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GEOCHEMICAL EFFECT OF THE ROCK CHEMISTRY AND THE ANTHROPOGENIC ACTIVITIES ON GROUNDWATER: THE CASE STUDY OF NW EUBOEA, GREECE

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Abstract

A geochemical study of NW Euboea island ground waters was undertaken, in order to examine the possible effect of the chemical composition of the country rocks of the area as well as of the anthropogenic activities, to the concentration of environmentally important elements and chemical compounds in the groundwaters. NW Euboea consists of a great variety of rock types showing a wide range in mineralogical and chemical composition. The main groups of rocks occurring in NW Euboea are: i) various types of sedimentary rocks e.g. shale and chert formations, carbonate and clastic rocks, ii) ophiolitic rocks including peridotite, gabbro, serpentinite etc, and iii) epizonally metamorphosed basic igneous rocks, with schist and phyllite intercalations. A number of hot springs also occur in the area. The main anthropogenic activity in the area is the agricultural land use, as any significant industrial activity is absent. For that purpose, 45 water samples were collected and analyzed by Spectrophotometry for the main anions and by FP and AAS for major and a number of trace elements. On the basis of those analyses, a number of the water samples were selected and analyzed by ICP-AES and ICP-MS for a large group of mainly metallic trace elements. The interpretation of the analytical data showed clearly that the content of the groundwater for a significant group of trace elements (e.g. Cr, Ni, Zn) was considerably influenced by the chemical composition of the surrounding rocks, especially the ophiolitic and metamorphic rocks. The anthropogenic activities also affect the groundwater quality, near areas where the use of fertilizers and pesticides for agricultural purposes is extensive, resulting to the increase of various anion concentrations (NO_3^-, SO_4^{-2}, PO_4^{-3}).

Key words: *groundwater geochemistry, trace element and anion concentration, NW Euboea, Greece.*

Περίληψη

Στη παρούσα μελέτη πραγματοποιήθηκε γεωχημική έρευνα των υπόγειων ψυχρών νερών της ΒΑ Εύβοιας. Στην ΒΑ Εύβοια εμφανίζεται πληθώρα γεωλογικών σχηματισμών με πλούσια ορυκτολογική σύσταση. Οι κυριότεροι τύποι πετρωμάτων που απαντώνται είναι: i) ιζηματογενή πετρώματα, ii) πετρώματα της οφιολιθικής σειράς όπως περιδοτίτες, γάββροι, σερπεντινίτες κ.α., iii) μεταμορφωμένα βασικά

εκρηξιγενή πετρώματα με παρεμβολές σχιστόλιθων και φυλλιτών. Επίσης, στη ΒΑ Εύβοια εμφανίζονται θερμές πηγές. Οι ανθρωπογενείς δραστηριότητες στην περιοχή μελέτης είναι κυρίως αγροτικής φύσεως, ενώ απουσιάζει οποιαδήποτε σημαντική βιομηχανική δραστηριότητα. Ένας από τους σκοπούς ευρύτερης έρευνας που διεξάγεται στην περιοχή, είναι ο εντοπισμός της επιρροής των φυσικών παραγόντων και των ανθρωπογενών δραστηριοτήτων στον χημισμό των υπόγεων νερών, εδαφών κλπ. Στα πλαίσια της παρούσας μελέτης συλλέχθηκαν 45 δείγματα υπόγειων νερών, τα οποία αναλύθηκαν φασματοφωτομετρικά για τον προσδιορισμό των κύριων ανιόντων/κατιόντων και με FP και AAS προσδιορίστηκαν κύρια στοιχεία και ιχνοστοιχεία. Επιλεγμένα δείγματα αναλύθηκαν με ICP-AES και ICP-MS για τον προσδιορισμό μια μεγάλης σειράς ιχνοστοιχείων. Από την επεξεργασία των αποτελεσμάτων διαπιστώθηκε πως οι συγκεντρώσεις στα νερά, διαφόρων στοιχείων (π.χ. Cr, Ni, Zn) επηρεάζεται από την χημική σύσταση των πετρωμάτων της περιοχής και κυρίως από τα οφιολιθικά και μεταμορφωμένα πετρώματα. Οι ανθρωπογενείς δραστηριότητες διαπιστώθηκε ότι επηρεάζουν την σύσταση των υπόγειων νερών, σε περιοχές στις οποίες υπάρχει έντονη χρήση λιπασμάτων και φυτοφαρμάκων, αυξάνοντας την συγκέντρωση ανιόντων (NO^{3-}, SO_4^{-2}, PO_4^{-3}) σε αυτά.
Λέξεις κλειδιά: *γεωχημεία υπόγειων νερών, συγκεντρώσεις ιχνοστοιχείων και ανιόντων, ΒΔ Εύβοια, Ελλάδα.*

1. Introduction

Groundwater, plays a basic role in human life. The existence of sufficient groundwater resources and the maintenance of their quality is of major importance for the survival of man. It is thus indispensable, to protect these resources and ensure their sustainability. Environmental deterioration has led to a growing public concern over the potential accumulation of harmful elements and other contaminants in groundwater (Kabata-Pendias, 1995). The contamination of groundwater can pose long term environmental and health implications (Kabata-Pendias, 2007; Mueller, 1994; Needleman, 1980).

Water, whose chemical composition controls the circulation of element in ecosystems, is the main carrier of trace elements for vegetation. The prevailing opinion is that high concentrations of trace elements, which at many cases are potentially toxic, are linked with anthropogenic activities. In the present paper, a non-industrial area, where only small scale agricultural activities take place, was studied. At the study area there are occurrences of ultramafic rocks from the ophiolitic sequence. Many studies have proven that from the weathering of that type of rocks, triggers the enrichment of specific elements in nearby soils e.g. Co, Ni, Cr, As, Fe, Mn (Kanellopoulos and Argyraki, 2013; Oze et al., 2003; Gasser & Dahlgren, 1994; Alexander et al., 1989; Gough et al. 1989; Brooks, 1987; Schreier et al., 1987).

The aim of this paper is to assess the impact of both anthropogenic and natural factors on the geochemistry of groundwater.

2. Geological Setting

Euboea Island is located in central Greece. The studied area lies between latitudes 38° 58′ and 38° 50.5′ and longitudes 22° 49.5′ and 23° 10.5′. It is characterized by rocky mountainous topography and some lowland areas.

The Northeastern part of Euboea island belongs geologically to the Pelagonian and Sub-Pelagonian units, which form the western part of the internal geotectonic units of Greece (Mountrakis, 1986; Aubouin, 1959).

The study area consists of non-metamorphic rocks of the ophiolitic series, including peridotite, gabbro and serpentinite, as well as of metamorphic rocks. Large parts of NW Euboea are covered by Post Alpine formations and sediments of Quaternary to Neogene age (Fig. 1).

In the centre of the northern Evoicos gulf, the volcanogenic islands of Lichades are located (Georgalas, 1938). They are made mainly of trachyandesite lava flows, dated at 0.5 Ma (Pe-Piper and Piprer, 2002). The whole area is highly faulted due to extensional tectonics (Vavassis, 2001, Le Pichon and Angelier, 1979; McKenzie 1970; 1972). In the studied area many hot springs exist (Gioni-Stavropoulou, 1983), showing high concentrations of a large group of major and trace elements (Kanellopoulos, 2011; 2006). Finally in the areas of Loutra Edipsou and Ilia, thermogenic travertine deposits exist, created by the local hot-springs (Kanellopoulos, 2012; 2011).

3. Materials and Methods

3.1. Groundwater Sampling and Analysis

A total of 45 groundwater samples were collected (Table 1) from springs, wells and drills mainly used for agricultural activities and water supply of villages. Sensitive physicochemical parameters such as, pH, Temperature, E.C., T.D.S. were measured in the field. All the samples were vacuum filtered, acidified to a final concentration of 2% nitric acid, stored in polyethylene bottles and preserved in a refrigerator.

All the 45 water samples were analyzed in the Laboratory of Economic Geology and Geochemistry, University of Athens. The anion concentrations were measured spectrophotometrically (bicarbonate was measured by titration) while the major and trace element concentrations were measured by Flame Photometry and Atomic Absorption Spectroscopy (AAS) (Table 2).

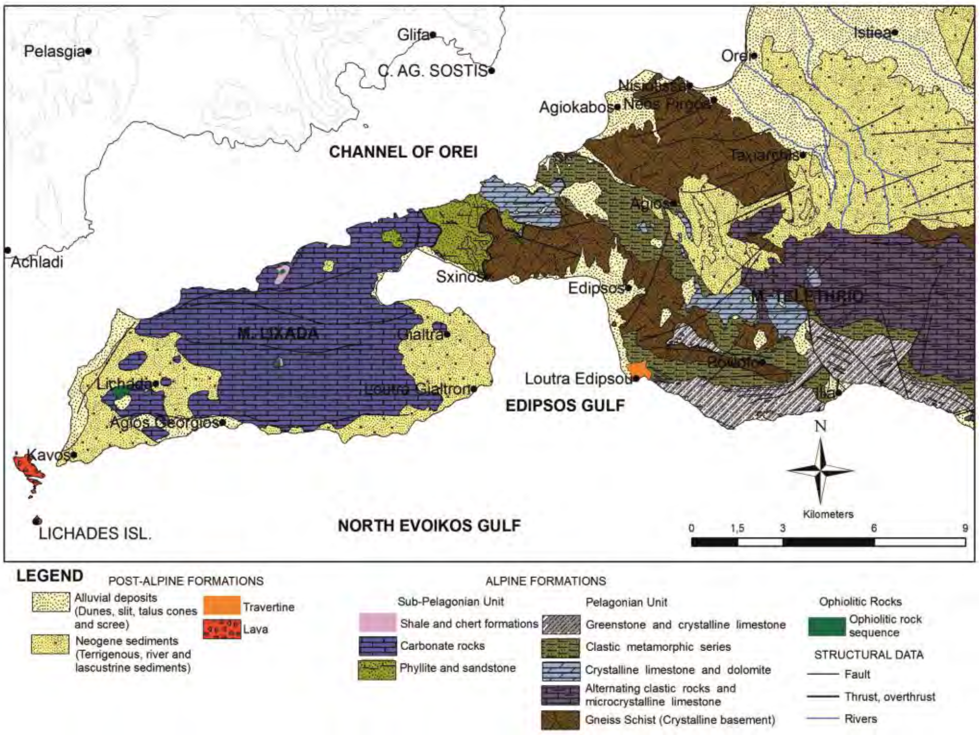

Figure 1 - Geological map of the study area (Kanellopoulos, 2011).

Table 1 - Samples locality, physicochemical parameters, hydrochemical type, SAR, EC, MH values and classification based on SAR-EC.

Code	Locality	Sampling site (depth in m)	T (ºC)	pH	TDS (g/lt)	EC* (mS/cm)	Hydroc. type	SAR-EC classif.	SAR	MH
AD-11	Edipsos-Schinos	well (4)	17.5	7.66	1.27	3.33	Ca-Cl	C3-S1	0.811	21.9
AD-22	Edipsos-Schinos	well (4)	21.9	7.85	1.77	3.55	Na-Cl	C3-S2	8.569	28.1
AD-10	Edipsos-Schinos	well (7)	23.2	7.1	3.63	7.26	Na-Cl	C2-S1	7.117	26.4
AD-16	Edipsos-Well Φ-18	well (10)	16	6.8	0.33	0.66	Ca-HCO_3	C1-S1	0.938	31.8
AD-17	Edipsos-Village	drill	14.45	7.45	0.41	0.84	Ca-HCO_3	C2-S1	0.949	43.9
AD-18	Edipsos-Old factory	drill (120)	12.2	6.99	0.475	0.96	Ca-HCO_3	C2-S1	1.214	35
HL-2	Ilia	spring	15	7.9	0.26	0.54	Mg-HCO_3	C1-S1	0.284	51.2
HL-10	Ilia	spring	18	8.27	0.25	0.51	Ca-HCO_3	C1-S1	0.397	46.7
AD-7	Polylofo-Vitsa	spring	15.3	7.7	0.39	0.78	Ca-HCO_3	C2-S1	0.759	26.1
AD-8	Polylofo- St. George M.	spring	12.7	8.1	0.27	0.53	Mg-HCO_3	C1-S1	0.266	50.3
GIA-1	Gialtra-3 springs	spring	21.3	6.96	0.69	1.36	Na-SO_4	C2-S1	2.4	43.6
GIA-2	Gialtra-Averof spring	spring	17.7	7.23	0.64	1.28	Na-NO_3	C2-S1	2.252	42.4
GIA-3	Gialtra	drill	19.1	7.6	0.33	0.69	Ca-HCO_3	C1-S1	0.997	45.1
GIA-5	Gialtra-Near Averof sp.	spring	14.1	7.7	0.37	0.74	Ca-HCO_3	C1-S1	0.8	49.4
GIA-6	Gialtra-3 springs	spring	20.1	8.06	0.66	1.34	Ca-HCO_3	C2-S1	1.838	47.3
GIA-10	Gialtra	spring	18	7.84	0.31	0.62	Mg-HCO_3	C1-S1	0.562	54.6
AGG-1	St. George vil.-Kamara	spring	19.9	6.96	1.18	2.37	Na-Cl	C3-S1	5.725	52.6
AGG-2	St. George village	spring	22.2	7.84	1.2	2.4	Na-Cl	C3-S1	6.224	55.2
LIX-1	Lichada	drill	17.9	7.27	0.54	1.09	Mg-HCO_3	C2-S1	0.506	60.2
LIX-2	Lichada	drill	23	7.85	0.52	1.05	Mg-HCO_3	C2-S1	0.513	60.6
AG-1	Agios	well (10)	15.35	6.91	0.61	1.23	Ca-HCO_3	C2-S1	1.33	25.4
AD-12	Agios-Platania	spring	12.7	7.6	0.25	0.51	Ca-HCO_3	C1-S1	0.273	48
AD-13	Agios-Old factory	drill (120)	14.3	7.33	0.46	0.93	Ca-HCO_3	C2-S1	1.026	38.6
BAR-1	Varvara	spring	15	7.39	0.51	1.03	Ca-HCO_3	C2-S1	0.571	41.7
AK-1	Agiokabos-Skepasti	spring	16.35	7.3	0.41	0.83	Ca-HCO_3	C2-S1	1.444	44.5
AK-2	Agiokabos-Xalasmata	drill	10.5	7.43	0.37	0.74	Ca-HCO_3	C1-S1	1.183	49.1
AK-3	Agiokabos-Restorant	drill (6)	14.3	7.25	0.39	0.8	Ca-HCO_3	C2-S1	0.774	33.7
AK-4	Agiokabos	drill (36)	15.8	7.3	0.32	0.64	Ca-HCO_3	C1-S1	0.643	40.4
AK-6	Agiokabos	drill (60)	15.2	7.19	0.33	0.66	Ca-HCO_3	C1-S1	0.636	38.9
AK-7	Agiokabos	drill (4)	18.3	7.96	0.46	0.93	Ca-HCO_3	C2-S1	1.17	28
NIS-1	Nisiotissa	well	13.1	7.24	0.42	0.85	Ca-HCO_3	C2-S1	1.299	31.5
NIS-2	Nisiotissa	well	14.6	7.19	0.41	0.84	Ca-HCO_3	C2-S1	1.696	32.8
NIS-3	Nisiotissa	drill	18.25	6.86	0.41	0.83	Mg-HCO_3	C2-S1	1.404	51.9
NP-1	N. Pirgos-Tsempetsis	well	17.7	7.23	0.56	1.13	Ca-HCO_3	C2-S1	2.19	41.2
NP-3	N. Pirgos-Lowland	drill (6)	17.5	7.45	0.53	1.07	Ca-HCO_3	C2-S1	0.712	45.7
NP-4	N. Pirgos-Lowland	drill (9)	15.6	7.3	0.48	0.93	Ca-HCO_3	C2-S1	0.837	41.6
NP-5	N. Pirgos-Arida	drill (50)	16.3	7.29	0.59	1.17	Ca-HCO_3	C2-S1	0.763	43.1
NP-6	N. Pirgos-New aqueduct	drill (60)	16.6	7.37	0.38	0.77	Ca-HCO_3	C1-S1	0.885	38.4
NP-7	N. Pirgos-Old aqueduct	drill (60)	16.6	7.36	0.9	0.44	Ca-HCO_3	C2-S1	0.852	44.1
NP-8	N. Pirgos-New church	well (3)	12.15	7.76	0.28	0.56	Ca-HCO_3	C1-S1	0.428	31.4
NP-9	N. Pirgos-Old church	drill	14.4	7.39	0.41	0.82	Ca-HCO_3	C2-S1	0.576	44
NP-10	N. Pirgos-Kolonaki	well (5)	14.1	7.13	0.42	0.86	Ca-HCO_3	C2-S1	1.278	47.4
NP-11	N. Pirgos-Kolonaki	well (5)	14.4	6.95	0.35	0.72	Ca-HCO_3	C1-S1	1.414	44.1
OR-1	Oreoi-School	spring	10.75	7.72	0.38	0.76	Ca-HCO_3	C1-S1	0.625	49.8

Table 2 - Concentrations of chemical parameters analyzed by AAS, FP, SP and titration.

	Cd	Co	Cr	Mn	Pb	Ni	Fe	Zn	Na	K	Mg	Ca	PO_4	NO_3	SO_4	Cl	HCO_3
	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
AD-11	0.1	1.8	<0.2	9	<1	3	22	420	42	8	34.1	200	0.21	9.2	160	650	320
AD-22	<0.1	<0.2	0.3	1	<1	<0.6	9	150	465	5	38.1	160.5	0.23	9.7	200	848	295
AD-10	0.3	0.3	0.3	0.6	<1	<0.6	2	5	-	-	-	-	0.353	1	70	410	283
AD-16	<0.1	<0.2	0.9	0.6	<1	<0.6	7	10	34	3	19.2	68	0.25	9.7	39	36	280
AD-17	<0.1	<0.2	0.4	1	<1	0.6	2	34	39	4	34.1	72	0.14	29	70	38	313
AD-18	<0.1	<0.2	0.9	0.7	<1	<0.6	3	10	51	4	28.4	87	0.24	19.8	26	66	381
HL-2	<0.1	0.5	0.4	0.8	<1	<0.6	3	9	10	3	29.3	46	0.13	7	20	9.9	154
HL-10	-	-	-	-	-	-	-	-	-	-	-	-	0.198	0.5	38.6	2.41	213
AD-7	<0.1	1.5	<0.2	<0.5	<1	<0.6	4	17	24	5	12	56	0.12	24.2	30	20.2	292
AD-8	0.4	1.3	0.3	<0.5	<1	<0.6	8	12	9	5	26.4	43	0.04	7	19	13	224
GIA-1	<0.1	0.6	1	<0.5	<1	<0.6	15	10	107	24	39.9	85	0.25	**225.5**	620	78	272
GIA-2	<0.1	1.3	1	<0.5	<1	<0.6	12	6	97	30	36.2	81	0.15	**250.8**	95	84	240
GIA-3	<0.1	0.6	6	1	<1	0.8	12	47	40	7	33.4	67	0.17	**166.1**	41	44	198
GIA-5	<0.1	2.9	0.7	1	<1	<0.6	10	23	30	6	32	54	0.27	15	37	21.3	255
GIA-6	<0.1	<0.2	0.6	<0.5	<1	<0.6	3	<2	81	19	42.3	77.6	0.28	**217.4**	80	140.8	283
GIA-10	-	-	-	-	-	-	-	-	-	-	-	-	0.121	0.8	26.2	27.5	267
AGG-1	<0.1	<0.2	0.2	1	<1	<0.6	3	4	275	9	55.8	83	0.1	7	80	478	330
AGG-2	<0.1	<0.2	0.3	<0.5	<1	<0.6	3	<2	290	9	55.1	73.8	0.09	4.4	74	604	258
LIX-1	-	-	-	-	-	-	-	-	-	-	-	-	0.446	15.5	43	7.57	347
LIX-2	-	-	-	-	-	-	-	-	-	-	-	-	0.514	8.9	42.9	15.45	343
AG-1	<0.1	0.2	0.2	120	<1	<0.6	2	5	60	13	23.8	115	3.04	**73.5**	94	64	298
AD-12	<0.1	<0.2	<0.2	<0.5	<1	<0.6	4	8	9	5	24.1	43	0.04	7	20	8.3	234
AD-13	<0.1	0.5	<0.2	<0.5	<1	<0.6	3	13	42	6	29.8	78	0.17	18	34	60	352
BAR-1	<0.1	<0.2	0.4	0.9	<1	0.9	2	3	27	4	42.9	99	0.32	29	55	52	410
AK-1	<0.1	0.2	<0.2	12	<1	<0.6	4	51	55	4	29.7	61	0.15	5.7	37	74	292
AK-2	0.2	0.9	0.3	0.5	<1	0.6	2	46	43	4	29.8	51	0.2	5.3	29	42	300
AK-3	0.3	<0.2	<0.2	3	<1	<0.6	1	3510	32	3	26.5	86	0.15	6.2	46	28	365
AK-4	<0.1	<0.2	<0.2	17	<1	0.8	3	30	24	3	25.9	63	0.12	6.6	34	40	270
AK-6	<0.1	0.4	0.4	1.8	<1	<0.6	2	8	24	4	25.5	66	0.06	7	40	28	285
AK-7	<0.1	<0.2	<0.2	3	<1	2	2	50	44	3	18.2	77.2	0.1	5.7	54	67.2	347
NIS-1	<0.1	<0.2	0.3	2	<1	<0.6	4	6	50	3	21.5	77	1.37	18.5	80	54	230
NIS-2	<0.1	<0.2	0.9	0.5	<1	<0.6	<2	6	61	3	19.5	66	1.11	7.5	64	76	270
NIS-3	<0.1	0.5	0.3	20	<1	<0.6	3	6	53	4	34	52	0.65	9.7	22	88	230
NP-1	<0.1	0.7	0.6	80	<1	5	7	15	88	7	30.6	72	2.02	40.5	44	72	386
NP-3	<0.1	<0.2	0.3	14	<1	<0.6	9	47	34	6	47.9	94	0.24	11.9	102.5	22.4	430
NP-4	<0.1	0.6	3	1.3	<1	<0.6	6	49	36	6	35.4	82	0.39	18	39	28	366
NP-5	<0.1	0.3	3	1.5	<1	<0.6	7	47	36	6	44.1	96	0.44	33.9	80	34	426
NP-6	<0.1	<0.2	<0.2	<0.5	<1	<0.6	7	22	33	6	24.6	65	0.19	10.1	25	20	277
NP-7	<0.1	<0.2	3	1	<1	0.6	13	11	37	6	38.2	80	0.22	15.8	40	13.1	378
NP-8	<0.1	0.2	2	0.9	<1	1	3	10	15	5	17.8	64	0.3	22.9	35	13	249
NP-9	<0.1	<0.2	3	0.8	<1	<0.6	<2	9	25	4	38.1	80	0.2	13.2	37	37	242
NP-10	<0.1	0.2	0.4	1.6	<1	<0.6	3	4	50	4	33.4	61	0.43	57.6	52	54	200
NP-11	<0.1	<0.2	0.3	0.7	<1	<0.6	13	4	50	7	25.4	53	0.63	31.2	55	46	230
OR-1	<0.1	0.3	0.3	260	<1	1	3	19	27	7	42.7	71	0.18	4.8	2	20.1	380
P.V.	**5**		**50**		**10**	**20**								**50**			

(P.V. = Parametric Value set by Directive 98/83/EC; with bold red color are the values exceed P.V.)

On the basis of the above analytical data, 11 of the water samples were analyzed by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) and by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the ACME Analytical Laboratories Ltd., Canada, for a series of elements (Table 3).

Detailed description of the used analytical methods as well as, the analytical quality control procedures, including analysis of blank and duplicate samples as well simultaneous analysis of Certified Reference water samples, are given in Kanellopoulos, 2011.

4. Analytical Results

4.1. Chemical Analysis

The location of the samples is presented in Table 1, while in Tables 1, 2 and 3, the physicochemical parameters analysed both in situ and in the lab, are presented.

In Figure 2A, the chemical analyses were plotted in the Piper diagram, in order to evaluate the hydrochemistry of the studied groundwater samples. In that Piper diagram, 39 of the studied groundwater samples are plotted in the same area and most of them have Ca-HCO_3 hydrochemical type (Table 1). From that group, only four samples have different hydrochemical type, as a result of the differentiation of the local bedrocks (Lichada area: LIX-1, LIX-2, Ilia area: HL-2, AD-8).

From all the studied samples only 6 are plotted separately due to their differed hydrochemical type, reflecting the impact of specific factors controlling the chemistry of the samples, like intrusion of sea water (AD-10, AD-11, AD-22, AGG-1 and AGG-2, hydr. type Na-Cl) or impact of fertilizers (GIA-1, hydr. type Na-SO_4). All the samples with Na-Cl hydrological type are from shallow aquifers located at a short distance from the shoreline (10-20m) and present high concentration of Cl (Table 2).

In order to visualize the spatial relationship between the concentrations and the geological features in the studied area, graduated symbol maps were created by plotting the results of the chemical analysis. Class intervals were selected on the basis of the statistical distribution for each element and appear with different sized symbol on the maps, representing the following concentration classes: (a) minimum- 1st quartile, (b) 1st quartile- median (baseline concentration), (c) median- 3rd quartile and (d) > 3rd quartile- maximum. These maps are presented in Figures 2E-2H.

The concentrations of Na and Cl vary in the same way (Fig. 2B), suggesting common source. The samples with higher concentrations of Cl (848 mg/L) and Na (642 mg/L) are from shallow aquifers located at short distance from the sea. For instance, samples AD-11, AD-22 and AD-10 were taken from shallow wells near the seashore at Schinos area (Fig. 2E).

The concentrations of K, NO_3, SO_4, PO_4 also co-vary satisfactorily (Fig. C), suggesting common source. The relation coefficient between K and NO_3 is 0.86. High concentrations are presented in samples located near lowlands, where agricultural activities take place (Fig. 2F).

Some samples present very high concentrations of NO_3 as compared to SO_4, PO_4 and K concentrations (e.g. GIA-1, GIA-2, GIA-3, AG-1 etc). These samples are located within or are adjacent to villages without sewerage.

Concentrations of Ni, Mg, Zn (Fig. 2G) and to a smaller extent Fe, Cr, Co show high values near the crystalline basement. These areas are mostly lowlands, usually covered by Post-Alpine formations, characteristic examples are the areas of Neos Pyrgos and Agiokampos. Also, the concentrations of Cr and Zn co-varies (Fig. 2D). Of the above elements, Zn shows some outlier values (>150 μg/L) like the AK-3 sample (3510 μg/L).

Table 3 - Concentrations of elements analyzed by ICP-MS.

		LIX-1	LIX-2	AGG-1	GIA-1	GIA-10	AD-10	HL-10	AD-18	AK-3	NIS-3	NP-7
Ag	**(μg/L)**	-	-	<0.05	<0.05	-	-	-	<0.05	<0.05	<0.05	<0.05
Al	**(μg/L)**	<100	<100	8	7	<100	<100	<100	10	5	9	6
As	**(μg/L)**	<1000	<1000	2.6	4.2	<1000	<1000	<1000	0.5	<0.5	<0.5	0 .7
Au	**(μg/L)**	-	-	<0.05	<0.05	-	-	-	<0.05	<0.05	<0.05	<0.05
B	**(μg/L)**	-	-	193	409	-	-	-	<20	91	25	48
Ba	**(μg/L)**	166	165	26	124	89	108	68	258	92	29	79
Be	**(μg/L)**	<0.11	<0.11	-	-	<0.11	<0.11	<0.11	-	-	-	-
Br	**(μg/L)**	-	-	1692	242	-	-	-	134	136	303	100
Ca	**(mg/L)**	83.1	82.4	113.6	117.1	56.6	454.2	51.5	120	109.6	67.2	103
Cd	**(μg/L)**	0.07	0.11	<0.05	<0.05	<0.05	<0.05	0.11	<0.05	0.29	<0.05	<0.05
Ce	**(μg/L)**	<0.24	<0.24	0.07	0.06	<0.24	<0.24	<0.24	0.06	0.06	0.06	0.04
Cl	**mg/L)**	-	-	522	102	-	-	-	88	46	113	35
Co	**(μg/L)**	<0.09	<0.09	0.15	0.18	<0.09	0.23	<0.09	0.21	0.14	0.16	0.15
Cr	**(μg/L)**	14	14	<0.5	0.7	<4	7	<4	1.1	<0.5	<0.5	2.4
Cs	**(μg/L)**	<0.09	<0.09	13.38	0.09	<0.09	<0.09	<0.09	0.03	<0.01	0.03	<0.01
Cu	**(μg/L)**	3	3	1.8	2.8	3	5	2	4.1	1.4	1.1	2.3
Fe	**(μg/L)**	<100	<100	600	520	<100	<100	<100	570	500	420	520
Ga	**(μg/L)**	<0.4	<0.4	-	-	<0.4	<0.4	<0.4	-	-	-	-
Ge	**(μg/L)**	<2	<2	-	-	<2	<2	<2	-	-	-	-
Hg	**(μg/L)**	-	-	0.4	<0.1	-	-	-	0.2	0.4	0.3	<0.1
K	**(μg/L)**	2630	2720	8130	21380	2250	9290	940	1140	560	950	1430
La	**(μg/L)**	<0.58	<0.58	0.06	0.05	<0.58	<0.58	<0.58	0.19	0.07	0.08	0.04
Li	**(μg/L)**	13.9	14.1	21.5	9.2	6.9	18.8	3.6	5.6	5.7	9.2	5
Lu	**(μg/L)**	<0.001	<0.001	<0.01	<0.01	<0.001	<0.001	<0.001	<0.01	<0.01	<0.01	0.01
Mg	**(mg/L)**	76.2	76.9	61.8	45	41.3	99	27.4	31.2	29	36.4	43.1
Mn	**(μg/L)**	<10	<10	1.36	0.29	<10	<10	<10	0.37	3.77	23.94	1.28
Mo	**(μg/L)**	<5	<5	1.2	0.3	<5	<5	<5	0.6	0.6	0.1	1.2
Na	**(mg/L)**	26.6	26.9	286.4	86	22.8	642.1	14.2	58.1	30.1	52.8	23.7
Nb	**(μg/L)**	<0.3	<0.3	-	-	<0.3	<0.3	<0.3	-	-	-	-
Ni	**(μg/L)**	4.9	4.4	<0.2	<0.2	1.5	6.1	1.2	0.4	<0.2	0.6	0.3
P	**(μg/L)**	<1000	<1000	44	79	<1000	<1000	<1000	41	41	41	66
Pb	**(μg/L)**	0.8	<0.4	0.1	<0.1	0.5	0.4	<0.4	<0.1	0.6	<0.1	0.1
Rb	**(μg/L)**	0.53	0.54	7.36	1.53	1.53	4.97	0.38	0.75	0.11	0.1	0.25
S	**mg/L)**	9.61	9.6	21	24	6.34	94.6	8.02	7	12	6	11
Sb	**(μg/L)**	<0.2	<0.2	<0.05	0.07	<0.2	<0.2	<0.2	0.21	0.08	<0.05	0.09
Se	**(μg/L)**	-	-	10.1	1.6	-	-	-	2.3	0.8	1.7	0.9
Si	**(μg/L)**	16100	16000	4200	13400	11800	10500	5000	12600	7600	13800	11000
Sn	**(μg/L)**	<0.8	<0.8	0.15	0.25	<0.8	<0.8	<0.8	0.31	0.21	1.15	1.71
Sr	**(μg/L)**	362	360	368	222	315	2599	240	324	264	204	289
Ta	**(μg/L)**	<0.03	<0.03	-	-	<0.03	<0.03	<0.03	-	-	-	-
Ti	**(μg/L)**	<1000	<1000	-	-	<1000	<1000	<1000	-	-	-	-
Tl	**(μg/L)**	<0.13	<0.13	<0.01	<0.01	<0.13	<0.13	<0.13	<0.01	<0.01	<0.01	<0.01
U	**(μg/L)**	1.4	1.41	2.82	0.98	1.51	9.02	1.01	2.73	1.72	0.2	3.51
V	**(μg/L)**	12.5	12.4	3	3.8	4.1	4.2	<1.3	0.6	0.3	0.5	1.2
W	**(μg/L)**	-	-	0.05	0.04	-	-	-	0.11	0.04	0.09	0.03
Y	**(μg/L)**	0.027	0.017	0.01	0.01	0.014	0.042	0.009	0.05	0.1	0.01	0.13
Zn	**(μg/L)**	30	25	11	11	<16	29	23	27	3020	12	12

(The samples LIX-1, LIX-2, GIA-10, AD-10, HL-10 analysed in Natural History museum of London labs and the rest of them in ACME labs)

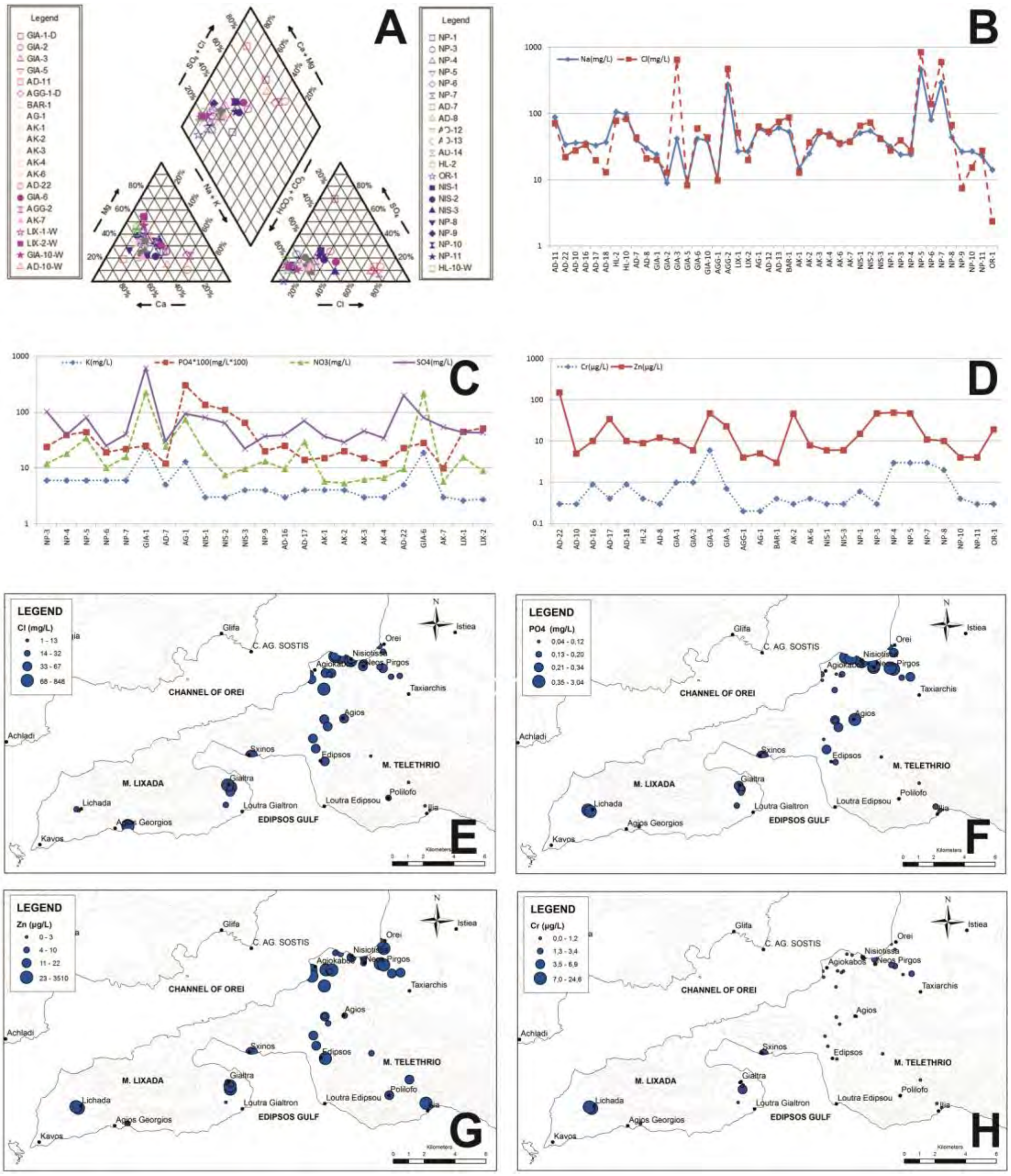

Figure 2 - (A) Chemical composition of groundwater samples plotted in Piper trilinear diagram. (B) Diagram presenting the co-varying of Na and Cl at groundwater samples. (C) Diagram presenting the variation of K, NO_3, SO_4 and PO_4 at groundwater samples from lowlands, where agricultural activities take place. (D) Diagram presenting the co-varying of Cr and Zn at groundwater samples (used only the samples in which both Fe and Zn concentrations are above detection limits). Geochemical maps showing the distribution of Cl (E), PO_4 (F), Zn (G) and Cr (H) in groundwater samples.

The water samples from the peninsula of Gialtra (Sample Codes: LIX-; AGG-; GIA- and samples AD-10, AD-11, AD-22) show the maximum concentrations for a series of elements, namely Cr (14.2 µg/L; Fig. 2H), Ni (6.1 µg/L) and Fe (35 µg/L), Zn (420 µg/L) and Co (3 µg/L).

The results of chemical analysis of groundwater samples by ICP-MS (Table 3) strongly support the relationships between elemental groundwater content and rock geochemistry.

4.2. Evaluation of Water Quality for Human Consumption

In order to assess the suitability of the studied groundwater samples, for human consumption, the analytical values with the parametric levels, imposed by the current relative legislation (Directive 98/83/EU) were compared. It is noted that the National Greek law is in agreement with that EU Directive 98/83/EU. Even though industrial activities are absent in the studied area and only agricultural activities take place, concentrations of some chemical parameters exceeded the indicator parametric value (17.7 %) and the parametric value (8.8 %) according to Directive 98/83/EC (Tables 1 and 2).

Analytically, the Mn content of the studied groundwater samples varies from 0.09 to 260 μg/L, while the parametric value given by Directive 98/83/EC is 50μg/L. This value was exceeded by three samples from the areas of Neos Pyrgos, Oreoi and Agios.

The Na content varies from 9 to 640mg/L, while the indicator parametric value is 200mg/L. Six samples, from Agios Georgios and Schinos of Edipsos exceed that value.

The Ca content ranges between 43 and 450mg/L, while the indicator parametric value is 100 mg/L. Four samples exceed it, from Agios Georgios and Schinos of Edipsos.

The NO_3 content varies from 0.5 to 250mg/L, while the parametric value is 50mg/L. Six samples from Gialtra, Agios Georgios and Neos Pyrgos exceed it.

The SO_4 content varies from 2 to 620mg/L, while the indicator parametric value is 250mg/L. Only one sample from the area of Gialtra exceeds it.

The conductivity values range between 0.4 and 7.3mS/cm, while the indicator parametric value is 2.5mS/cm. Three samples exceed it, and all these samples are from the area of Schinos of Edipsos. All the others studied chemical parameters are within the parametric values given by the Directive 98/83/EC.

4.3. Evaluation of Water Quality for Irrigation

In order to assess the suitability of groundwaters for irrigation, their quality status was assessed through Sodium Adsorption Ratio (SAR) and Magnesium Hazard (MH). The SAR in the studied groundwater samples ranges from 0.2 to 8.6 (Table 1) which, combined with the measured values of Electrical Conductivity (EC) gave information about their classification, based on the fields suggested by U.S. Salinity Laboratory (1954). So the studies samples were classified (Table 1) as follows: S1-C1 (58%), S1-C2 (33%), S1-C3 (7%) and S2-C3 (2%). The MH (Magnesium Hazard) values, in the studied samples, ranges from 21.9 to 60.6 and 18% of the samples have MH>50 (Table 1), meaning that they are not recommended for irrigation.

5. Discussion - Conclusions

The results from the study of cold groundwater, undertaken in the area of NW Euboea Greece, show that the chemical composition of the groundwater is controlled by the following three main factors: (i) the chemical composition of the local rocks (ultramafic and metamorphic), (ii) the sea, for the samples located near the seashore and (iii) the anthropogenic activities (mainly the extensive use of fertilizers and pesticides).

The results of chemical analyses through the spatial distribution of the concentrations of the various elements, show that the two main rock formations that have affected the chemical composition of the studied groundwater are the ultramafic rocks from the ophiolitic sequence as well as the metamorphic rocks occurring in the area.

In the peninsula of Gialtra, small surface occurrences of ultramafic rocks from the ophiolithic sequence are present. The water samples from that area (Lichada, Agios Georgios, Gialtra, Schinos), show the highest concentration of Cr (up to 14μg/L), Ni (6.1μg/L) as well as high concentrations of Co (up to 3μg/L), Fe (up to 35μg/L) and Zn (up to 450μg/L). Enrichment of groundwater in these elements can be attributed to the impact of ultramafic rocks. Kanellopoulos (2011) and Kanellopoulos and Argyraki (2013) proved that soils and some plant species (e.g. Alyssum chalcidicum) also present high concentrations of the same elements, especially Cr and Ni, even at long distances from the surface occurrences of the local ultramafic rocks.

High concentrations of Zn, Mg, Ni and to a smaller extent Fe, Cr, Co are observed near the metamorphic basement (e.g. Neos Pyrgos and Agiokampos). Enrichment of groundwater in those elements is attributed to the impact of metamorphic rocks dominating in this region. It must be noted that the soils in these areas also present high concentrations of the same elements and after geochemical and mineralogical analysis found that they have been enriched by the weathered material of the metamorphic rocks (Kanellopoulos, 2011). Of the above elements, Zn, shows some outlier values (>150 μg/L) like the AK-3 sample (3510 μg/L). These cases may be influenced by anthropogenic sources.

The co-variation of Cl and Na suggests that they have common source. The spatial distribution of their concentrations, points out that the samples with the highest concentrations (848 mg/L Cl; 642 mg/L Na) are from shallow aquifers near the seashore, which have been affected from the seawater and they have Na-Cl hydrochemical type, like the case of Schinos area.

Also the co-variation of K, NO_3, SO_4, PO_4, suggests their common source. The spatial distribution of their concentrations, points out that the samples with the highest concentrations located near lowlands, where agricultural activities take place. Their source is the use of fertilizers and the variability which could be observed from area to area is related to the different degree of use of each type of fertilizer. Some samples present disproportionately high concentrations of NO_3 compared to SO_4, PO_4 and K concentrations. These samples are within or adjacent to villages without sewerage, so the high concentration of NO_3 is related to residential wastewater.

It is profound that both natural and anthropogenic factors affect the groundwater quality for human consumption to such an extent that 17.7 % exceed at least one indicator parametric value and 8.8 % exceed at least one parametric value of the Directive 98/83/EC. Finally, the studied groundwater samples quality for irrigation classified based on SAR-EC as S1-C1 (58%), S1-C2 (33%), S1-C3 (7%) and S2-C3 (2%) and based on the MH (Magnesium Hazard) 18% of the samples have MH>50 and they are not recommended for irrigation.

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