

Isotope Geochemistry Survey in Ierissos Gulf Basin, North Greece

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Abstract. Major element chemistry of water samples in Ierissos gulf basin is dominated by Ca^{2+} , Mg^{2+} and HCO_3^- ions. Water rock interaction is an important mechanism in the mineralization of waters. A link between Skouries and Gomati samples (Mg-HCO_3) was detected reflecting the well documented M. Panagia-Gomati fault. In Neochori and M. Panagia samples were identified fluids with different origin. Regarding surface waters, extended bicarbonates action of meteoric waters and reductive conditions, probably control *As* concentration in surface water. Generally, surface waters in Kokkinolakas basin exceed the WHO limits for *As*, *Sb*, *Cr*, *Ni*, *Cd*, *Pb*, *Mn*, *Fe* in great rates as natural immobilization mechanisms are suspended.

1. Introduction

The basin of Ierissos Gulf in Chalkidiki, north Greece, is characterized by a dynamic geomorphologic regime with sharp slopes and dense hydrographic network (large rivers and mountain streams). Kokkinolakas River, with a NW to SSE direction, constitutes the body of hydrographic network with a permanent flow throughout the year. The land uses that predominate are woodlands followed by agricultural land. Mining activities, that have been taking place in this area since the last decade of 19th century, occupy the smaller percentage than the traditional productive sector and although there is a need for a variety of papers regarding the geochemical regime of the area (soil, water, air) and the interaction with inhabitants and their activities (fishing, animal husbandry, agriculture), only few studies have been published demonstrating the elevated heavy metal concentrations in stream sediments and waters [1, 2, 3, 4, 5]. This study was carried out in order to highlight gaps in our knowledge about the geochemical model of the wider area of Ierissos Gulf basin. Therefore, thirty-six samples were collected in three different sampling periods and subjected to chemical and isotopic analysis. The isotope analyses were performed in the Laboratory of Stable Isotopes and Radiocarbon in Nanoscience and Nanotechnology Institute, NCSR Demokritos, Greece. Major ions (Cl^- , HCO_3^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , Mg^{2+}), heavy metals (Ba, As, Sb, Hg, Cr, Ni, Cd, Pb, Co, Mn, Fe, Cu, Zn) and B^+ were determined according to standard analytical methods [6]. The $\delta^{18}\text{O}$ compositions of water were determined from CO_2 equilibrated with the water [7]. Surface water was collected three days after an extreme precipitation episode where acidic runoff was observed in Kokkinolakas basin.



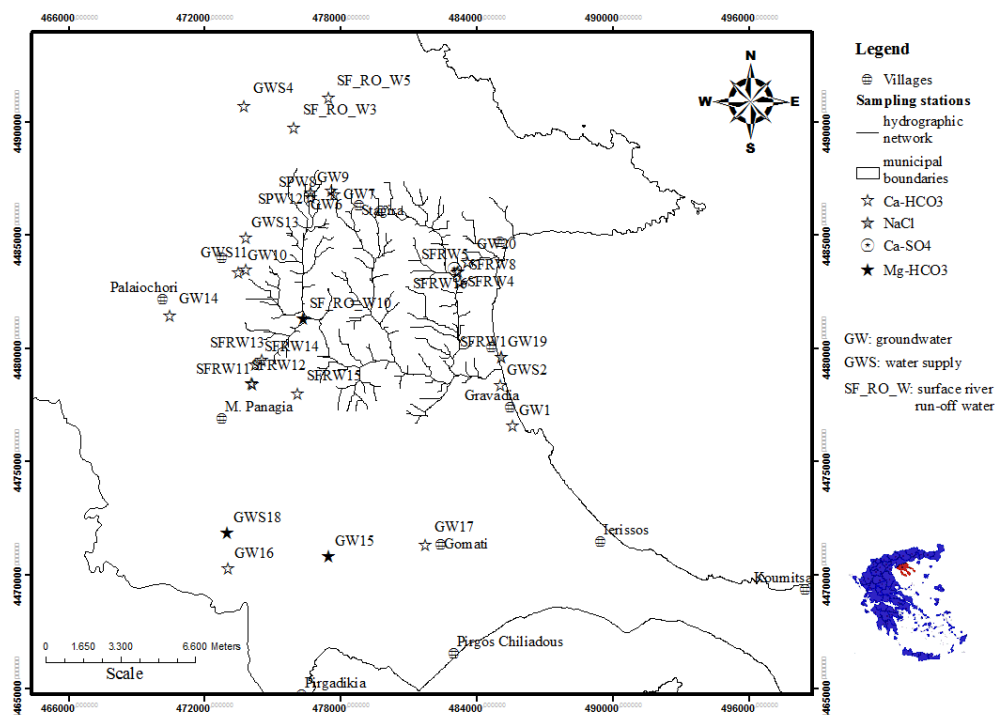


Figure 1. Study area of Ierissos gulf basin and sampling sites

2. Hydrochemistry

All sampled water exhibited neutral to alkaline pH (7.2-8.5) values. Four different chemical types were found (Figure 1): Ca-HCO₃, Mg-HCO₃, Ca-SO₄ and Na-Cl. Ca-HCO₃ group represents low SO₄²⁻ and Cl⁻ concentrations concerning both groundwater and surface water samples. Ca-SO₄ water type concerns surface water sample SFRW16 in the upper part of Kokkinolakas River and downstream the mining plants of Madem Lakkos area. Kelepertzis E. et al. [3] have also reported elevated Ca, Mg and SO₄ as a result of draining episodes of polymetallic sulphide deposits. Based on Figure 2 (left), a variation was detected with respect to Mg/Ca ratio. Mg-HCO₃ samples (GW15, GW18, SFRW10) were mainly controlled by an excess of Mg/Ca ratio with a stable Na/Ca ratio (Figure 2, right) and a circulation pattern in the rock substrate where both silicate and carbonate weathering effect results in the release on K⁺ and Mg²⁺ ions (Figure 2, left). Considering that sample SF_RO_W10 represents Skouries area, its grouping (Mg-HCO₃ type) with Gomati samples (GW15, GW18) probably reflects the well documented M. Panagia-Gomati fault [8, 9, 10, 11]. In fact, the pronounced magnesium concentrations could be attributable to the conclusions of Kroll T. et al. [10] for crustal contamination based on relatively high ⁸⁷Sr/⁸⁶Sr ratios. Given that water equilibrates with calcite and dolomite under room temperature resulting in an ideal molar Mg/Ca ratio of about 0.8 [12], it seems that rest of samples (except SFRW1) that represented Mg/Ca ratio below the line of 0.8, probably reflect a simultaneous equilibration with the calcite and dolomite. Sample SFRW1 presents a trend to seawater confirming its Na-Cl chemical type and its sampling site at the outflow of Kokkinolakas River where there is an interaction with sea water.

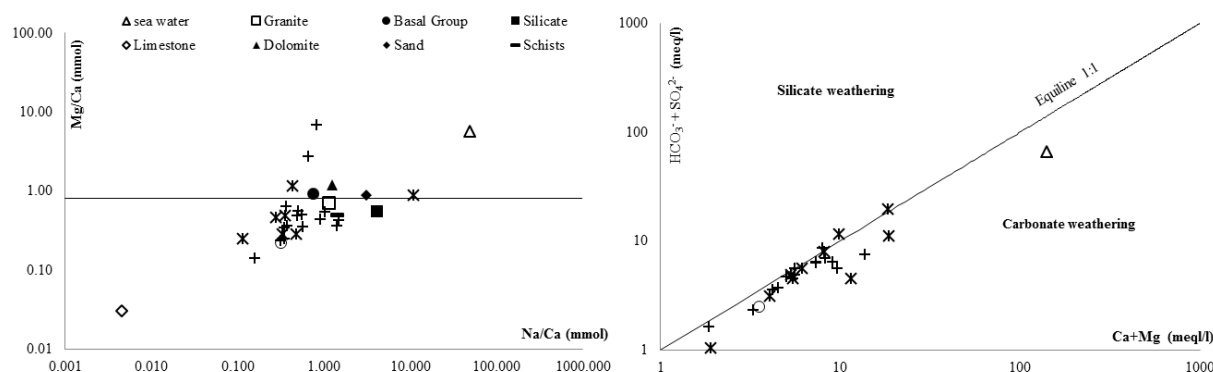


Figure 2. On the left: diagram of Mg/Ca versus Na/Ca and on the right: $[\text{HCO}_3^- + \text{SO}_4^{2-}]$ versus $[\text{Ca}^{2+} + \text{Mg}^{2+}]$

3. Oxygen stable isotopes

Oxygen isotopic data ranged from -9.5‰ to -7.3‰ for groundwater and from -8.6‰ to -6.5‰ for surface waters. These values were consistent with the reported ones by Voutsas D. et al. [4] and Gilg et al. [13] for the area. In $\text{Cl}-\delta^{18}\text{O}$ (Figure 3, left) diagram the position of samples highlights three different mechanisms. Samples (GWS2, GW4, GW6, GW7, GW9, GWS13, GW14, GW16, GW19, SPW8, SF_RO_W3, SFRW11, SFRW13, SFRW14) align along the fresh water-sea water mixing line implying a seawater end-member. However, chemical data (mean Cl^- concentration of 32.9 ppm for groundwater and 12.7 ppm for surface water) do not imply a marine component, except sample SFRW1 with NaCl chemical type. Probably this trend highlights the seawater signature through sea sprays and aerosols, as Ierissos Gulf presents a dynamic wind circulation pattern [2]. This is further supported by the strong correlation ($r^2=0.78$) between Na-Cl in all samples despite their low values. Regarding samples that grouped above mixing line (SFW4, SFW5, SFW12, SFW16, SF_RO_W10), a $\delta^{18}\text{O}$ enrichment can be observed without any strong variation to Cl^- ppm values. Considering a typical isotopic gradient 0.3‰/100 m [14] for $\delta^{18}\text{O}$, a variation of about 2.1‰ (-8.6‰ to -6.5‰) could be attributable to the altitude effect ($\Delta h=700$ m). However, such hypothesis is rejected as the more enriched values correspond to higher altitudes. Therefore, the enrichment in $\delta^{18}\text{O}$ values is rather attributable to water-rock interaction process. Groundwater samples present a typical picture where the more depleted $\delta^{18}\text{O}$ values (-9.5‰ to -7.3‰) correspond to higher altitudes and the $\delta^{18}\text{O}$ variation corresponds to the isotopic gradient. Last group, below the mixing line, presents a trend to slight higher Cl^- values (ppm) and a strong correlation factor between the samples (GW10, GW11, GW17, GW20). These samples exhibit a slight shift from the mixing line and for this reason they could be considered to belong to a wider area that reflects the signature of sea sprays and aerosols. However, their strong correlation could imply a dilution by different origin fluids that can be characterized by a bit higher and enriched Cl^- (ppm) and $\delta^{18}\text{O}$ (‰) values respectively. The samples correspond to Neochori (GW10, GW11) and M. Panagia (GW17, GW20). Kroll T. et al. [10] characterized this area as hydrothermal alteration zone and reported the high hydrothermal magnetite with intense oxygen fugacity. Indeed, sample GW17 is accompanied by field observations concerning the strong sulphur odour and degas episode while sample GW20 presented intense carbonate precipitation in the surroundings of borehole. The position of SFRW1 sample probably reflects an evaporation effect as the increase of Cl^- is observed without strong alteration to $\delta^{18}\text{O}$ values.

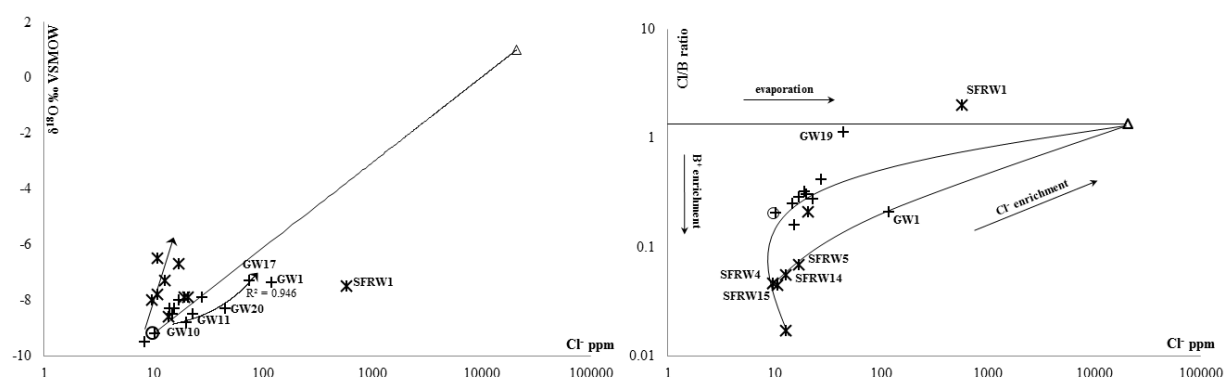


Figure 3. $\delta^{18}\text{O}$ VSMOW versus Cl^- ppm (left) and Cl/B versus Cl^- ppm (right)

In order to highlight the above mechanisms, the soluble ions (Cl^-) and the rock-forming elements (B^+) were used. The main pathways that these ions transport are meteoric water, water-rock interaction (for B^+) and mixture with marine groundwater (for Cl^-). The Cl/B ratio for meteoric waters reflect the one of sea water as a result of sea sprays and aerosols. When this water interacts with the rock substrate Cl^- and B^+ are dissolved, stoichiometrically, from the surrounding rocks. Given that rocks are rich in B^+ , the Cl/B ratio of the water becomes lower than that of seawater. Rest of samples present a Cl/B ratio below that of sea water suggesting a water-rock interaction process [14]. However, based on their ratio two trends are distinguishable. The first follows a ratio between 0.3 and 0.2. These samples concern mainly groundwater and spring water suggesting the rock contribution of boron, except the sea sprays signature. The unique surface run-off sample that is grouped to this category is SF_RO_W3 implying that this sample, which outflows to Kokkinolakas river with high As (140 ppb) and Sb (94 ppb) concentrations, originates from groundwater aquifer. The second trend concerns SFRW4, SFRW5, SFRW14, SFRW15 samples with Cl/B ratio between 0.04 and 0.2. This pronounced reduction of Cl/B ratio is because of the increased boron concentration in surface waters. This could be attributable to the interaction with fine sediment material and suspended dust in the water resulting in elevated boron concentration. In more detail, surface samples SF_RO_W5, SFRW4, SFRW5, SF_RO_W10 (NE part of Kokkinolakas basin) present a positive strong correlation ($r^2=0.96$) between Pb and B with the corresponding values of sulphate to be elevated (59.5-463 ppm), reflecting the lead/zinc/silver sulphide background of this area. This was also evident in Kelepertzis et al. [3] for Kokkinolakas samples where a strong positive correlation ($r^2=0.84$) between Pb and SO_4 can be observed. Groundwater sample from Ierissos (GW1), at the lower part of Kokkinolakas basin, also grouped in this trend implying an interaction between surface and underground water table. This observation is strengthened considering that groundwater circulation on the downstream of Ierissos Gulf basin is in a shallow water table where the alluvial deposits (permeable) predominate. However, this could not be further supported as it is represented only by one sample. Finally, sample SF_RO_W10 from Skouries area presents a strong contribution of boron content confirming the previous observations of crustal contamination.

4. Distribution of heavy metals

The concentration of heavy metals exhibited elevated values for the elements As (GWS4, GW6, GW7, SFRW4, SFRW5, SFRW14, SFRW16, SF_RO_W10, SPW8, SPW12), Sb (SF_RO_W3, SF_RO_W5, SPW8), Cr (SF_RO_W10), Ni (SFRW5, SFRW8, SF_RO_W5, SF_RO_W10), Cd (SFRW1, SFRW5, SFRW8, SFRW16, SF_RO_W5), Pb (SFRW4, SFRW5, SFRW8, SFRW13, SF_RO_W5, SF_RO_W10), Co (SF_RO_W5), Mn (GW6, GW7, GW9, GW17, GW19, SFRW1, SFRW4, SFRW5, SFRW8, SFRW13, SFRW14, SFRW15, SFRW16, SF_RO_W5, SF_RO_W6, SF_RO_W10), Fe (GW7, GW9, GWS13, GW16, GW17, SFRW4, SFRW5, SFRW14, SFRW16) and Zn (SFRW8, SF_RO_W10) about 15-87%, 50-90%, 55%, 34-79%, 2-87%, 10-93%, 85%, 16-99%, 3-94%, 43-53% over the WHO drinking guidelines [15], respectively (Table 1).

Table 1. Heavy metal (ppb) for groundwater and surface water samples that exceed WHO drinking guidelines

WHO limits	Ba 1000	As 10	Sb 5	Cr 50	Ni 20	Cd 5	Pb 10	Co 1-2	Mn 50	Fe 300	Zn 5000
GWS4	196	20.4	5	1	<5	<5	0	<1	13	14	1147
GW6	40.6	87	4.2	1	<5	<5	<5	<1	80	84	171
GW7	54.5	90	4.3	1	<5	<5	0	<1	714	1000	1743
GW9	66.6	6	<1	1	<5	<5	0	<1	90	571	1838
GW10	54.9	25	2	1	8	<5	<5	<1	20	24	1162
GWS13	59.8	<1	<1	1	<5	<5	<5	<1	16	825	1167
GW16	33.8	<1	<1	0	<5	<5	0	<1	22	325	10
GW17	193.7	<1	<1	1	<5	<5	<5	<1	347	2387	<5
GW19	311	<1	<1	1	<5	<5	5	<1	69	137	6
SFRW1	57	17	<2.8	<2	13.6	5.19	<5	-	1319	23.6	2240
SFRW4	218	13.5	<2.8	2.06	9.1	0.747	82.15	-	229	320	1470
SFRW5	214	69.4	2.95	4.39	65.8	23.4	106.6	-	6988	478	3640
SFRW8	92.7	25	4.33	<2	144	73.9	23.72	-	750	98	16200
SFRW13	91.6	<1	<2.8	4.57	9.4	0.626	12.18	-	69.8	129	2240
SFRW14	103	14.3	<2.8	2.38	<5	0.483	7.089	-	89.7	1165	1790
SFRW15	1363	2.1	<2.8	<2	<5	0.366	<5	-	176	91.4	1370
SFRW16	138	84.7	3.73	3.73	14.8	5.79	6.965	-	3650	699	963
SF_RO_W3	124	140	94	5	<5	<5	<5	<1	-	13	1452
SF_RO_W5	102.5	9	15	5	41	55	14	25	12250	130	12480
SF_RO_W6	1644	5.41	<2.8	2.07	<5	0.439	<5	-	126	26.5	1640
SF_RO_W10	218	41.2	<2.8	173	172	2.62	291.8	-	244	10510	1870
SPW8	65.9	66	24	1	<5	<5	0	<1	29	12	1227
SPW12	57	15	3	1	<5	<5	<5	<1	<10	<10	1096

Many authors [16, 17, 18] have reported the positive correlation between boron and arsenic in groundwater as they are both soluble minerals found in hydrothermal deposits. However, this study presents samples with no correlation between boron and arsenic (Figure 4, left) implying a different origin of these ions. The positive strong correlation between As and HCO_3^- (Figure 4, right) for surface samples and the respective negative correlation between As and SO_4^{2-} (Figure 5, left) indicates that As values mainly gathered by an extended interaction with meteoric water bicarbonates and the dissolution of arsenic into groundwater under reductive conditions, although there are some exceptional cases (treated waters). Both of these mechanisms suggest the disruption of natural immobilization mechanisms that have been reported by Gamaletsos et al. [1] such as the formation of insoluble Fe-arsenate phases or the natural scavenging of As into Fe(III)-oxy-hydroxy-sulfate phases. Indeed, the competitive behavior of bicarbonates on As adsorption reactions onto iron oxide minerals, resulting in increased concentrations of As remaining in solution as the bicarbonate concentration increases, it is well documented [16, 18, 19]. Figure 5 (right) highlights this observation with the absence of correlation between Fe and As concentrations. Generally, it should be noted that surface waters exceed the WHO drinking guidelines for all the above mentioned elements. Lazaridou et al. [5] concluded that heavy metal pollution is responsible for the reduction of the abundance and diversity of benthic macroinvertebrates in the streams of Olympias and Skouries catchments and that minor heavy metal load bioaccumulation of metals affected higher trophic levels (fish).

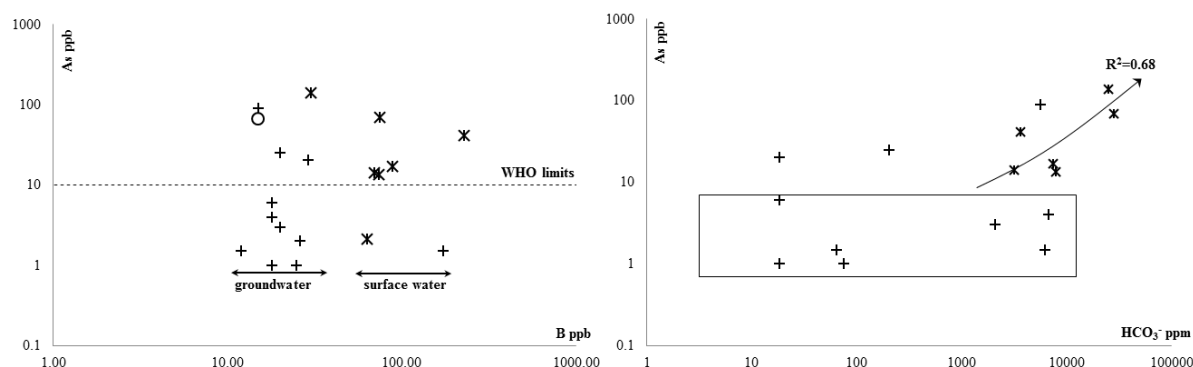


Figure 4. As ppb versus B ppb (left) and As ppb versus HCO₃⁻ ppm (right)

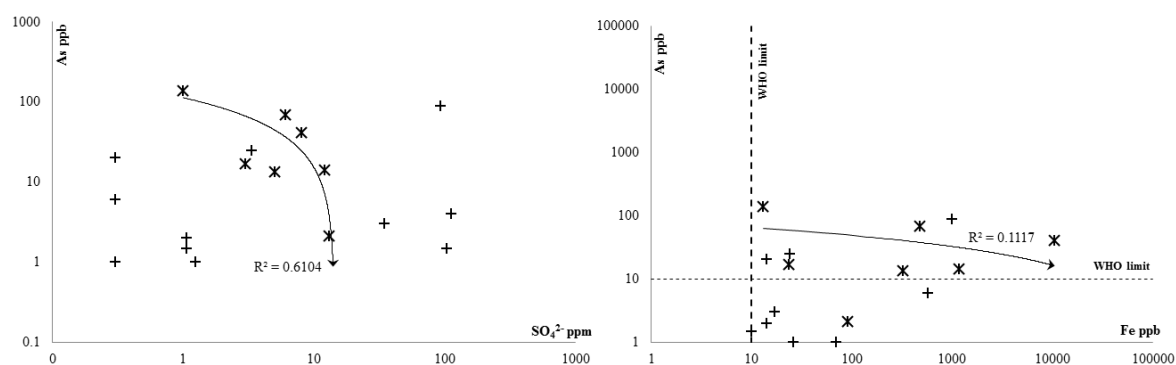


Figure 5. As ppb versus SO₄²⁻ ppm (left) and As ppb versus Fe ppb (right)

5. Conclusion

Within this study the primary conclusions concern: a) the correlation between Skouries and Gomati groundwater through M. Panagia-Gomati fault, b) the different origin of fluids that participate in heavy metal load of Neochori and M. Panagia groundwater, c) a surface run-off with high As and Sb concentrations and groundwater origin d) the action of bicarbonates and reductive conditions in arsenic values in surface water. M. Panagia, Neochori and Gomati areas should be protected as overpumping threatens the quality of groundwater. The variation of arsenic concentrations in water samples is an important consideration for monitoring and treatment projects. Environmental and health studies are imposed in Chalkidiki study area.

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References

- [1] Gamaletsos P., Godelitsas A., Dotsika E., Tzamos E., Göttlicher J., Filippidis A., 2015. "Geological sources of as in the environment of Greece: A review", Handbook of Environmental Chemistry, 40, pp. 77-113.
- [2] Chantzi P., Albanakis K., Krestenitis I., Kombiadou K., Konstadinou Z., 2014. "Investigation of coastal sediment transport in the Ierissos Gulf, Chalkidiki", Book of Abstracts of the International Conference on Adaptation Strategies to Global Environmental Change in the Mediterranean City and the Role of Global Earth Observations. The Mediterranean City, 2014: p16

- [3] Kelepertzis E., Argyraki A., Daftsis E., 2012. “Geochemical signature of surface water and stream sediments of a mineralized drainage basin at NE Chalkidiki, Greece: A pre-mining survey”, *Journal of Geochemical Exploration*, Volume 114, Pages 70-81
- [4] Voutsas D., Dotsika E., Kouras A., Poutoukis D., Kouimtzis Th., 2009. “Study on distribution and origin of boron in groundwater in the area of Chalkidiki, Northern Greece by employing chemical and isotopic tracers”, *Journal of Hazardous Materials*, Volume 172, Issues 2–3, Pages 1264-1272
- [5] Lazaridou-Dimitriadou M., Koukoumidis C., Lekka E., Gaidagis G., 2004. “Integrative evaluation of the ecological quality of metalliferous streams (Chalkidiki, Macedonia, Hellas)”, *Environmental Monitoring and Assessment* 91, 59–86.
- [6] APHA, AWWA, WPCF, 1985. Standard Methods for the Examination of Water and Wastewater (16th ed).
- [7] Epstein, S., Mayeda, T., 1953. “Variation of ^{18}O content of waters from natural sources”, *Geochim. Cosmochim. Acta* 4, 213–224.
- [8] Chatzipetros A., Michailidou A., Tsapanos Th. and Pavlides S., 2005. Morphotectonic-seismotectonic study of Stratoni-Varvara and Gomati-Megali Panagia faults (eastern Chalkidiki), *Bulletin of the Geological Society of Greece*, 37, 127-142.
- [9] Michailidou A., Chatzipetros A. and Pavlides S., 2005. “Quantitative analysis - morphotectonic indices for the Stratoni-Varvara and Gomati-Megali Panagia faults (eastern Chalkidiki)”, *Bulletin of the Geological Society of Greece*, 38, 14-29.
- [10] Kroll T., Müller D., Seifert T., Herzig P.M., Schneider A., 2002. “Petrology and geochemistry of the shoshonite-hosted Skouries porphyry Cu–Au deposit, Chalkidiki, Greece”, *Mineralium Deposita* 37, 137-144.
- [11] Pavlides S.B., Tranos M.D., 1991. “Structural characteristics of two strong earthquakes in the North Aegean: Ierissos (1932) and Agios Efstratios (1968)”, *Journal of Structural Geology*, Volume 13, Issue 2, Pages 205-214
- [12] Appelo, C.A.J., Postma, D., 1993. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam.
- [13] Gilg A., Frei R., 1994. “Chronology of magmatism and mineralization in the Kassandra mining area, Greece: The potentials and limitations of dating hydrothermal illites”, *Geochimica et Cosmochimica Acta*, Volume 58, Issue 9, Pages 2107-2122
- [14] Dotsika E., 2015. H–O–C–S isotope and geochemical assessment of the geothermal area of Central Greece, *Journal of Geochemical Exploration*, Volume 150, Pages 1-15.
- [15] WHO, Guidelines for drinkingwater quality Health Criteria and Other Supporting Information, vol. 2, 2nd ed., World Health Organisation, Geneva, Switzerland, 1996, pp. 940–949.
- [16] Bhattacharya P., Claesson M., Bundschuh J., Sracek O., Fagerberg J., Jacks G., Martin R.A., Storniolo A., Thir M., 2006. “Distribution and mobility of arsenic in the Rio Dulce alluvial aquifers in Santiago del Estero Province”, Argentina, *Sci. Total Environ.* 358, 97-120.
- [17] Smedley P.L., Nicolli H.B., MacDonald D.M.J., Baros A.J., Tullio J.O., 2002. “Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina”, *Appl. Geochem.* 17, 259-284.
- [18] Kim M.J., Nriagu J., Haack S., 2000. “Carbonate ions and arsenic dissolution by groundwater”, *Environ. Sci. Technol.* 34, 3094-3100
- [19] Kim M.J., Nriagu J., Haack S., 2003. “Arsenic behaviour in newly drilled wells”, *Chemosphere* 52, 623-633.