

**GROUNDWATER FLOW REGIME AND QUALITY ASSESSMENT
OF THE ALLUVIAL AQUIFER IN THE DELTAIC ENVIRONMENT
OF RIVER PINIOS (THESSALY)**

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Abstract

This study aims at defining the groundwater flow regime and the principal hydro-geochemical processes controlling groundwater quality in the deltaic plain of River Pinios (Thessaly-Greece) and investigating whether seawater intrusion and pollution are influencing groundwater quality. Groundwater level monitoring from October 2012 to September 2013 shows that groundwater flow is seawards and that the water table of the phreatic aquifer is mainly declining during the summer period when it is over-pumping and natural recharge limited. Major ions analysed in 49 groundwater samples reveal that groundwater is mainly affected by four factors: (i) dissolution of calcite and dolomite; (ii) weathering of silicate minerals; (iii) seawater intrusion; and (iv) contaminant enrichment (e.g., NH₄) mainly caused by point sources of pollution. High enrichment of Na and Cl near the coast gives an indication of seawater intrusion into the aquifer as also supported from the Na–Cl signature on the Piper diagram and the Revelle coefficient. The dissolution of calcite and dolomite results in Ca–HCO₃ and Mg–HCO₃ groundwater types, whereas natural geochemical processes are considered responsible for the aquifer's enrichment in minor elements (e.g., Fe, Mn). Based on the simulation results performed using PHREEQC model, groundwater is mainly supersaturated with respect to calcite and dolomite minerals, supporting a long residence time hypothesis. The relation between seasonal water level fluctuation and hydrochemistry shows that both are mainly controlled by the aquifer's recharge process.

1. Introduction

Nearly sixty percent of the world's population lives in coastal and deltaic regions (Richter and Kreitler 1993) vulnerable to seawater intrusion and groundwater contamination due to groundwater over-exploitation to meet increasing water demands associated with population growth and anthropogenic activities (e.g., agriculture). This vulnerability is also expected to exacerbate by future climate change and associated sea-level rise (Taylor *et al.* 2013). Seawater and freshwater have differing hydrochemistry, with the former being characterized by nearly uniform chemistry where chloride (Cl) and sodium (Na) make up around 84% of the total ionic composition. On the other hand, while freshwater composition varies widely, calcium (Ca) and bicarbonate (HCO₃) commonly dominate (Richter and Kreitler 1993). Although seawater intrusion is

an influential factor of groundwater quality, processes such as hydro-geochemical reactions, shoreline geomorphology, biological processes, and aquifer flow, are some of the factors that can eventually define the groundwater hydrochemistry and its potential use (e.g., irrigation) (Matiatos *et al.* 2014). Hence, the knowledge of the factors controlling the regional groundwater flow and quality regime is important for planning and management of the groundwater resources. The present study is an integrated hydrogeological and hydrochemical approach through the use of both water chemistry and hydraulic data for providing a better understanding of the groundwater movement as well as the hydro-geochemical processes responsible for the water quality characteristics in the deltaic plain of River Pinios. The study is conducted in the framework of the project Thalys – Daphne, whose general scope is to investigate the consequences of climate change on deltaic plains, as one of the most vulnerable coastal and wealth-producing ecosystems.

2. Materials and Methods

2.1 Physiographic setting

The study area represents the deltaic plain of River Pinios (Thessaly-Greece) covering an area of approximately 68 Km² and located between 22°36' to 22°44' E longitude and 39°51' to 39°58' N latitude. The plain is surrounded to the East by Thermaikos Gulf, to the West-Northwest by the mountainous area of Kato Olympos and to South-Southeast by Mt. Ossa (Figure 1). The modern alluvial deposits of the river give the deltaic plain a valley relief with gentle slopes. A number of radial riverbeds, maiandrisms, and isolated parts of old riverbeds, which operate only during flood events, are also present. Moreover, anthropogenic activities, e.g., agriculture, have influenced the plain relief of the area resulting in the disappearance of old riverbed parts.

2.2 Geological and Hydrogeological Setting

According to Katsikatsos and Migiros (1982), the wider area of the deltaic plain of River Pinios is occupied by both alpine and post-alpine geological formations (Figure 1). The alpine formations of Ossa Unit (i.e., crystalline limestones and dolomites followed by metamorphic flysch) of over 1000 m in thickness are overlaid by the Ampelakia Unit metamorphic formations (mainly shales with crystalline marble intercalations) and the Pelagonic Unit (i.e., a pre-Upper Cretaceous complex of metamorphic ophiolites, amphibolites, shales and prasinites followed by Cretaceous marbles) which cover the largest part of Ossa and Kato Olympos area. The Neogene deposits, mainly marly formations which successively become conglomerates in the upper parts and of over 300 m in thickness, followed by the Pleistocene sediments (i.e., debris cones, screes and fluvial terraces) lie mainly in the areas of Platamonas and Pyrgos along the western and northern outcrops of the deltaic plain. The alluvial sediments (e.g., sands, clays) constitute the youngest formation covering the largest part of the plain, whereas in the coastal areas sand dunes and coastal sediments (e.g., sands) prevail.

From a hydrogeological aspect, groundwater occurs in the alluvial sediments of the deltaic plain of River Pinios. Although groundwater has been identified in deeper geological formations (Panagopoulos *et al.* 2001), the present study focuses only in the upper phreatic aquifer of medium capacity and thickness (approximately 7-10 m, as derived from preliminary geophysical results), which shows lithological heterogeneities in both horizontal and vertical direction. In particular, the alluvial sediments occurring on both sides of River Pinios are essentially composed of coarse grained material, whereas clays and silts are mainly located in the estuarine zone where river water velocities decline. In the vertical direction, the pore spaces developed in the alluvium sediments act as a shallow granular aquifer and form potential water-bearing zones, whereas the clay and silt intercalations decrease the overall permeability of the formation. As a result, a series of successive superimposed semi-confined or unconfined aquifers of limited extent are expected to occur inside the alluvial sequence. However, despite the described

heterogeneity, on a regional scale a single unconfined aquifer may be considered. The region accounts for approximately 140 wells and boreholes through which groundwater resources are being abstracted. Most of the boreholes are shallow (up to 7 m depth) of small-diameter and operate using suction pumps thus taking advantage of the very shallow groundwater levels along most of the deltaic plain. The hydraulic interaction between the aquifer and River Pinios has been proposed by Panagopoulos *et al.* (2001). In particular, the authors suggest that in the eastern part of the area, where the river enters the plain, the river recharges the aquifer, whereas in the central and eastern part of the plain, the authors assume that the river recharges the aquifer and vice-versa depending on the exact location, the season and the relation between the river stage and the potentiometric surface. In the present study, the hydraulic connection between River Pinios and the aquifer is not examined.

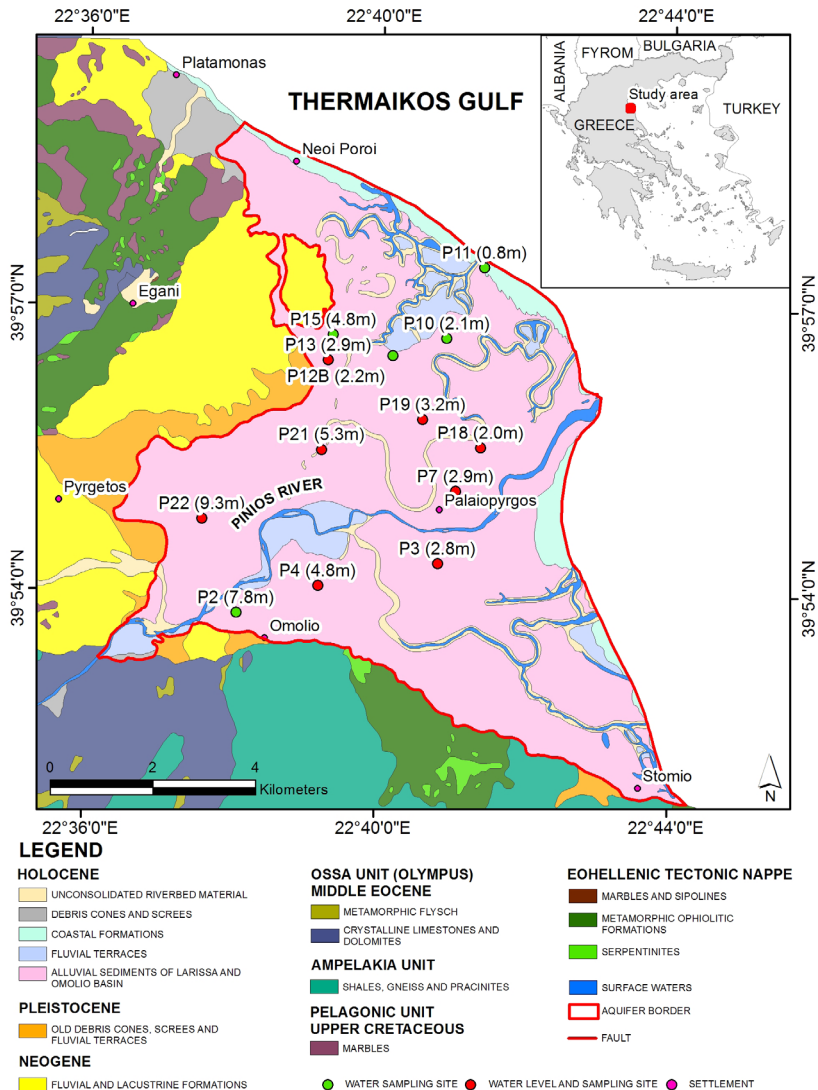


Figure 1. Geological map of the study area and the locations of the groundwater monitoring sites. The numbers in the parentheses indicate the altitude.

2.3 Groundwater Monitoring

Field campaigns were carried out between October 2012 and September 2013 in the deltaic plain for the purpose of investigating the groundwater dynamics and the water quality characteristics. Measurements of groundwater levels were performed on a monthly basis in eight (8) shallow monitoring boreholes (Figure 1). The exact location and altitude of the boreholes was defined using a Topcon Differential GPS. Sampling campaigns were performed in 13 boreholes (Figure 1) on a seasonal basis, i.e. October 2012, January 2013, April 2013 and July 2013.

Groundwater samples collected from the boreholes were stored in thoroughly cleaned 2L Nalgene bottles. In situ measurements of water temperature, pH and Electrical Conductivity (EC) were performed with a YSI 63 portable multimeter. After sampling, the water samples were filtered within 24 hours and refrigerated until filtration; the latter was conducted using a Nalgene filtration apparatus and Millipore membrane filters (mixed cellulose esters types with 8 μ m and 0.45 μ m pore diameter). Cation determinations (Ca, Mg, K and Na) were performed in the laboratory by using flame emission atomic spectrometry (FAAS, Varian SpectraAA 200) or titrimetrically (APHA 2012). The quantification of the anions (Cl and SO₄) was done by ion chromatography (Metrohm 820 IC Separator Center, 819 IC Detector). Nutrients (NO₃, NO₂, NH₄, PO₄) were measured spectrophotometrically with a Varian Cary 1E UV-visible spectrophotometer (Grasshoff *et al.* 1999). For the trace element (Cd, Cu, Fe, Mn, Pb, Ni, Zn) measurements, aliquots of the filtered water samples were pre-concentrated using Chelex 100 resin (Dassenakis *et al.* 1997) before measured by means of atomic absorption spectrometry (FAAS Varian SpectraAA 200, Graphite Furnace AAS Varian GTA 100-Zeeman 640Z with autosampler). Once arriving at the laboratory, all samples were immediately measured for total dissolved Cr with Graphite Furnace AAS (Varian GTA 100-Zeeman 640Z). The analytical precision of the chemical analyses ranged from below 5% for the main constituents to 15% for the trace elements (e.g., Cd, Pb, Cu).

3. Results and Discussion

3.1 Groundwater levels

The variations of the groundwater levels were monitored on a monthly basis (Table 1). The results reveal that the water flows from the outcrops of the deltaic plain towards the sea. Groundwater level fluctuation data shows that the hydraulic heads decline from middle spring through summer and recover partially by the end of the fall. Two potentiometric surface maps of two representative periods are illustrated in Figure 2.

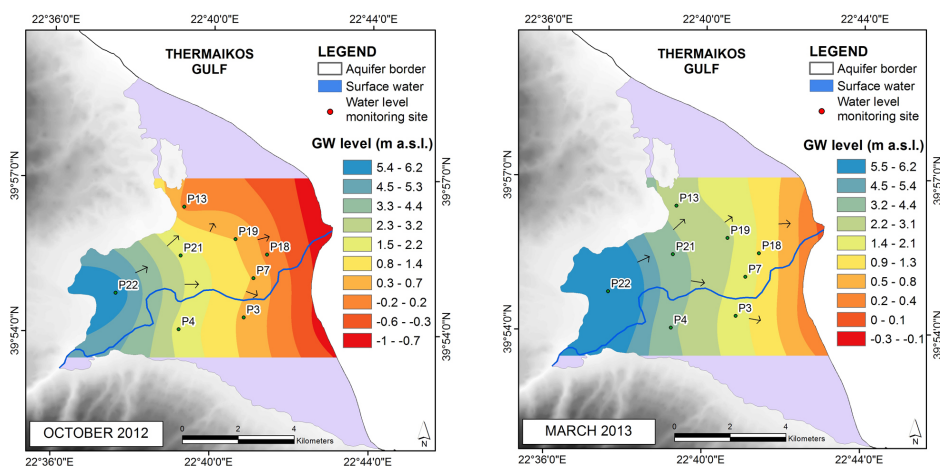


Figure 2. Potentiometric surface maps of "October 2012" and "March 2013".

In particular, the water level measurements of "October 2012" and "March 2013" were chosen; The first represents the end of the irrigation period when the water levels have declined due to pumping (hence marks the start of the recovery period), whereas in "March 2013" the water levels have recovered due to the natural recharge received mainly in the form of direct infiltration of rain water which has precipitated during the winter and also lateral inflows from the surrounding formations. Thus, the hydraulic heads of "March 2013" are higher than those observed in the period of October 2012; this means that the recharge process mainly controls the seasonal variations in the groundwater flow. Moreover, during "October 2012" the lowest hydraulic heads are observed near the coastal zone indicating a small-scale seawater intrusion potential (negative groundwater levels), whereas in "March 2013" no negative hydraulic heads were monitored in the area. The latter means that the aquifer, after the winter recharge, increases its discharge and pushes back the potential seawater mixing zone.

Table 1. Hydraulic heads recorded in the monitoring sites.

Sample	Oct-12	Nov-12	Dec-12	Jan-13	Feb-13	Mar-13	Apr-13	May-13	Jun-13	Jul-13	Aug-13	Sep-13
P3	0.6	0.3	1.0	1.5	2.3	1.6	1.2	1.1	0.7	-	0.4	0.5
P4	1.8	1.7	2.9	3.3	3.6	3.3	3.0	3.2	2.5	2.3	2.0	1.9
P7	0.7	0.5	1.6	1.8	2.3	1.7	1.5	1.2	0.8	0.5	0.4	0.3
P13	0.0	0.1	1.3	2.2	-	2.4	2.1	1.7	1.3	-	-	0.1
P18	-	0.3	1.2	1.4	-	1.2	1.1	0.9	0.4	-0.1	0.1	0.2
P19	0.7	0.6	1.4	2.3	2.9	2.3	1.9	1.7	1.1	0.6	0.4	0.4
P21	2.1	2.0	3.8	3.5	4.1	3.5	3.2	3.4	2.6	2.4	2.2	2.2
P22	6.2	5.8	6.9	8.0	8.6	8.0	7.7	7.7	6.8	6.7	6.6	5.9

3.2 Groundwater hydrochemistry

3.2.1 Physical-chemical parameters

The pH values were found to lie inside a normal range of 6.5–9.5 in all samples. The EC values ranged from 230 to 9180 $\mu\text{S}/\text{cm}$ with the maximum values recorded at the sampling site P10 (Figure 1) only during the summer periods. The concentrations of the analyzed chemical constituents are presented as box plots in Figure 3. Wide ranges and great standard deviations occur mainly for the concentrations of Na and Cl exhibiting ranges of 6.1–1,407 mg/L and 5.3–3,190 mg/L, respectively. The concentrations of Ca, Mg and SO_4 showed lower variations with ranges of 20.8–140.2, 6.3–214.9 and 0.5–161.4 mg/L, respectively. These distributions indicate that chemical composition is affected by multiple processes, including seawater mixing (Park *et al.* 2005). The substantial amounts of HCO_3 , Ca and Mg reflect contribution by water– rock interaction (Hem, 1985).

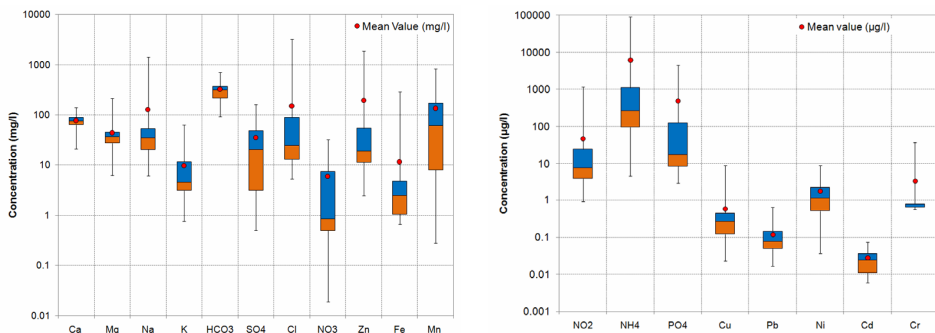


Figure 3. Box plots of the major and minor elements in the groundwater.

The NO_3 concentration ranges from 0.02 to 31.8 mg/L without exceeding the threshold value of 50 mg/L set for water intended for human consumption (Directive 98/83/EC). This outlines that nitrate contamination in the specific sampling sites due to anthropogenic activities (e.g., agriculture) is limited. The extremely high NH_4 content (89.6 mg/L) in sampling site P4 is attributed to a point source of pollution, i.e. ammonium fertilizer carelessly spread around the borehole. The majority of the trace elements (e.g., Cd, Pb) exhibits extremely low concentrations as illustrated in the boxplots of Figure 3. However, Fe, Mn and Zn contents show the widest ranges in between samples which most probably originate from natural weathering of iron, manganese and zinc bearing minerals and rocks.

3.2.2 Groundwater classification

Groundwater samples were classified according to the Piper (1944) classification system (Figure 4). From the analysis of the Piper diagram, Cl^- and HCO_3^- are the dominant anions whereas Ca^{2+} and Na^+ are the most dominant cations. The Piper diagram shows that the dominant water types in aquifer are Ca-HCO_3 , Mg-HCO_3 and Na-Cl . The Ca-HCO_3 water type indicates dissolution of calcite, whereas the Mg-HCO_3 water type can be attributed to Mg-bearing minerals found in several geological formations (e.g., ophiolites, dolomites). Two sampling sites (P10, P13) showed the Na-Cl water type. At the P10 sampling site the increased Na and Cl content is attributed to the seawater influence, whereas at the P13 sampling site the salinity is probably attributed to mineral dissolution or to an isolated old groundwater body. The latter needs further investigation. Moreover, sampling site P11, although very close to the coastline, its water quality is not affected by seawater which is attributed to a local impermeable fine-grained barrier that prevents seawater from intruding inland. Although the Ca-Cl water type was not recorded in any of the sampling sites, groundwater paths of hydrochemical evolution are expected to take place leading to from a Ca-HCO_3 or Mg-HCO_3 to a Na-Cl type. These patterns indicate that the identified groundwater chemistries are changed by cation exchange reaction, as well as simple mixing (Appelo and Postma 1999).

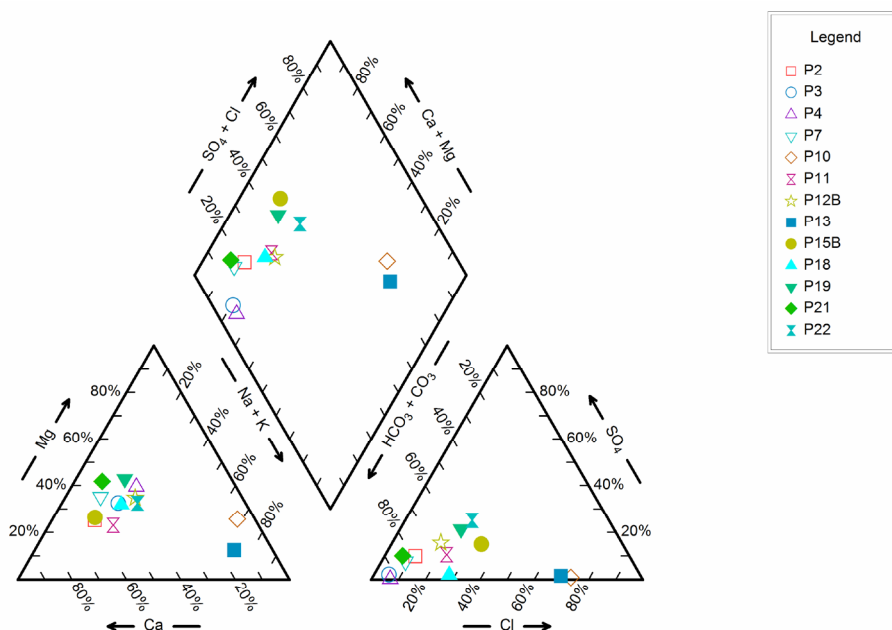


Figure 4. Piper diagram with classification of major ions and groundwater types.

3.2.3 Saturation indices

Saturation index (SI) calculations of some common minerals using the PHREEQC geochemical code (Parkhurst and Appelo 1999) were employed to determine whether a mineral species is likely to dissolve or precipitate in the groundwater flow system. Mineral phases that are clearly undersaturated ($SI \leq -0.1$) will tend to be dissolved, whilst mineral phases that are clearly oversaturated ($SI \geq +0.1$) will precipitate these mineral phases out of solution (Adams *et al.* 2001); equilibrium is achieved for SI values between -0.1 and $+0.1$. According to Jawad & Hussien (1986), the higher SI values are related to aquifers, where diffuse flow dominates and hence, a longer groundwater residence time is expected. The saturation indices of some common carbonate minerals (calcite and dolomite) are shown in Table 2. Groundwater samples vary from undersaturated to oversaturated with respect to calcite and dolomite. These minerals are hosted in rock formations (limestones and dolomites) observed in the study area. Around 77% and 62% of the groundwater samples are supersaturated with respect to calcite and dolomite, respectively. No groundwater sample was found undersaturated with respect to calcite, whereas 23% of the samples were classified as undersaturated with respect to dolomite. The SI results indicate that the dissolution of carbonate rocks is taking place within the groundwater system, with the highest values being related mainly to the precipitation of the calcite mineral. Moreover, the majority of the samples are classified as "supersaturated" with respect to SI, indicating a long residence time of the groundwater.

Table 2. Calculated saturation indices obtained from PHREEQC geochemical code and Sodium Adsorption Ratio (SAR) values. Mean concentrations were used in the calculations.

Sample	SI _{calcite}	SI _{calcite} classification	SI _{dolomite}	SI _{dolomite} classification	SAR
P2	0.04	In equilibrium	-0.13	Undersaturated	0.53
P3	0.12	Supersaturated	-0.05	In equilibrium	0.54
P4	0.04	In equilibrium	-0.13	Undersaturated	0.84
P7	0.17	Supersaturated	7.96E-04	In equilibrium	0.40
P10	0.62	Supersaturated	0.46	Supersaturated	12.48
P11	0.49	Supersaturated	0.33	Supersaturated	0.89
P12B	0.63	Supersaturated	0.47	Supersaturated	1.30
P13	-0.02	In equilibrium	-0.19	Undersaturated	11.74
P15B	0.52	Supersaturated	0.35	Supersaturated	0.79
P18	0.62	Supersaturated	0.46	Supersaturated	0.78
P19	0.45	Supersaturated	0.28	Supersaturated	0.83
P21	0.50	Supersaturated	0.33	Supersaturated	0.43
P22	0.55	Supersaturated	0.39	Supersaturated	1.16

3.2.4 Bivariate plots

From the scatter plots, the factors affecting the chemical composition of groundwater in the study area can be deduced. In the bivariate diagram of Cl/HCO_3 versus Cl (Figure 5) some samples present much higher ratios compared to the others. The ratio of Cl/HCO_3 (Revelle coefficient) ranges between 0.03 and 1.54. The salinization effect of the groundwater was classified using the Cl/HCO_3 ratio <0.5 for unaffected groundwater, $0.5-6.6$ for slightly and moderately affected, and >6.6 for strongly affected groundwater (Revelle 1941). Considering the values of Cl concentration and the ratio Cl/HCO_3 , around 85% of groundwater samples are unaffected and around 15% of groundwater samples are slightly or moderately affected by the saline water. The unaffected water samples originate from boreholes located away from the coastline and are characterized as fresh groundwater, whereas the moderately affected water samples are from borehole P10 located closer to the coastline. As discussed earlier, contamination by seawater leads to elevated Cl and EC values. Generally, fresh groundwater that is not affected by pollu-

tion is characterized by low values of EC, Cl and Ca–Mg–HCO₃ water type. The latter represents freshwater that has recently infiltrated into the zone of recharge, while high values of EC and Cl are attributed to salinization by seawater intrusion.

The scatter plot of (Ca+Mg) versus (HCO₃+SO₄) is used as an indicator of the geochemical processes occurring in the aquifer. According to Elango & Kannan (2007), the samples falling above the equiline 1:1 indicate that carbonate minerals dissolution is prevailing, whereas those plotted below the equiline 1:1 are mainly characterized by silicate minerals dissolution. As illustrated in Figure 5, the fresh water samples are allocated below and above the equiline 1:1, indicating that there are sites where silicate dissolution prevails against carbonate dissolution and vice-versa, respectively. This is attributed to the composition of the alluvial sediments where both mineral categories are included.

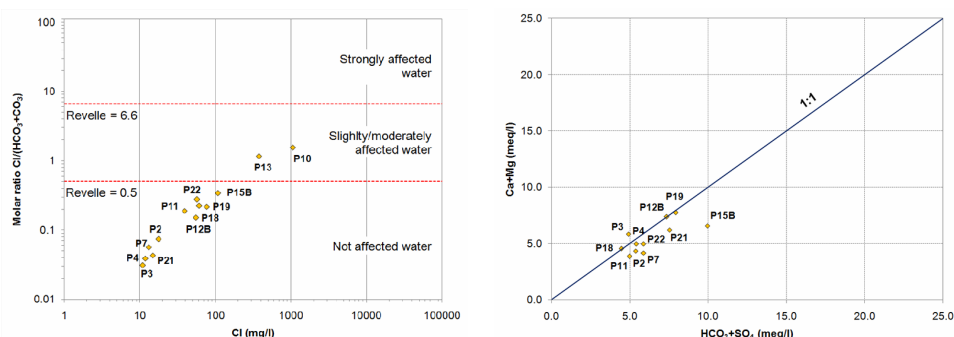


Figure 5. Scatter diagram of a) $\log Cl/HCO_3$ ratio (or Revelle coefficient) versus $\log Cl$ (mg/L) (left); and (Ca+Mg) versus (HCO₃+SO₄) (right). Sampling sites P10 and P13 were excluded in the right diagram due to their brackishness.

3.2.5 Groundwater for irrigation purposes

The United States Department of Agriculture (USDA) (1954) classifies irrigation water with respect to its Sodium Adsorption Ratio (SAR). SAR is calculated from the following formula, all concentrations expressed in milli-equivalents per litre:

$$SAR = Na / [(Ca+Mg)/2]^{0.5} \quad (1)$$

The calculated SAR ranges from 0.4 to 12.48 (Table 2). According to Wilcox diagram (1955), that is widely used and is especially implemented to classify groundwater quality for irrigation (Ebraheem *et al.* 2012; Ganyaglo *et al.* 2011), water can be grouped into sixteen (16) classes. The conductivity (horizontal axis) is classified into low (C1), medium (C2), high (C3) and very high (C4) salinity zones; these zones (C1–C4) have the value of EC <250, 250–750, 750–2250 and >2250 $\mu S/cm$, respectively. The SAR (vertical axis) is subdivided into four classes, with decreasing limiting values as EC increases: low (S1), medium (S2), high (S3) and very high (S4) sodium hazard. The results show that 84% of all samples from the study area was classified as suitable for irrigation use (classes C₂S₁ and C₃S₁) with some caution required with regards to sensitive crops and heavy soils, while 16% as unsuitable or suitable under specific conditions (classes C₄S₄ and C₃S₃).

3.3 Relation between seasonal water level fluctuation, precipitation and hydrochemistry

Seasonal variations in groundwater chemistry in any area occur principally due to variations in groundwater recharge, pumping, lithology and geochemical reactions (Scheytt 1997). In the study area, precipitation generally occurs during the winter according to Stomio meteorological station (Figure 6). The comparison between precipitation and the water table indicates that the

effect of rise in water level is noticed when the monthly precipitation increases. As the boreholes are located in the alluvial formations, the water level may respond differently due to the presence of silt/clay layers. Hence, these factors play a major role in the seasonal variation of electrical conductivity in groundwater. The variation in groundwater hydrochemistry with respect to seasonal water level fluctuation is illustrated in Figure 6. When the water table rises, the EC value decreases due to the enrichment of groundwater with fresh water associated with precipitation. The recharge process reduces the ionic concentration in the groundwater through the mixing of fresh infiltrated water with groundwater. On the contrary, lowering of water table is accompanied by increasing EC due to evaporation. Thus, the seasonal variations in hydrochemistry and groundwater level are mainly controlled by the recharge process.

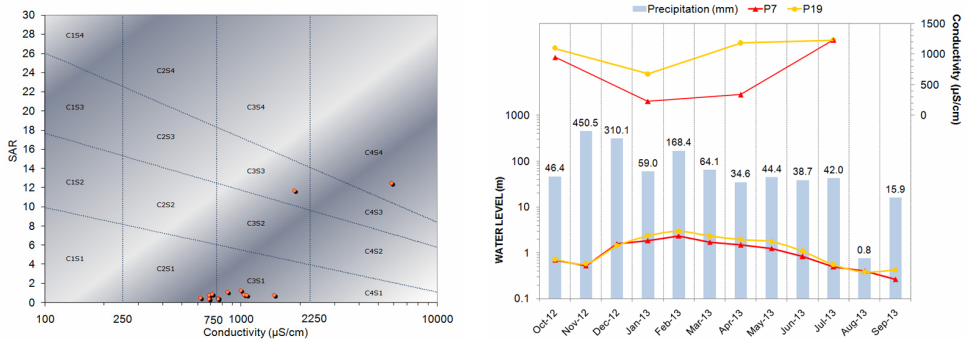


Figure 6. Assessment of groundwater suitability for irrigation purposes based on Wilcox diagram (left) and temporal variation in precipitation (Stomio meteorological station), groundwater table and EC in two representative sampling sites (right).

4. Conclusions – Remarks

The investigation of the groundwater flow regime in the deltaic plain of River Pinios showed that the groundwater flows from the western outcrops of the aquifer towards the sea. The seasonal variations in the groundwater table monitored for twelve (12) consecutive months revealed an elevation in the winter and a decline at the end of the summer. The groundwater quality characteristics are mainly controlled by the geological environment and the anthropogenic activities (e.g., increased NH_4 concentrations in specific locations). The majority of the sampling sites showed a (Ca or Mg)– HCO_3 water type leading to the conclusion that weathering of carbonate minerals is the main hydro-geochemical process controlling the hydrochemical composition. This is also supported by the saturation indices suggesting saturation with respect to calcite and dolomite and a long residence time. Silicate weathering is also concluded by the ion-ratio processing, while trace elements (e.g., Fe, Mn) are attributed to local dissolution of the trace element bearing minerals inside the alluvial sediments. The results also revealed that seawater intrusion is of small scale and mainly taking place in the summer period. Water brackishness is observed in two sampling sites (P10 and P13), which are classified as moderately affected waters (Revelle > 0.5) and unsuitable or suitable under specific conditions (classes C_3S_3 and C_4S_4) for irrigation purposes according to SAR index. The relation between seasonal water level fluctuation and hydrochemistry showed that both are mainly controlled by the aquifer's recharge process.

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