

GROUNDWATER QUALITY OF THE HYDROLOGICAL BASIN OF AMYROS RIVER, AGIA AREA THESSALY, GREECE

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Abstract

The area of Agia (Thessaly, Central Greece) is a highly cultivated region, whose hydrogeochemical status is influenced both by natural and manmade factors. Chemical analyses of 40 groundwater samples from the examined area, revealed that geology has a significant impact to aquifers chemistry, mainly expressed through the presence of carbonate rocks and evaporitic minerals of the Neogene formations of the area., as well as the ultrabasic rocks of the substrate. The manmade influence is assessed through the elevated values of nitrates (values up to 168,7 mg/L). Furthermore, the analytical results of the groundwaters revealed that NO₃⁻, Fe and Se, in several samples, exceeded the EC and SMCL (USEPA) limits. More specifically, the 20% of NO₃⁻ samples exceeded the EC limits as well as the 2,5% of Se in samples. The 2,5% of Fe in samples exceeded both the EC and SMCL (USEPA) limits.

Key words: hydrogeochemistry, environment, risk assessment, Agia area, Thessaly.

1. Introduction

The hydrogeochemistry of natural waters is mainly influenced by the chemical composition of the predominant geological formations of a hydrological basin. The specific hydrogeochemical characteristics depend on the chemistry of rock-forming minerals including metal sulfide minerals such as pyrite FeS₂. The physical process of erosion creates favourable conditions for mineral dissolution, that leads to enrichment of ions, metals or metalloids, which often tend to reach hazardous concentrations in terms of toxicity for the natural or mankind environment (Alexakis and Kelepertsis 1998; Vardaki and Kelepertsis 1999; Kelepertsis et al. 2001; Robinson and Ayotte, 2006; Negrel 2006; Lang et al., 2006, Tziritis et al., 2008). According to Kelepertsis et al. (2006b), elevated concentrations of As and Sb were detected in natural waters of Eastern Thessaly, a fact which has been mainly attributed to the occurring sulfide mineralization of the area (arsenopyrite, orpiment realgar, etc.).

Moreover, physicochemical (temperature, pH, Eh) and biological parameters (microbial catalysis), as well as other geochemical processes (adsorption, ion-exchange, complexation etc) have a great impact to ground and surface waters, affecting either direct or indirect their quality status (Kelepertsis, 2000; Siegel, 2002). Other factors, such as rainwater or climatic conditions seem to affect water chemistry, but only in specific cases, were favorable conditions occurring. Apart from natural factors of enrichment, mankind effect seems to be dominant in many regions, especially in sites of agri-

cultural, industrial and mining activities (Shivkumar et al. 1997; Kabata – Pendias and Pendias, 1999; Kabata – Pendias, 2001; Djabri et al., 2003, Tziritis, 2009).

The study area (Amyros river Basin) is situated in the Prefecture of Larissa, Eastern Thessaly, Central Greece, about 400 km northern of Athens. The basin extends in an E-W direction between latitudes 39° 041'00" – 39° 045'00" and longitudes 22° 041'00" -22° 047'00". Relief is smooth with low hills and cultivated areas of apple and cherry trees, surrounded by the mountains of Kissavos and Maurovouni.

The scope of the present research aims to:

- 1) Research and define the spatial distribution of heavy metals and metalloids in natural waters of Agia region, Thessaly.
- 2) Define the relation between geology and groundwaters.
- 3) Assess the level of potential pollution in terms of potability regarding the EC Directive and determine the pollution sources.

2. Geological setting

The alpine substrate of the basin (Fig.1) (Greek Pelagonian zone) is consisted from bottom to top of (Katsikatos,; Migiros 1983; IGME 1981 and 1984):

- Paleozoic (Pre-Carboniferous) crystalline basement of the Pelagonianzone. It includes gneiss-schists, amphibolite schists and amphibolites.
- Neopaleozoic – Lower Mesotriassic formations. They include a variety of metamorphic rocks of sedimentary origin and coarse-grained marble and cipolines .
- Middle Upper Cretaceous – Upper Jurassic marbles.
- Pre-Upper Cretaceous tectonic cover. It is wholly metamorphosed with a thickness of 1000m. It includes a variety of formations and an ophiolitic complex.
- Marbles of Agia (Upper Cretaceous).
- Neogene sediments: composed of marly limestones, marls and conglomerates.
- Quaternary sediments: consisting of unconsolidated material with sand and rounded and angular pebbles in the torrent beds and alluvial sediments.

In the southeastern part of the studied area there are many small occurrences of iron oxides-hydroxides with copper and antimony arsenic mineralization Kelepertsis et al. (2006b). Copper occurs as malachite $[\text{Cu}_2(\text{CO}_3)(\text{OH})_2]$, antimony as stibnite (SbS_3) and arsenic as arsenopyrite (FeAsS). There are also outcrops of manganese oxides. All the above ore occurrences are found within the metamorphic rocks of the basement and the ophiolitic bodies (Migiros 1993). No mining activity has been reported in the whole mineralised area, although some of the ore deposits may show an economic interest.

In general, in the wider area of Agia the predominant geology is dominated by the existence of the Pelagonian zone, as it has been already mentioned, especially in the southern, northern and north-eastern parts of mountain Ossa, where there are developed the Upper-Cretaceous formations of the tectonic nappe (mainly serpentinites, metamorphic basic and ultrabasic rocks and secondary marbles). The aforementioned tectonic nappe is characterized by intense tectonism which created sec-

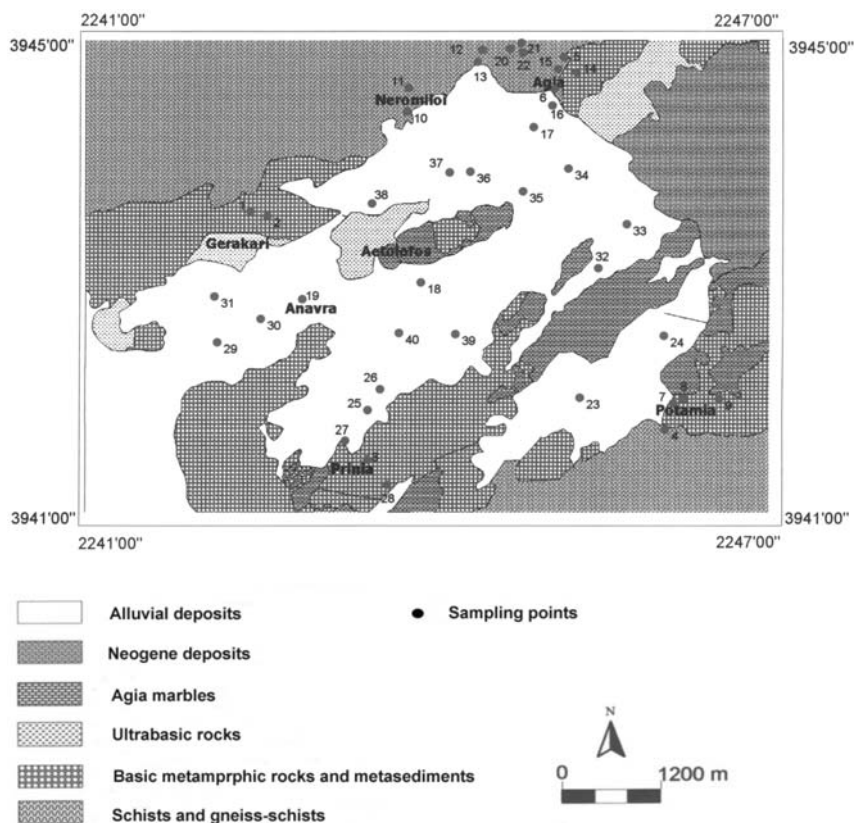


Fig. 1: Sites of groundwater samples and geological map of the area.

ondary tectonic fractions and a vast number of mylonitized zones. The above fact poses favorable conditions for water flow, and the permeability of these formations seems to be elevated. In this hydrogeological system it can be also added the aquifer of the karstified marbles. These aquifers impose the deeper hydrogeological system of the tectonic nappe. Apart from this deeper system, in the area Agia basin there are developed clastic fluvial formations, whose permeability vary, both vertical and horizontal. These clastic formations compile the upper hydrogeological system, which is quite inhomogeneous and frequently develop local aquifers with different hydrogeological properties.

3. Materials and methods

3.1 Sampling and analysis

Totally forty groundwater samples were collected during field work (January-March 2006) from all the available boreholes and springs, covering an area of 65km² (Fig. 1). During sampling, all necessary precautions were taken in order to avoid any possible contamination. Totally 27 parameters were determined (Table 1), including major ions (Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻) and trace elements (B, Ba, Br, Cr, Cu, Fe, Li, Mn, Ni, P, Pb, Se, Si, Sr, U and Zn). Samples were vacuum filtered through a 0,45 µm pore size membrane, acidified to a final concentration of about 1% nitric acid and then stored in a polyethylene container in order to be analyzed. Major anions were

Table 1. Results of chemical analyses for the analyzed parameters of the 40 groundwater samples and risk-based parametric values.

				Parametric value (EC ^a)	MCL (USEPA ^b)	SMCL (USEPA ^b)
	Mean	Minimum	Maximum			
Ca ⁺⁺ (µg l ⁻¹)	83.596	32.570	180.800	None	None	None
Mg ⁺⁺ (µg l ⁻¹)	24.230	7.660	58.480	None	None	None
K ⁺ (µg l ⁻¹)	1.875	910	3.540	12.000	None	None
Na ⁺ (µg l ⁻¹)	11.522	3.380	24.980	200.000	None	None
HCO ₃ ⁻ (µg l ⁻¹)	308.777	145.070	483.900	None	None	None
NO ₃ ⁻ (µg l ⁻¹)	32.450	1290	168.700	50.000	None	None
SO ₄ ⁻ (µg l ⁻¹)	33.603	8.810	148.700	250.000	None	250.000
Cl ⁻ (µg l ⁻¹)	14.275	4990	33.240	250.000	None	250.000
B (µg l ⁻¹)	25	7	76	1.000	None	None
Ba (µg l ⁻¹)	13	3	34	None	2.000	None
Br (µg l ⁻¹)	420	17	4.561	None	None	None
Cr (µg l ⁻¹)	5	0	26	50	100	None
Cu(µg l ⁻¹)	3	0	27	2.000	None	1.000
Fe (µg l ⁻¹)	65	0	1.143	200	None	300
Li (µg l ⁻¹)	3	0	6	None	None	None
Mn (µg l ⁻¹)	6	0	123	50	None	50
Ni (µg l ⁻¹)	1	0	9	20	None	None
P (µg l ⁻¹)	50	20	146	None	None	None
Pb(µg l ⁻¹)	1	0	1	10	15	None
Se (µg l ⁻¹)	2	0	19	10	50	None
Si (µg l ⁻¹)	9.210	4.881	16.205	None	None	None
Sr (µg l ⁻¹)	196	48	575	None	None	None
U (µg l ⁻¹)	1	0	9	None	None	None
Zn (µg l ⁻¹)	18	3	147	None	None	5.000

NA: not applicable

measured photometrically using attach DR/4000 apparatus (except HCO₃⁻ which were measured with titration), while the rest of the parameters (major cations and trace elements) were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS). Data quality was assured by introduction of internal reference samples and by analyzing duplicates of 10 samples. The precision was calculated and found between the international standards.

3.2 Statistical analysis

The data obtained from chemical analyses was statistically processed, in order to extract potential correlations between the examined parameters and the relevant natural or manmade processes. For this purpose, correlation and R-mode factor analysis were performed. In correlation analysis, the possible linkage between two single variables was assessed with the estimation of correlation coefficient (Pearson Correlation Coefficient - r). Values close to 1 state absolute (high) correlation while the sign denotes if it is proportional or not (Drever 1997). Results are shown on Table 2.

On the other hand, R-Mode Factor Analysis is a technique of management, simplification, and assessment of data bases, in order to extract and grade correlations between parameters and to specify their contribution into a common polyparametric process. The basic aim is to specify individual factors, few in number, which will explain the variation of a large number of variables and data (Kelepertzis et al. 2006; Panda 2006). Initial data has been standardized in order to eliminate the influence from different units. Principal Components Analysis (Davis 1984) was performed as an extraction technique, because it explains properly the extracted results, even in cases of non-normal distribution of initial data input (Brown, 1998). Finally, factor loadings were optimized with Varimax rotation method. Results are shown on Table 3.

4. Geochemical results and discussion

The results of chemical analyses were compared with the upper acceptable limits of the 98/83/EU Directive (EC 1998) and the maximum contaminant levels as well as the secondary maximum contaminant levels of EPA (EPA 2001) for drinking water. The mean values of all the analyzed parameters do not exceed as much the EC limits (1998) as the EPA limits (2001). There is an exception concerning the maximum fluctuation values for NO_3^- (1290-168700 $\mu\text{g l}^{-1}$), Fe (0-1143 $\mu\text{g l}^{-1}$), Mn (0-123 $\mu\text{g l}^{-1}$) and Se (0-19 $\mu\text{g l}^{-1}$). According to the chemical analyses there is an excess of the critical levels in 11 groundwater samples in Agia, Thessaly area. Contamination of NO_3^- (sampling sites A2, A23, A25, A26, A27, A30, A31, A38), Fe (sampling sites A8), Mn (sampling sites A32), Se (sampling sites A13) over the risk-based drinking water criteria given by the EC (1998) and EPA (2001) of the Agia Thessaly groundwaters was observed. The percentages (%) of the total groundwater samples, which exceed the critical levels of EC (1998), are as follows: 20% of the samples for NO_3^- , 2,5% for Fe, 2,5% for Mn and 2,5% for Se, while, regarding the critical levels of EPA (SMCL), is 2,5% for Fe and 2,5% for Mn.

The areas with high values of NO_3^- , that exceed as much the critical levels of EC (1998) as well as the levels of EPA (2001), are those where the boreholes are found in direct geological relation with the basic metamorphic rocks and metasediments of the Pre-Upper Cretaceous tectonic nappe and are presented in the studied area as follows: (Gerakari, Prinia west part sampling sites A2, A25, A26, A27, A30, A31, A38 and Potamia southeast part sampling sites A23). Regarding the Fe, Mn, Se, only in one sample of each element (sampling A8, A32, A13 respectively) the values exceed the critical levels of EPA (SMCL).

Table 2 shows that the parameters Ca^{2+} , Mg^{2+} , K^+ , Na^+ , HCO_3^- , NO_3^- , SO_4^{2-} , Cl, B and Sr are inter-correlated and associated with the carbonate-Neogene rocks of the area such as the Cretaceous limestones and marls, and also with the evaporitic minerals of the Neogene formations. Another important fact is the strong correlation between Br and Se ($r = +0,95$) and this should be attributed to man-made origin due to pesticide sprayings in the broader cultivated area.

Principal component factor analysis with a varimax rotation was applied to the data in order to cre-

Table 2. Correlation coefficient matrix from Agia for the parameters of the analyzed groundwater samples.

	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	B	Ba	Br	Cr	Cu	Fe	Li	Mn	Ni	P	Pb	Se	Si	Sr	U	Zn
Ca ²⁺	1																							
Mg ²⁺	0,68	1																						
K ⁺	0,38	0,44	1																					
Na ⁺	0,55	0,78	0,40	1																				
HCO ₃ ⁻	0,75	0,77	0,31	0,73	1																			
NO ₃ ⁻	0,75	0,71	0,33	0,44	0,39	1																		
SO ₄ ²⁻	0,77	0,67	0,52	0,55	0,41	0,78	1																	
Cl ⁻	0,77	0,88	0,50	0,79	0,70	0,80	0,73	1																
B	0,61	0,80	0,43	0,59	0,49	0,72	0,75	0,79	1															
Ba	0,15	0,28	0,49	0,27	0,10	0,11	0,37	0,20	0,31	1														
Br	-0,27	-0,23	-0,20	-0,15	-0,21	-0,24	-0,19	-0,30	-0,31	-0,23	1													
Cr	0,43	0,55	0,34	0,15	0,30	0,55	0,46	0,38	0,62	0,29	-0,21	1												
Cu	0,04	0,39	-0,03	0,68	0,44	0,01	-0,04	0,32	0,23	-0,08	0,02	-0,14	1											
Fe	-0,16	-0,13	-0,05	0,08	-0,06	-0,19	-0,16	-0,14	-0,19	0,06	0,17	-0,15	0,20	1										
Li	0,35	0,65	0,21	0,65	0,61	0,23	0,35	0,56	0,59	0,31	-0,18	0,11	0,44	-0,06	1									
Mn	0,16	0,12	0,39	0,27	0,12	-0,12	0,41	0,18	0,16	0,42	-0,05	-0,13	-0,06	-0,03	0,19	1								
Ni	0,07	0,25	0,44	0,05	0,24	-0,08	0,10	0,10	0,19	0,38	-0,13	0,52	-0,08	-0,01	0,07	0,37	1							
P	0,34	0,39	0,55	0,16	0,16	0,40	0,43	0,38	0,52	0,27	-0,37	0,52	-0,16	-0,13	0,06	0,08	0,12	1						
Pb	-0,35	-0,21	-0,06	-0,03	-0,31	-0,25	-0,10	-0,20	-0,03	0,17	0,03	-0,15	0,17	0,32	-0,12	0,17	0,05	-0,01	1					
Se	-0,25	-0,20	-0,17	-0,10	-0,20	-0,24	-0,11	-0,26	-0,26	-0,21	0,95	-0,25	0,02	0,16	-0,14	0,06	-0,10	-0,37	0,07	1				
Si	0,44	0,73	0,37	0,42	0,58	0,49	0,32	0,59	0,60	0,22	-0,34	0,65	0,12	-0,18	0,44	-0,12	0,30	0,52	-0,29	-0,38	1			
Sr	0,79	0,85	0,49	0,68	0,61	0,81	0,88	0,82	0,83	0,37	-0,19	0,51	0,11	-0,16	0,51	0,20	0,07	0,47	-0,18	-0,14	0,56	1		
U	0,25	0,19	0,15	0,25	0,27	-0,01	0,28	0,15	0,20	0,39	-0,14	-0,06	-0,20	-0,03	0,58	0,41	0,06	-0,04	-0,06	-0,09	-0,03	0,32	1	
Zn	0,08	0,11	0,11	0,20	0,08	0,10	0,07	0,09	0,06	0,18	0,03	-0,02	0,20	0,90	0,04	-0,01	-0,02	0,11	0,28	0,02	0,04	0,14	0,10	1

Table 3. Varimax rotated factor loadings and percentage of variance for the 5 extracted factors of the analyzed groundwater samples.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Ca ²⁺	0,85				
Mg ²⁺	0,79	0,50			
K ⁺	0,52				
Na ⁺	0,64	0,65			
HCO ₃ ⁻	0,56	0,61			
NO ₃ ⁻	0,88				
SO ₄ ²⁻	0,94				
Cl ⁻	0,66				
B	0,78				
Ba					0,59
Br				-0,78	
Cr				0,52	
Cu		0,84			
Fe			0,57		
Li		0,61			0,49
Mn					0,67
Ni				0,39	
P				0,57	
Pb			0,58		
Se				-0,81	
Si				0,62	
Sr	0,93				
U					0,80
Zn			0,68		
% Variance	29,5	12,1	10,8	8,1	6,5

ate factors each representing a cluster of interrelated variables within data set. The proportion of the variance explained by five factors the rotated factor loadings and the communality are presented in Table 3. In the present study, the element distribution in the groundwater samples of the Agia area is explained through five factors, which interpret the 67% of the total variance of the data set. The first factor explains the 29,5% of the total variance, with high positive factor loadings the parameters of Ca²⁺, Mg²⁺, K⁺, Na⁺, HCO₃⁻, NO₃⁻, SO₄²⁻, Cl⁻, B, Sr. This factor interprets the impact of the carbonate rocks and the evaporitic minerals of the Neogene formations in the area. The second factor explains the 12,1% of the total variance and as the parameters of Na⁺, HCO₃⁻, Cu and Li with high positive factor loadings (0,61 to 0,84). This factor possibly reflects the anthropogenic impact which is associated with phosphate fertilizers. The third factor explains the 10,8% of the total variance and includes as the parameters of Fe, Pb and Zn with medium factor loadings and explains the co-pre-

cipitation of Pb and Zn with Fe oxides. The fourth factor explains 8,1% of the total variance and shows positive loadings for Cr, Ni, P, Si and negative for Br and Se. Table 3 shows highly negative factor loadings for the parameters Br and Se and interprets the various sprayings with pesticides that take place in the cultivated fields of the studied area. We can also assess that the parameters of Cr, Ni, U, Li present positive factor loadings that emanate from the ultrabasic rocks of the area. Finally, the fifth factor explains the 6,5% of the total variance, and consists the parameters of Ba, Mn, U, Li which are associated with the weathering process of schists and micaschists of the metamorphic substrate.

5. Conclusions

The area of Agia (Thessaly, Central Greece) is a highly cultivated region, whose hydrogeochemical status is influenced both by natural and manmade factors. Chemical analyses of 40 groundwater samples from the examined area, revealed that geology has a significant impact to aquifers chemistry, mainly expressed through the presence of carbonate rocks and evaporitic minerals of the Neogene formations of the area., as well as the ultrabasic rocks of the substrate. The manmade influence is assessed through the elevated values of nitrates (values up to 168,7 mg/L. As far as the risk assessment for the manmade environment is concerned, the analytical results revealed that NO_3^- , Fe and Se, in several samples, exceeded the EC and SMCL (USEPA) limits. More specifically, the 20% of NO_3^- samples exceeded the EC limits, posing a direct threat to manmade environment. Furthermore the 2,5% of Se in samples, also exceeded the highest parametric levels. The 2,5% of Fe in samples exceeded both the EC and SMCL (USEPA) limits. Factor analysis grouped the elements in five factors. These factors interpret the main processes that affect the hydrogeochemical variance of aquifers. The five factors explained the 67% of the total variance. The first factor reflects the presence of carbonate rocks and evaporitic minerals of the Neogene formations of the area, and is related to the elements Ca^{2+} , Mg^{2+} , K^+ , Na^+ , HCO_3^- , NO_3^- , SO_4^{2-} , Cl⁻, B, Sr.. The second factor with positive loadings for the parameters of Na^+ , HCO_3^- , Cu and Li explains their anthropogenic origin, which owed to the fertilization that take place in the cultures of the studied area. The third factor includes the elements Fe, Pb and Zn and reflects the co-precipitation of Pb and Zn with Fe oxides, while the fourth interprets the presence of ultrabasic rocks in the studied area. Finally, the fifth factor includes the elements Ba, Mn, U, Li, which are associated with the weathering products of schists and micaschists. Conclusively, the hydrogeochemical status of Agia aquifers is majorly influenced by both anthropogenic and natural factors. The above factors in general se good quality conditions for the uses of groundwater, except few samples, where the concentration of nitrates exceeds the upper limits of potability, as they are set by EU.

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