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HYDROCHEMICAL CHARACTERISTICS OF THE OROPOS COASTAL AQUIFERS, ATTICA, GREECE.

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Abstract

This article deals with the hydrochemistry of coastal aquifers of the Oropos plain, Attica, Greece. It is the first study which presents hydrochemical data of the Oropos plain groundwater. Groundwater samples from 34 wells were collected and analyzed for major and heavy metal constituents. Groundwater was differentiated between the Pleistocene confined aquifer and the group of the Holocene, the Miocene and the Mesozoic aquifers based on the electrical conductivity (EC) values and the chlorides content. Groundwater in the Pleistocene sediments presented EC values ranging between 766 and 971μS/cm and chlorides between 95-163mg/l. The group of the rest aquifers presented EC values up to 3770 μS/cm and chlorides up to 993mg/l. The Pleistocene aquifer seems to be protected from seawater intrusion, although, it is located adjacent to the shoreline. In addition, most of the heavy metal concentration exceeded the EU limits. Cd, Fe, Pb, Ni have been determined at 82, 2500, 817, 217 μg/lit respectively. Groundwater was, also, categorized into 2 main water types that of Ca-Mg-HCO3 type indicating recharge of fresh water and that of Ca-Mg-Cl type indicating reverse cation exchange of old Na-Cl waters.

Keywords: *coastal aquifer, hydrochemistry, seawater intrusion, Oropos plain*

Περίληψη

Αυτό το άρθρο ασχολείται με την υδροχημεία των παράκτιων υδροφορέων του Ωρωπού Αττικής. Για το σκοπό αυτό πραγματοποιήθηκαν χημικές αναλύσεις σε 34 δείγματα υπόγειων νερών και 1 επιφανειακό από τον Ασωπό ποταμό. Τα υπόγεια νερά διαφοροποιήθηκαν μεταξύ του πλειστοκαινικού υπό πίεση υδροφόρου ορίζοντα και των ολοκαινικών, μειοκαινικών και μεσοζωικών ιζημάτων με βάση τις τιμές ηλεκτρικής *αγωγιμότητας (EC) και την περιεκτικότητα σε χλωριόντα. Τα υπόγεια νερά στα ιζήματα του Πλειστοκαίνου παρουσίαζαν τιμές EC κυμαινόμενες μεταξύ 766 και 971μS/cm και χλωριόντων μεταξύ 95-163mg/l. Τα νερά των υπολοίπων υδροφορέων παρουσίασαν τιμές EC μέχρι 3770 μS/cm και χλωριόντα μέχρι 993mg/l. Τμήμα του πλειστοκαινικού υδροφόρου ορίζοντα, αν και βρίσκεται δίπλα στην ακτογραμμή, φαίνεται να προστατεύεται από τη διείσδυση θαλασσινού νερού. Επιπλέον, το μεγαλύτερο μέρος της συγκέντρωσης βαρέων μετάλλων υπερέβη τα όρια της ΕΕ. Τα Cd, Fe, Pb, Ni έχουν προσδιοριστεί στα 82, 2500, 817, 217 μg/l, αντίστοιχα. Τα υπόγεια ύδατα ταξινομήθηκαν επίσης σε 2 κύριους τύπους νερού. Ο πρώτος είναι του τύπου Ca-Mg-HCO3 που υποδηλώνει τροφοδοσία γλυκού νερού και ο δεύτερος του τύπου Ca-Mg-Cl που δείχνει αντίστροφη ανταλλαγή κατιόντων από παλαιότερα νερά Na-Cl.*

Λέξεις κλειδιά: *παράκτιος υδροφορέας, υδροχημεία, θαλάσσια διείσδυση, Ωρωπός*

1. Introduction

Coastal aquifers have been extensively studied over a century by many researchers (Post, 2004; Bear et al., 1999; Stigter et al., 1998; Stuyfzand, 1993; Todd, 1980; Freeze and Cherry, 1979; Stringfield et al., 1969; Henry, 1964; Herzberg, 1901; Ghyben, 1888). The main problem of coastal aquifers is seawater intrusion. This phenomenon takes place when coastal aquifers are hydraulically connected to the sea resulting in seawater intrudes inland due to natural and/or anthropogenic factors. However, in confined aquifers, which extend adjacent to the shoreline and which they are separated from seawater by thick confining clay layers, fresh groundwater can be preserved by salinisation (Hermides, 2018; Post et al., 2013; Post, 2004; Lloyd et al., 1985). This study presents the hydrochemistry of groundwater in part of the Pleistocene sediments located adjacent to the Oropos shoreline which is appeared to be preserved by salinisation. Chemical data from the Oropos groundwater are very few (Stamatis et al., 2011). The wide area has been hydrogeologically investigated the last decades by some researchers (Pagounis, 1994; Dounas et al., 1980). However; hydrogeology of the study area is not fully elucidated. The interaction of tectonic and stratigraphic factors (Katsikatsos, 2000; Mettos, 1992; Parginos et al., 1989; Perissoratis, 1989) combined with eustatic changes (Lambeck, 1996) established a complex hydrogeological regime where successive confined/leaky aquifers have been formed. Groundwater in part of the Pleistocene sediments which are underlain the Holocene deposits, seems to retain its quality against the intrusion of seawater. The objective of this article is to highlight the occurrence of good quality groundwater which is hosted in the confined aquifer of the Pleistocene sediments located adjacent to the shoreline of the Oropos coastal area.

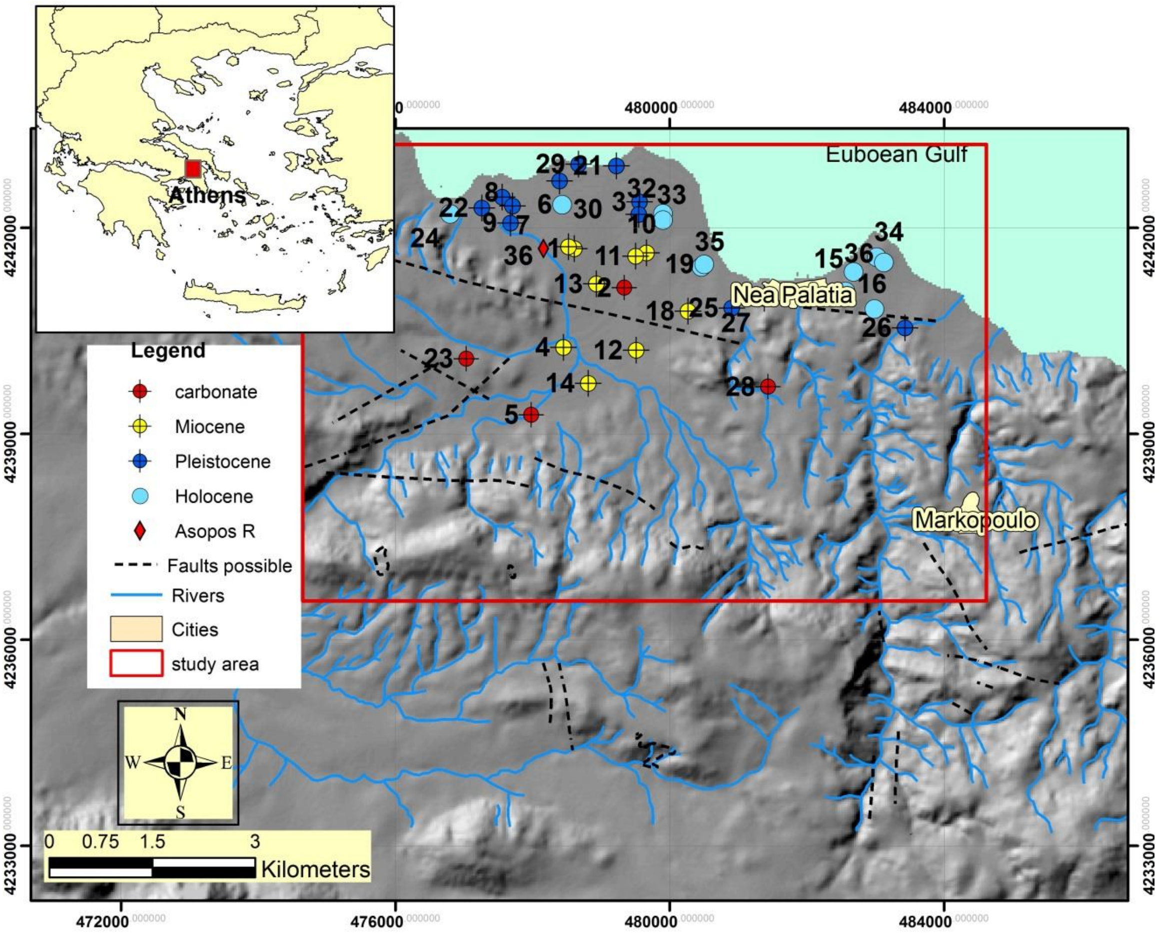

Fig. 1: Study area and sampling points (map projection GCS_GGRS_1987).

2. Study area

Oropos plain is located 40 km north of Athens (Fig. 1). Most of the plain which extends up to 50 km^2 is occupied by cultivated land. The surface topography of the plain is gently sloped from the elevation of 400 m in the south towards the Euboean Gulf to the north. Semi-arid climate prevails in the wide area with mean annual precipitation of 460 mm while the mean annual temperature is 16.2 ^{o}C. The plain is highly contaminated as a result of the heavy industry development.

Asopos River flows through the plain locally feeding the Quaternary sediments. Aquifers are tapped by hundreds of dug wells and boreholes.

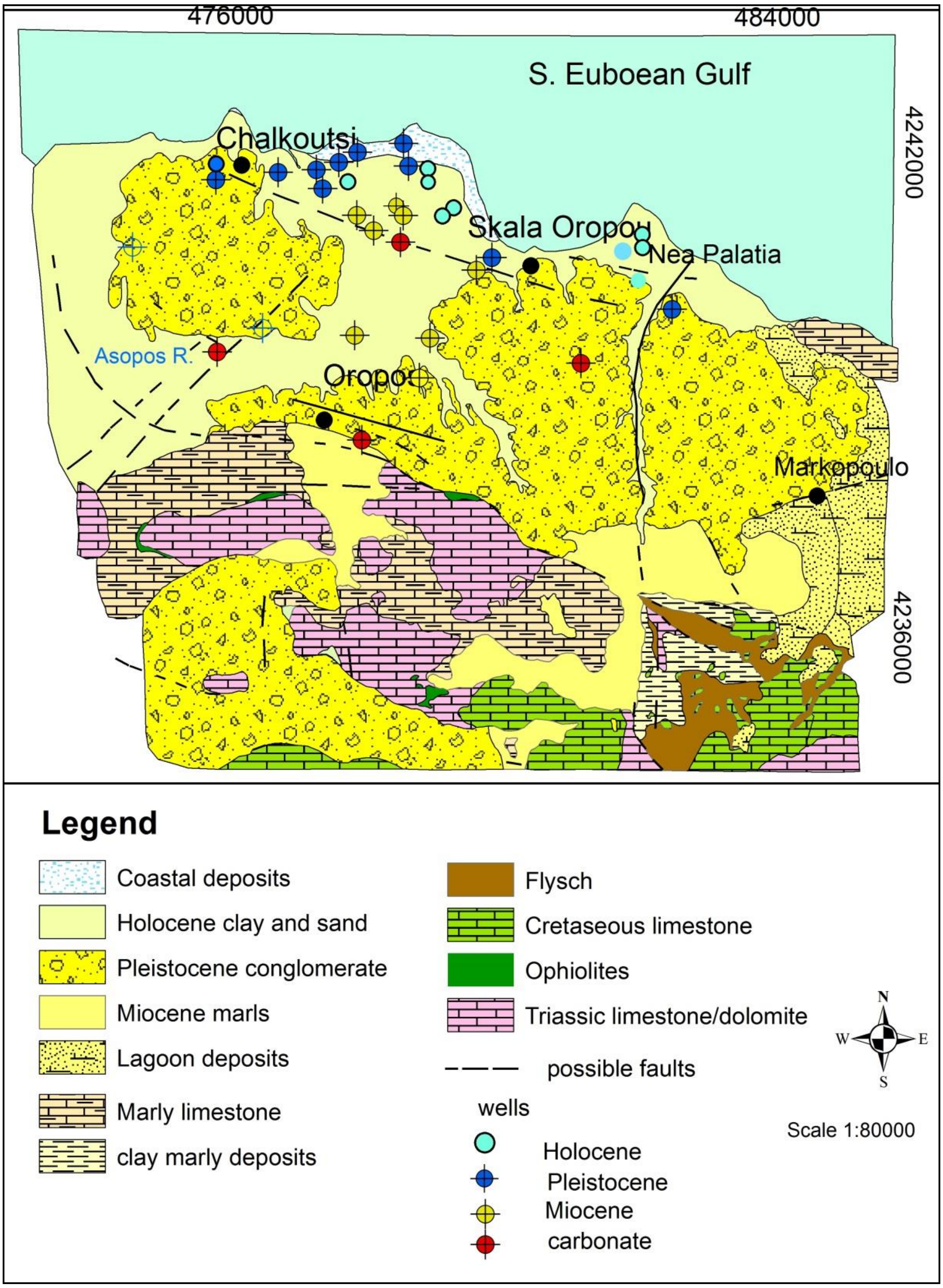

Fig. 2: Geological map after Parginos et al., (1989); Katsikatsos, (2000) and sampling points (map projection GCS_GGRS_1987).

3. Geological setting

The geological structure of the study area (Fig. 2) is complex consisting of alpine and post-alpine sediments (Katsikatsos, 2000; Mettos, 1992; Parginos et al., 1989, Perissoratis, 1989). Alpine sediments comprise: (i) Permo-Triassic shales, sand, greywackes, phyllites and conglomerate with basic volcanic rocks intercalations of 400 m thick which consist of the basement of the study area; (ii) Triassic limestone, dolomitic limestone and dolomite 700 m in thickness; (iii) ophiolites which consist of the basement of the wide area; (iv) Cretaceous limestone 150 m thick; and (v) Cretaceous flysch of 150 m thick. Post-alpine sediments comprise: (i) lacustrine and lagoon Upper-Miocene marls, marly limestone at the base and torrential clay, sand and conglomerate at the top 200-300 m thick; (ii) torrential Pleistocene conglomerate/breccia and clay; and (iii) Holocene clay, sand and conglomerate.

The Oropos plain is a NE-SW oriented neotectonic depression. It has been affected by W-E, NE-SW and NW-SE striking tectonic and neotectonic faults that caused uplift or subsidence of the area during the Pleistocene (Papanikolaou et al., 1989; Perissoratis, 1989; Papanikolaou et al., 1988). It has been also affected by the Pleistocene sea level fluctuations (Lambeck, 1996). As a result the basin was filled with torrential, lacustrine and lagoon sediments depending on the actual sea level.

4. Hydrogeology

The interaction of tectonic and stratigraphic factors combined with eustatic changes established a complex hydrogeological regime where successive confined/leaky aquifers have been formed (Pagounis, 1994; Dounas et al., 1980). In total, four aquifers occur in the study area. The upper aquifer occurs in the Holocene sediments which is unconfined and locally confined. Many wells located in the topographic lows are ‘flowing artesian wells’. The second aquifer, which is confined, occurs in the Pleistocene sediments. Potentiometric surface stands 2-5 m below ground surface. The third aquifer occurs in the Miocene conglomerate and the last one in the Mesozoic carbonate. Many wells tap 2-3 aquifers standing up to 100 m in depth. The pumping rate ranges between

10-40 m^3/h. Wells located at the topographic highs tap the limestone from the depth of up to 220 m and the pumping rate ranges between 30-50m^3/h.

5. Methods and materials

The hydrochemistry of Oropos groundwater has been investigated using major and heavy metal constituents. Groundwater samples from 34 wells (Holocene aquifer samples 10; Pleistocene aquifer samples 11; Miocene aquifer samples 9; and carbonate aquifer 4 samples) and one sample from Asopos River surface water were collected during 2006. Chemical analyses were performed in the Mineralogy-Geology Laboratory of Agricultural University of Athens. Physico-chemical characteristics of Temperature T (^{o}C), pH and Electrical Conductivity EC (μS/cm) were measured in situ. The method of titration was used for Ca^{2+}, Mg^{2+}, HCO_3^-, and Cl^- determination. Hack Dr 3000 Spectrophotometer was used for NO_3^-, PO_4^{3-}, NH_4^+ and SiO_2 determination. The concentration of Na^+ and K^+ was determined using the CORNING Flame Photometer 410. Heavy metals such as Sr, Cd, Cu, Fe, Mn, Ni, Pb, Cr VI και Zn were determined using AAS GBS 908 Atomic Absorption Spectrophotometer. Ion balance error which was better than 5% was calculated summing the ions concentration.

6. Results-Discussion

Statistics of physico-chemical characteristics of the groundwater are presented in Table 1 grouped by aquifer geology.

Table 1: Statistics of physico/chemical parameters grouped based on the aquifer geology.

Parameters	**Units**	**Carbonate**		**Miocene**		**Pleistocene**		**Holocene**		**Asopos R.**
		range	Median	range	median	range	median	range	median	
Ph		7,2-7,8	7.4	7,2-8,0	7.48	7,5-8,0	7.71	7,4-7,9	7.62	8.38
Temperature (T)	^{o}C	17,9-25,0	20.55	15-18,8	17.49	17-20	17.77	16,6-19	17.93	
Electical Conductivity	(μS/cm)	1120-2350	1605	845-2790	1455	766-971	854	526-3770	2097	14500
Hardness T/CaCO3	mg/l	23,6-63,5	39.63	19,1-60,0	35.16	19,2-26,4	22.26	5,73-67,41	34.75	115

Bicarbonate	mg/l	457-604	524	366-640	491	390-445	414	347-1701	717	488
Chlorides (Cl^-)	mg/l	184-478	270	99-815	266	96-163	121	32-992	372	5141
Sulphates (SO_4^{2-})	mg/l	17-300	135	23-134	73	Ιουν-27	16	15-355	177	750
Calcium (Ca^{2+})	mg/l	46,4-155	105	52-156	104	52-78	65	24-136	93	22
Magnesium (Mg^{2+})	mg/l	74-181	108	36-165	89	49-68	56	17-224	102.8	394
Sodium (Na^+)	mg/l	77-176	139	60,5-226	120.1	44-81,4	62.2	16-689	279	2890
Potassium (K^+)	mg/l	0,0-4,4	1.93	0,0-4,4	1.5	1,1-6,6	2.69	0,0-17,6	6.38	114
Αμμωνιακά NH^{4+}	mg/l	0,0-0,4	0.11	0,0-0,1	0.02	0,0-0,1	0.02	0,0-1,61	0.43	1.7
Nitrates ($NO^{-}{}_{3}^{-}$)	mg/l	24-259	88	8-182	54	7,9-29	20	4,4-79	21.6	24
Silicon dioxide (SiO_2)	mg/l	22,8-40,8	28.94	17,8-39,3	28.74	22,3-27,6	25.59	14,5-31	21.4	8.8
Phosphates (PO_4^{3-})	mg/l	0,2-2,1	0.94	0,1-0,4	0,19	0,1-1,4	0.31	0,1-2,8	0,5	1,49
Iron (Fe Tot)	mg/l	0,148-0,176	0.163	0,112-0,415	0.194	0,127-0,268	0.169	0,144-2,514	0.432	0.206
Manganese (Mn)	mg/l	-	-	-	-	-	-	0,022-0,507	0.175	-
Lead (Pb)	mg/l	0,005-0,048	0.027	0,007-0,068	0.05	0,013-0,144	0.069	0,031-0,09	0.059	-
Nickel (Ni)	mg/l	0,04-0,07	0.049	0,002-0,124	0.049	0,021-0,113	0.058	0,014-0,127	0.059	0.021
Copper (Cu)	mg/l	0,056-0,072	0.062	0,041-0,067	0.053	0,048-0,081	0.063	0,043-0,078	0.059	0.082
Zinc (Zn)	mg/l	0,067-0,106	0.087	0,003-0,817	0.209	0,021-0,475	0.161	0,005-0,024	0.013	-
Cadmium (Cd)	mg/l	0,045-0,082	0.061	0,025-0,066	0.049	0,044-0,071	0.056	0,042-0,066	0.058	0.056
Strontium (Sr)	mg/l	0,913-3,847	2204	1289-3827	2282	0,0-1619	0.745	0,0-4443	2561	8489
Chromium Tot (Cr)	mg/l	0.015-0.034		<0.001-0.024	0.011	0.002-0.014	0.005	<0.001-0.002		

Hydrochemistry of groundwater in the Holocene, Miocene and Mesozoic sediments indicated seawater influence. Figure 3 shows the concentration of the major components. Electrical conductivity (EC) values ranged between 526 and 3770 μS/cm with a median at 2098 μS/cm. Chlorides ranged between 31 and 993 mg/l with a median at 260 mg/l. On the contrary, groundwater quality in part of the Pleistocene conglomerate, occurring below the Holocene sediments of about 10 m in thickness, was very good. Wells and pump depth that tap the Pleistocene aquifer are between 22-40 m. The EC values which ranged between 766 and 971μS/cm with a median at 854 μS/cm and chlorides which ranged between 95 and 163 mg/l with a median 121 mg/l led to the conclusion that this coastal aquifer is protected from seawater intrusion, despite the fact that it is located adjacent to the shoreline. This happens because in many cases the torrential Pleistocene sediments are anisotropic and inhomogeneous due to occasional clay deposition. Clay plays determinant role in groundwater flow resulting in hydraulic differentiation through the formation extent. The value of 854μS/cm would probably was lower if water from the upper layers did not insert in the borehole through the well screens. The rest part of the Pleistocene aquifer indicates seawater influence with chlorides ranging between 141-815mg/l, although in 2-3 wells water quality is good with chlorides ranging around 100mg/l but they are located far from the shoreline. Water quality degradation either occurs through the well screens coming from the contaminated Holocene strata or the recharge from the return of contaminated irrigation water coming from pumping of the underlain Miocene or Cretaceous strata.

The NO_3^- and PO_4^{3-} concentrations were increased in the agricultural area which is attributed to fertilizers. Most of the heavy metal concentration such as Cd, Fe, Pb and Ni exceeded the EU limits which they have been determined at 82, 2500, 817, 217 μg/lit, respectively. It is worth mentioning the occurrence of Cd in all the samples all over the Oropos plain (Fig. 4). It is probably attributed to fertilizers (Kabata-Pendias and Pendias, 1992). It is also worth highlighting that chromium VI concentration was not exceeded the EU limits. It is likely that it was adsorbed on the clay matrix of the aquifers.

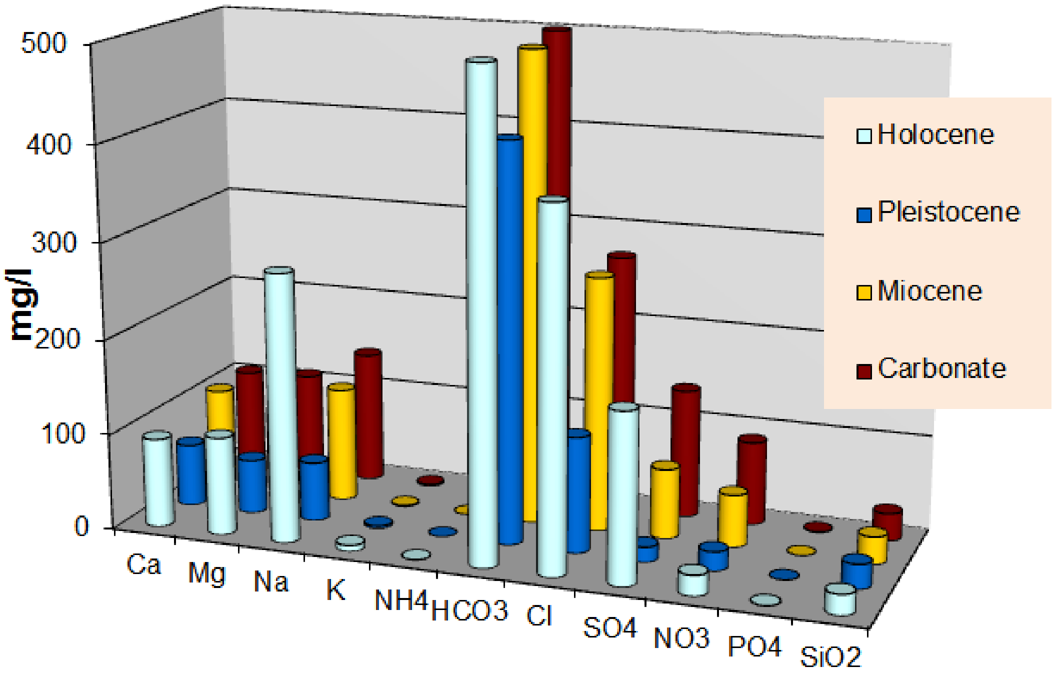

Fig. 3: Chemical analyses graph showing the low chloride concentration of the Pleistocene sediments groundwater

The Na/Cl mass ratio in 12 samples ranged between 0.52-0.59 (0.79-0.90 meq ratio) indicating that seawater has influenced groundwaters; in 10 samples the ratio ranged between 0.28-0.50 (0.43-0.77 meq ratio) indicating reverse cation exchange; and in 11 samples the ratio ranged between 0.60-1.01. (0.93 -1.54 meq ratio) indicating cation exchange processes. The mass ratio values around 0.35 reveal strong reverse cation exchange which may indicate that groundwater is hosted in the aquifer for many years.

The Cl/SO_4 mass ratio in five samples ranged between 10.82-28.58 (29.4-77.4 meq ratio) indicating sulphates reduction processes and in the most samples the ratio ranged between 0.79-5.01 (2.0-13.8 meq ratio) indicating evaporites or fertilizes influence. The Cl/SO_4 mass ratio in five samples ranged from 5.08 to 8.58 (14-22 meq ratio) indicating influence of seawater. Evaporites occurrences may be possible in the Pliocene sediments that form the corresponding aquifer. Based on the Piper diagram (Fig. 5) most of the samples showed Ca-Mg-Na-HCO3 water type and some samples showed no dominant ion which means mixing processes are in progress.

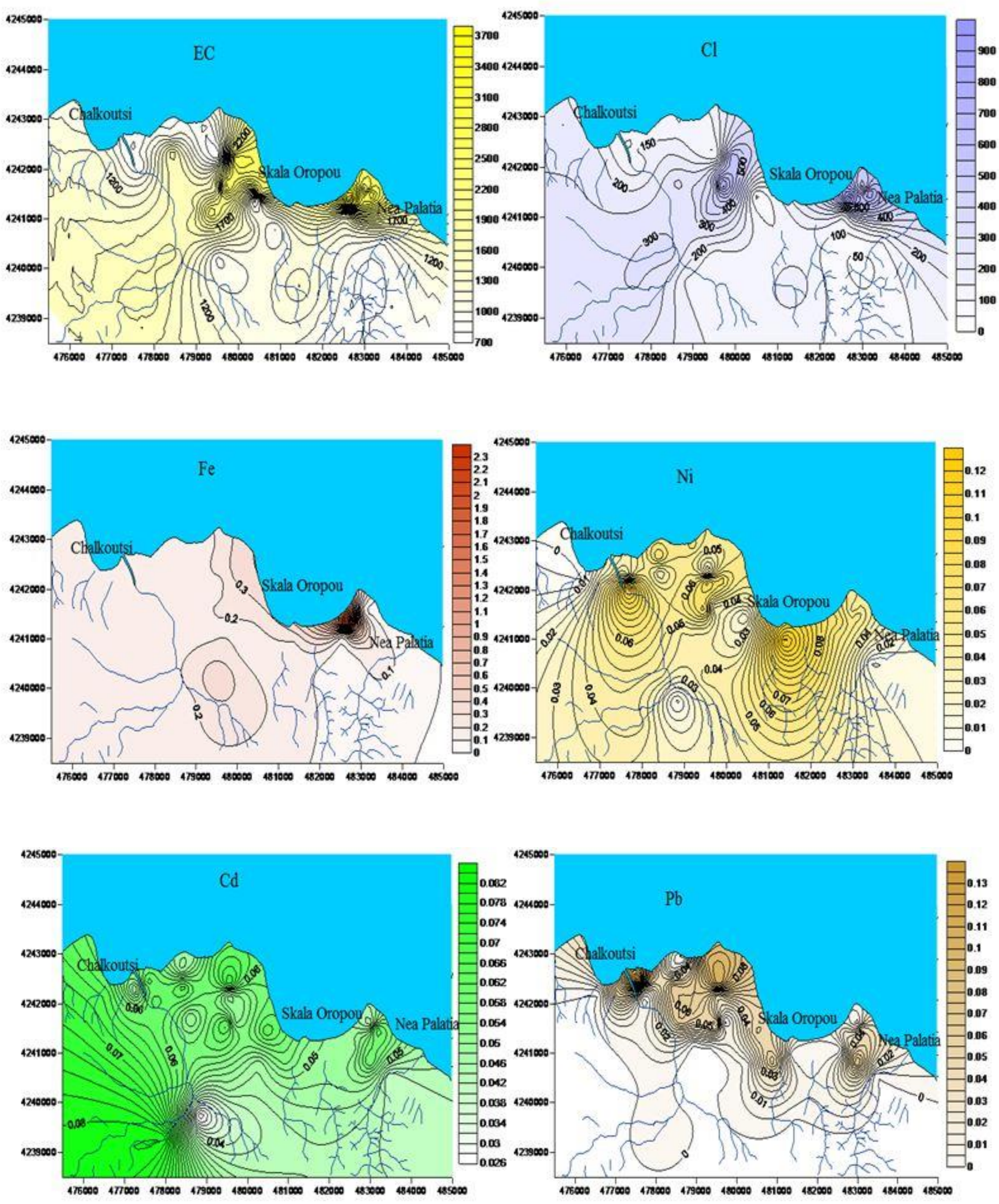

Fig. 4: EC, Cl, Cd, Fe, Ni and Pb spatial distribution of in the Oropos plain groundwaters.

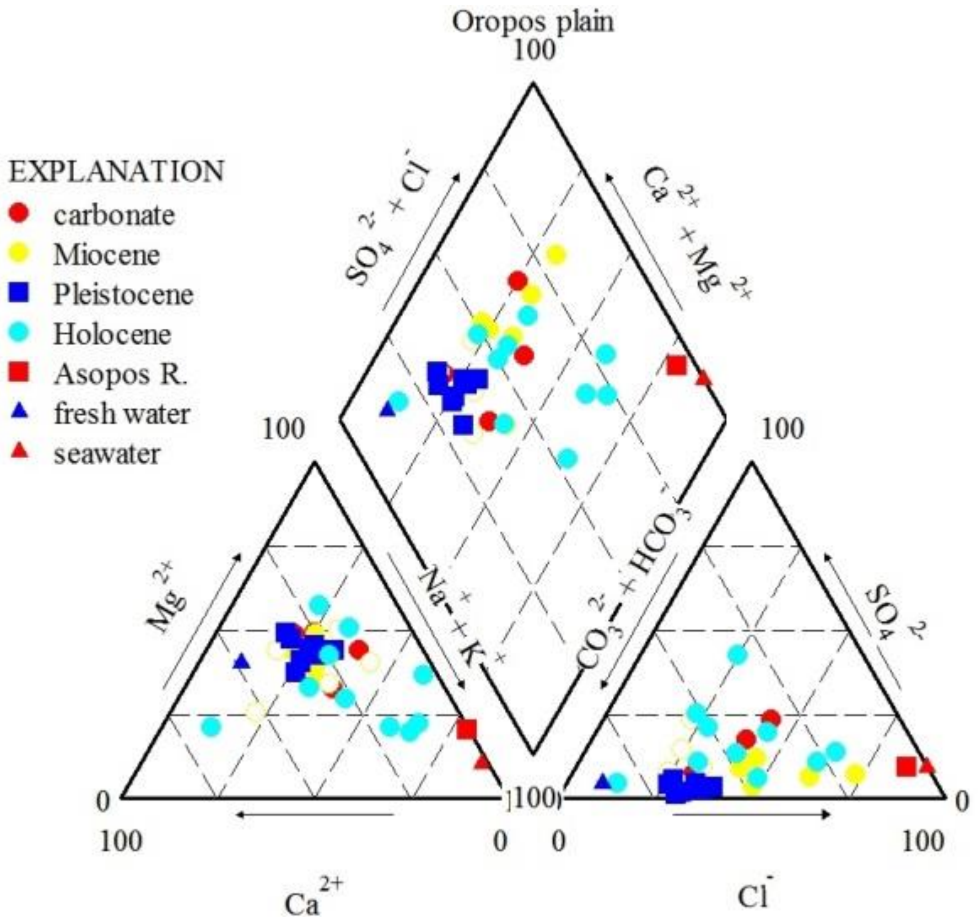

Fig. 5: Piper diagram shows i) earth alkaline with high alkali content bicarbonate (chloride) and ii) an ambiguous water type of Ca-Mg-Na-HCO3(-Cl) for the most groundwater samples

This process could take place by pumping and through the well screens or through the clay layers due to the phenomenon of diffusion Post, 2004). Groundwater was categorized into two (2) main water types based on the expanded Durov diagram (Lambrakis, 1991) which mainly presents the geochemical evolution of groundwater (Fig. 6): (i) the first group was mainly depicted on the field 2 with no dominant cation indicating fresh groundwater of Ca-Mg-HCO3 water type; and (ii) the second group was depicted on the field 8 that is Ca-Mg-Cl water type indicating reverse cation exchange of old Na-Cl waters (Lloyd et al., 1985). The Asopos River surface sample was projected on the field 9 indicating Na-Cl type contaminated by seawater because the sample was taken close to the shoreline. The expanded Durov diagram also gives a second view of the hydrogeological paths of groundwater flow. The fact that no samples are depicted in 4, 6 and 7 fields could be explained that aquifers are not in hydraulic connection each other (Alam, 2010; Lloyd and Heathcote, 1985).

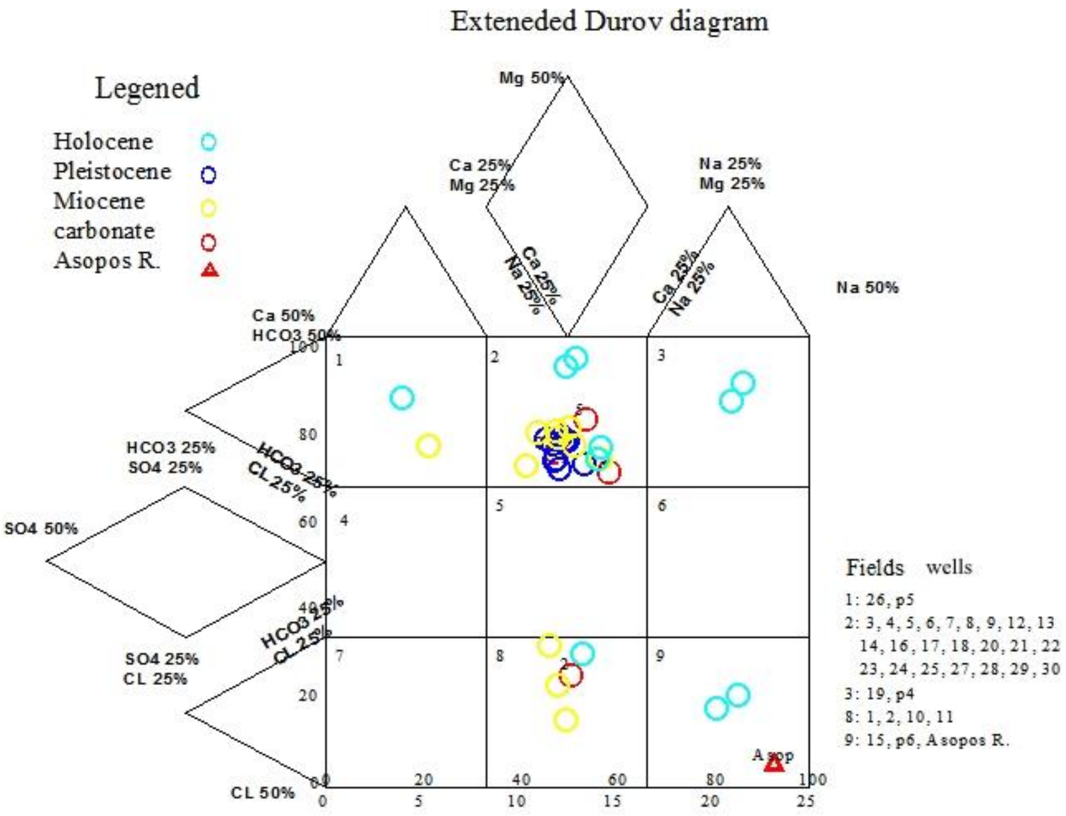

Fig. 6: Expanded Durov diagram shows Ca-Mg-HCO3 water type for the most groundwaters samples

However, the Piper diagram shows mixing processes of different groundwater. The apparently divergence of the two diagrams could be explained by the fact that the mixing processes could take place through the screens of the wells during pumping and not through the aquifers. In addition, depending on the pressure of the aquifers maybe water is mixed through the screens in non-pumping conditions.

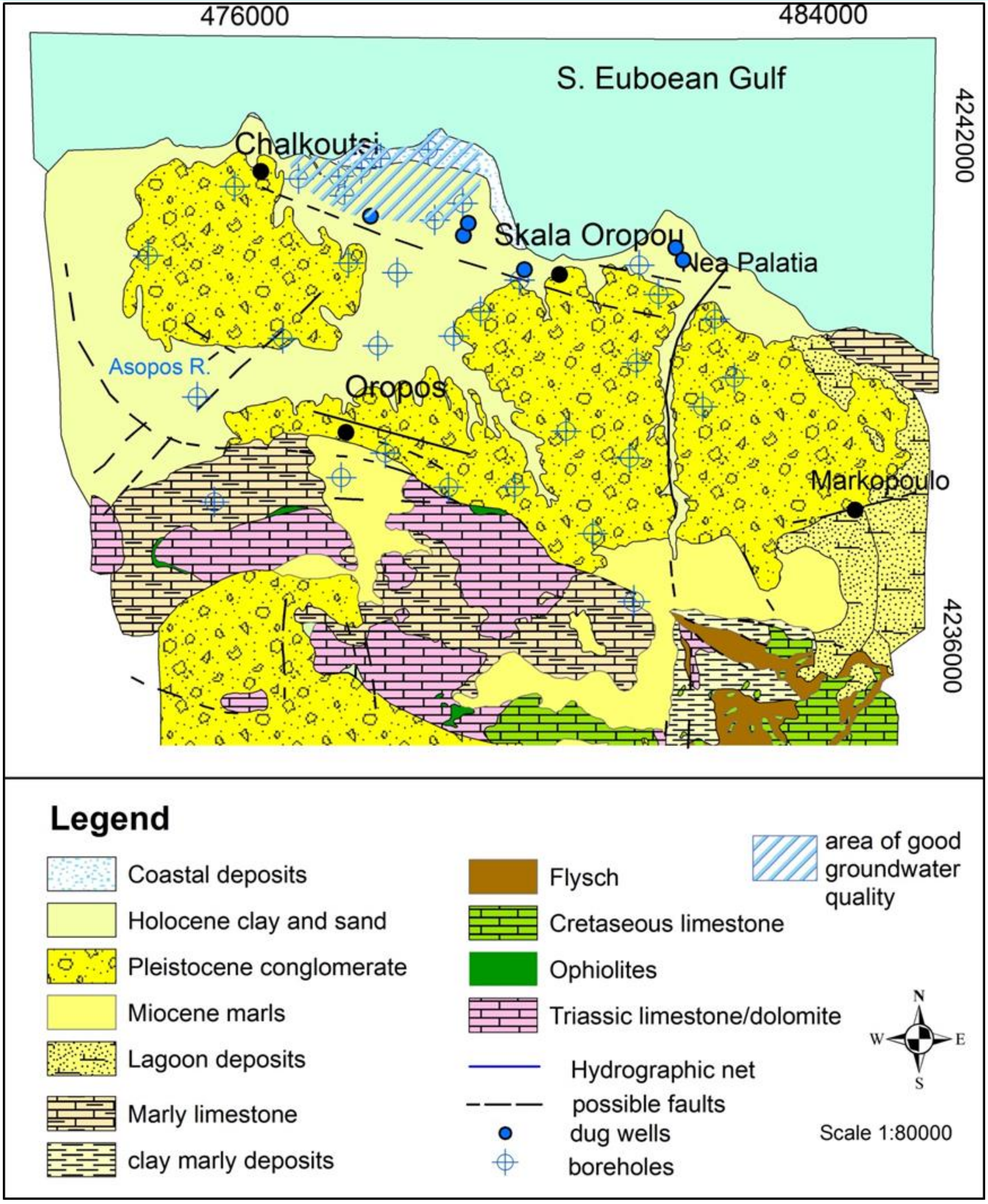

Fig. 7: The extent of the area located adjacent to the Oropos shoreline where good groundwater quality of the Pleistocene sediments was found (map projection GCS_GGRS_1987).

In Figure 7 is illustrated the area located adjacent to the shoreline of Oropos plain where groundwater quality was good. The aquifer which is formed in part of the Pleistocene sediments underlain the Holocene ones, seems to retain its good quality water protected from seawater due to very low hydraulic conductivity of clay.

7. Conclusions

A preliminary hydrochemical study on the Oropos plain groundwaters was carried out to investigate the extent of any contamination. Seawater intrusion possibly takes place through the Holocene, the Pliocene and the Carbonate aquifers. Heavy metals concentration of Cd, Fe, Pb, and Ni exceeded the EU limits while Cd concentration is attributed to fertilizers. The Pleistocene conglomerate seems to retain its good water quality against the seawater despite the fact that it is located adjacent to the shoreline and represent a reserve of good quality water which needs to be properly managed.

Groundwater was categorized into 2 main water types based on the expanded Durov diagram: (i) the first group was mainly depicted on the field 2 indicating fresh groundwater of Ca-Mg-HCO3 type; and (ii) the second group was depicted on the field 8 that is Ca-Mg-Cl type indicating reverse cation exchange of old Na-Cl waters. Based on the Piper diagram most of the samples showed Ca-HCO3 type and some samples showed no dominant type (ambiguous) which means mixing processes are in progress.

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