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Statistical approach of groundwater quality parameters at Almopia basin, Macedonia, North Greece.

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Introduction

The aim of this work is to present the groundwater quality characteristics and to identify the hydrochemical processes of the central alluvial part of the Almopeos river basin that administratively belongs to Almopia Municipality (Macedonia, North Greece) and covers an area of 240 km^2. The main geological formations that outcrop in the river basin are gneisses, schists, marbles, ophiolitic rocks, volcano-sedimentary series, limestones and flysch. The central part that constitutes the study area, is covered by sediments that are mainly composed of: clayey, clayey-sandy, clayey-gravely depositions, clay-sand-gravel material, colluvial deposits, conglomerates and pyroclastic volcanic material. A system of successive confined and unconfined aquifers is developed in these sediments. The main anthropogenic activities that have impact on the environment in the area are agriculture and livestock farming. There are also a few food processing units and touristic activities at Pozar thermal springs area. The main cultivations are fruit bearing trees and irrigated crops (such as maize, clover, vineyards, sunflower). Regarding the hydrogeological regime of the study area, the alluvial aquifers are recharged by the precipitation and lateral by the mountainous karstic formations that surround them (Mattas et al 2017). Groundwater level measurements that were implemented by I.G.M.E. during the decades of 1980, 1990 and 2000 recorded a continuous water level drawdown but this trend seems to reverse according to measurements that were implemented by the authors of this work in the year 2017 (Mattas et al 2017).

Materials and methods-Results-Discussion

A total of 52 groundwater samples were collected over the dry and wet periods of the years 2004 to 2007 by I.G.M.E.. In situ measurements of the physicochemical parameters (EC, pH) took place and chemical analyses for the main ions (Ca, Mg, Na, K, HCO_3, Cl, SO_4 and NO_3) were performed. We chose to study the data from this period, since during these three years there were not significant changes regarding the hydrogeological-climate conditions or the exploitation regime of the water resources. The available hydrochemical data were statistically processed with classical methods and the joint use of multivariate statistical methods. The Pearson method, the R-mode factor analysis and K-means cluster analysis were used to investigate the relation between the parameters in order to identify the prevailing hydrogeological procedures that determine the hydrochemical regime of the area. All mathematical and statistical computations were made using the Microsoft Excel 2010 and IBM SPSS statistics 20 software.
The results of the conventional statistical process are presented in Table 1. According to these results, the majority of

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

(n=52)	**pH**	**EC**	**Ca**	**Mg**	**Na**	**K**	**HCO_3**	**Cl**	**SO_4**	**NO_3**
MEAN	7,54	423,25	53,10	16,18	9,15	2,69	219,70	10,23	27,41	9,65
MIN	6,77	140,4	22,44	0,97	3	1	62,22	3,54	9,3	0
MAX	8,11	1369	206,17	44,76	62	6	835,7	113,47	70	47,08

the samples correspond to typical good quality waters since these values do not exceed the maximum permissible limit for drinking or irrigation purposes. The Pearson coefficient is a statistical tool to show the degree of dependency of one variable with the other and is used to measure and establish the relationship between two variables. According to the results presented in Table 2, Pearson coefficient has revealed a high correlation between EC-Ca–Mg–HCO_3, which is expected as EC is a dependent variable and depends on the values of ions that determine the composition of water. This correlation is attributed to the dissolution of karstic rocks. Additionally, a high correlation was observed between Na-Cl and pH-SO_4. This is probably due to the existence of the geothermal field that is developed 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 as it is illustrated in Table 3 that interpret 74.726% of the total variance. The Kaiser-Meyer-Olkin coefficient is 0.604 (>0.5), and hence the method is valid. Electrical Conductivity, Ca, Mg and HCO_3 participate in Factor 1. These variables are associated to the procedures of carbonate rocks dissolution by water and Factor 1 has positive value in the northwestern and eastern boundaries of the area (Figure 1) where lateral recharge of the alluvial aquifers from karstic rocks take place. In Factor 2 pH, Na and Cl participate and it has positive values (Figure 1) mainly at the western boundaries and could be attributed to the existence of the geothermal field. K and SO_4 participate in the Factor 3 showing positive values at the north and western parts of the basin. This could be explained by the existence of the geothermal field at the western boundaries and due to agricultural activities. The K-means cluster analysis groups the samples according to their similarities. A subjective decision must be taken by the researcher regarding the final number of groups and in this case study three groups were selected. The results are shown in Table 4. The samples of the first group mainly appear at the western boundaries of the study area that lateral recharge of aquifers from mountainous rocks takes place and the samples of the second group at the eastern boundaries following groundwater flow that passes through the sediments of the plain part of the basin. The third group includes one sample with different water quality compared to the other samples close to an area that a geothermal spring exists.

Table 2. Pearson correlation matrix of Almopeos river basin.

n=52	EC	pH	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3
EC	1	-0,215	**0,884**	**0,754**	0,57	0,041	**0,859**	0,491	0,412	0,414
pH	-0,215	1	-0,121	-0,032	-0,452	0,129	-0,093	-0,499	**0,089**	-0,027
Ca	**0,884**	-0,121	1	0,51	0,36	-0,072	**0,857**	0,271	,246	0,295
Mg	**0,754**	-0,032	0,51	1	0,258	0,263	**0,73**	0,248	0,456	0,347
Na	00,57	-0,452	0,36	0,258	1	0,100	0,31	**0,897**	,217	0,101
K	0,041	0,129	-,072	0,263	0,100	1	0,007	0,119	0,331	0,012
HCO_3	**0,859**	-0,093	**0,857**	**0,73**	0,310*	0,007	1	0,204	0,185	0,272
Cl	0,491	-0,499	,271	0,248	**0,897**	0,119	0,204	1	0,286	0,003
SO_4	0,412	**0,089**	,246	0,456	0,217	0,331	0,185	0,286	1	0,355
NO_3	0,414	-0,027	0,295	0,347	0,101	0,012	0,272	,003	0,355	1

Table 3. Varimax rotation factor loadings.

	Component		
	1	2	3
EC	0,906	0,373	0,119
pH	-0,004	-0,736	0,257
Ca	0,889	0,193	-0,112
Mg	0,764	0,077	0,381
Na	0,235	0,888	0,157
K	-0,071	0,015	0,816
HCO_3	0,928	0,117	-0,060
Cl	0,130	0,922	0,219
SO_4	0,330	0,079	0,743
NO_3	0,503	-0,101	0,228

Table 4. Final Cluster centers.

	Component		
	1	2	3
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_3	160,49	274,96	835,7
Cl	5,79	14,86	46,09
SO_4	23,94	32,27	29,30
NO_3	6,24	14,96	0,44

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