JOURNAL OF WATER
AND LAND DEVELOPMENT
J. Water Land Dev. No. 15, 2011: 127–144

Geochemical status and interactions between soil and groundwater systems in the area of Akrefnio, Central Greece. Risk assessment, under the scope of mankind and natural environment

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Abstract: Totally 50 samples of groundwater and soil were collected from the area of Akrefnio (central Greece), in order to assess the geochemical status and the risk for humans and natural environment. The analytical results and processing of the initial data revealed that the main factors controlling hydrogeochemistry are the natural enrichment from calcareous substrate and the manmade pollution through extensive use of N-fertilizers. Soil geochemistry was mainly influenced by the occurrence of lateritic horizons, which gave raise to elevated concentrations of Ni and Cr in the majority of soil samples. Although most of the geochemical enrichment processes between soil and groundwater are common, the above geochemical systems don't seem to interact, and act most of the times independently. Risk assessment of natural and mankind environment revealed that groundwater is suitable for drinking but not for irrigation, due to high salinity. Finally, soils are highly polluted by Ni and Cr, and thus are inappropriate for the existing agricultural land uses.

Key words: *Akrefnio, central Greece, geochemistry, groundwater, risk assessment, soil*

INTRODUCTION

The study area is located in the vicinity of Akrefnio city, which lies about 100 km northern of Athens, central Greece. The western part of wider area is a part of a great polje which have been affected by intense karstification and tectonism. Land use has been changed over the last 100 years. More precisely, the aforementioned area was a marshy region, frequently changing between a periodic lake and a swamp. The last few years, the entire area has been drought and since then its fertile parts are under extensive agricultural practices.

The geology of the area is mainly characterized by karstic limestone formations and a thick sequence of Quaternary deposits. More precisely, the Alpine substrate consists in succession from bottom to top: Triassic dolostones and dolomitic limestones, a Jurassic volcanoclastic complex compiled of schists, sandstones and ultrabasic blocks, a Cretaceous sequence of pelagic limestones which hosts locally at their upper boundary Fe-Ni rich lateritic horizons and finally the typical Eocenic flysch (PAGOUNIS *et al.*, 1994). The Post-Alpine sediments have a great thickness and embrace in succession clays, breccias, sandstones, lacustrine marls of Plio-Plistocenic age, and a few lignitic intercalations. The upper sequence is consisted of Quaternary terrestrial and torrential phases with alluvial deposits (ALLEN, 1986; PAGOUNIS *et al.*, 1994).

The existence of Fe-Ni-rich ores has been reported by several researchers in the wider area of Kopaida (ALBANTAKIS, 1984; ALBANTAKIS and KOUNDOUROS, 1984; KOUMANTAKIS, 1975; PARASKEVAIDIS, 1972). Their occurrences are found only in the northeastern extremities of the area (Aghios Ioannis) (Fig. 1) but their presence in the substrate of the area is significant due to the specific tectonic conditions (ALBANTAKIS and KOUNDOUROS, 1984).

The hydrogeological setting is mainly influenced by the specific geological and tectonic conditions. The stratigraphic contacts between formations of different permeabilities as well as the tectonic nappes and the various deformation episodes, formed three individual aquifers. The upper one is developed in the Cretaceous limestone and is characterized by high permeability and karstic flow. The middle one is developed in Jurassic limestones with elevated values of hydraulic conductivity, and the lower one is consisted of dolostones and dolomitic limestones and is differentiated from superincumbent aquifers due to the considerable decrease of permeability and karstic development. The general groundwater flow is towards east, with local differentiations. Piezometric level is variable, ranging between 20 and 160 m depending on local lithologic and tectonic conditions (TZIRITIS *et al.*, 2008). The three aquifers may be considered as united in most of the cases. Discharges vary between 40 and 300 $km^3 \cdot h^{-1}$, depending on the type of the aquifer. Finally, the alluvial aquifer is of minor importance and practically ignored.

The soils of the area are generally characterized by red or brownish-red colour, with heavy texture and frequent presence of breccias. They are mainly consisted of non-evoluted calciferous lacustrine sediments and therefore are classified as “Typic Haplaquent” in most of the cases, while a minor part of them is classified as “Mollic Haplaguent” (THEOCHAROPOULOS *et al.*, 1995). The presence of root systems is frequent and the boundaries among the different horizons are abrupt and wavy. Soil structure and cohesion form satisfactory conditions concerning plant growth and biological activity.

The scope of the present paper is dual. Firstly the study aims to describe the natural and manmade processes that affect the chemistry of soils and groundwater, as well as to define the possible interaction between them. Secondly the study makes an assessment of the general environmental conditions of both soils and groundwater regarding the potential threats and the relative legislation.

METHODS

Totally fifty samples of both groundwater (32 samples) and soil (18 samples) were collected during field work, covering an area of about 170 km^2. Samples were collected during June of 2009. Regarding groundwater, samples were collected from all available boreholes of the karstic aquifer (Fig. 1).

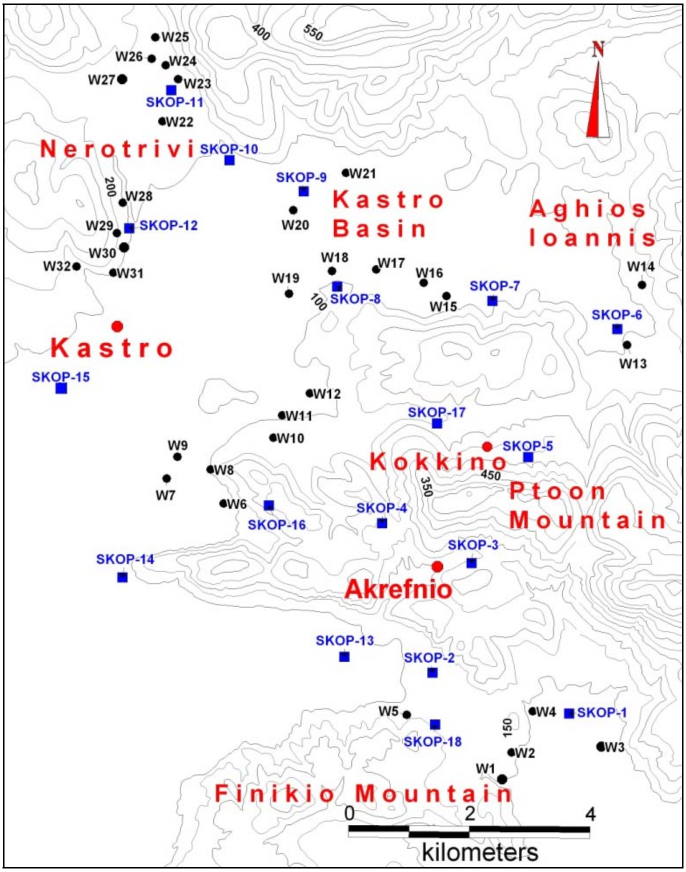

Fig. 1. Sites of groundwater (W) and soil (SKOP) samples

During sampling, all necessary precautions were taken in order to avoid any possible contamination. Totally 19 parameters were determined (Tab. 1), including major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-} and HCO_3^-), trace elements (Al, Ba, Cr, Cu, Fe, Mn, Ni and Zn) and physicochemical parameters (pH, EC and TDC) that were measured in situ. Data quality was assured by introduction of internal reference samples and by analyzing duplicates of 10 samples. The precision was calculated and found within the international standards.

Soil samples were collected with the use of an auger sampler from a depth of 30 cm while surface debris and vegetation was before removed. After the proper preparation the soil samples were digested with a mixture of $HClO_4$, HNO_3, HCl, HF and analyzed by an ICP-MS for the following 10 chemical parameters: Al, Ba, Ca, Cu, Cr, Fe, Mg, Mn, Ni and Zn. Data quality was assured by introduction of internal reference samples and by analyzing the duplicates of 5 samples. The precision was calculated from these duplicates and it was found within the international standards. The results are shown in Table 3.

The initial analytical data was processed statistically in order to extract potential correlations between the parameters and assess the contribution of natural and manmade processes to the chemical status of groundwater and soils. Data have been standardized through logarithmic normalization and R-mode factor analysis was applied for both soil and groundwater samples. R-mode factor analysis is a handful method which is frequently used to similar studies (KELEPERTZIS *et al.*, 2006; PANDA *et al.*, 2006; TZIRITIS, 2009) and aims to specify individual factors, few in number, in order to explain the variation of a large number of variables and data. Each factor joins separate variables and finally correlates them directly or indirectly with a common process. The extraction technique for the application of factor analysis was the "principal components analysis" (DAVIS, 1984) and the results were optimized following the "Varimax rotation" method. The interpretation of each examined parameter's contribution depends on its communality, which in the case of well described parameter should be above 0.80 (ZHU *et al.*, 2007). In other cases, where communality is below 0.80, other processes which are not described in factor analysis might occur. The results of the R-mode factor analysis for groundwater samples are shown in Table 2 and for soils in Table 4.

A further geochemical process for the groundwater samples included the estimation of quality indices, in order to assess the quality status of the samples regarding their potential pollution or salinization. In more details, quality status was assessed through Contamination Index (C_d) and Sodium Adsorption Ratio (SAR). The above process was followed in order to assess more thoroughly the suitability of groundwaters for human consumption and irrigation, apart from the classic procedure of comparing the analytical values with the maximum parametric levels, imposed either by the current relative legislation (Directive 98/83/EU) or the proposed international standards (FIPPS, 2003).

In more details, the quality status of an aquifer can be assessed with the use of environmental factors and indices, which include a wide spectrum of parameters. Such factors may become a valuable tool for the assessment of environmental conditions of an area. According to BACHAM *et al.* (1997), Contamination Index (C_d) may be considered as a good quality environmental indicator, if we take into account the measured concentrations of the examined parameters and the upper permissible parametric levels of a contaminant. According to RAPANT *et al.* (1995) the Contamination Index is defined as:

$$C_d = \sum_{i=1}^{n} C_{fi} \quad (1) \quad \text{and} \quad C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \quad (2)$$

where:

C_d Contamination Index,
C_{fi} contamination factor of the *i*-th component,
C_{Ai} analytical value of the *i*-th component,
C_{Ni} upper permissible concentration of the *i*-th component (defined by choice according to relative legislation or proposed international standards).

Contamination Index (C_d) is calculated individually for each water sample, as a sum of the contamination factors of single components that exceed the maximum contaminant levels. In that way, contamination index summarizes the combinational effects of several quality parameters that may have harmful impacts to human environment. The scale value consists of three ranges (RAPANT *et al.*, 1995), $C_d < 1$ for low contamination, $1 < C_d < 3$ for medium contamination and $C_d > 3$ for high contamination. It should be noted that contamination index provides only a qualitative approach to contamination and not the levels of environmental hazard, since the effects to mankind and natural environment form e.g. Cr and Ni which may be toxic are different from the effects of SO_4^{2-}. Results are shown on Table 3.

Furthermore, the Sodium Adsorption Ratio (*SAR*) was calculated for each groundwater sample, in order to assess the levels of salinization and to provide a holistic approach of quality status in combination with the other data. The estimation of *SAR* was made through the relation $SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$ (3) in $meq \cdot l^{-1}$ (RICHARDS, 1969) and its combination with the measured values of electrical conductivity gave information about the geochemical class of water. Results are shown on Table 3.

RESULTS AND DISCUSSION

As can be assessed from Table 1, the values of calcium in groundwater are relatively elevated, ranging from 37.8 $mg \cdot l^{-1}$ to 162 $mg \cdot l^{-1}$, with a mean value of 90,5 $mg \cdot l^{-1}$, and the highest measured concentrations in samples W7 (127 $mg \cdot l^{-1}$), W12 (131 $mg \cdot l^{-1}$) and W13 (162 $mg \cdot l^{-1}$). Magnesium ranges between 17.6 $mg \cdot l^{-1}$ and 99.4 $mg \cdot l^{-1}$ with a mean value of 43.4 $mg \cdot l^{-1}$, and appear elevated values in samples W9 (88 $mg \cdot l^{-1}$), W18 (90 $mg \cdot l^{-1}$) and W22 (99 $mg \cdot l^{-1}$). The ions of Na^+, Cl^- and SO_4^{2-} appear elevated concentrations in samples W7, W9 and W18, which probably denote a common factor of enrichment. The highest values of Na^+ are found in samples W7 (67 mg·l^{-1}), W9 (57 mg·l^{-1}) and W18 (83 mg·l^{-1}), for Cl^{-} in W7 (117 mg·l^{-1}), W9 (86 mg·l^{-1}) and W18 (124 mg·l^{-1}), and for SO$_4^{2-}$ in W7 (169 mg·l^{-1}), W9 (217 mg·l^{-1}), W12 (112 mg·l^{-1}) and W18 (256 mg·l^{-1}). Furthermore, the concentrations of K^{+} show a small variance and range between 1 mg·l^{-1} and 16 mg·l^{-1} with a mean value of 2.3 mg·l^{-1}. The highest measured values are found in samples W1 (14 mg·l^{-1}) and W27 (16 mg·l^{-1}). Nitrates appear elevated concentrations (above 40 mg·l^{-1}) in the 25% of the samples. Their concentrations range between 4 and 64.6 mg·l^{-1}, with a mean value of 25.3 mg·l^{-1}. The maximum concentrations are found in samples W5 (65 mg·l^{-1}), W12 (55 mg·l^{-1}) and W22 (55 mg·l^{-1}). Finally, the concentrations of HCO$_3$, show greater variances denoting the existence of different populations with values ranging from 205 to 451 mg·l^{-1}, with a mean of 297 mg·l^{-1}, and highest values in samples W22 (428 mg·l^{-1}) and W27 (439 mg·l^{-1}).

Table 1. Analytical results and descriptive statistics of groundwater samples; values for major elements and TDS are in mg·l^{-1}, for trace elements in μg·l^{-1} and for *EC* in μS·cm^{-1}

Parameters	Major elements							
	Ca	Mg	K	Na	Cl	NO$_3^-$	SO$_4^{2-}$	HCO$_3^-$
Min	37,8	17,6	1,0	9,0	12,0	4,0	2,0	205
Max	162,0	99,4	16,4	72,9	123,6	64,6	256,0	451
Mean	90,5	43,6	2,6	25,3	36,0	25,3	55,8	297
Range	124,2	81,8	15,4	63,9	111,6	60,6	254,0	246
St. Dev.	24,7	18,0	3,4	15,3	26,1	15,5	57,6	65
Variance	612,3	325,3	11,6	234,6	683,2	241,7	3 318,4	4 262

	Trace elements and physicochemical parameters										
	Al	Ba	Cr	Cu	Fe	Mn	Ni	Zn	EC	TDS	pH
Min	3	17	0	1	0	0	0	5	530	260	7,0
Max	33	130	33	237	245	72	14	424	1300	650	8,3
Mean	13	40	6	15	63	5	2	60	737	371	7,8
Range	30	112	33	236	245	72	14	419	770	390	1,3
St. Dev.	8	24	6	44	82	13	3	84	191	97	0,4
Variance	69	555	37	1 896	6 800	165	9	7 065	36467	9 447	0,1

Regarding the analytical values of trace elements and physicochemical parameters, all metals in general are in the range of normal values for natural waters (DREVER, 1997). A slight enrichment in some samples in comparison with the rest is observed for the parameters of Ba, Cu, Cr, Ni, Mn and Zn. More precisely, elevated values of Ba are found in samples W6 (89 μg·l^{-1}) and W7 (130 μg·l^{-1}) while the mean value is 40 mg·l^{-1}. Elevated values for Cu are found in samples W3 (237 μg·l^{-1}), W27 (99 μg·l^{-1}) and W30 (39 μg·l^{-1}), while the mean value is 15 μg·l^{-1}. Furthermore, Cr appear elevated values in samples W13 (13 μg·l^{-1}) and W22 (33 μg·l^{-1}) while mean value is 6 μg·l^{-1}, Ni in sample W24 (14 μg·l^{-1}) while mean value is

2 μg·l^{-1}, Mn in sample W7 (72 μg·l^{-1}) while mean value is 5 μg·l^{-1}, and Zn in samples W10 (221 μg·l^{-1}), W13 (424 μg·l^{-1}) and W18 (210 μg·l^{-1}) while the mean value is 60 μg·l^{-1}. Finally, the values of *EC* and TDS present great variance, denoting the impact from different factors, while pH is slightly alcalic, reaching values up to 8.3.

The application of R-mode factor analysis in groundwater samples resulted to the existence of five factors (Tab. 2) that control 77.1% of the hydrogeochemical status. Depending on their communalities, only the parameters TDS, *EC*, Na^+, SO_4^{2-}, Mg^{2+}, Cl^-, Ba^{2+}, Cr, pH, Ca^{2+}, Al and NO_3^- appear values equal or greater than 0,80 and can be well interpreted.

Table 2. Sorted Rotated Factor Loadings and Communalities for groundwater samples, values below 0.4 are presented as zero for simplification

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
TDS	0.967	0.000	0.000	0.000	0.000	0.950
EC	0.962	0.000	0.000	0.000	0.000	0.941
Na	0.897	0.000	0.000	0.000	0.000	0.856
SO_4	0.835	0.000	0.000	0.000	0.000	0.844
Mg	0.790	0.000	0.000	0.000	0.000	0.886
Cl	0.770	0.000	0.000	0.000	0.000	0.897
Ba	0.730	–0.491	0.000	0.000	0.000	0.837
HCO_3	0.551	0.529	0.000	0.000	0.000	0.622
Mn	0.512	0.000	0.000	–0.452	0.000	0.559
Ni	0.467	0.000	0.441	0.000	0.000	0.676
K	0.405	0.000	0.000	0.000	0.000	0.565
Cr	0.000	0.872	0.000	0.000	0.000	0.860
pH	0.000	0.849	0.000	0.000	0.000	0.874
Zn	0.000	0.579	0.000	0.000	0.000	0.639
Ca	0.000	0.000	0.882	0.000	0.000	0.824
Al	0.000	0.000	0.000	–0.813	0.000	0.795
Cu	0.000	0.000	0.000	–0.716	0.000	0.576
NO_3	0.000	0.000	0.000	0.000	0.930	0.899
Fe	0.000	0.000	0.439	0.000	–0.513	0.553
Variance	6.1680	2.9590	1.9813	1.9134	1.6312	14.6530
% Var	0.325	0.156	0.104	0.101	0.086	0.771

The first factor explains 32.5% of the chemical variance and includes with high positive factor loadings the parameters of TDS, *EC*, Na^+, SO_4^{2-}, Mg^{2+}, Cl^-, with medium positive factor loadings the parameters of Ba^{2+}, HCO_3^-, Mn, and with weak positive loadings the parameters Ni and K^+. This factor includes saline water related parameters which may have an origin from different sources, such as seawater intrusion or dissolution of evaporitic minerals.

The second factor explains 15.6% of chemical variance and includes with high positive factor loadings the parameters of Cr and pH, with medium positive factor loading the parameters of Zn and HCO_3^-, and with weak negative loading Ba^{2+}. A possible interpretation of this factor would be the impact of the lateritic horizons which are Cr-rich and the contribution of pH as regulatory parameter controlling solubility and mobility of the aqueous solution.

The third factor explains 10.4% of the chemical variance and includes with high positive factor loading Ca^{2+}, and with weak positive loadings the parameters Ni and Fe, and possible interprets the influence of the calcareous substrate through the process of karstification. The negative values of factor loadings of Ni and Fe probably denote the lithological differences and the local spatial dominance of the ultrabasic blocks of the volcanoclastic formation where limestones are absent.

The fourth factor explains 10.1% of the chemical variance and includes with high negative factor loading Al, with medium negative loading Cu and with weak negative loading Mn, and probably interprets the contribution from the ultrabasic blocks of the volcanoclastic formation.

Finally, the fifth and last factor explains 8.6% of the total chemical variance and includes with high positive factor loading the parameter of NO_3^- and with medium negative loading the parameter of Fe. The possible interpretation of this factor should be attributed to the impact of mankind pollution, through the extensive use of fertilizers. The negative value of Fe probably refers to local reducing conditions (TZIRITIS, 2009), where NO_3^- and Fe^{3+} are depleted because of reduction, and the aqueous solution is enriched in N and Fe^{2+}.

As can be assessed from Table 3 the majority of groundwater samples belong to Ca-HCO_3 water type denoting the significant influence of the calcareous substrate, and only few of them to Mg-HCO_3 type due to the impact of ultrabasic formations and dolomitic aquifer. It is quite noticeable that although the contamination index of the groundwater samples is rather low, salinity which is expressed through the values of SAR is elevated in many of them. This assessment is due to the fact that contamination index embraces parameters that are harmful to human environment as they are imposed by the relative legislation, while *SAR* and salinity hazard refers to the irrigation quality of groundwater, thus takes into account the natural environment. The elevated values of *SAR* should be attributed to local elevated values of Na^+ which might be related with several origins of salinization, such as seawater intrusion, dissolution of evaporitic minerals, connate water etc.

Comparing the analytical results with the parametric values of the 98/83/EU Directive, it can be concluded that only in 5 samples the maximum acceptable limits are exceeded. In more details, the maximum concentration of NO_3^- (50 $mg \cdot l^{-1}$) is exceeded only in samples W5, W8 and W22, while the maximum concentrations of SO_4^{2-} (250 $mg \cdot l^{-1}$) and Mn (50 $\mu g \cdot l^{-1}$) are exceeded only in samples W18 and W7 respectively. Regarding the parametric values of heavy metals and metalloids

Table 3. Summary table depicting water type for groundwater samples, ionic ratios of Mg:Ca, SAR values, the relative salinity hazard, as well as Contamination Index (C_d) and levels of contamination

	Water type	Mg:Ca meq	SAR	Salinity Hazard	Cd	Cfi	Contamination
W1	Ca-HCO_3	0.614	385×10^{-3}	medium	0	–	none
W2	Ca-HCO_3	0.837	904×10^{-3}	medium	0	–	none
W3	Ca-HCO_3	0.747	101×10^{-3}	medium	0	–	none
W4	Ca-HCO_3	0.557	805×10^{-3}	medium	0	–	none
W5	Ca-HCO_3	0.718	467×10^{-3}	medium	0.3	NO_3^-	low
W6	Ca-HCO_3	0.616	523×10^{-3}	high	0	–	none
W7	Ca-HCO_3	0.830	1.21	medium	0.4	Mn	low
W8	Ca-HCO_3	0.867	965×10^{-3}	medium	0	NO_3^-	none
W9	Mg-HCO_3	1.330	983×10^{-3}	high	0	–	none
W10	Ca-HCO_3	0.704	550×10^{-3}	medium	0	–	none
W11	Ca-HCO_3	0.705	480×10^{-3}	medium	0	–	none
W12	Ca-HCO_3	0.494	374×10^{-3}	high	0.1	–	low
W13	Ca-HCO_3	0.241	271×10^{-3}	medium	0	–	none
W14	Ca-HCO_3	0.685	328×10^{-3}	medium	0	–	none
W15	Ca-HCO_3	0.784	365×10^{-3}	medium	0	–	none
W16	Ca-HCO_3	0.697	329×10^{-3}	medium	0	–	none
W17	Ca-HCO_3	0.748	338×10^{-3}	medium	0	–	none
W18	Mg-HCO_3	1.559	1.29	high	0.1	SO_4^{2-}	low
W19	Ca-HCO_3	0.891	520×10^{-3}	medium	0	–	none
W20	Ca-HCO_3	0.937	421×10^{-3}	high	0	–	none
W21	Mg-HCO_3	1.075	414×10^{-3}	medium	0	–	none
W22	Mg-HCO_3	4.335	737×10^{-3}	high	0.1	NO_3^-	low
W23	Ca-HCO_3	0.773	251×10^{-3}	medium	0	–	none
W24	Ca-HCO_3	0.816	635×10^{-3}	medium	0	–	none
W25	Ca-HCO_3	0.881	625×10^{-3}	high	0	–	none
W26	Mg-HCO_3	1.225	336×10^{-3}	medium	0	–	none
W27	Ca-HCO_3	0.682	373×10^{-3}	medium	0	–	none
W28	Ca-HCO_3	0.706	400×10^{-3}	medium	0	–	none
W29	Ca-HCO_3	0.689	375×10^{-3}	medium	0	–	none
W30	Ca-HCO_3	0.746	121×10^{-3}	high	0	–	none
W31	Ca-HCO_3	0.920	560×10^{-3}	high	0	–	none
W32	Ca-HCO_3	0.624	225×10^{-3}	medium	0	–	none

for long and short term exposure of vegetation (Fipps, 2003), it should be concluded that none of the samples exceeds the maximum imposed values.

SOILS

From Table 4 it shown that the concentrations of calcium in soils range between 0.6 and 31% w.w., with a mean value of 11% w.w., and the highest values in samples S7, S8, S9, S15 and S16. Magnesium ranges between 0.4 and 8.1% w.w. with a mean of 1.4% w.w., and the highest values in samples S2 (3.3% w.w.) and S12 (8.1% w.w.). The concentrations of Nickel appear to be elevated, ranging between 36 and 1569 $mg \cdot kg^{-1}$, with a mean value of 472 $mg \cdot kg^{-1}$. The highest values are found in samples S3 (876 $mg \cdot kg^{-1}$), S5 (1569 $mg \cdot kg^{-1}$), S6 (976 $mg \cdot kg^{-1}$), S10 (857 $mg \cdot kg^{-1}$) and S12 (1160 $mg \cdot kg^{-1}$). The values of Cr range between 19 and 921 $mg \cdot kg^{-1}$ with a mean of 241 $mg \cdot kg^{-1}$, and the highest values are found in samples S5 (591 $mg \cdot kg^{-1}$) and S6 (921 $mg \cdot kg^{-1}$). The concentrations of Al range between 0.2 and 2.8 % w.w. with a mean value of 1.5% w.w. and the highest concentrations in samples S3 (2.78% w.w.) and S11 (2.76% w.w.). Furthermore, the highest concentrations compared to other samples for Zn are found in samples S3 (124 $mg \cdot kg^{-1}$) and S5 (98 $mg \cdot kg^{-1}$), for Mn in samples S3 (1295 $mg \cdot kg^{-1}$) and S11 (1113 $mg \cdot kg^{-1}$), for Fe in samples S3 (5.3% w.w.), S5 (6.9% w.w.) and S6 (6.2% w.w.), for Cu in samples S3 (41 $mg \cdot kg^{-1}$) and S6 (41 $mg \cdot kg^{-1}$), and finally for Ba in samples S1 (147 $mg \cdot kg^{-1}$) and S11 (145 $mg \cdot kg^{-1}$).

Table 4. Analytical results and descriptive statistics of soil samples; values are on $mg \cdot kg^{-1}$ except of Ca, Mg, Al and Fe where are on % w.w.

Parameters	Ca	Mg	Al	Cu	Zn	Ni	Mn	Fe	Cr	Ba
Min	0.6	0.4	0.2	6	20	36	185	0.3	19	39
Max	31.0	8.1	2.8	41	124	1 569	1 295	6.9	921	147
Mean	11.0	1.4	1.5	22	60	472	585	2.9	241	95
Range	30.3	7.7	2.6	35	104	1 533	1 110	6.7	902	108
St. Dev.	10.3	1.8	0.7	11	27	447	299	1.9	242	30
Variance	106.7	3.3	0.5	114	739	200 079	89 148	3.6	58 403	910

According to Table 5 which depicts the extracted factors of the applied R-mode factor analysis, the chemical variation of soils is interpreted through three factors that explain the 88.7% of the total variance. The communalities for the examined parameters exceed the value of 0.80, thus all parameters are well described. The first factor explains 54.7% of total variance and includes with high positive factor loadings the parameters of Ni, Cr, Fe, Mn, Zn, Al and with medium ones the parameters of Cu and Mg. The interpenetration of this factor should be related with the lateritic horizons of the area as well as with the ultrabasic blocks of the volcanoclastic formation. The second factor explains 18% of total variance and includes with high positive factor loading Ca, while Al and Cu appear antithetic negative medium loadings. This factor probably interprets the influence of the calcare-

Table 5. Sorted Rotated Factor Loadings and Communalities for soils; values below 0.4 are presented as zero for simplification

Variable	Factor 1	Factor 2	Factor 3	Communality
Ni	0.954	0.000	0.000	0.959
Cr	0.944	0.000	0.000	0.932
Fe	0.906	0.000	0.000	0.958
Mn	0.869	0.000	0.000	0.805
Zn	0.817	0.000	0.000	0.882
Al	0.752	–0.501	0.000	0.834
Cu	0.693	–0.567	0.000	0.824
Ca	0.000	0.933	0.000	0.919
Ba	0.000	0.000	–0.933	0.919
Mg	0.542	0.000	0.716	0.835
Variance	5.4689	1.8026	1.5959	8.8675
% Var	0.547	0.180	0.160	0.887

ous substrate. Finally, the third factor which explains the 16% of total variance includes with high negative loading Ba and with antithetic medium positive loading Mg, probably interpreting the influence from Triassic dolostones.

Regarding groundwater, the prevailing calcareous substrate is the main factor that characterizes the hydrogeochemical conditions. Totally 26 out 32 samples appear calcium values greater than 75 $mg \cdot l^{-1}$, a threshold that defines the impact of calcareous basins (APPELO and POSTMA, 2005). Elevated values of calcium are accompanied in most of the cases with elevated values of HCO_3^- confirming the existence of karstification process which is expressed through the reaction $CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$ and is significant in the area due to the large number of karstic caves and katavothraes. In a few cases, the simultaneous elevated values of calcium and magnesium (e.g. W7, W9 and W18) denote the impact of the Triassic dolostone, which is hosted in the substrate. The elevated values of calcium are not spatially related, but insignificantly scattered, probably related more with underground topography of the substrate rather than the geological formations over the surface. When calcium values are low and magnesium on the contrary elevated (compared with the rest of the samples) the influence of the ultrabasic blocks of the volcanoclastic formation is significant in hydrogeochemistry, mainly through the dissolution of Mg-rich silicate minerals, such as olivine, amphibole and pyroxene.

An interesting assessment is made through the estimation of ionic ratios of Mg:Ca (Tab. 3), which reveals that in 13 (42%) of the samples the ratio is ranging between 0.5 and 0.7 denoting impact of calcareous formations (Jurassic and Cretaceous limestones), 12 (37%) of the samples range between 0.7 and 0.9 denoting impact of dolostones, and 7 (21%) of the samples have values above 0.9 denoting impact of ultrabasic formations. The percentage of dolomitic impact is not relative with the analytical values, as well as with the water types since Mg-HCO_3 type is found only in 5 samples, thus leading to the conclusion that the scattered existence of ultrabasic blocks has given a rise to the total concentration of magnesium, resulting to groundwater samples whose ionic ratios of Mg:Ca are similar with those of dolomitic impact. The above fact was confirmed by field works, where the outcropping dolostones had minor spatial existence, and from the hydrogeological conditions which impose that the Triassic dolomitic aquifer is not extended due to statigraphic and tectonic factors.

Nevertheless, the weathering of limestones and generally the karstification phenomena seems to be the main factor that controls the geochemistry of soils. In total 7 out of 18 samples appear elevated values of calcium (13.4 to 31%) but the compare with the neighbouring groundwater samples reveals that (apart from samples W13-S6) there is no significant spatial correlation between the elevated values of Ca in soils and those in groundwater. The same happens for magnesium, as there is no correlation between the Mg elevated values in soils and groundwater. This should be attributed to the fact that the main enrichment source of Mg are the ultrabasic formations of the substrate which rarely have surface occurrences in the area, thus the weathering that mainly affects the geochemistry of soils has limited impact on the upper horizons. On the contrary, the existence of volcanoclastic formations in various depths affect frequent the hydrogeochemistry of groundwater.

The presence of Ni and Cr in groundwater samples is less than expected, according to the presence of lateritic horizons in the lithological sequence of the area and the concentrations of the aforementioned metals in soil samples. In more details, nickel in groundwater is present in minor concentrations, ranging from 6 ppb to 14 ppb, only in few samples (W3, W11, W12, W13 and W24), while chromium appears slightly elevated concentrations (ranging from 12 ppb to 33 ppb) compared with nickel in samples W2, W13, W14, W22 and W28. Despite the fact that Cr and Ni possible have the same origin (lateritic horizons and ultrabasic rocks) they don’t appear similar elevations in their concentrations of groundwater samples, apart from sample W13. In all other cases the fluctuation of their concentrations is different, probably denoting regulation from external factors. A more thorough assessment of the analysis reveals that the elevated values of Cr related with pH values ranging from 8.1 to 8.4 and relatively the elevated values of Ni are related with pH values ranging from 7 to 7.8, denoting a possible influence, a fact which is in accordance with the results of the second factor of R-mode analysis (Tab. 2) which includes pH and Cr with high positive factor loadings. In addition, the differences in mobility of Cr and Ni and subsequently in the variation of their concentrations in aqueous solutions might be attributed to other geochemical phenomena. In more details, a significant increase in the mobility of Ni might occur when nickel is associated with carbonates (BINOTTO *et al.*, 2000), a fact which is confirmed by the chemical analyses and the third factor of R-mode analysis.

On the contrary, Ni appears high concentrations in soils, which should be attributed to the impact of the Ni-rich lateritic horizons that occur at the geological substrate of the area. The elevated values of Ni in soils are accompanied in most of the cases with elevated values of Fe, Cr, Al and Mn, which exist in the weathering crusts of laterite in the wider area (SKARPELIS, 2006). Only in few cases (northern of Kastro and southern of Aghios Ioannis) the elevated values of Ni and Cr are related with an increase in the concentrations of Ni and Cr in groundwater. In all other cases soil and groundwater geochemistry are not related, regarding the values of Cr and Ni.

The assessment of the statistical processing of initial data, revealed the impact of a single factor to hydrogeochemistry that was not clearly indicated directly through chemical analysis. As we can assess by the first factor of R-mode analysis, there is an elevation in some samples in the values of TDS, *EC*, Na^+, SO_4^{2-}, Mg^{2+} and Cl^-, which probably denotes a common source of enrichment. All the aforementioned parameters are seawater related (HEM 1985), so a scenario that would adopt a potential seawater intrusion in the eastern parts of the study area might interpret this phenomenon. But the hydrogeological evidences (PAGOUNIS *et al.*, 1994) show that there is not such a case for the area, leading to the conclusion that the increased salinity may be attributed to another factor. Since the enrichment from airborne sea-spray should be excluded due to the local climatic conditions (general annual wind direction) and topography (the study area is surrounded by mountains), the salinization should attributed to the paleo-environmental conditions of the area.

In more details, the study area was a part of the former Lake of Kopais, which periodically had frequent changes in water level accompanied by high temperatures (ALLEN, 1984). The above fact played a major role for the formation of evaporitic fluoresences in the limestone outcrops that were revealed after the periodic decrease of water level (TZIRITIS, 2008). Similar fluoresences are frequently present with the form of crusts in Lakes with high organic content and specific climatic conditions (high temperature and evapotranspiration) with the form of trona ($Na_2CO_2 \cdot NaHCO_3 \cdot 2H_2O$), tenardite ($Na_2SO_4$) and halite (NaCl), over organic debris or fine bedded sandy depositions (TSIPOURA and STAMATAKIS, 2004; 2005). All the above conditions resemble with the paleo-environment of the area, resulting to the fact that the salinization source of enrichment should be attributed to evaporitic crusts. This scenario is also confirmed, apart from the hydrogeological evidences, by two more important notes. If salinization were related with seawater intrusion, apart from the elevated values of the aforementioned seawater related parameters, the concentrations of K^+ should be also elevated. This fact is not valid, so the origin of Na^+, SO_4^{2-} and Cl^- should be different, for example dissolution of tenardite or halite. Moreover, if seawater intrusion had occurred that would mean a more widespread spatial distribution of salinization, and not a local one, such as in our case which occurs only for samples neighbouring with limestone outcrops.

An interesting note is made for Ba^{2+} which appears elevated concentrations (related to other samples) in some of the groundwater samples (W6, W7, W8 and W18) ranging from 70 to 130 ppb. These samples (except W18) are spatially related concluding to the fact of a common source of enrichment. This source should be possibly attributed to the dissolution of barite ($BaSO_4$), as the highest values of sulphates appear also in these samples. The occurrence of barite, although it was not detected by mineralogical methods, it is quite possible to exist since barite can be formed in organic rich calcareous sediments through diagenetic processes (STAMATAKIS and HEIN, 2004). On the contrary, Ba^{2+} concentrations in soils are low and even those samples which appear slightly elevated values compared with the others, do not appear any spatial correlation with the elevated values in groundwater samples. This might be interpreted by the existence of a secondary source of enrichment which is major for soil geochemistry, such as the content of the volcanoclastic formations in Ba^{2+}.

The elevated values of copper in groundwater samples W3, W27 and W30 (237 ppb, 99 ppb and 39 ppb respectively) are not associated with any other parameter. In fact, all other parameters in these samples appear decreased values compared with other samples, except W30 which appear elevated value for nitrates (44 ppm). This fact may interpret the elevated values of Cu which might be related with nitrate fertilizers and/or pesticides which are used intensively in the area. In other case, secondary geochemical processes might occur (e.g. complexation) which increases the mobility and concentrations of copper, while the rest heavy metals (e.g. Cr, Ni, Zn, Fe) which are related either with the volcanoclastic formations or the lateritic horizons are low. On the contrary, copper is correlated in the geochemistry of soils samples with Zn, Mn, Fe and Ni, since their highest values co-exist in the same samples, probably denoting the impact from a weak sulfide mineralization.

Finally, an important factor which influences the chemical status of groundwater is the manmade pollution, which derives from the extensive use of N-fertilizers. Totally 8 samples (W5, W12, W20, W21, W22, W25, W30 and W31) out of 18 appear elevated concentrations ranging from 40 ppm to 65 ppm. The spatial distribution of the above samples denote that there is not an extended contaminated plume, but local contaminated areas which are probably due to specific enrichment conditions related with infiltration and magnitude of enrichment (use of fertilizers). It is quite noticeable that in samples with elevated NO_3^- values the concentrations of Fe are low, while in the samples with the highest Fe concentrations nitrates are abnormally decreased. The above fact, which is confirmed also by the fifth factor of R-mode analysis, interprets the local reducing conditions which are developed in some areas (TZIRITIS, 2009), where NO_3^- and Fe^{3+} are depleted because of reduction, and the aqueous solution is enriched in N and Fe^{2+}.

The risk assessment for the quality status of groundwater and soils, regarding the impact to biota and fauna, resulted to the following. Groundwater is in general suitable for drinking, as no extended contamination phenomena were detected. The contamination index is negligible for the majority of the samples, and only five of them appear minor contamination conditions, regarding the parametric values imposed by the relative legislation (Directive 98/83/EU). In more details, the main pollutant of groundwater are nitrates which appear elevated concentrations (above 40 $mg \cdot l^{-1}$) in the 25% of the samples, while three of them (W5, W12 and W22) appear concentrations which exceed the proposed levels of 50 $mg \cdot l^{-1}$ for use as potable water (Directive 98/83/EU). In addition, Mn and SO_4^{2-} exceed the maximum parametric values of the relative Directive in samples W7 (72 ppb) and W18 (256 ppm) respectively. On the contrary, the salinity conditions of the samples as were assessed by the values of *SAR*, denote that most of the samples are not suitable for irrigation, especially for plants which are sensitive to high salinization. The content of heavy metals in groundwater has no impact to plants either for short or long term exposure, except the value of Cu in W3 for long-term exposure (Tab. 6).

Table 6. Maximum parametric levels for irrigation waters regarding long and short term use (FIPPS, 2003)

Constituent	Long-term use, $mg \cdot l^{-1}$	Short-term use, $mg \cdot l^{-1}$
Al	5.0	20
Cr	0.1	1
Cu	0.2	5
Fe	5.0	20
Mn	0.2	10
Ni	0.2	2
Zn	2.0	10

Regarding soils, as can be extracted from Table 7, the concentrations of Ba, Cu, and Zn are below the parametric values of both Canadian and Dutch limits. Serious environmental problems derive form the concentrations of Ni, which exceed the maximum imposed parametric values of both Canadian and Dutch standards in many soil samples. In more details, the Canadian limit for Ni is exceeded in 11 samples, while the Dutch in 10 samples. The above fact raises a significant environmental pressure regarding Nickel concentrations in soils, and poses the fact that most of the soils covering the area are inappropriate for specific uses, such as agricultural land. It should be noted that the majority of the area is used for agricultural purpose, such as the cultivation of green vegetables which are intended for human consumption. The maximum concentrations for Cr are exceeded in two of the samples regarding the Canadian limits, and in 5 samples regarding the Dutch ones which have lower values.

Table 7. Canadian and Dutch maximum parametric values for soils concerning the examined parameters of the soil samples

Parameter	Canadian limits, mg·kg^{-1} agricultural land	Dutch limits, mg·kg^{-1} soils (general) – urgent action
Ba	750	625
Cr	750	380
Cu	150	190
Ni	150	210
Zn	600	720

Source: Canadian Soil Quality Guidelines for the Protection of Environmental Human and Health; The new Dutch list.

CONCLUSIONS

The analytical data as well as the geochemical and statistical processing revealed that hydrogeochemical status of groundwater is influenced mainly by the extensive use of fertilizers, which impose elevated values of nitrate. Additionally, the paleo-environmental conditions gave rise to the formation of evaporitic crusts, which define locally the chemical status of groundwater through their dissolution. Other natural factors that control hydrogeochemistry are the calcareous substrate and lateritic horizons.

Soil geochemistry is majorly influenced by the geological formations of the area, and more specifically by the volcanoclastic formations as well as from the limestones.

The common impact of the above factors to soil and groundwater chemical status was observed only in very few cases. That means that these two geochemical systems act independently and don’t seem to be related.

The risk assessment of both soil and groundwater samples revealed that there is no significant environmental threat regarding groundwater, a fact which differentiates for soils as the elevated values of Ni and Cr in most of the samples pose a serious environmental problem.

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STRESZCZENIE

Stan geochemiczny i oddziaływania między glebą a systemem wód podziemnych na obszarze Akrefnio, środkowa Grecja. Ocena zagrożeń dla ludzi i środowiska naturalnego

Słowa kluczowe: *Akrefnio, geochemia, gleba, ocena ryzyka, środkowa Grecja, woda gruntowa*

Pobrano 50 próbek gleby i wody gruntowej z obszaru Akrefnio (środkowa Grecja) do oceny stanu geochemicznego i zagrożeń ludzi i środowiska naturalnego. Wyniki analiz i przetworzenie danych ujawniły, że głównymi czynnikami hydrogeochemicznymi są zasilanie z wapiennego podłoża i antropogeniczne zanieczyszczenia, pochodzące z nadmiernego stosowania nawozów azotowych. Geochemia gleby podlegała silnym wpływom laterytowych poziomów, które zwiększały stężenie niklu i chromu w większości próbek glebowych. Choć większość procesów geochemicznych między glebą a wodami gruntowymi ma charakter powszechny, opisany system nie wykazywał interakcji, a jego elementy funkcjonowały w większości niezależnie. Ocena zagrożeń naturalnego środowiska wykazała, że woda gruntowa nadaje się do spożycia, ale nie do nawodnień z powodu silnego zasolenia. Gleby są w wysokim stopniu zanieczyszczone niklem i chromem, dlatego są nieodpowiednie do obecnego wykorzystania rolniczego.

Received 22.11.2010