

**Research Paper****STATISTICAL APPROACH OF GROUNDWATER QUALITY ASSESSMENT  
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**Abstract**

*Groundwater quality is substantial for social and economic activities in Greece since the majority of the cultivated land is irrigated by water abstracted from aquifers, via a large number of wells and boreholes. The main sources of groundwater pollution are the fertilizers used in agriculture, and the disposal of untreated wastewater from domestic and industrial use. The plain part of Almopia basin, North Greece, is a rural area with intense agricultural activities (including livestock), without significant industrial activity or urban centers. Mild touristic activity has been developed during the last decades in the area of Loutraki, due to the exploitation of the local geothermal field (Pozar springs) for balneotherapy. The aim of this paper is to evaluate the groundwater quality using conventional statistical methods, as well as to employ multivariate statistical methods (factor analysis, cluster analysis) in order to identify the main hydrogeological processes or human activities that affect and determine the water character. The area was selected because of the extended cultivating activities that take place within its boundaries and the availability of adequate data. According to the results of the implemented research, the groundwater samples are of good quality, whereas the chemical composition is mainly formed by the interaction between the water and the geological formations.*

**Keywords:** *Almopia, groundwater quality, multivariate statistics.*

## Περίληψη

*Η ποιότητα των υπόγειων νερών είναι σημαντική για την κοινωνία και την οικονομία στην Ελλάδα, καθώς η πλειονότητα των καλλιεργούμενων εκτάσεων αρδεύεται από το νερό που αντλείται από τους υδροφορείς μέσω μεγάλου αριθμού πηγαδιών και γεωτρήσεων. Οι κύριες πηγές ρύπανσης των υπόγειων νερών είναι τα λιπάσματα που χρησιμοποιούνται στη γεωργία και η διάθεση ακατέργαστων λυμάτων από οικιακή και βιομηχανική χρήση. Το πεδινό τμήμα της λεκάνης της Αλμωπίας είναι μια αγροτική περιοχή με έντονες γεωργικές δραστηριότητες (συμπεριλαμβανομένης της κτηνοτροφίας), χωρίς σημαντική βιομηχανική δραστηριότητα και αστικά κέντρα. Στην περιοχή αναπτύσσεται γεωθερμικό πεδίο που συμβάλλει στην ανάπτυξη ήπιων τουριστικών δραστηριοτήτων γύρω από την περιοχή Λουτρακίου τις τελευταίες δεκαετίες. Σκοπός της εργασίας είναι η αξιολόγηση της ποιότητας των υπόγειων νερών με τη χρήση συμβατικών στατιστικών μεθόδων και η χρήση πολυμεταβλητών στατιστικών μεθόδων (ανάλυση παραγόντων, ανάλυση σε συστάδες) προκειμένου να προσδιοριστούν οι κύριες υδρογεωλογικές διεργασίες ή οι ανθρώπινες δραστηριότητες που επηρεάζουν και προσδιορίζουν τον χαρακτήρα του νερού. Η περιοχή επελέγη για μελέτη λόγω των εκτεταμένων καλλιεργητικών δραστηριοτήτων εντός των ορίων της και της διαθεσιμότητας επαρκών δεδομένων. Τα αποτελέσματα της έρευνας έδειξαν ότι η ποιότητα των υπόγειων νερών είναι καλή και διαμορφώνεται κυρίως από την αλληλεπίδραση του νερού με τους γεωλογικούς σχηματισμούς.*

*Λέξεις κλειδιά:* Αλμωπία, ποιότητα υπόγειου νερού, πολυμεταβλητή στατιστική.

## 1. INTRODUCTION

Water is one of the most important substances on earth, since plants, animals and humans need water to survive and grow. Fresh water can be found in rivers, lakes or in aquifers (as groundwater), which usually interact. For example, changes to river flow regime can affect the recharge of the local aquifers, or, on the other hand, a change in the groundwater level could affect the river flow regime, resulting in alterations of the ecosystems' fauna and flora (Harwood et al. 2017). Human abstractions, in order to meet drinking, irrigation and industrial demands, often cause severe damages to the natural circle of the water resources, especially in cases of overexploitation, where the abstraction rate exceeds the replenishment rate. The combination of overexploitation and climate change, assert pressure on water resources and environment, threatening food security and human well-being.

The sustainability of many regions in Greece relies on groundwater, since it constitutes a major part of the available fresh water resources. Therefore, the monitoring of its quality and quantity is crucial for achieving effective integrated management and designing appropriate policies. Groundwater quality and quantity status is determined by the characteristics of the geological formations, the climatic conditions, the land use, and the human activities (Burri et al., 2019; Helena et al., 2000; Chan, 2001).

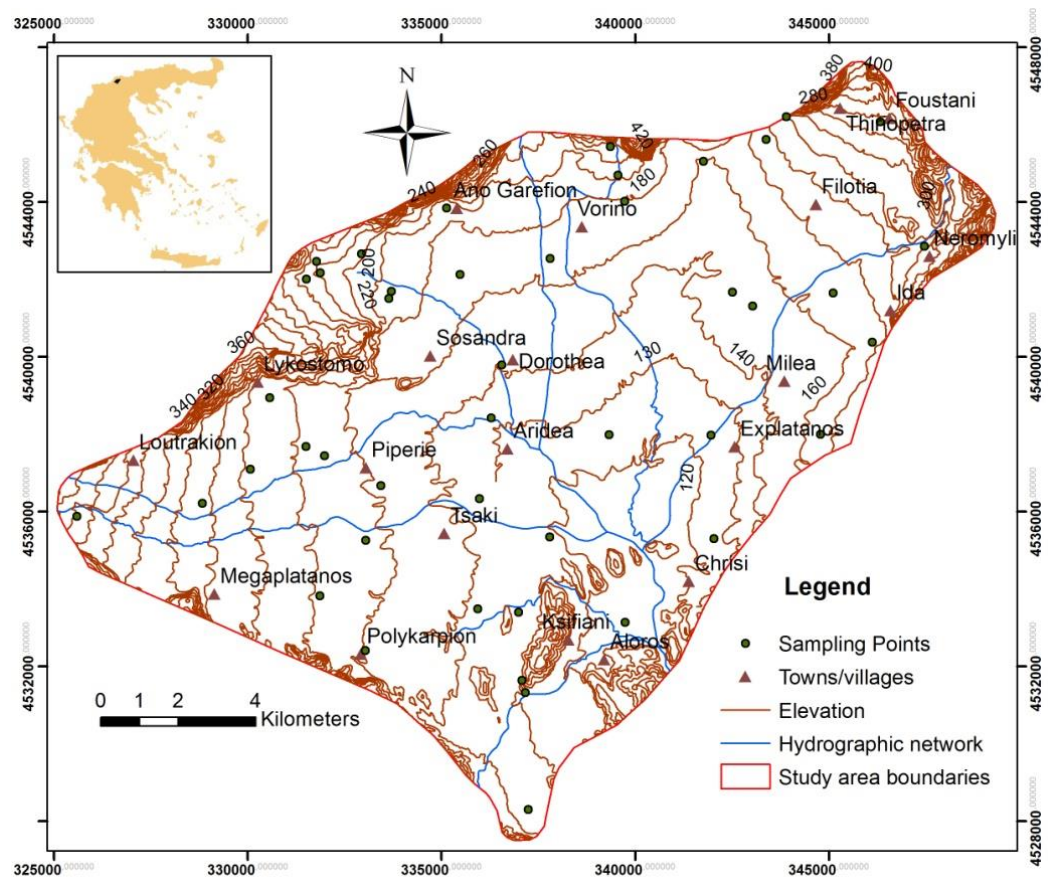
There are many different approaches for the water quality investigation, based on statistics, graphical methods, ratios etc. All these methods have been used over the years to classify water samples in groups and to identify the main processes and the origin of groundwater (Freeze and Cherry, 1979; Karanth, 1987; Sara and Gibbons, 1991; Kim et al. 2002; Zhu et al. 2007). The disadvantage of the aforementioned methods is that they do not take into account the human activities and their impact on groundwater quality. Therefore, multivariate statistical techniques (Dehghanzadeh et al., 2014; Subyani and Al Ahmadi, 2010; Purushothaman et al., 2014; Suresh et al., 2009; Saleem et al., 2015) have been enabled the last decades as a useful tool for the distinction of anthropogenic and geogenic factors that shape water composition in complex geological and hydrogeological systems.

The most common methods used in literature are Factor Analysis and Cluster Analysis. Geostatistical techniques constitute another tool of major importance for scientists, managers and policy makers the recent years (Jha et al., 2007; Steube et al., 2009; Machiwal and Jha, 2010), especially when they are combined with multivariate statistical techniques. Geostatistical techniques applied in a GIS context provide mapping of parameters values, depiction of spatio-temporal variation, as well as simultaneous combined illustration of large volume of different types of data on different layers (Jeong, 2001; Güler and Thyne, 2004; Valdes et al., 2007). Kriging includes a group of geostatistical techniques that are used to interpolate observed values at unobserved locations in a random field (Guey-Shin et al., 2011). The coupling of these methods allows the identification of all the possible factors that determine the chemical characteristics of water systems.

The aim of the work presented in this paper, is to identify hydrogeological or human processes that control the groundwater quality in the aquifers developed in the central alluvial part of the Almopeos River basin (Region of Central Macedonia, north Greece).

## 2. STUDY AREA

The study area administratively belongs to the Almopia Municipality of the Region of Central Macedonia and covers an area of 240 km<sup>2</sup>. The mean altitude is 175.5 m. The minimum and maximum altitudes are 111.5 m and 492 m, respectively (Fig. 1). According to data from the rain gauge installed in Exaplatanos village, the annual rainfall is 610 mm for the time period 1975-2006. The main geological formations that outcrop in the river basin are gneisses, schists, marbles, ophiolitic rocks, volcano-sedimentary series, limestones and flysch (Fig. 2). The central part of the basin, i.e. the study area, is covered by sediments that are mainly composed of clayey, clayey-sandy, clayey-gravelly depositions, clay-sand-gravel material, colluvial deposits, conglomerates and pyroclastic volcanic material (Mercier, 1966; Mountrakis, 2010). The thickness of the sediments at the area of Sossandra village ranges from a few tens of meters to 760 m. According to geological and geophysical data from the area, the maximum thickness of the sediments exceeds 2 km (Thanasoulas, 1985; Vougioukalakis, 2002).

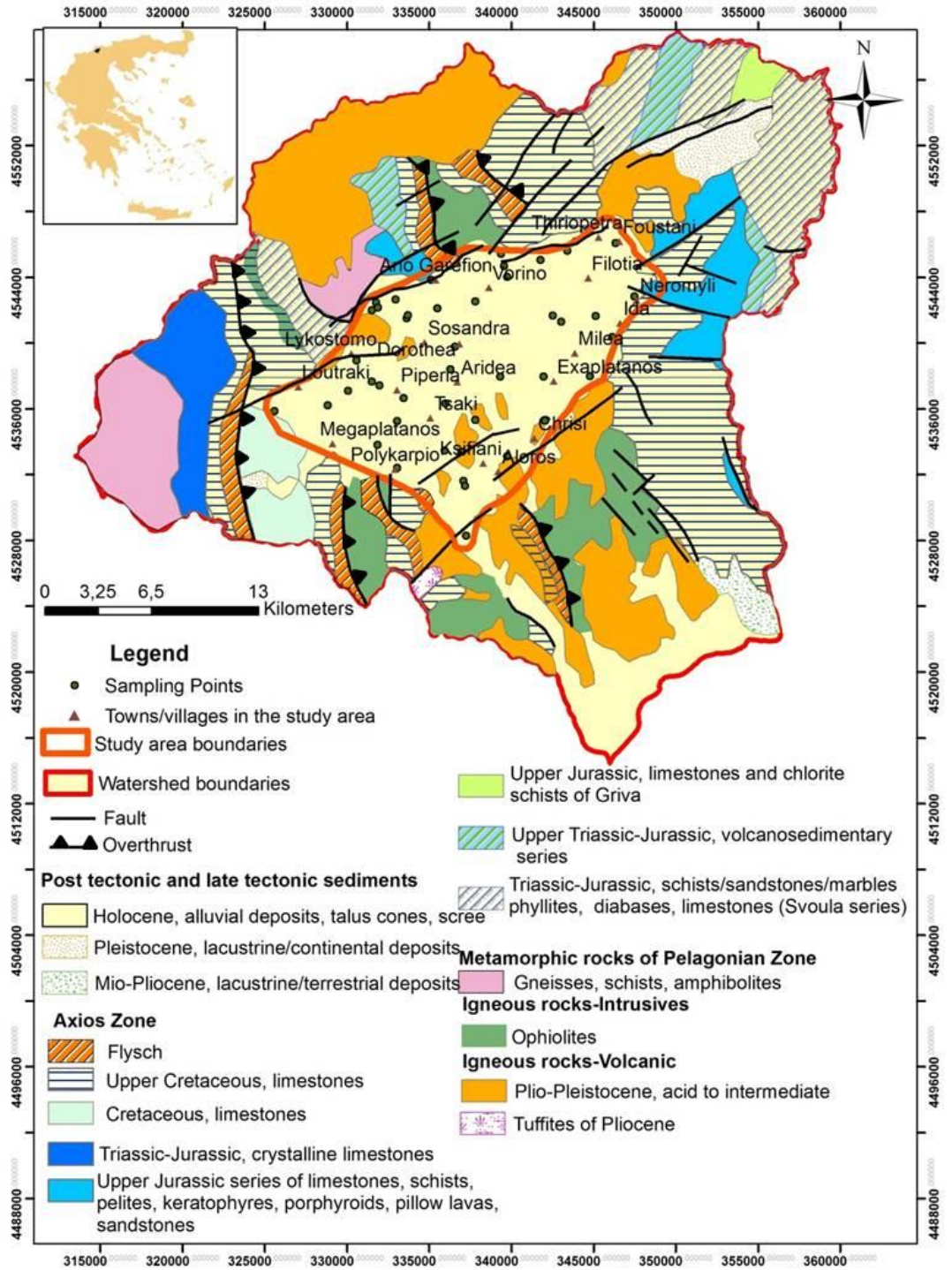


**Fig. 1:** Topographic map of the study area.

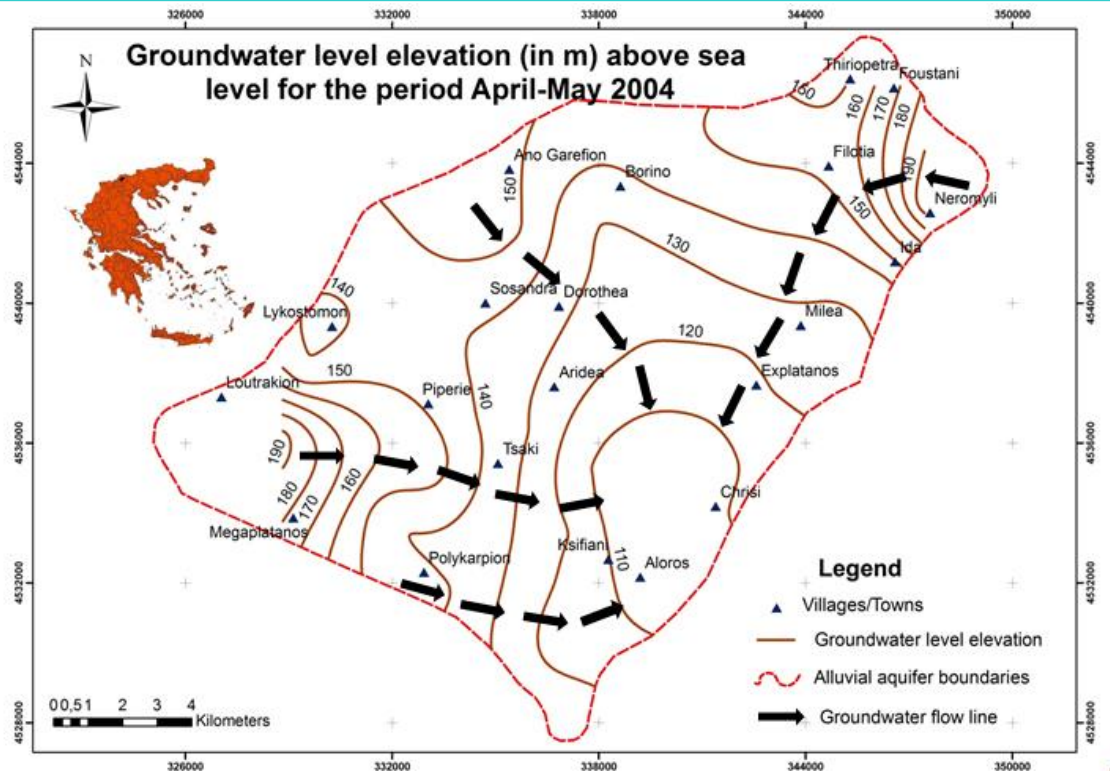
A system of successive confined and unconfined aquifers is developed inside these sediments and the mean thickness of the aquifers is approximately 52 m. The hydraulic conductivity ranges from  $10^{-4}$  m/s to  $10^{-6}$  m/s in the alluvial deposits that occupy the largest part of the study area. The talus cones and scree manifestations at the boundaries of the aquifer system have small extent and show high to medium hydraulic conductivity values ( $10^{-4}$  m/s to  $10^{-5}$  m/s). The volcanic rocks (tuffs) at the south-southeast part of the study area are characterized by medium to low hydraulic conductivity values ( $10^{-5}$  m/s to  $10^{-7}$  m/s). The groundwater discharge rates from the wells in the study area range between 25 and 280 m<sup>3</sup>/h (Veranis et al., 2010), with the mean value at 105 m<sup>3</sup>/h (sample of 100 wells).

The higher flow rates are observed at the north-east part of the study area, near the villages Neromyli, Filotia, Milea (Fig. 1). As regards the hydrogeological regime, the alluvial aquifers are recharged by precipitation and laterally by the surrounding mountainous karst formations (Mattas et al., 2017). The groundwater flow follows the main axes of the hydrographic network and the surface topography (Fig. 3). Groundwater level measurements implemented by I.G.M.E. during the decades of 1980, 1990 and 2000, recorded a continuous water level drawdown of 0.16 m per year over the period 1984-2007 (Veranis et al., 2010). However, this trend seems to have been reversed, as it is evidenced by the measurements performed by the authors in 2017 (Mattas et al., 2017).

Twenty-one (21) villages are located within the boundaries of the study area, with a population of 27556 inhabitants, according to the 2011 census. The population density is relatively low (114.8 inhabitants/km<sup>2</sup>). The main anthropogenic activities that have affected the groundwater quality are agriculture and livestock farming. The main cultivations are fruit bearing trees and irrigated crops (such as maize, clover, vineyards, sunflower). In addition, a few food processing units, as well as touristic resorts and a balneotherapy center (in Pozar thermal springs) exist in the area. Domestic wastes and old landfills constitute possible pollution sources. According to the available data derived from the research conducted by I.G.M.E. (Veranis et al 2010), the groundwater samples are of good quality and are appropriate for domestic and irrigation purposes. In a small number of samples, the concentration of Fe, Mn, B and As exceed the maximum permissible value for drinking purposes set by the World Health Organization. This is attributed to the nature of the geology formations and the existence of the low temperature geothermal system (Veranis et al., 2010; Veranis et al., 2015).



**Fig. 2:** Geological map of the Almopeos River basin, based on the Geological Map of Greece, scale 1:500000 published by I.G.M.E (Bornovas and Rondogianni-Tsiambaou, 1983) and Ganas et al. (2013).



**Fig. 3:** Groundwater flow for the period of April - May 2004 (Mattas et al., 2017).

### 3. MATERIALS AND METHODS

A total of 52 groundwater samples were collected during the dry and wet periods of the years 2004 to 2007 by I.G.M.E. (Veranis et al., 2010). The sampling points are illustrated on the map of Fig. 1 and Fig. 2. The depth of the wells ranges from 30 m to 220 m from the ground surface. The samples come from different depths of the successive unconfined and confined aquifers that are developed in the Quaternary deposits. According to Veranis et al (2010) there is hydraulic connection between the confined and unconfined aquifers and therefore the samples in many cases are the result of a mixing process. This can also be attributed to the great range of the depth of the wells that drill different successive aquifers. The sampling network is adequately distributed and, therefore, is considered representative for the area. The measurement of the physicochemical parameters such as the Electrical Conductivity (EC) of water and pH was performed in situ, whereas the chemical analyses for the main ions (Ca, Mg, Na, K,  $\text{HCO}_3$ , Cl,  $\text{SO}_4$  and  $\text{NO}_3$ ) was conducted in the laboratory of the Institute of Geology and Mineral Exploration in Thessaloniki.

The groundwater samples were collected from wells, after sufficient pumping time, so as to obtain steady pH and EC values, securing that the water comes from the examined

aquifer and was not stagnant in the borehole. Samples were collected in prewashed high-density polypropylene bottles and were in situ washed with the sampled water. The bottles were transferred to the laboratory in a portable cooler box very soon after they were collected. The samples were acidified with  $\text{HNO}_3$ . This time period that was chosen for this study, was selected because during these four years (2004-2007) no significant changes of the hydrogeological and climate conditions or of the water resources exploitation regime were observed, that could result in insignificant variation in the quality status. For the treatment of the data set, classical descriptive statistical methods combined with multivariate statistical methods were used.

Descriptive statistics include mean-minimum-maximum value and standard deviation. These parameters are used to evaluate water quality in an initial stage, by comparing the samples with typical values proposed in literature and by legislation or international organizations standards (e.g. World Health Organization, Water Framework Directive 2000/60 etc.). The standard deviation was used as a measure of the amount of variation of the data set. The samples were divided in groups according to the sampling period. Twenty (20) samples were collected during the dry period of the years 2004-2007 and thirty two (32) samples over the wet period of the same years. Each group of samples was investigated separately using descriptive statistics. The Correlation Coefficient Matrix (Pearson Correlation) is a statistical tool that shows the degree of dependency between two variables. It is used to measure and establish the relationship (Belkhiri et al., 2011; Khan, 2011) that depicts the influence of water rock interaction on water quality (Athuman and Nkotagu, 2012; Ukandu et al., 2011). The R-mode factor and K-means cluster analyses were implemented to investigate the relation between various parameters, in order to identify the prevailing hydrogeological processes that determine the hydrochemical regime of the area. Factor analysis (FA) is a multivariate statistical technique, which has been widely used in environmental and hydrogeological research. The relationship among a large number of observed quantitative variables is represented by a small number of independent variables, which are called factors. The credibility of the applied method on the dataset is investigated by using the Kaiser-Meyer-Olkin coefficient. Values higher than 0.5 are considered valid. Factors that show eigenvalues higher than one are selected to explain the total variance (Cattell, 1978). The ordinary kriging method (spherical model) was applied for the interpolation of the factor scores and the construction of spatial distribution maps. Factor score values equal or greater than zero reveal that the corresponding factor has an impact on the area. Negative values show that there is no impact of the process the factor describes on that area.



K-means clustering uses criteria to classify the samples of a dataset, into K clusters (groups or categories), based on intrinsic characteristics, proximity, or degree of similarity (Bonansea et al., 2015), represented by centroids (Hancer and Karaboga, 2017). For the application of the multivariate statistical methods all the collected samples were treated together. These methods have been applied by many scientists that investigate the quality of water resources and the factors that affect it in several case studies in Greece for several case studies in Greece (Lappas et al., 2014; Tziritis et al., 2016; Tziritis et al., 2017; Kazakis et al., 2017).

#### 4. RESULTS-DISCUSSION

The results of the descriptive statistical methods are presented in Table 1. The samples correspond to typical good quality waters, since these values do not exceed the maximum permissible limit for drinking or irrigation purposes set by the World Health Organization, the European Water Framework Directive 2000/60 and the Greek legislation. According to the results presented in Table 2, Pearson coefficient shows strong correlation between EC-Ca-Mg-HCO<sub>3</sub>, which is rather expected as EC is a dependent variable and depends on the values of ions that exist in water. This correlation is attributed to the dissolution of karstic rocks. Additionally, high correlation was observed between Na-Cl and pH-SO<sub>4</sub>, probably due to the existence of the geothermal system at the western boundaries and the central part of the alluvial plain (Arvanitis et al., 2008).

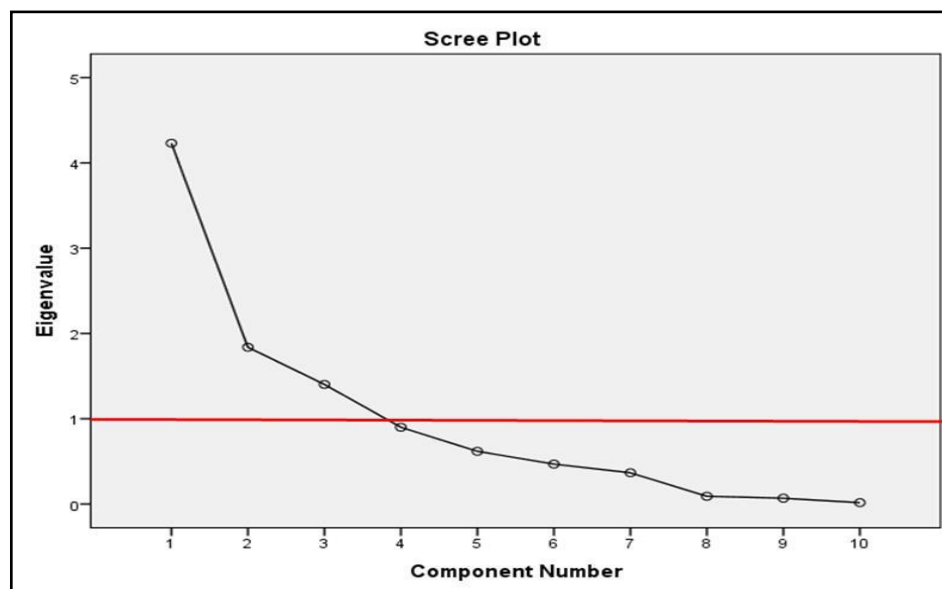
The R-Factor analysis resulted in three (3) factors showing eigenvalues higher than one (Fig. 4) that interpret 74.726% of the total variance. The Kaiser-Meyer-Olkin coefficient is 0.604 (>0.5), and, hence, the method is considered valid. The parameters that participate in each Factor are shown in Table 3. The spatial interpolation of the factor scores is depicted in Figures 5, 6, 7. EC, Ca, Mg and HCO<sub>3</sub> participate in Factor 1. These variables are associated to the carbonate rocks dissolution by water and it has positive value in the northwestern and eastern boundaries of the area (Fig. 5), where lateral recharge of the alluvial aquifers from karstic rocks take place. It could also be an indicator of meteoric water or of small residence time inside the aquifer. This hypothesis is enhanced by the ionic ratios of (Ca+Mg)/(Na+K), Na/Ca and Na/(Na+Ca) that have been estimated in previous studies (Veranis et al., 2010), and reveal that the recharge zone is near the samples' locations, as well as that the recharge of the aquifers is continuous.

**Table 1.** Summary statistics of the groundwater samples quality characteristics.

	(n=20)	pH	EC	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	NO <sub>3</sub>
<b>DRY PERIOD</b>	MEAN	7.5	417.4	47.9	16.7	8.0	2.4	213.1	7.4	27.8	11.6
	MIN	7.3	267.0	24.1	3.9	3.0	1.0	123.8	3.5	15.7	0.9
	MAX	7.8	776.0	67.3	34.0	29.0	6.0	455.7	28.4	51.2	45.3
	STDEV	0.2	138.7	14.1	8.2	6.0	1.0	80.5	5.6	8.5	10.4
	(n=32)	pH	EC	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	NO <sub>3</sub>
<b>WET PERIOD</b>	MEAN	7.54	426.91	56.37	15.85	9.91	2.88	223.83	11.96	27.18	8.40
	MIN	6.77	140.40	22.44	0.97	3.00	1.00	62.22	3.54	9.30	0.00
	MAX	8.11	1369.00	206.17	44.76	62.00	6.00	835.70	113.47	70.00	47.08
	STDEV	0.33	234.49	33.96	11.33	12.11	1.24	141.96	20.11	14.63	10.97

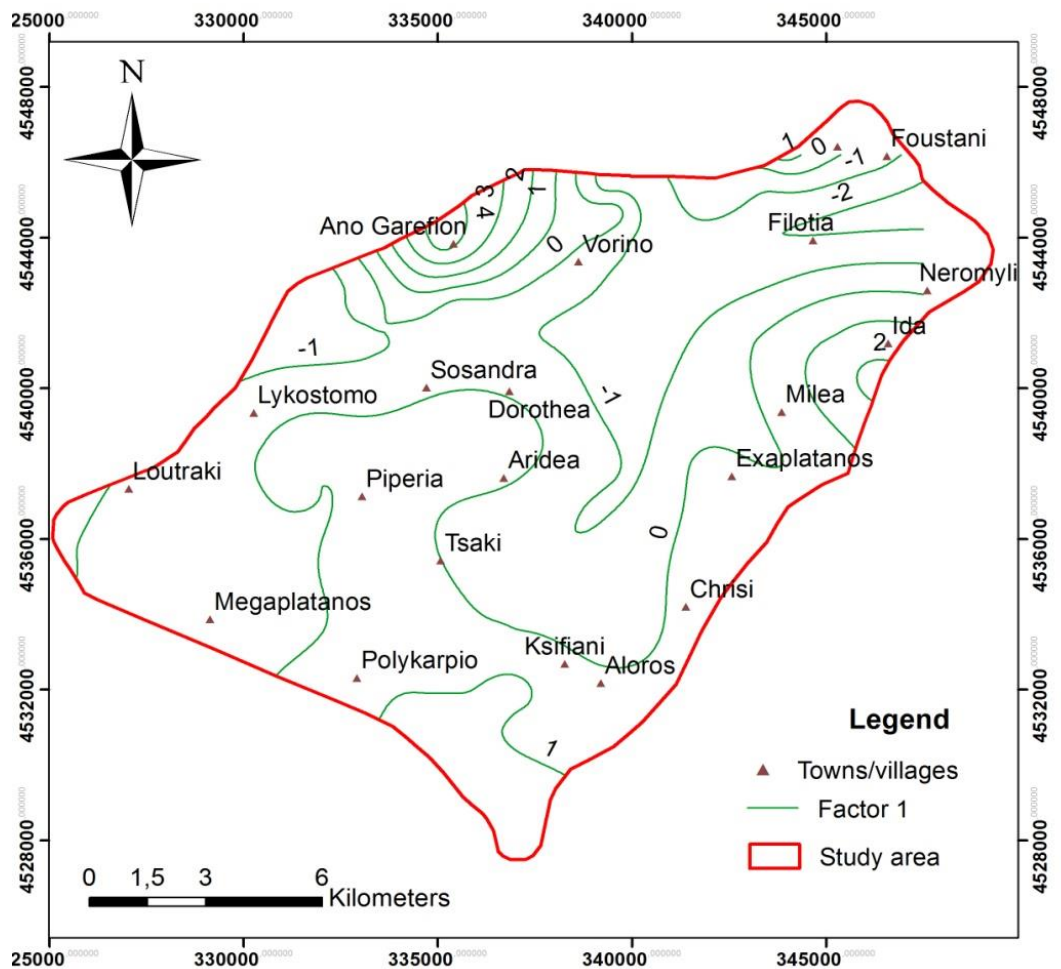
**Table 2.** Pearson coefficient of the total number of samples for the 2004-2007 period.

	EC	pH	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	NO <sub>3</sub>
EC	1	-.215	<b>0.884</b>	<b>0.754</b>	0.57	.041	<b>0.859</b>	0.491	0.412	0.414
pH	-.215	1	-.121	-.032	-0.452	.129	-.093	-0.499	<b>.089</b>	-.027
Ca	<b>0.884</b>	-.121	1	0.51	0.36	-.072	<b>0.857</b>	.271	.246	0.295
Mg	<b>0.754</b>	-.032	0.51	1	.258	.263	<b>0.73</b>	.248	0.456	0.347
Na	0.57	-0.452	0.36	.258	1	.100	0.31	<b>0.897</b>	.217	.101
K	.041	.129	-.072	.263	.100	1	.007	.119	0.331	.012
HCO <sub>3</sub>	<b>0.859</b>	-.093	<b>0.857</b>	<b>0.73</b>	.310*	.007	1	.204	.185	.272
Cl	0.491	-0.499	.271	.248	<b>0.897</b>	.119	.204	1	0.286	.003
SO <sub>4</sub>	0.412	<b>.089</b>	.246	0.456	.217	0.331	.185	0.286	1	0.355
NO <sub>3</sub>	0.414	-.027	0.295	0.347	.101	.012	.272	.003	0.355	1

**Fig. 4:** Scree plot depicting eigenvalues versus components. The Kaiser criterion (eigenvalues equal or higher than one) is shown with red line.

**Table 3.** Factor analysis results for the hydrochemical data.

	Component		
	FACTOR 1	FACTOR 2	FACTOR 3
EC	<b>0.906</b>	0.373	0.119
pH	-0.004	<b>-0.736</b>	0.257
Ca	<b>0.889</b>	0.193	-0.112
Mg	<b>0.764</b>	0.077	0.381
Na	0.235	<b>0.888</b>	0.157
K	-0.071	0.015	<b>0.816</b>
HCO <sub>3</sub>	<b>0.928</b>	0.117	-0.060
Cl	0.130	<b>0.922</b>	0.219
SO <sub>4</sub>	0.330	0.079	<b>0.743</b>
NO <sub>3</sub>	0.503	-0.101	0.228

**Fig. 5:** Spatial distribution of Factor 1 scores.

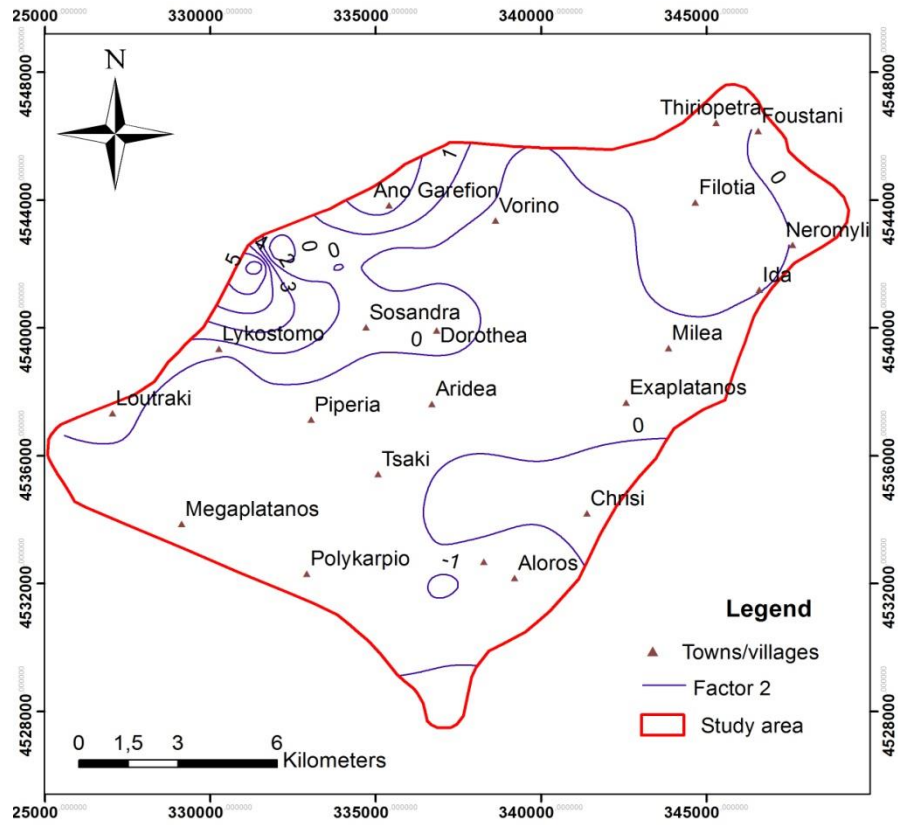


Fig. 6: Spatial distribution of Factor 2 scores.

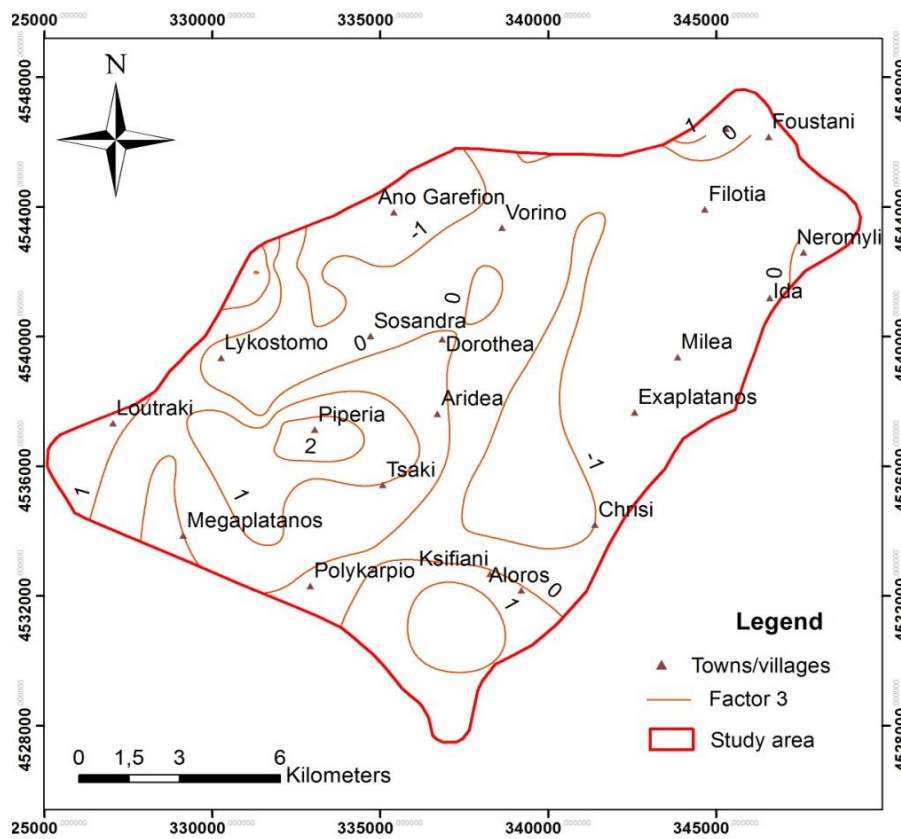


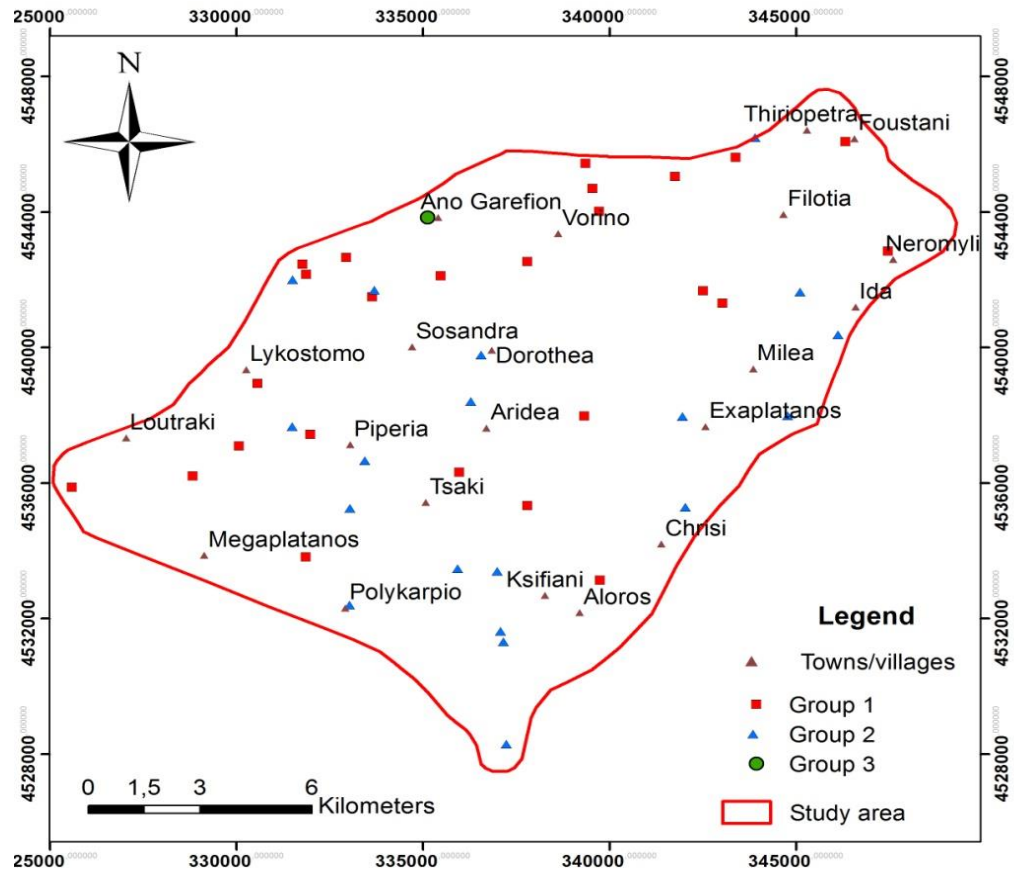
Fig. 7: Spatial distribution of Factor 3 scores.

Na, Cl and pH participate in Factor 2, and have positive values (Fig. 6) almost everywhere inside the basin, with higher values at the western boundaries. The sodium (Na) values could be attributed to the ion-exchange between water and volcanic-schistolithic rocks, whereas chloride (Cl) to the pollution from geothermal fluids. K and SO<sub>4</sub> participate in Factor 3 showing positive values at the north and western parts of the basin (Fig. 7). This could be explained by the existence of the geothermal field at the western boundaries and the agricultural activities. The K-means cluster analysis groups the samples according to their similarities. The final number of groups is a subjective decision made by each researcher. In this case study, three groups were selected. In K-means clustering, each cluster is represented by its centre (i.e., *centroid*), which corresponds to the mean of points classified to the cluster. The results are shown in Table 4.

The samples of the first group mainly appear at the western boundaries of the study area, where lateral recharge from the mountainous rocks takes place (Fig. 8). The samples of the second group are located at the eastern boundaries and they obtain higher values compared to the first group. This is mainly due to the ionic exchange between the geological formations and the water as it flows through the sediments of the plain part of the basin (Fig. 8). The third group includes only one sample with different water quality. This sample was collected at a site close to a geothermal spring and is probably affected by the geothermal fluids.

**Table 4.** Final Cluster Centers.

	Cluster Centres		
	1	2	3
Number of samples	30	21	1
EC	299.02	555.69	1369.00
pH	7.55	7.55	7.02
Ca	40.39	64.00	206.20
Mg	10.72	22.62	44.76
Na	5.83	12.48	39.00
K	2.57	2.90	2.0
HCO <sub>3</sub>	160.49	274.96	835.7
Cl	5.79	14.86	46.09
SO <sub>4</sub>	23.94	32.27	29.30
NO <sub>3</sub>	6.24	14.96	0.44



**Fig. 8:** Spatial distribution of clusters.

## 5. CONCLUSIONS

The groundwater resources of the study area are of good quality and fulfill the requirements of both domestic and irrigation demands. The main factor that determines the chemical composition of the water is the local geology and the existence of the geothermal field, which however affects the water quality of very few samples at a local scale. The anthropogenic activities have a very small impact on the groundwater quality. A very small number of samples show increased values of nitrates coming from fertilizers, yet, they do not exceed the maximum allowable value set by the World Health Organization for human consumption.

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