	15,5	466,7	61	8,6	11,9	15,8	0,39	0,14	(Ca-Mg)-HCO3
L1	7,4	586,1	330	40	63,24	0,9	6,8	404,3	19	10	9,68	4,5	1,58	0,11	Mg-HCO3
M1	7,19	692	407	109,2	32,5	0,6	6,8	435	30	5,5	7,04	14	0,30	0,13	Ca-HCO3
P15	7,05	544,1	312	87,6	23,44	6,2	8,2	346	12	7,5	13,64	44,6	0,27	0,51	Ca-HCO3
P16	7,17	601,3	344	102,4	15,4	6,1	8,3	343,2	19	12,6	10,56	59,8	0,15	0,58	Ca-HCO3
P17	7,16	667,7	383	106,4	26,85	7	10,2	440	42	10,3	16,6	50,3	0,25	0,47	Ca-HCO3
P18	7,35	722,8	413	116	24,91	5,8	7,9	408,9	37	10,4	15,84	50,4	0,21	0,43	Ca-HCO3
P21	7,12	765,6	437	97	33	1,7	6,9	390	52	11,5	19,36	11,8	0,34	0,12	Ca-HCO3
P23	7,08	574	330	73,6	14,4	6,5	24	331,5	28	23,5	3,08	68,9	0,20	0,94	Ca-HCO3
P24	7,16	633	360	98,4	22,9	8	8,9	382,2	19	18,8	19,8	22	0,23	0,22	Ca-HCO3
P35	7,17	631	356	98,4	35,5	3,7	9,2	412	43	10,6	8,8	21,5	0,36	0,22	Ca-HCO3
X4	7	666,7	375	101	35,1	1	8,1	390,5	52	8	13,64	11,1	0,35	0,11	(Ca-Mg)-HCO3

The distribution of the hydrochemical results on the triangular diagram of Piper (1944) enables us to separate the waters with the same hydrochemical characteristics and the mixing processes between different water types. From the three-linear diagram, three major chemical facies can be identified (Table I; Davis and DeWiest, 1967): Ca-HCO₃, Mg-HCO₃ and (Ca-Mg)-HCO₃. The first facies is representative of waters coming from carbonate rocks, the second facies indicates feeding from fracture zones crossing the ophiolites of Lefkadia area (well L1, Fig 2), while the third facies results from the mixing of these two extreme types of waters.

It is well known that from the characteristic ratio of some ions and the index of saturation relative to different minerals it is possible to infer the provenance of the waters and the lithological characteristics of the permeated rocks (Plummer and Back, 1980; Hem, 1978; Matthes, 1982). In particular, for the Skydra area the Mg/Ca and SiO₂/Ca ratios (tab. I) have been calculated and analysed. The former is in the range 0.15-0.54, thus clearly indicating an alimentation from carbonate rocks, with the exception of the Lefkadia

area, where the ratio is anomalously high (1.58). The latter ratio (SiO₂/Ca) shows values between 0.11 e 0.58 which are much lower than commonly assumed for water coming from volcanic materials. The only exception is represented by P23 well, in the northern part of the study area (Fig 2), with a higher ratio of 0.93, probably indicating a 'volcanic' provenance of the waters. Moreover, the same well shows a positive value of the saturation index in Quartz (+1.17), thus further emphasising the local alimentation of the aquifer system from the volcanic formation of Maurovouni (Fig 2) consisting of latites and latitic-andesites (Eleftheriadis, 1977) whose main components are SiO₂ (4.0%), Na₂O (3.8%), K₂O (4.0%) and Al₂O₃ (17.4%).

Statistical analysis

The multivariate statistical techniques here applied allow to analyse and interpret numerous hydrochemical data in order to detect possible relationships among several variables and the similarities among samples (Davis, 1973; Ashley and Lloyd, 1978; Dalton and Upchurch, 1978; Lawrence and Upchurch, 1982; Greenacre, 1984). The principal aim of

these techniques is to reduce an initial large number of variables, as obtained from a huge amount of measurements, to a small number of new variables representing linear relationships between the initial variables. In the present research, the R-mode factor analysis has been applied. However, before the analysis, data have been standardised according to some of the criteria proposed by Davis (1973), while the correlation coefficient matrix has been generated with the requirement of a normal distribution of all variables. This correlation matrix gives the intercorrelation value among the set of variables. The factor extraction is performed with a minimum acceptable eigenvalue equal to 1 (Kaiser, 1958).

In order to further simplify the interpretation of the results, the factor loading matrix is rotated to a simpler system, according to varimax rotation. This procedure returns a new rotated factor matrix, where each factor is

described in terms of only these variables. This matrix thus allows the grouping of variables or factors and the estimation of the influence on particular samples as factor scores. Any variable may appear in one or more factors and its coherence to a particular group is expressed in terms of factor loading. According to the factor loadings, the communalities and the obtained eigenvalues, from the selected variables it is possible to distinguish the different chemical processes which occurred in the aquifer and to evaluate the importance of the major elements in terms of the total data set as well as of single factors. By applying the R-mode factor analysis to the hydrochemical data of the volcano-sedimentary aquifer of Skydra, five factors are emphasised which explain about 88.8% of the total variance of the analytical data (Tabl. 2). In the following, each factor is separately discussed.

Table 2: Varimax rotated factor matrix of major ions.

variable	factor I	factor II	factor III	factor IV	factor V	communality
Cl	0.889	0.041	-0.117	-0.191	-0.0003	0.84
K	0.787	-0.165	-0.0806	0.295	0.404	0.90
SiO ₂	0.735	-0.240	-0.162	0.387	0.006	0.77
Na	0.719	0.364	-0.225	-0.117	-0.442	0.91
SO ₄	0.28	0.909	-0.277	-0.081	0.110	0.92
E.C.	-0.102	0.857	0.270	0.219	0.052	0.87
pH	-0.082	-0.207	0.869	-0.176	-0.071	0.87
HCO ₃	-0.273	0.210	0.797	0.250	-0.033	0.82
Ca	-0.037	0.235	0.144	0.937	0.136	0.97
Mg	-0.447	0.391	0.375	-0.643	0.069	0.91
NO ₃	0.046	0.175	-0.182	0.061	0.948	0.97
eigenvalue	3,52	2,15	1,78	1,41	0,90	
variance (%)	32.1	19.6	16.2	12.8	8.2	

Factor I accounts for the 32.1% of the total variance of the element concentrations and is characterised by very strong positive loadings relative to the ions of chloride (79% of the chloride variance), potassium (54%), silicate (62%) and sodium (the 52%). This factor can be associated with the existence of tuff materials, which increases the concentration of the above listed ions, with maximum values in the P23 well. In fact, the area distribution of factor scores for this particular factor (Fig. 4a), shows very strong values around the Maurovouni area, thus indicating that the alimentation of the aquifer system comes from the volcanic formations as further confirmed by the piezometric map (Fig 3).

Factor II accounts for the 82.6% of the sulphate variance, the 73.5% of the electrical conductivity variance and the 19.6% of the total variance. This factor can be labelled as the 'electrical conductivity factor'. From the areal distribution of the loadings of this factor (Fig 4b), it is also possible to observe a progressive increase of positive scores from west to east, corresponding to a similar increase of the

electrical conductivity along the flow lines.

Factor III consists of 75.6% of the pH variance, of 63.6% of the bicarbonate variance and accounts for 16.2% of the total variance. This factor can be labelled as the 'pH factor' and indicates the alkalic character and the quick renewal of the waters. Also, by comparing the areal distribution of the loadings of this factor (Fig 4c) and the pH values (Fig 5a), the existence of strong relationships between these two parameters can be clearly envisaged.

Factor IV accounts for 12.8% of the total variance of the element concentrations and is characterised by very strong positive loadings in the ions of calcium (88% of the calcium variance) and magnesium (41.3%). This factor is here labelled as the 'calcium factor' and is straightforwardly associated to the presence of carbonate formations in the surrounding mountains. In fact, in the Lefkadia area, where the underground water circulation mainly occurs across fracture zones pervading the ophiolitic formation, the loadings of factor IV show strong negative values (-2.5). Eventually, the areal distribution of factor scores for this

factor, indicates a very strong correlation with the spatial distribution of the calcium concentration (Fig. 5b).

At last, *factor V* accounts for 8.2% of the total variance of the element concentrations and is characterised by very strong positive loadings in the ions of nitrate (90% of the nitrate variance). This factor is labelled as the 'pollution factor' and is obviously related to the diffuse agriculture

practices and the application of chemical fertilisers. Also, the areal distribution of the loadings of this factor and the NO_3 values (Fig. 5c), indicates the strong relationship between these two parameters, as emphasised by positive loading values and high concentrations in NO_3 in the central sector of the study area.

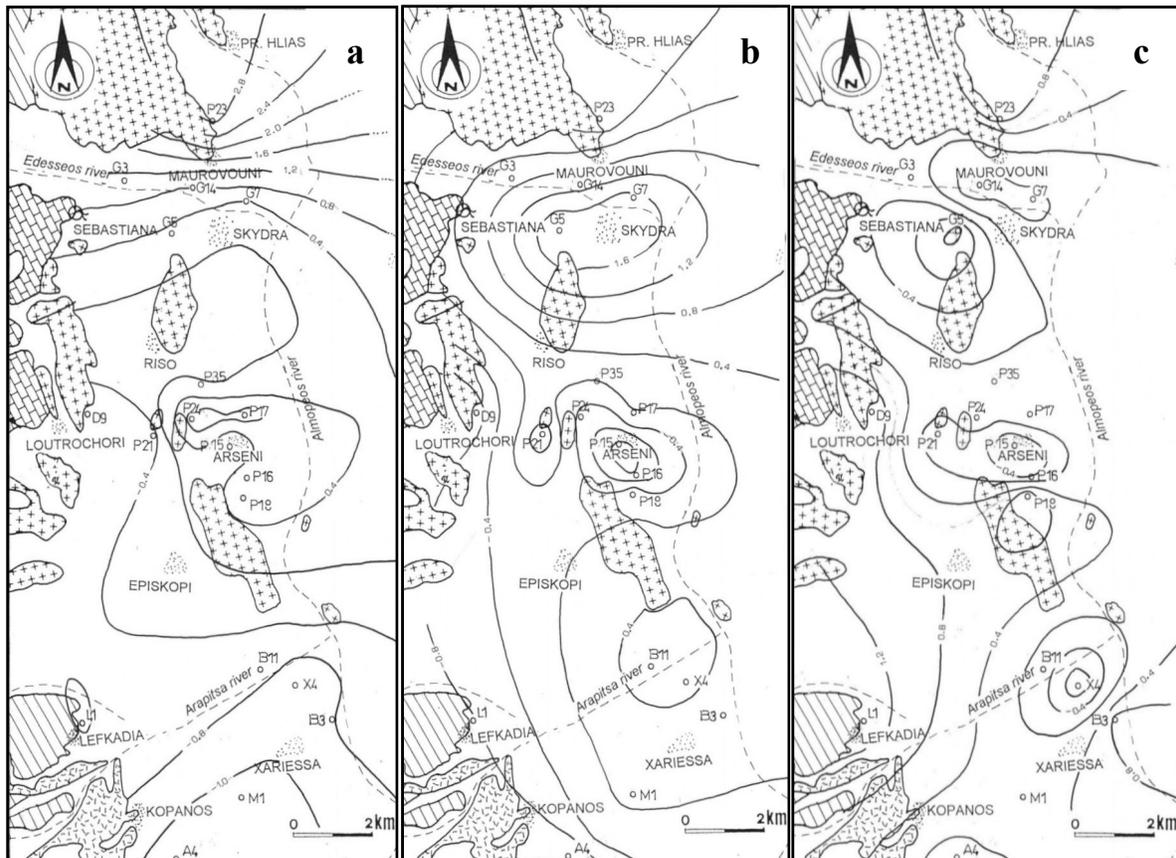


Figure 4: Distribution of a) I factor; b) II factor; c) III factor; and location of samples collection. See text for further explanations.

Concluding remarks

The investigated volcano-sedimentary multiaquifer of the Skydra region is mainly developed within tuffs materials, with alternating layers or lenses of sand and pelites. Although there is a general southward increase of the total thickness, values vary between a minimum of 25 m and a maximum observed value of 250 m.

The geomorphologic evolution of the area, the Pliocene-Quaternary volcanic activity in the northern sectors and the areal distribution of carbonate and metamorphic rocks, along the western border of the plain have clearly strongly influenced the hydrogeological setting and the hydrochemical characteristics of the aquifer.

The principal alimentation area of this multiaquifer system is represented by the lithological formations outcropping in the western sector of the investigated area, as clearly emphasised by the trends of the piezometric map

(Fig 4). Secondary contribution is the direct infiltration (15.6%) of the atmospheric precipitation.

From the analysis of the concentrations of the principal ions it can be observed that the predominant cations and anions in decreasing order are $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3 > \text{SO}_4 > \text{Cl} > \text{NO}_3$, respectively, while the ionic concentration in SiO_2 varies between 9.1 and 68.9 mg/l.

Furthermore, in the waters of this volcano-sedimentary aquifer three hydrochemical facies can be distinguished: i) the Ca-HCO_3 , in the central sector of the investigated area, is clearly related to the western provenance across the carbonate rocks (Fig 2); ii) the Mg-HCO_3 , characterising the Lefkadia area, is due to the alimentation from numerous fracture zones cross cutting the ophiolitic formations and iii) the Ca-Mg-HCO_3 , in the northern and southern sectors, is probably associated to mixing phenomena of the two above described facies.

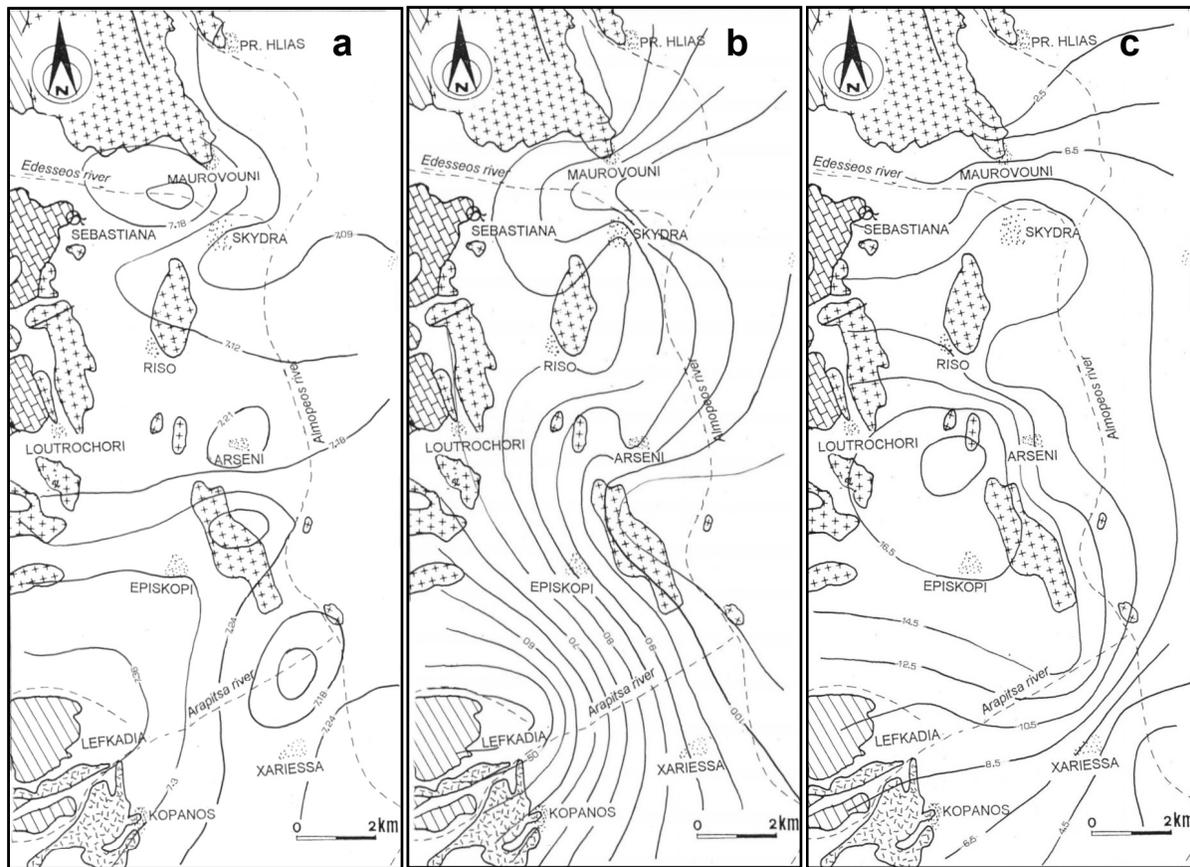


Figure 5: Distribution of a) pH values; b) Ca (mg/l); and c) NO_3 (mg/l) concentration.

From the application of the factor analysis to the investigated volcano-sedimentary aquifer and due to the existence of multiple source areas, it is not possible to recognise a dominant factor solely accounting for most of the initial variance. Nevertheless, five factors with comparable weight and accounting for the 88.8% of the total variance have been distinguished. Accordingly, these factors well describe the aquifer alimentation from volcanogenic materials in the northern sector (factor I) and the water pollution due to high contents of nitrates (factor V).

Eventually, with the present research I wish to emphasise that the integrated study of the hydrochemical characteristics of the underground waters performed with

classical hydrogeological approaches and compared to multivariate statistical techniques offers interesting results by permitting a more comprehensive recognition and detailed grouping of the hydrochemical facies, of the mixing phenomena and of the alimentation sources. These encouraging results are further reinforced by the fact that the factors obtained from the multivariate analysis properly reflect, and correlate with, the regional geology and the human impact.

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