TEMPORAL EVOLUTION AND ASSESSMENT OF GROUNDWATER QUALITY IN COASTAL AGRICULTURAL AREAS. THE CASE OF PINIOS RIVER DELTA

[1]PISINARAS V., [1]ILIAS A., [1]PARASKEVAS C., [2]POULOS S., [2]MATIATOS I., [3]ALEXOPOULOS J.D., [4]KOTSOPOULOS S., [5]ALEXIOU I., [4]LAZOGIANNIS K., [1]ARAMPATZIS G., [1]KALOGIANNI H., [1]TSEKOURA D. and [1]PANAGOPOULOS A.*

[1] Land Reclamation Institute, D.G. Agricultural Research, Hellenic Agricultural Organization DEMETER, 57400, Sindos, Greece, panagopoulosa@gmail.com,
[2] Department of Geography & Climatology, Faculty of Geology & Geo-Environment, University of Athens, Panepistimioupoli, Zografou, 15784, Athens, Greece,
[3] Department of Geothysics & Geothermy, Faculty of Geology & Geo-Environment, University of Athens, Panepistimioupoli, Zografou, 15784, Athens, Greece
[4] Department of Civil Engineering, Technological Educational Institute (TEI) of Thessaly, 41110 Larissa, Greece
[5] Institute of Soil Mapping and Classification, D.G. Agricultural Research, Hellenic Agricultural Organization DEMETER, 57400, Sindos, Greece

Keywords: Groundwater quality, Seawater intrusion, Piper diagrams, Pinios river delta, Hydrochemical evolution.

Abstract

The present study aims to assess the current groundwater quality and investigate its temporal evolution in the two identified aquifers (shallow and deep) located in the sedimentary sequence of Pinios River estuary. Significant land use changes mark groundwater management practices of the shallow aquifer over the past years, as traditional crops of high water requirements have been partly substituted by less water demanding crops, and groundwater abstractions have been reduced and substituted by surface water from Pinios River to cover irrigation needs over a large part of the study area. To study the effect of aforementioned land use changes, major groundwater physicochemical parameter values for the year 2013 were assessed and compared to the corresponding data for the years 1998 and 1999. The results indicate that the quality of the shallow aquifer in terms of groundwater salinization and nitrate pollution may be considered as satisfactory with higher groundwater salt content observed in the northern and southern parts of the system. The water quality characteristics of the deep aquifer are overall worse than the shallow aquifer as groundwater salt content is increasing towards the coast. The temporal comparison of the water quality characteristics demonstrates no significant changes for seawater intrusion related parameters such as Electrical Conductivity, and Na^+ and Cl^- concentrations, but also for pollution related parameters such as NO_3^- concentrations.

1. Introduction

Groundwater constitutes a vital source of usable water around the globe and that is the case for Greece, as it serves the major part of potable and irrigation water demands of the country. The last decades, due to the increment of potable water needs and the intensification of agriculture, significant deterioration of the groundwater quantitative regime has been observed in several groundwater bodies in Greece (Petalas *et al.* 2009). Similarly, groundwater quality has been found to be significantly affected mainly by agricultural activities (Voudouris *et al.* 2004; Mattas *et al.* 2007; Alexandridis *et al.* 2014) due to the non-rational application of agrochemicals, but also by industrial activities and urban pollution. Moreover, as Greece is surrounded by the sea, seawater intrusion phenomena are observed in several coastal aquifers (Voudouris *et al.* 2000; Stamatis *et al.* 2001; Lambrakis and Marinos 2003; Panagopoulos *et al.* 2004; Petalas and Lambrakis 2006; Petalas *et al.* 2009). Land use and water management in the study area, along with its hydrogeological setup have been reported to affect groundwater quality (Panagopoulos *et al.* 2001).

This study aims to investigate the current groundwater quality status of the two coastal aquifers in the deltaic plain of Pinios River (Central Greece). Moreover, recent groundwater quality data, in the frame of the AGROCLIMA project, is compared to corresponding data from years 1998 and 1999 in order to identify changes in the temporal and spatial distribution of the major groundwater chemical constituents and relate them to changes identified in agricultural and groundwater management practices adopted in the study area.

2. Materials and Methods

2.1 Study Area Description

The study area is situated in the deltaic plain of Pinios River and covers an area of about 76 Km^2. Pinios River basin that is the largest fully developing basin in Greece, is of high significance in terms of regional and national socio-economic development and stability, as it is one of the highest productive basins of the country. It is located in Thessaly (central Greece) that has total surface area of approximately 11.000 Km^2, it is characterized by highly diversified geological, hydrological and hydrogeological conditions and marked by the systematic exploitation of water resources since early 1960's. Due to water resources mismanagement, signs of overexploitation have appeared as early as mid 1980's and a deficient water balance has been established in the last 3 decades (Panagopoulos *et al.* 1995).

In contrast to the surrounding mountainous area, Pinios River deltaic plain presents low relief with ground elevation ranging between 0 and 15 m above mean sea level (amsl), gently sloping eastwards. The geomorphological evolution of the study area is directly related and controlled by the geotectonic evolution of the wider area during Holocene and to the erosion-deposition mechanisms induced by river flow during this period. As river outflow to the sea is estimated to have formed during the Quaternary, the deltaic plain is also estimated to be recently formed. This evidence, in addition to the fact that the modern talus cones and scree along the margins of the basin are covered by recent deltaic depositions, justify the small area of Pinios River deltaic plain, despite the fact that it receives the sediment depositions of the largest basin fully developing in Greece.

Moreover, the development of deltaic plain is limited by the sediment transport processes observed in sea. The modern deltaic depositions of Pinios River demonstrate a typical arcuate section with radial growth eastwards. Due to the recent deposition of deltaic sediments and low slopes observed in the study area, river course evolution presents a composite structure, hence complex meanders and multiple courses with radial arrangement are observed.

Geologically, two major formations are observed in the wider study area: sequences of folded alpine formations and plio-quaternary deposits in which the deltaic plain is situated. More detailed, Neogene formations crop out at the western margin of the deltaic plain, which are considered to be the bedrock of the overlying Pleistocene and Holocene sediments. According to the geological mapping carried out by I.G.M.E. (1989), the thickness of the Neogene formations in the wider study area is up to 200 m and indicates high lithological heterogeneity. Pleistocene deposits include talus cones and screes developed in the western boundary of the deltaic plain consisting mainly of breccio-conglomerates of variable size and composition. Finally, the Holocene deposits include the following formations: a) the alluvial sequence of Omolio basin, consisting mainly by sands, breccia-pebbles and clay, b) coastal formations consisting mainly by sand and clay and c) recent incoherent sediments which include contemporary river deposits consisting mainly by sands, clays and breccia-pebbles of varying size and lithological composition.

In terms of hydrogeological properties, the formations that are of importance for the deltaic plain are the Quaternary sediments and especially the alluvial deposits. In general, a trend is observed in the alluvial deposits that become finer shifting from the margins of the basin towards the coast to the east. Therefore, the percentage of silty and clayey sediments is increasing with subsequent impact on the hydraulic properties of the aquifer. This trend is locally disturbed along the river course (old and current) in which coarser fractions are observed as a result of the river sediment deposition process.

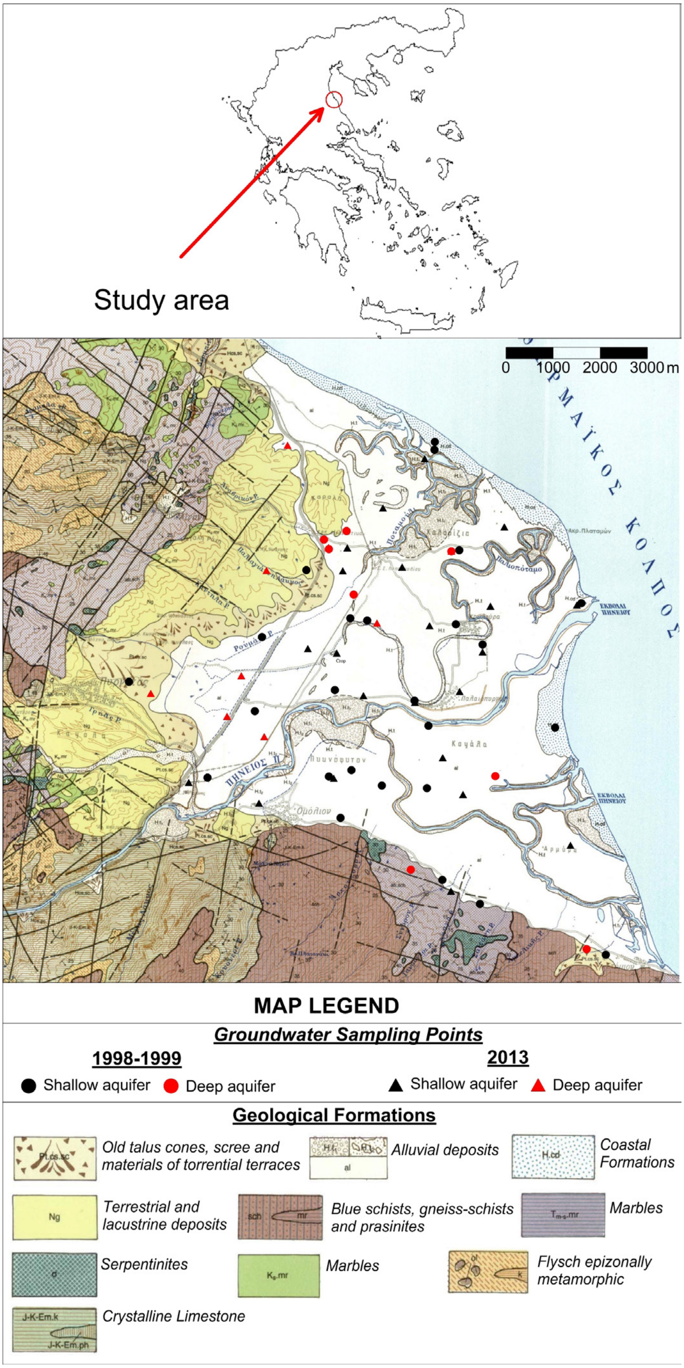

Figure 1. Geological map and location map of groundwater sampling wells in the study area (based on the geological mapping by the I.G.M.E. (1989)).

The stratigraphic structure of the deltaic plain is typical alluvial with continuous alterations of fine (silts and clays) and coarse sediments (sands). The thickness of these layers, which are not uniformly distributed in the study area, is up to 4 meters, while the total thickness of the structure is up to 30-40 m. Below this structure, a sequence of clay layers are observed, as indicated by wells logs, while a deep confined aquifer consisting mainly by conglomerates is formed below the sequence of clay layers. Therefore, two major aquifer systems are defined: the phreatic (referred to as shallow aquifer) and the confined (referred to as deep aquifer).

Precipitation data collected from the meteorological station in Pirgetos village (35 m amsl), for the period 1960-1993, yields average annual precipitation 795.6 mm. The driest month for the study area is July (19.4 mm) followed by August (23.1 mm) will the wettest month is January (105.3 mm) followed by December (103.1 mm). Two major categories of land use are identified in the deltaic plain of Pinios Rrver: agricultural and urban-touristic. The last two decades, significant residential and touristic infrastructures development is observed, almost exclusively in the coastal part of the study area. Also, significant changes are observed during the last decade in crop pattern distribution. The major crops cultivated during 90s' were corn, wheat, cotton, alfalfa and sugar-beet, while during the last years, the major crops are wheat, sunflower, kiwi-fruit and alfalfa. Therefore, a change to less water-demanding crops is observed, as sunflower and wheat are not irrigated in the study area. Moreover, a significant part of irrigation water demands that used to be covered by groundwater, are nowadays catered by river water diverted in irrigation-drainage canals.

2.2 Dataset Collection and Processing

Following a comprehensive wells' and boreholes' census carried out in the study area, a groundwater monitoring network was established (Figure 1), which consists of 23 wells considered as representative of the shallow aquifer (depth < 30 m) and 9 boreholes considered as representative of the deep aquifer (depth > 30 m). A groundwater sampling survey during the summer of 2013, in which Temperature (T), pH and Electric Conductivity (EC) were measured in-situ, while major ions and nitrogen compounds concentrations were determined in the accredited Laboratory of the Land Reclamation Institute using standard methods.

In order to compare the impacts of changes in cultivated crops and groundwater management practices in the study area, groundwater quality data from the Hellenic Institute of Geology & Mineral Exploration referring to the summer of years 1998 and 1999 were used. Similarly to the dataset of year 2013, data were categorized, depending on the depth of the monitoring well, as representative of the shallow or the deep aquifer. Due to the fact that there were no significant variations observed in groundwater quality between the two successive datasets (1998 and 1999), the parameters were averaged when two samples were available for the same sampling well. In total, 33 groundwater sampling points were included in the analysis from which 25 are representative of the shallow aquifer and 8 are representative of the deep aquifer.

In order to investigate the variation of the major hydrochemical constituents within the two datasets, hence the two periods of time (1998-1999 vs 2013), typical statistical parameters such as mean, median, minimum and maximum values were calculated, while Piper diagrams were also compiled. Study of the groundwater salinity distribution was based on spatial EC distribution maps for the shallow aquifer. For the deep aquifer, bar charts of EC were used instead due to the fact that the quantity and the spatial distribution of groundwater samples were not sufficient to justify the compilation of isoparametric maps. Finally, the results of analyses described below were compared in order to identify changes between the two datasets.

3. Results and Discussion

3.1 Groundwater quality evolution of the shallow aquifer

The statistical analysis results of the variation of the major hydrochemical constituents in the shallow aquifer between the examined sampling periods are presented in Table 1. Despite the fact that groundwater quality for both sampling periods is considered satisfactory in terms of groundwater salinization and nitrate pollution affection, there are a few samples in both sampling periods in which values of parameters related to seawater intrusion such as EC and Na^+ and Cl^- concentrations are increased. This is also illustrated at the Piper diagram presented in Figure 2a, which suggests that the majority of groundwater samples for both sampling periods are freshwaters of Ca^{2+}-HCO_3^- hydrochemical type, while a few samples are of Na^+-Cl^- hydrochemical type, thus indicating possible groundwater salinization processes. Moreover, several samples are scattered in the central part of the tri-linear diagrams, indicating a complex transgressive hydrochemical type that may not be assigned a definite hydrochemical type. The mean, minimum and maximum values of EC and Na^+, Cl^- for 6 coastal aquifers in Greece which are subject to seawater intrusion are presented in Table 2. All aquifers indicate a larger variation range of the three parameters presented, thus indicating stronger influence by seawater intrusion. Moreover, Na^+ and Cl^- concentrations and EC values were on the average higher for all aquifers presented in Table 2, except from the case of Northern Korinthia aquifer (Voudouris *et al.* 2000) in which the corresponding values are close to those of the shallow aquifer in the study area.

Table 1. Statistical analysis results of the values of the key physicochemical parameters for the shallow aquifer over the two sampling periods

	pH		**T (°C)**		**EC (μS/cm)**		**K^+ (mg/L)**	
	1998-99	**2013**	**1998-99**	**2013**	**1998-99**	**2013**	**1998-99**	**2013**
Mean	7.54	7.00	17.39	18.50	1061	977.63	8.52	9.36
Median	7.54	7.05	17.13	18.50	910	979.00	5.08	7.25
Min	6.96	6.33	12.50	13.30	207	270.40	0.39	1.10
Max	7.91	8.01	24.70	21.50	2849	2130.00	44.96	26.00
	Na^+ (mg/L)		**Ca^{2+} (mg/L)**		**Mg^{2+} (mg/L)**		**Cl^- (mg/L)**	
	1998-99	**2013**	**1998-99**	**2013**	**1998-99**	**2013**	**1998-99**	**2013**
Mean	74.06	61.94	97.36	87.87	35.16	38.89	82.15	97.55
Median	25.52	36.56	95.79	80.80	35.99	43.15	38.99	35.70
Min	3.45	7.07	33.27	24.93	5.35	12.10	7.09	9.82
Max	432.76	220.82	183.57	190.65	75.39	83.00	452.85	474.13
	HCO_3^- (mg/L)		**SO_4^{2-} (mg/L)**		**NO_3^- (mg/L)**			
	1998-99	**2013**	**1998-99**	**2013**	**1998-99**	**2013**		
Mean	435.92	421.39	67.84	29.45	9.06	9.81		
Median	429.53	431.60	45.15	19.36	4.96	2.52		
Min	95.79	151.00	0.48	0.11	1.24	0.55		
Max	860.28	783.50	247.36	119.47	52.08	37.98		

Comparative study between the results of the two examined sampling periods with regards to pH values, shows lower mean and median values and larger variation range for year 2013 compared to the corresponding values for the period 1998-1999. Both the average and median T values are higher in 2013 compared to 1998-1999. EC variation demonstrates higher mean but lower median value for 1998-1999. Despite the fact that K^+ variation range was higher for 1998-1999 compared to 2013, average and median values were lower. Similar changes were also presented for Mg^{2+}. Na^+ and HCO_3^- concentrations mean values for the year 2013 were found to be lower when compared to the corresponding value for the period 1998-1999. Average and median Ca^{2+} and SO_4^{2-} concentrations were lower for the year 2013. Average Cl^- and NO_3^- concentrations were higher in 2013 compared to the 1998-1999 period, but median values were lower. Overall, the observed differences in the major hydrochemical constituents presented above are not considered as significant either in terms of average or median values. Even for hydrochemical parameters related to seawater intrusion such as EC, Na^+ and Cl^-, mean and median values are very close in both sampling periods, thus indicating that the average chemical quality of the shallow aquifer has not been significantly influenced by the change of groundwater management practices. EC and Na^+ concentration maxima were higher for the period 1998-99 compared to year 2013, indicating locally higher influence by possible salinization processes.

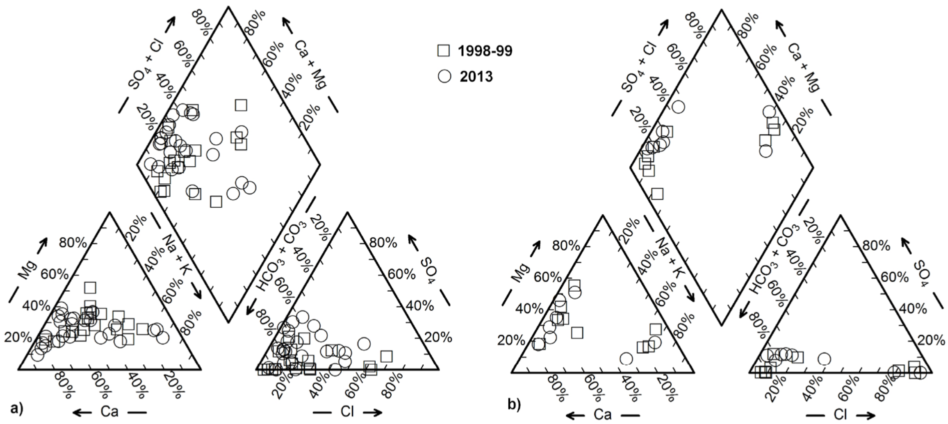

Figure 2. Piper diagrams for a) the shallow aquifer and b) the deep aquifer.

The spatial distribution of EC for both sampling periods is illustrated in Figure 3. There are several spatial trends that are common for both sampling periods. Hence, higher EC values are recorded in the northern and southern parts of the study area, with the highest values being observed in the former part and during the first sampling period (1998-1999). Moreover, lower EC values are presented in the central part of the study area, along the current Pinios River course, suggesting direct infiltration of Pinios River water to the shallow aquifer. Also, the western part of the shallow aquifer demonstrates lower EC values which could be attributed to lateral cross-flows from the surrounding hydrogeological environment.

Table 2. Mean, minimum and maximum values of EC, Na^+ and Cl^- concentrations for some coastal aquifers in Greece

Parameter		Voudouris *et al.* (2000)	Stamatis *et al.* (2001)	Lambrakis and Marinos (2003)		Petalas & Lambrakis (2006)	Petalas *et al.* (2009)
				Gouves aquifer	Malia aquifer		
EC (μS/cm)	**Mean**	1,328	3,732	2,674	1,035	2,240	3,789
	Min	550	795	900	290	365	554
	Max	4,120	8,470	4,080	5,000	11,000	14,300
Na^+ (mg/L)	**Mean**	88	504	407	170	152	226
	Min	19	23	83	12	21	61
	Max	440	1,200	670	1,200	1,024	931
Cl^- (mg/L)	**Mean**	97	990	669	369	590	1,155
	Min	15	99	155	22	19	62
	Max	694	2,198	1,045	2,180	3,992	5,158

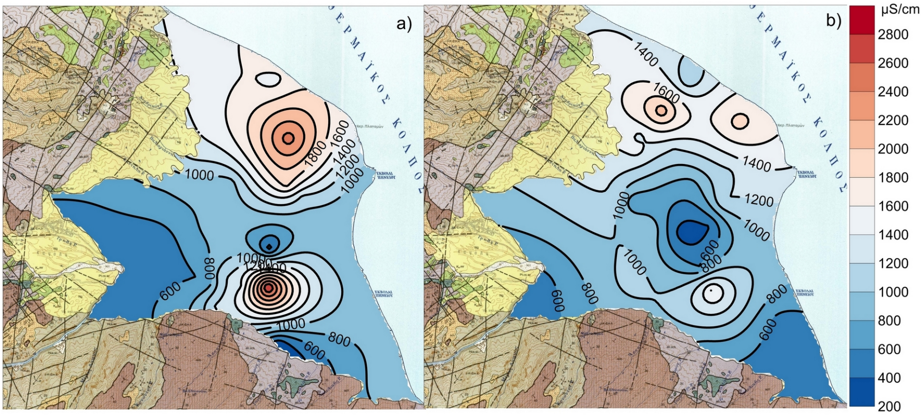

Figure 3. EC spatial distribution in the shallow aquifer a) summer periods of 1998-99 and b) summer period of 2013.

3.2 Groundwater quality evolution of the deep aquifer

The statistical analysis results of the variation of the major hydrochemical constituents in the deep aquifer between the examined sampling periods are presented in Table 3. Parameters related to groundwater salinization such as EC, Na^+ and Cl^- present a very wide range of variation for both sampling periods, indicating significant differences in groundwater salt content, and obviously suggesting variations in the dominant mechanisms that control hydrochemical evolution of the system. This is also justified by the large difference between mean and median values of EC and Na^+, Cl^- concentrations, as well as by the projection of the analysed water samples at the Piper diagram presented in Figure 2b. Two major groups are clearly distinguished in the Piper diagram for both sampling periods. The first group, defined by the groundwater samples located in the left side of the diagram, indicates freshwaters of low ion content and of Ca^{2+}-HCO_3^- hydrochemical type. The second group referring to groundwater samples found in the right side of the diagram suggests groundwater of Na^+-Cl^- hydrochemical type, which is indicative of groundwater affected by salinization processes. In terms of nitrate pollution, mean and median nitrate concentrations were <10 mg/L for both sampling periods indicating that the change in land use over the years had no significant impact on the nitrate content of the aquifers. The comparison of the groundwater quality characteristics of the two aquifer, showed a higher salt content in the deep aquifer as reflected both on the mean and median values, while higher variation range of groundwater salinization related parameters is also observed. Moreover, a more scattered distribution of the groundwater samples from the shallow aquifer than from the deeper aquifer, as presented in the Piper diagram (Figure 2a), indicates that more complex hydrochemical processes, including mixing, are occurring in the shallow aquifer. The comparison of average, minimum and maximum EC values and Na^+ and Cl^- concentrations of the deep aquifer with the corresponding values of the six coastal aquifers presented in Table 2, indicate that EC and Cl^- maximum values in the deep aquifer are higher than the maxima observed in the studies of Voudouris *et al.* (2000) and Lambrakis and Marinos (2003). Moreover, higher average Na^+ and Cl^- concentrations are observed for the deep aquifer compared to the studies of Voudouris *et al.* (2000) and Lambrakis and Marinos (2003) (Malia aquifer).

The temporal comparison indicates that, in terms of pH, T, SO_4^{2-} and NO_3^- lower mean and median values were presented for year 2013 compared to the corresponding values for the period 1998-1999. On the contrary, mean and median Na^+, K^+, Mg^{2+} and HCO_3^- concentrations were found to be higher for the year 2013 compared to the period 1998-1999. Concerning average EC values and Ca^{2+} concentrations, these were found to be lower for the year 2013, but increased on the median, when compared to the corresponding values for the period 1998-1999. The opposite trend was observed for Cl^- concentrations, which were found to be increased on the average and decreased on the median. Similarly to the shallow aquifer, the overall temporal changes of hydrochemical parameters between the two sampling periods are not considered significant.

Table 2. Statistical analysis results of the variation of the major physicochemical constituents for the deep aquifer over the two sampling periods

	pH		T (°C)		EC (μS/cm)		K^+ (mg/L)	
	1998-99	**2013**	**1998-99**	**2013**	**1998-99**	**2013**	**1998-99**	**2013**
Mean	7.36	7.08	16.09	15.99	1964.25	1887.78	3.54	11.38
Median	7.38	6.95	16.10	16.00	931.75	1010.00	1.17	2.20
Min	6.82	6.75	15.00	14.40	607.50	698.00	0.78	1.00
Max	7.78	7.87	17.70	18.00	6105.00	6510.00	10.16	76.00
	Na^+ (mg/L)		**Ca^{2+} (mg/L)**		**Mg^{2+} (mg/L)**		**Cl^- (mg/L)**	
	1998-99	**2013**	**1998-99**	**2013**	**1998-99**	**2013**	**1998-99**	**2013**
Mean	171.28	239.89	137.98	110.93	49.67	72.63	397.69	495.75
Median	16.32	24.54	101.80	115.35	45.72	47.80	45.64	28.05
Min	7.59	10.80	74.55	52.55	15.32	17.55	19.50	14.88
Max	695.63	1158.05	340.68	141.50	91.44	268.00	1784.00	2448.96
	HCO_3^- (mg/L)		**SO_4^{2-} (mg/L)**		**NO_3^- (mg/L)**			
	1998-99	**2013**	**1998-99**	**2013**	**1998-99**	**2013**		
Mean	444.33	479.00	33.80	17.51	10.50	9.15		
Median	403.29	460.12	39.63	11.81	8.21	3.47		
Min	214.77	36.42	0.00	0.11	1.55	1.02		
Max	878.58	922.83	66.76	45.58	20.46	37.27		

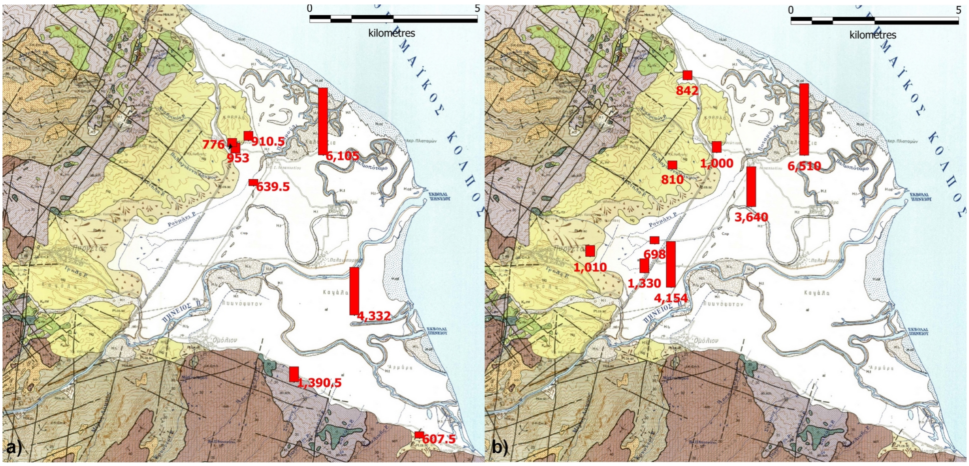

Figure 4. EC spatial distribution in the deep aquifer a) summer periods of 1998-99 and b) summer period of 2013.

The spatial distribution of EC, which is considered as indicative of the total salt content, for the two sampling periods is presented in Figure 4. Despite the fact that groundwater samples are not evenly distributed in the study area for the two sampling periods, the EC values increases as the distance from the coast decreases and the distance from the western margin of the deltaic plain increases.

Therefore, groundwater of low ion content is found near the western margins of the deep aquifer where the alpine formations including karstified carbonate rocks crop out and marginal fans develop.

4. Conclusions

In the present study, the basic groundwater quality characteristics of the two aquifers in the deltaic plain of Pinios River were assessed based on hydrochemical data from the summer period of year 2013, mainly in terms of groundwater salinization, while the results were compared with data from the summer periods of years 1998-1999. Overall, groundwater quality of the shallow aquifer was fair, while in the northern and southern parts of the study area, increased Na^+ and Cl^- concentrations as well as EC values were observed, thus indicating possible influence from seawater. Despite the fact that the local land uses have changed considerably over the last decade, as groundwater abstractions for irrigation have been substituted in a significant degree by surface water abstractions from Pinios River, the chemical quality of the shallow aquifer has not changed significantly. Compared to the shallow aquifer, the deep aquifer presents higher groundwater salt loads. Moreover, the comparison of groundwater quality characteristics for the two sampling periods indicates that no significant changes have occurred, which was expected as groundwater exploitation from the deep aquifer is rather limited. Further investigation of groundwater quality characteristics is required for the study area including seasonal groundwater sampling in order to study in more detail the effects of groundwater management practices, identify the dominant groundwater recharge mechanisms and determine their relative importance in groundwater quality evolution. Moreover, due to the fact that deep aquifer exploitation is limited, further hydrogeological and hydrochemical investigation is required in order to identify its exploitation potential.

5. Acknowledgements

This research work was elaborated in the framework of the project “AGROCLIMA”, under the national action "COOPERATION 2011: Partnerships of Production and Research Institutions in Focused Research and Technology Sectors" that is co-funded by the European Regional Development Fund of the EU and National Resources. The authors wish to acknowledge the valuable contribution of the former Hellenic Institute of Geology and Mineral Exploration and in particular Dr A. Manakos, for providing hydrochemical data from groundwater quality assessment studies (years 1998-1999) and borehole logs from drilling projects operated in the area.

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