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Surface–ground water interactions and hydrogeochemical evolution in a fluvio-deltaic setting: The case study of the Pinios River delta

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ABSTRACT

River deltas sustain important ecosystems with rich biodiversity and large biomass, as well as human populations via the availability of water and food sources. Anthropogenic activities, such as urbanization, tourism and agriculture, may pose threats to river deltas. The knowledge of the factors controlling the regional water quality regime in these areas is important for planning sustainable use and management of the water resources. Here, hydrochemical methods and multivariate statistical techniques were combined to investigate the shallow aquifer of the Pinios River (Thessaly) deltaic plain with respect to water quality, hydrogeochemical evolution and interactions between groundwater and surface water bodies.

Water quality assessment indicated that most of the river and groundwater samples fully comply with the criteria set by the Drinking Water Directive (98/83/EC). The river is recharged mainly from springs of the Tempy valley and the shallow aquifer, and to a lesser degree from precipitation, throughout the year. The hydrogeochemical characteristics indicated a cation (Ca, Mg, and Na) bicarbonate water type, which evolves to calcium-chloride, sodium-bicarbonate and sodium-chloride water type, in the northern part of the delta. Calcite and dolomite dissolution determined the major ion chemistry, but other processes, such as silicate weathering and cation exchange reactions, also contributed. In the northern part of the plain, the interaction with the deeper aquifer enriched the shallow aquifer with Na and Cl ions.

Principal Component Analysis showed that five components (PCs) explain 77% of the total variance of water quality parameters; these are: (1) salinity; (2) water-silicate rocks interaction; (3) hardness due to calcite dissolution, and cation exchange processes; (4) nitrogen pollution; and (5) non-N-related artificial fertilizers. This study demonstrated that the variation of water hydrochemistry in the deltaic plain could be attributed to natural and anthropogenic processes. The interpretation of the PCA results dictated the parameters used for the development of a modified Water Quality Index (WQI), to provide a more comprehensive spatial representation of the water quality of the river delta.

1. Introduction

Over 500 million people live in river deltas, despite these areas account for only 5% of the global land mass. River deltas are areas of ecological and societal value, because they host fresh surface and groundwater resources, sustain biodiversity, and provide large flat areas for agricultural and urban uses. These multiple conflicting human activities apply significant pressures and risks to deltaic and coastal ecosystems (Kuenzer and Renaud, 2012).

The status of fresh surface water and groundwater quality in the deltaic areas is affected by natural factors, such as the high lateral and vertical granulometric variability of deltaic depositional sequences, the

hydrogeochemical reactions between water and sediments and the surface water-groundwater interactions, which modify the hydrochemical characteristics of the surface water and groundwater resources on a spatial and temporal basis (Brunke and Gonser 1997; Ezzy et al., 2006; Menció and Mas-Pla, 2008; Torres-Rondon et al., 2013).

Seasonal variations of precipitation, river discharge and water table level can cause a reduced replenishment of the water system leading to limited availability of water. Groundwater over-extraction can trigger sea water intrusion, causing a degradation of the deltaic freshwater quality and shortage of drinking water supplies. Nutrients, such as nitrogen and phosphorus, in agricultural practices can contaminate aquifers and surface waters via infiltration and direct runoff,

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respectively (Barrett et al., 2002; Kim et al., 2009; Mondal et al., 2011; Sarma et al., 1982).

The detailed knowledge of the factors controlling the surface water and groundwater quality is recognized as critical for water resources management, especially in the semi-arid southern coastal parts of Europe (i.e. Mediterranean coast). Conventional hydrochemical methods of data analysis combined with multivariate statistical techniques, such as Principal Component Analysis (PCA), are widely applied in surface and groundwater studies to identify the natural and anthropogenic factors that control water quality (Ahmed Baig et al., 2010; Cloutier et al., 2008; Fan et al., 2010; Matiatis et al., 2014a; Okiongbo and Douglas, 2015; Tanasković et al., 2012; Qin et al., 2013; Ujević Bošnjak et al., 2012).

Water Quality Indices (WQIs) are used to describe the overall 'quality' of a water body by assigning to a set of critical parameters a single value (e.g. Abbasi and Abbasi, 2012; Debels et al. 2005; Dhanasekarapandian et al., 2016; Şener et al., 2017). The 'quality' of a water system can be evaluated in a more easily and rapidly comprehensible manner, assisting decision makers and regulatory authorities to determine priorities and evaluate the impact of various environmental management practices (Pusatli et al., 2009; Sadiq et al., 2010; Song and Kim, 2009). The application of WQIs facilitates the comparison of the water quality between different sampling sites and sampling events in a single or multiple geographical areas.

The deltaic plain of Pinios River lies in central Greece and is of significant ecological importance. It is characterized by rich fresh surface water availability supporting a great biodiversity of flora and fauna. It is classified as "Special Protection Area" of the NATURA 2000 network (GR1420015) and a CORINE biotope (A00020006) and includes riparian forests, an estuary with riparian woodland, marshes, small freshwater lakes, sand dunes and coastal zones. The area combines the natural-biological features of the regions placed under protection by the international treaties of Bonn (Convention on the Conservation of Migratory Species of Wild Animals), Bern (Convention on the Conservation of European Wildlife and Natural Habitats), Barcelona (Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean) and Washington (Convention on International Trade in Endangered Species) (Economou, 2005).

This study uses hydrochemical and multivariate statistical techniques and aimed to a) define the possible interactions between groundwater and surface water bodies in the deltaic plain of Pinios River; b) identify the main hydrogeochemical processes and mechanisms that control the water quality in the deltaic environment and the suitability of the water for drinking purposes, and c) test the suitability of a modified Water Quality Index for describing the overall water quality. The major pressures exerted on deltaic aquifers worldwide are reviewed and compared to the results of this study. The outcomes of this work could be easily used by the local authorities, stakeholders and water managers as an operational tool for the effective management of the water resources.

2. Study area

The deltaic plain of Pinios River (Thessaly, Greece) covers approximately 70 km², where the river flows in a WSW-ESE direction, discharging into Thermaikos Gulf (Fig. 1). Literature data show that river discharge levels have their maxima between November and April and minima between May and September (Lazogiannis et al., 2014). Before exiting Tempi valley, the river is recharged from karstic spring waters (Fytianos et al., 2002; Migiros et al., 2011). The deltaic plain is characterized by a flat relief and encompasses radial riverbeds, meanders and isolated parts of old riverbeds, which operate only during flood events, indicative of the gradual geomorphological evolution of the plain over the years (Karymbalis et al., 2016). The delta has a Mediterranean climate with mean annual precipitation and air

temperature of 800 mm and 14.0 °C, respectively (Matiatis et al., 2014b).

2.1. Geological and hydrogeological setting

The largest part of the Pinios River deltaic plain comprises alluvial sediments (e.g. sands, clays, silts) of Holocene age, whereas sand dunes and coastal sediments (mostly sands) prevail along coastal areas (Fig. 1). The western and northern boundaries of the deltaic plain comprise Neogene deposits (marls and conglomerates) and Pleistocene formations (debris cones, scree and fluvial terraces), whereas the rest of the plain is surrounded by metamorphic rocks, such as crystalline limestones and dolomites, shales and ophiolites (Katsikatos and Migiros, 1982).

This study focuses on the shallow aquifer system hosted in the alluvial sediments, which are composed mostly of coarse-grained sands, with clays and silts located mainly in the broader river mouth area. On the basis of the vertical distribution of electrical resistance the aquifer is confined below 5–10 m depth (Alexopoulos et al., 2014).

The aquifer is recharged through: (i) the debris cones and scree of Pleistocene age at the inland limit of deltaic plain, where the Pinios River exits the Tempi valley and enters the deltaic plain; (ii) precipitation; and (iii) lateral less permeable formations, such as the Neogene sediments. Previous studies (e.g. Matiatis et al., 2014b; Panagopoulos et al., 2001) show hydraulic interaction between the river and the aquifer, especially in the central part of the plain, depending on location, season and groundwater level fluctuation.

Land use in the deltaic plain is mainly agricultural (kiwi, olive trees, corn, sunflower, cotton plantations), but there are areas for animal grazing. Irrigational water is obtained by groundwater and river water extraction. Potable water demand is met by groundwater pumped from boreholes outside the deltaic plain. Groundwater inside the plain is mostly extracted from shallow boreholes with suction pumps.

3. Materials and methods

3.1. Sampling and analytical procedures

Groundwater levels and river water discharge were measured monthly from October 2012 to September 2013. River water discharge (in m³/s) was measured at two river sites, one just before the river enters the delta area (site GA) and one close to the river mouth (site GP, see Fig. 1), using a current flow meter (Valeport BFM 001/002). Groundwater levels were measured in 13 boreholes with a contact gauge (OTT KL 010). RTK-GPS was used to map the position of the boreholes to an accuracy of ~10 mm.

Monthly rainfall data were obtained from meteorological stations (Davis Vantage Pro2 Plus), at Stomio (RS) and at Palaiopyrgos (RP) within the deltaic plain, at an altitude of 9 m and 6.5 m, respectively.

Groundwater samples from 13 boreholes were collected in different seasons (October 2012, January 2013, April 2013 and July 2013). Two springs were sampled on monthly basis for the first year (2012–2013) and on seasonal basis for the second year (2013–2014). The same sampling pattern was followed for river water samples collected from 7 sampling stations in and out of the deltaic plain. River water samples were collected by lowering horizontal sampling bottles from bridges. Both groundwater and surface water samples were collected in pre-cleaned high-density polyethylene 2-L bottles.

In situ parameters (temperature, pH, electrical conductivity) were measured by means of an YSI 63 multi-parameter instrument. All water samples were field filtered through 8 µm and 0.45 µm Millipore filters (mixed cellulose esters), into sample bottles with appropriate storage and preservation methods (refrigeration, freezing, acidification, addition of chloroform). Chemical analyses included major ions (Ca, Mg, K, Na, HCO₃, Cl and SO₄), nutrients (NO₃, NO₂, NH₄, and PO₄) and dissolved trace elements (Fe, Mn and Zn). Major cations were determined

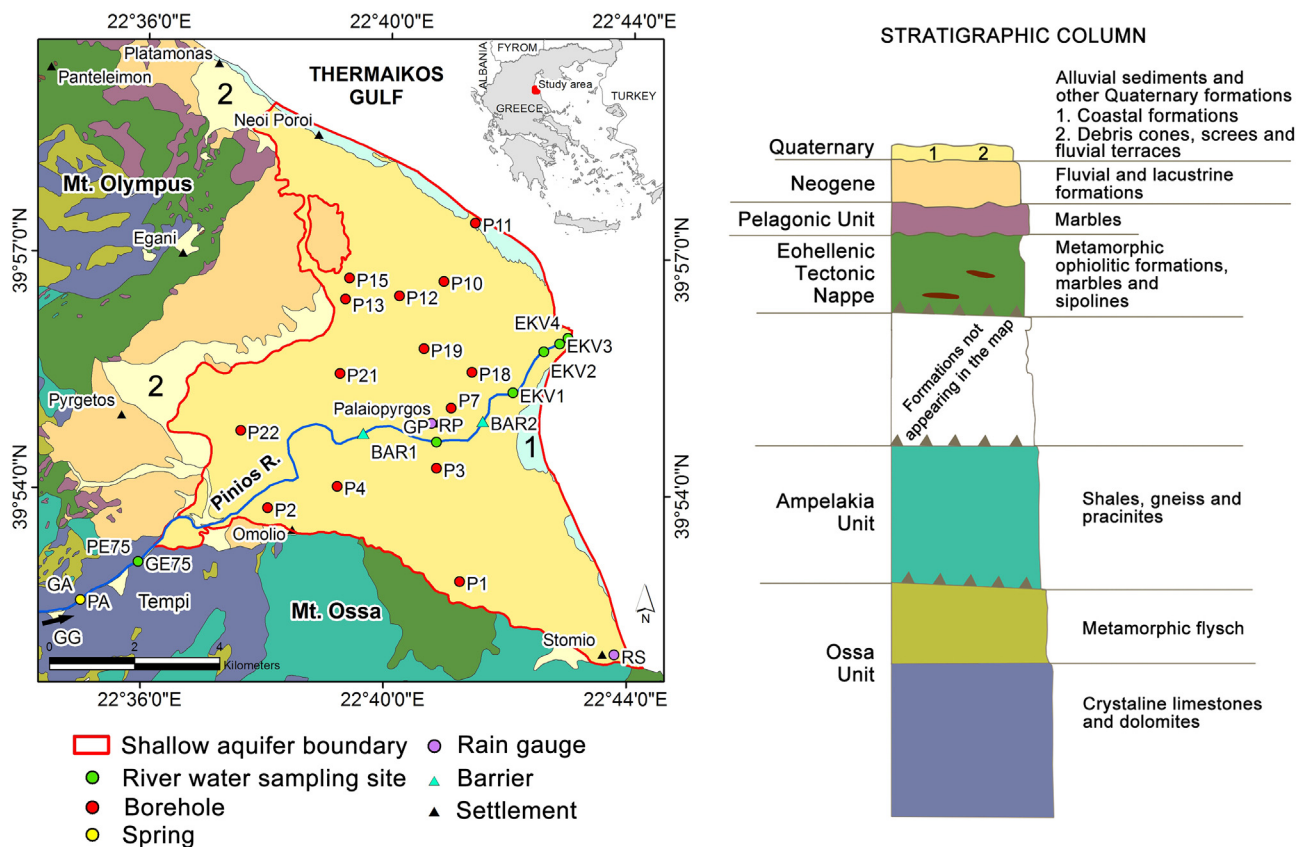


Fig. 1. Location, geology and sampling points of the study area (geological map based on Katsikatos and Migiros, 1982).

by flame atomic emission (K, Na) and adsorption (Ca, Mg) spectrometry (Varian SpectrAA 200). Alkalinity was measured by titration and anions Cl and SO₄ by ion chromatography (Metrohm 820 IC Separator Center, 819 IC Detector). Nutrients were measured spectrophotometrically with a Varian Cary 1E UV–vis spectrophotometer, and the dissolved trace elements using flame or graphite furnace atomic absorption spectrometry (Varian GTA 100-Zeeman 640Z) after pre-concentration of an aliquot of filtered water sample in a Chelex-100 resin. Details about the detection limits and the certified references used to check the accuracy can be found in the [supplementary material](#). Total dissolved solids (TDS) were not measured *in situ*, but calculated from electrical conductivity (EC) to be used in the bivariate plots.

Some results from river stations were excluded from our statistical analysis due to missing values in key parameters. In total, 124 samples with 18 physical-chemical parameters (temperature, pH, EC, TDS, Ca, Mg, Na, K, HCO₃, SO₄, Cl, NO₃, NO₂, NH₄, PO₄, Fe, Mn, and Zn) were used.

Procedural blanks, duplicate samples and certified reference materials were analysed for quality control purposes in all chemical methods. All hydrochemical analyses were checked for electro-neutrality below 5%. The per cent relative standard deviation (% RSD) from the duplicate analysis ranged between 1 and 10% and recoveries from the reference materials ranged between 80 and 115% depending on the complexity of each analytical procedure. Concentrations below the detection limit were replaced by the detection limit.

The methodologies followed for sampling, chemical analysis and data preparation for statistical analysis are summarized in [Fig. S1 of supplementary material](#).

3.2. Saturation index

Using PHREEQC (Parkhurst, 1995), calcite and dolomite saturation indices were calculated for water samples collected from boreholes and

springs. The calcite and dolomite saturation indices were defined by Appelo and Postma (1993):

$$\text{Calcite Saturation Index} = \log\left(\frac{\{Ca^{2+}\} \times \{CO_3^{2-}\}}{K_{\text{calcite}}}\right) \quad (1)$$

$$\text{Dolomite Saturation Index} = \log\left(\frac{\{Ca^{2+}\} \times \{Mg^{2+}\} \times \{CO_3^{2-}\}}{K_{\text{dolomite}}}\right) \quad (2)$$

where K values are the thermodynamic solubility product constants and “{ }” denotes activities of ions.

3.3. Multivariate statistical analysis

Although a large number of parameters were measured for each water sample, dependent and redundant parameters (e.g. TDS) were excluded from the dataset, to optimize the multivariate statistical analysis, based on the approach of Cloutier et al. (2008). After data processing, the following parameters were retained: pH, EC, Ca, Mg, Na, K, HCO₃, SO₄, Cl, NO₃, Zn, Fe, and Mn. Multivariate statistical analysis was applied on normalized (log-transformed) data to address the wide range of concentrations, especially between the major and the minor elements (Davis, 1986).

The dataset of thirteen variables (pH, EC, Ca, Mg, Na, K, HCO₃, SO₄, Cl, NO₃, Zn, Fe, and Mn) was used for PCA ([Fig. S1 of supplementary material](#)). Before applying PCA, a correlation matrix of the selected variables was created and inspected to examine if there was an appropriate number of correlations (Pearson Correlation Coefficient- PCC above 0.3) between the variables (Tabachnick and Fidell, 2006). Two statistical tests, the Barlett test of Sphericity (*p* below 0.05) and the Kaiser-Meyer-Olkin (KMO) (Measure of Sampling Adequacy (MSA) above 0.5) were performed to examine the correlation between the variables (Hinton et al., 2014).

To extract the principal components or factors and to calculate the eigenvectors, the eigenvalues and the loadings, the Kaiser criterion was

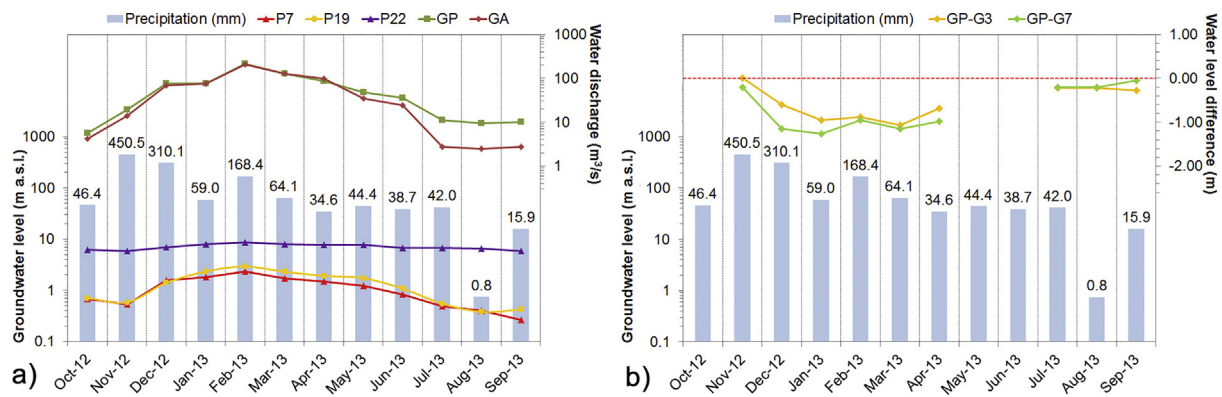


Fig. 2. Temporal variation of: (a) groundwater level (P2, P19, P22) and river water discharge (GA, GP), and (b) water level difference between river water and groundwater, compared to monthly rainfall (vertical bar charts).

applied, for which only the components with eigenvalues greater than 1 were retained (Kaiser, 1958). To maximize the variance of the principal axes, the Varimax normalized rotation was applied. The terms ‘strong’, ‘moderate’, and ‘weak’, as applied to principal component loadings, refer to absolute loading values of > 0.75, 0.75–0.5 and 0.5–0.3, respectively.

3.4. Water Quality Index

To characterize the quality of the various water types in the Pinios River deltaic plain, a WQI was calculated for each sample. The aim was to provide a five-class scoring, in line with the Water Framework Directive (WFD) quality classification (2000/60/EC): “High”, “Good”, “Moderate”, “Poor” and “Bad”, to characterize water quality in the study area with greater detail compared to the dual “good” – “failing to achieve good” scheme, which is currently used in WFD reporting of chemical status.

The equation, proposed by Debels et al. (2005) to describe water pollution of a river system affected by agricultural activities, was used for the calculation of the WQI for each sample:

$$WQI = \frac{\sum_{i=1}^n C_i \times P_i}{\sum_{i=1}^n P_i}$$

where n represents the total number of parameters used for the calculation, C_i is the normalized concentration of parameter i , and P_i is the weight of the parameter.

The chemical parameters, normalization factors, weights and parameter value ranges are presented in Table 1 of the Supplementary material.

The chemical parameters considered in the calculations were EC, Na, Cl, Ca, NO_3 , SO_4 , and Mn, as the most representative of the five factors extracted from the PCA analysis, with the addition of NH_4 , NO_2 , to include all parameters for which quality standards are set by the Drinking Water Directive (98/83/EC).

The weights were set from 1 to 4 (Loukas, 2010; Şener et al., 2017). Since salinization and nitrate pollution were considered the most important threats to the deltaic system, a weight of 4 was assigned to NO_3 , NO_2 , NH_4 , EC, Na and Cl. Manganese, SO_4 and Ca were assigned the weights 3, 3 and 1, respectively. The variables were normalized-transformed to one of four corresponding scores (0–25–50–100) (Table 1 of supplementary material).

The normalization factors used to transform each measured concentration were limited to four (0–25–50–100), in contrast to eleven (0–100 incremented by 10) used by Debels et al. (2005), because this was dictated by the concentration ranges set by the European

legislation limits and other water quality criteria (Loukas, 2010) (see Supplementary material for the mathematical calculation of increments).

The classification scale was modified by Debels et al. (2005) taking into account that spring waters produced WQI values ranging from 100 to 85. This range was set as the “High” quality class. To set the last class [“Bad” (< 25)] a mock calculation was performed with a hypothetical sample that scored 25 for all parameters. For the three intermediate classes that needed to be set in order to comply with WFD categories it was decided that the scoring range of 25–84 be equidistantly incremented by 20 units. The intermediate classes were set as “Good” (84–65), “Moderate” (64–45), “Poor” (44–25). For higher resolution between samples of the same class the three intermediate classes were further subdivided into sub-classes (a and b), i.e. “Good(a) – Good(b)”, “Moderate(a) – Moderate(b)” and “Poor(a) – Poor(b)”. The higher (a) values corresponded to samples closer to the immediately better classification class and the lower (b) values to the next worst.

4. Results and discussion

4.1. Hydrological conditions

The temporal variation of groundwater levels in the middle part of the deltaic plain (e.g. P7, P19; Fig. 2a) follows roughly the seasonal patterns of precipitation with higher water table values observed during the wet season and the lower ones during the dry season. In the beginning of the dry season (October–November) water levels of the shallow aquifer were relatively low, increased until February and dropped gradually to reach the lowest values during the end of the dry season (August–September). On the other hand, the groundwater level in borehole P22 in the western part of the plain remained constant throughout the year, indicating that rainfall recharge played a secondary role in this area of the delta. Here, shallow aquifer recharge seems to be related to a lateral groundwater supply from the surrounding mountainous area.

River water discharge variation patterns did not closely follow the high and low peaks of precipitation on a monthly basis, indicating that the river was also recharged from different sources (springs and groundwater). Both river discharge and groundwater levels followed roughly the same temporal pattern (Fig. 2a), indicating that there is interaction between the two. Both reached their highest peak in February and showed a smooth temporal variation with higher values in the wet season and lower values in the dry season.

During the dry season, a temporary dirt barrier (BAR1 in Fig. 1), is emplaced to divert part of the river water flow towards an irrigation canal in the SE. From June to September, river water discharge downstream (site GP) was higher than upstream (site GA), despite the diversion of river flow in May. The comparison of water levels in the

river channel at GP to water levels in the nearby boreholes G3 and G7 (Fig. 2b) showed that groundwater levels were constantly higher than the water in the river channel, indicating that in this part of plain, there is an inflow of water from the aquifer to the river during the dry period.

4.2. Hydrochemistry of the deltaic plain

Tables 2–5 of the supplementary material summarize the mean, minimum and maximum values and the standard deviation of the 19 hydrochemical variables determined from the spring, groundwater and river water samples.

4.2.1. River water

The data of river water upstream of the mouth were slightly alkaline with pH values in the range of 6.8–8.6. Water temperature and EC ranged from 9.2 to 29.9 °C and from 349 to 771 $\mu\text{S}/\text{cm}$, respectively. River water samples showed lowest mineralization compared to other water samples, by the low EC values (mean = 563 $\mu\text{S}/\text{cm}$) and TDS values (mean = 343 ppm).

On average, Ca, Mg, Na, and K accounted for 31.5%, 12.3%, 11.6%, and 0.8%, respectively, of the total dissolved cationic charge ($\text{TZ}^+ = \text{Na} + \text{K} + 2\text{Mg} + 2\text{Ca}$ in meq/l) of the analysed river water samples. The cation concentrations followed the order of $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$ at sampling sites GG and GP and $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ at sampling sites GE75 and GA. Sodium (mean = 0.9 mmol/l) was higher than Cl (mean = 0.5 mmol/l), indicating that salt is not the sole Na source in river waters.

Bicarbonate was the major anion accounting for approximately 88% of the total dissolved anionic charge ($\text{TZ}^- = \text{Cl} + 2\text{SO}_4 = \text{HCO}_3 + \text{NO}_3$ in meq/l). The anion concentrations followed the order $\text{HCO}_3 > \text{Cl} > \text{SO}_4 > \text{NO}_3$ in river sampling sites GG, GE75, GA and GP. Electrical conductivity, as well as the concentrations of K, Na, Mg and Cl, were higher during the dry period than the wet period, which can be attributed to evaporation and or recharge from groundwater, e.g. during baseflow conditions. NO_3 concentrations ranged from ~0 to 7.5 mg/l, less than the 50 mg/l acceptable concentration for human consumption (Directive 98/83/EC). The nitrate values increased during the wet period, as a result of increased precipitation and subsequent agricultural runoff.

At the mouth area downstream of the second river barrier (BAR2 in Fig. 1), river water at sites EKV1-EKV4 had temperatures between 8.1 and 16.8 °C and EC between 481 and 1240 $\mu\text{S}/\text{cm}$. Water chemistry was dominated by HCO_3 and Cl accounting for 77.6% and 13.9% of the TZ^- respectively. The molar anion concentrations in the mouth area were $\text{HCO}_3 > \text{Cl} > \text{SO}_4 > \text{NO}_3$. Ca, Mg, Na, and K accounted for 29.3%, 13.0%, 14.5%, and 0.9% of the TZ^+ of the river water, respectively. The molar cation concentrations followed the order $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$. NO_3 concentrations ranged from 1.1 to 7.9 mg/l.

4.2.2. Spring water

Spring water samples from sites PA and PE75 were neutral to slightly alkaline with an average pH value of 7.6. The temperature of spring waters ranged from 13.3 to 20.8 °C and EC ranged from 448 to 851 $\mu\text{S}/\text{cm}$ with an average value of 684 $\mu\text{S}/\text{cm}$. The mineralization of the spring water samples was attributed to water-rock interaction. On average, Ca, Mg, Na, and K account for 38.3%, 9.9%, 3.3%, and 0.3% of the TZ^+ of the spring water samples, respectively. Cation concentrations followed the same order and levels as those of the river water sampling sites GE75 and GA indicating recharge of the river by springs. The dominant anion, HCO_3 , accounted for approximately 95% of the TZ^- in the spring waters. The molar anion concentrations of the spring waters followed an order of $\text{HCO}_3 > \text{Cl} > \text{SO}_4 > \text{NO}_3$. The ionic concentrations of the spring waters were similar to the river waters at sampling sites GE75 and GA. Nitrates and nitrites were below the threshold values of 50 mg/l, and 0.5 mg/l, respectively (Directive 98/83/EC).

4.2.3. Groundwater (shallow aquifer)

The pH of groundwater ranged from 6.9 to 8.2, with EC values between 230 and 9180 $\mu\text{S}/\text{cm}$ and a mean value of 1365 $\mu\text{S}/\text{cm}$. Among the different categories of water samples, groundwater had the highest EC values and concentrations of Total Dissolved Solids, TDS (mean: 874 mg/l). The highest mean EC values were in the northern part of the plain (P10: 5849 $\mu\text{S}/\text{cm}$, P13: 1868 $\mu\text{S}/\text{cm}$, P15: 1472 $\mu\text{S}/\text{cm}$, P19: 1067 $\mu\text{S}/\text{cm}$ and P12: 994 $\mu\text{S}/\text{cm}$). These elevated values indicated the influence of saline water in this part of the plain.

Calcium, Mg, Na, and K accounted for 15.1%, 13.4%, 41.2%, and 2.0% of the TZ^+ of the groundwater, respectively. However, after excluding brackish samples at sites P10 and P13, Ca, Mg, Na, and K accounted for 21.7%, 19.2%, 15.3%, and 2.8% of the TZ^+ of the groundwater, respectively. Molar cation concentrations followed the order $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and HCO_3 was the dominant anion accounting for 78.5% of the TZ^- . The anion concentrations of groundwater followed the order $\text{HCO}_3 > \text{Cl} > \text{SO}_4 > \text{NO}_3$. Of the major ions, SO_4 was below the threshold value of 250 mg/l set by the EU Directive for drinking water. Sodium exceeded the value of 200 mg/l only in borehole P10, while Cl exceeded the EU threshold value of 250 mg/l in 12% of the samples.

Nitrates and nitrites were generally below the EU threshold values of 50 mg/l and 0.5 mg/l, respectively (Directive 98/83/EC), whereas ammonium exceeded the EU threshold value of 0.5 mg/l in 38% of samples. The highest NO_3 (from 10.9 to 31.8 mg/l) and NH_4 (from 0.8 to 89.7 mg/l) concentrations were observed in the western (e.g. P2, P4, P22) and northern part of the plain (e.g. P10, P11, P15). The higher NO_3 and NH_4 concentrations in groundwater compared to river water signifies that the aquifer is contaminated not only from agricultural runoff, but also from point sources of contamination in places, e.g. domestic effluents at the built-up coastal area (e.g. P11).

The concentrations of Fe, Mn and Zn showed the highest values in the groundwater samples (Tables 2–5 of the supplementary material), probably originating from natural weathering of iron, manganese and zinc bearing minerals and rocks. Only manganese concentration exceeded the EU threshold value of 50 $\mu\text{g}/\text{l}$ in 56% of the samples (max: 826 $\mu\text{g}/\text{l}$), which could be attributed to an additional source of Mn, such as the application of Mn-enriched fertilizers (see also Section 4.6).

4.3. Water Quality Index

The Water Quality Index results and classification for all sampling sites and periods are found in Tables 6 and 7 of the supplementary material. A spatial summation of the WQI results is presented in Fig. 3.

The classification of the groundwater samples showed that 13% of the samples were classified as “High” quality, 73% as “Good” quality, and the remaining 14% as “Moderate” (8%) and “Poor” (6%) quality waters. Furthermore, 63% of the good quality groundwater samples were classified into the subcategory of “Good (b)” water quality, which is closer to the “Moderate” water quality class. In the northern part of the plain, groundwater samples showed a “Poor (b)” (P10) to “Moderate” (P13) water quality. No seasonal variation was observed on the WQIs of the groundwater samples.

Considering the riverine water body, of 52 river water samples 11 were classified as of “Good (a)” water quality and the remaining as of “High” water quality. The upstream river sampling site GG, located outside the deltaic plain, had a “Good” quality, which was attributed to enrichment with contaminants originating from the agricultural plain of Thessaly, the city of Larisa and its industrial zone. The contribution of spring waters to the river, as it enters the plain, resulted in the classification of the river water samples at site GE75 as of “High” quality. In the central part of the plain, 82% of the water samples of sampling site GP were classified as of “High” quality, whereas 50% of the river water samples from the mouth area were classified as of “Good”, 29% as of “High” and 21% as of “Moderate” water quality. The deterioration of the water quality in the mouth area samples is limited

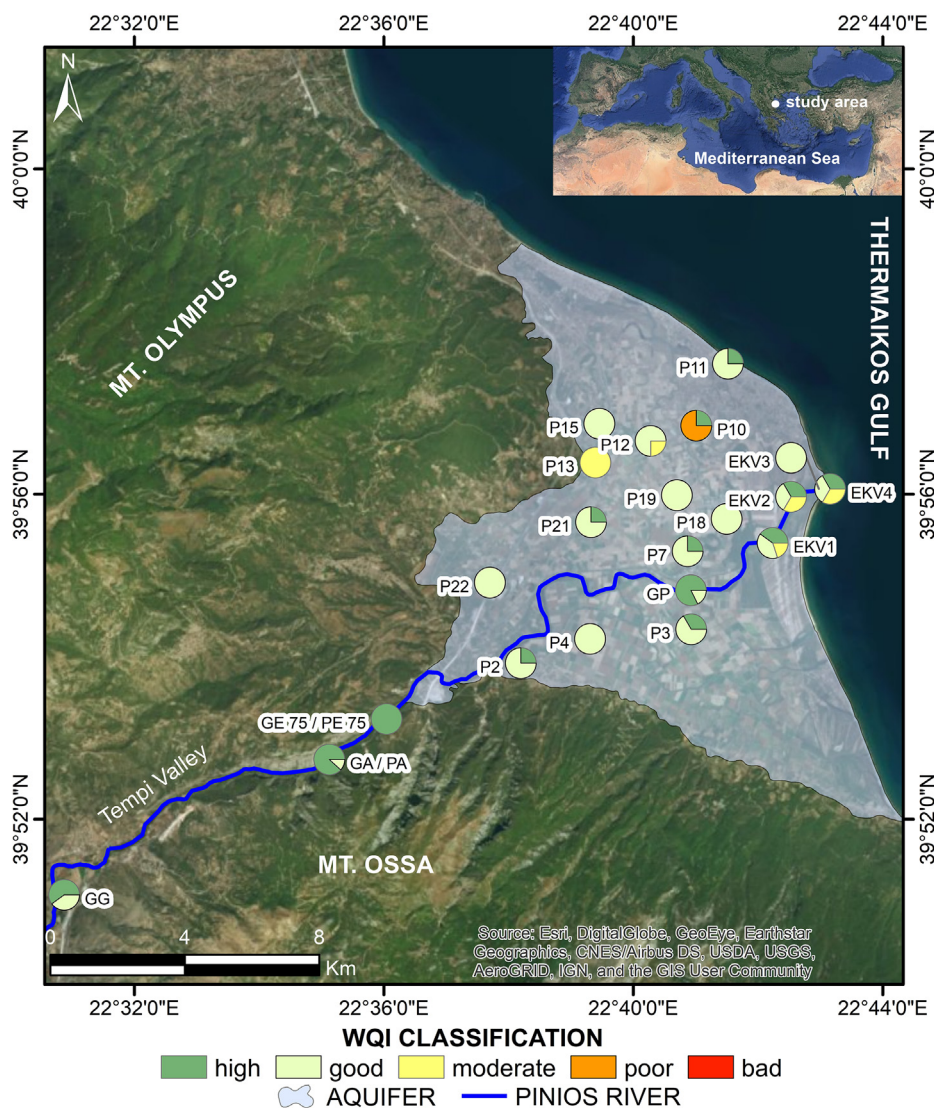


Fig. 3. Spatial distribution of WQI values in the study area.

and due to seawater intrusion.

4.4. Hydrochemical evolution

Water types were defined for all samples (river, mouth area, springs, groundwater) using cations and anions plotted on a Piper diagram (Piper, 1944). Six water types are shown in Fig. 4. Since it was not possible to discriminate the Ca–Mg–HCO₃, Ca–HCO₃, and Mg–HCO₃ water types, a Ca/Mg ratio and a ternary Ca–Mg–Cl diagram were used, as discussed later.

River water samples upstream and at the mouth area showed mainly a Ca–Mg–HCO₃ water type. Two river water samples, one collected inside the plain (site GP) in November 2012 and one outside the plain (site GG) in September 2013, as well as a groundwater sample collected from site P13 in November 2012 showed a Na–HCO₃ water type. The river water samples at the mouth area were taken only during the wet period and were not enriched in Cl (mean = 39.4 mg/l) except sampling site EKV1 which showed a Na–Cl type in October 2013, due to increased Cl concentration (225 mg/l) because of seawater intrusion.

Spring water samples showed a Ca–HCO₃ water type throughout the year indicating a constant mineralization source. Groundwater samples were mainly concentrated in the water types Ca–Mg–HCO₃, Ca–HCO₃, and Mg–HCO₃. The samples close to the river (e.g. P2, P3, and P7)

showed the same water type (Ca–Mg–HCO₃) as the river samples of site GP, indicating possible interaction between the two water bodies. In the northern part of the plain, groundwater quality evolved locally (e.g. P10, P13) to a Na–Cl water type, indicating enrichment in Na and Cl and influence from a saline source. Borehole P15 showed a hydrochemical evolution to a Ca–Cl water type, indicating occurrence of hydrogeochemical processes, as discussed later.

In the western part of the plain, borehole P4 exhibits a NH₄-HCO₃ water type due to the extremely high NH₄ concentration (mean = 60 mg/L) attributed to a point source of agricultural pollution. However, after removing the NH₄ contamination, the water varied between the Ca–Mg–HCO₃ and the Mg–HCO₃ water type throughout the year.

As illustrated in Fig. 5, as the river flows towards the river mouth area, the Ca/Mg ratio changed, because of interaction with spring waters and groundwater. Outside the plain, sampling site GG showed a mean Ca/Mg ratio of 1.8, which increased to 2.3 at the river sampling site GA, as a result of mixing with the spring waters of Ag. Paraskevi (site PA), which showed a mean Ca/Mg ratio of 3.0. Before entering the deltaic plain, the river is recharged by the spring waters near Rapsani (site PE75, mean Ca/Mg = 4.9), as confirmed by the increase of the Ca/Mg ratio at the river water sampling site GE75 (mean Ca/Mg = 3.9). As the river crosses the deltaic plain, the mean Ca/Mg ratio decreased to

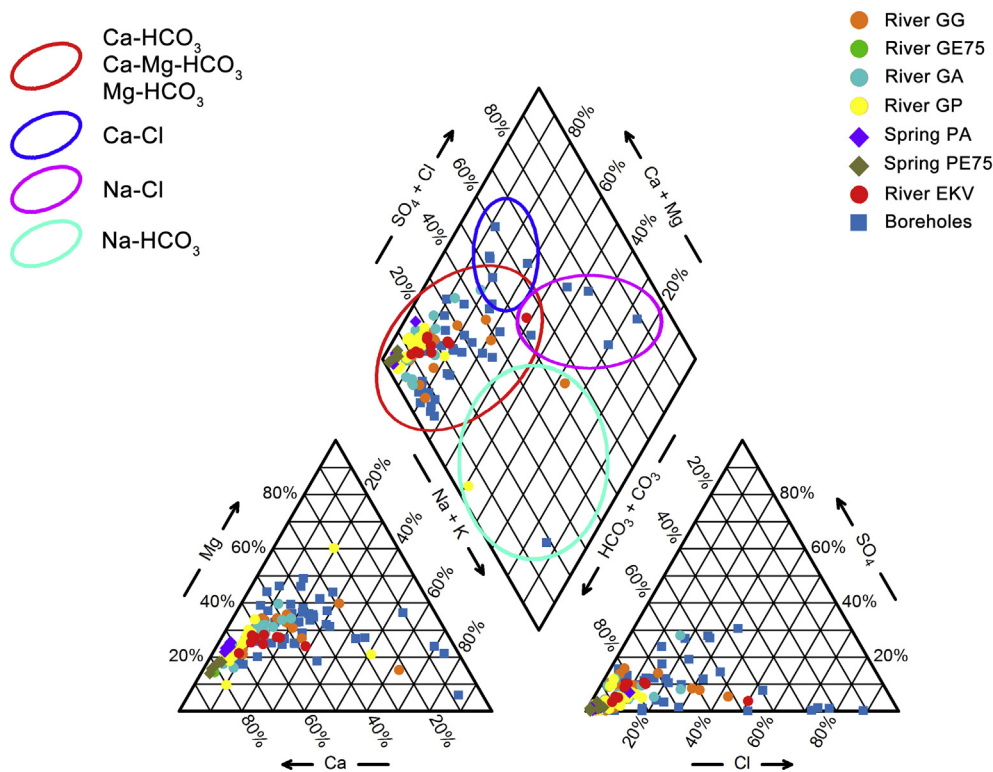


Fig. 4. Piper diagram of water samples and group clusters according to the water type.

2.8 at the river water sampling site GP, indicating water enrichment in Mg, probably due to the interaction with groundwater (mean Ca/Mg = 1.5). At sites EKV1-EKV4 the river water samples exhibited a mean Ca/Mg ratio (2.1–2.4) like that of sampling site GP (2.8).

Groundwater samples showed no particular pattern in terms of Ca/Mg ratio. The groundwater samples close to the river (e.g. P2, P3, and P7) showed similar Ca/Mg ratios (mean Ca/Mg = 2.0) to the river samples of site GP (mean Ca/Mg = 2.8), indicating possible interaction between the river and the aquifer. In the western part of the plain, the P2 sampling site exhibited the highest Ca/Mg ratio (3.0), which was close the Ca/Mg ratio of the river site GE75 (3.9), suggesting that interaction between the river and the aquifer is likely to occur. In the

northern part of the plain, groundwater shows a high variation in terms of Ca/Mg ratio. This is because the aquifer in this area is influenced by saline sources with low Ca/Mg ratios and high Cl concentration. For example, the P10 sampling site exhibited the highest mean EC value (3743 μS/cm), a mean Ca/Mg of 0.7 and a mean Cl value of 1297 mg/l.

4.5. Water-rock interactions and mixing

Gibbs (1970) proposed that the TDS versus Na/(Na + Ca) can be used to explore the relative importance of the major natural mechanisms controlling water chemistry. As illustrated in Fig. 6a and b the samples collected from the river, the springs and the boreholes fall

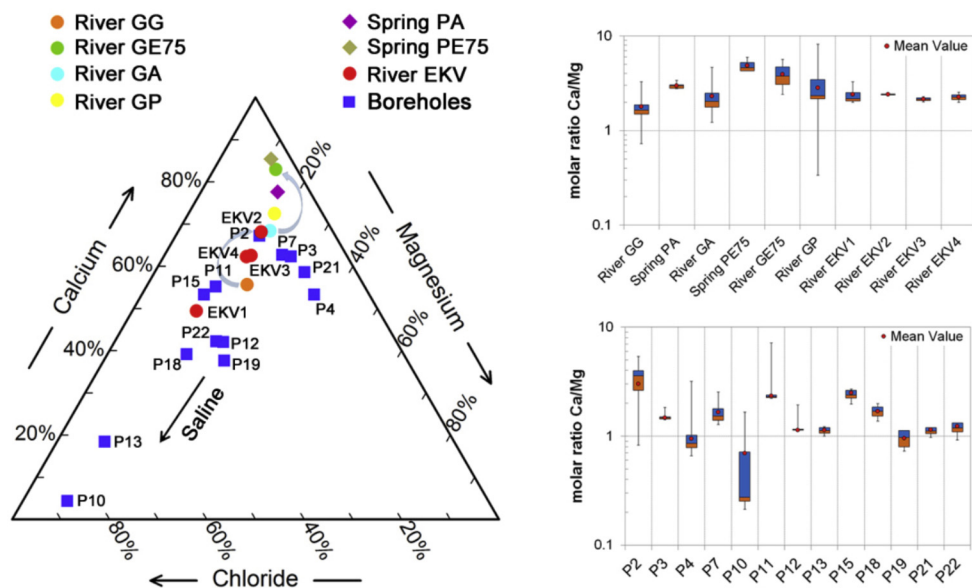


Fig. 5. Ca-Mg-Cl ternary diagram of the water samples. The arrows indicate the hydrochemical evolution between the sampling sites.

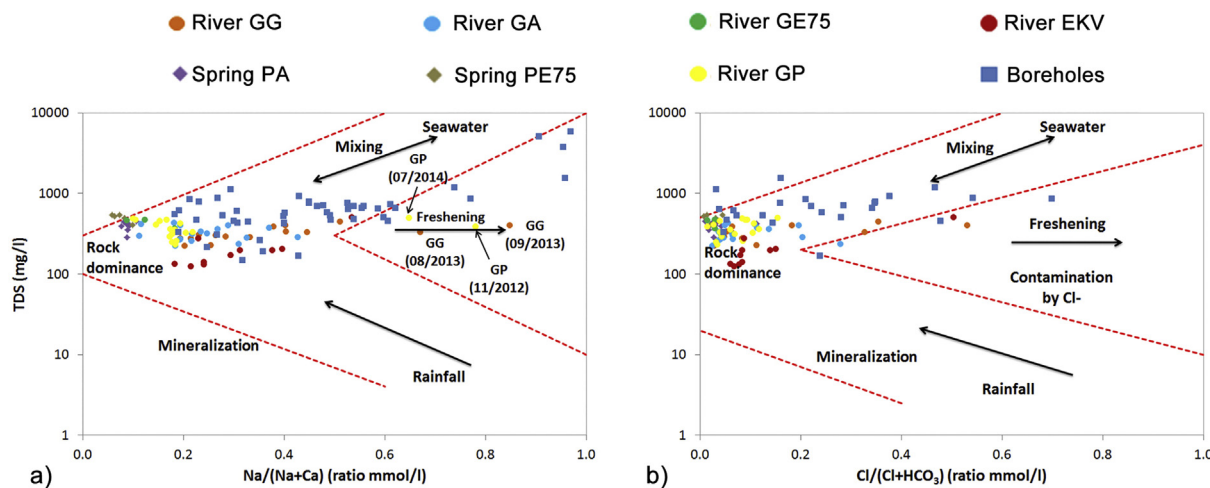


Fig. 6. Identification of the main processes on Gibbs diagrams (adapted from Gibbs 1970) according to a) the Na and Ca ratio (left) and b) the Cl and HCO₃ ratio (right).

mainly in the domain influenced by geology. Only a few groundwater samples in the northern part of the plain (e.g. P10) underwent some mixing with saline water.

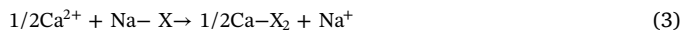
To further investigate the salinization effect, the Revelle (1941) index (RI = Cl/(HCO₃ + CO₃)) was used (Fig. 7). River water samples upstream of the mouth area showed a RI ranging between < 0.1 and 1.1, representing mainly fresh water, except for the river water samples of site GG, which became slightly brackish in the summer of 2013. The river site GG lies outside the deltaic plain, thus seawater intrusion cannot explain the increase in Cl concentration, which was probably due to evaporation phenomena combined with low river flow. At the river mouth area, the water exhibited low RI values (< 0.5), indicating no brackishness due to seawater intrusion in the wet period. However, in October 2013 the site EKV1 showed a RI of 1.0, which indicated a seawater intrusion influence.

Most of the groundwater samples (77.1%) showed a RI < 0.5. Fewer groundwater samples (14.6%), collected mostly in the dry season, fell in the “slightly brackish water” domain. Moderately or very brackish waters accounted for 8.3% of the groundwater samples. As illustrated in Fig. 7, in the northern part of the plain sampling sites P10 and P13 exhibited a strong enrichment in Cl, as a result of a saline source influence. In this part of the plain the groundwater level remained above the absolute sea water level throughout the year (Matiatos et al., 2014b), while the RI values did not reach their maximum during the summer season. Thus, it can be concluded that the aquifer became enriched in Cl not because of seawater intrusion but due

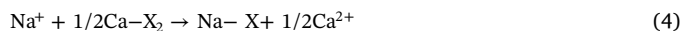
to mixing with the brackish deeper aquifer (Pisinaras et al., 2014).

4.5.1. Cation exchange processes

The cation exchange reaction taking place during freshening of the aquifer is given by Appelo and Postma (1993):



When saline water intrudes on a freshwater aquifer, Na replaces part of the Ca on the solid surface, as demonstrated in the following equation:



where X represents the cation exchanger.

To investigate cation exchange processes a scatter plot of Na versus Ca was constructed (Fig. 8). Inside and outside the deltaic plain river water samples exhibited constant calcium and sodium values, except for river water at site GP which showed a strong increase of sodium concentration (8.7 mmol/l) and a decrease in calcium concentration (2.5 mmol/l) in November 2012, which was attributed to recharge from groundwater influenced by cation exchange processes.

In the northern part of the deltaic plain, groundwater at site P13 showed excess sodium in October 2012, resulting in a water type of Na-HCO₃, which was attributed to cation exchange reactions during freshening of the aquifer. Calcium concentration at sampling site P15 increased from October 2012 to January 2013, but sodium concentration decreased, resulting in a Ca-Cl water type indicative of cation

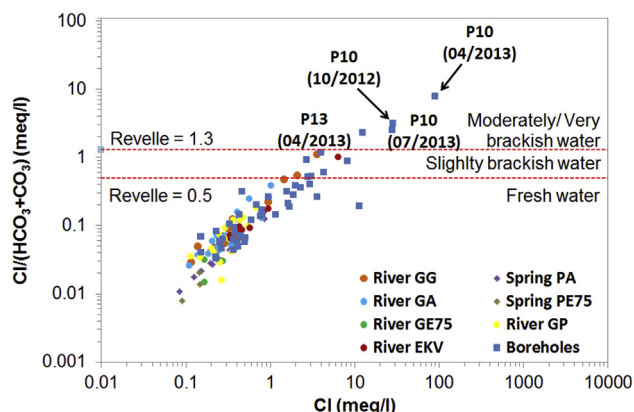


Fig. 7. Scatter plot of Cl vs Cl/(HCO₃ + CO₃) of water samples in the study area.

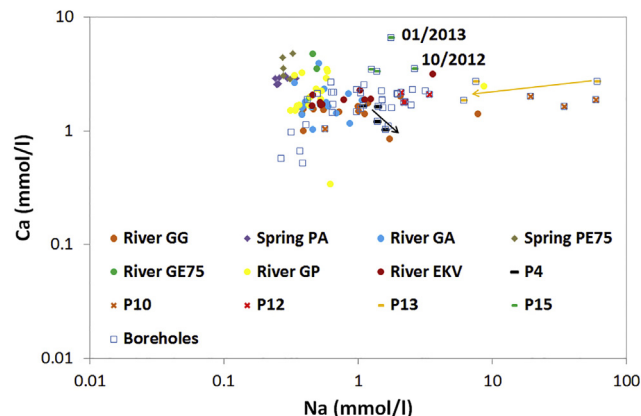


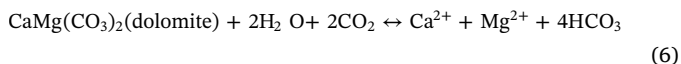
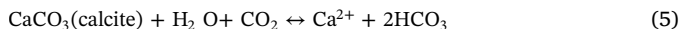
Fig. 8. Scatter plot of Na vs Ca of water samples in the study area. The arrows show the hydrogeochemical evolution.

exchange reactions due to mixing with saline water.

The Na–HCO₃ water of site P4 of October 2012 showed that fresh-water is flushing saline water from the aquifer, which results in uptake of Ca and Mg by the exchangers with release of Na. As illustrated in Fig. 8, the groundwater samples showed a decrease in calcium concentration with respect to sodium concentration and thus ion exchange reactions occur.

4.5.2. Carbonate dissolution and silicate weathering

The reaction of calcite and dolomite with water and carbon dioxide can be written as follows (Appelo and Postma, 1993):



The Mg/(Ca + Mg) ratio can provide evidence of the carbonate dissolution. Most samples showed a Mg/(Ca + Mg) ratio below 0.5 indicating a limestone-dolomite dissolution process (Hounslow, 1995). When calcite and dolomite dissolve according to reactions (5) and (6), respectively, the molar proportions of Ca/HCO₃ and (Ca + Mg)/HCO₃ are expected to be linear, with a slope of 0.5. As illustrated in Fig. 9a, calcite dissolution alone cannot explain the high HCO₃ concentrations. Surface and groundwater samples that plotted close to the (Ca + Mg) = 0.5·HCO₃ line indicated that dolomite could explain the excess HCO₃ and enrichment in Mg (Fig. 9b). All water samples were super-saturated with respect to calcite and dolomite, except for the samples collected from boreholes P2, P7, P15 and P18 during April and July 2013 and the spring water sample of site PE75 collected during April 2013.

The water samples that plotted above the theoretical line of dolomite dissolution were highly enriched in calcium and magnesium in relation to bicarbonate ((Ca + Mg)/HCO₃ > 0.5). Mg-enrichment could be attributed to silicate weathering. The plot of (Ca + Mg) vs

(HCO₃ + SO₄) confirms that Ca and Mg enrichment is also due to the weathering of silicates (Fig. 9c).

Temporal variations of groundwater hydrochemistry were related to the fluctuations of water table levels. Low EC and ionic concentrations were observed during high recharge, whereas the increased residence time during low flow recharge produced higher EC and ionic concentrations. Although the solubility of calcite and dolomite are similar, the kinetics of dolomite dissolution is slower than calcite (Plummer et al., 1978). Thus, increased dolomite dissolution and higher Mg concentrations are expected during low flow recharge. As depicted in Fig. 9d, in the central part of the plain, boreholes P7 and P19 were enriched in Mg when groundwater level is lower (low recharge). When the groundwater level raised, the EC and Mg concentrations decreased due to the mixing of groundwater with fresh water.

4.5.3. Dedolomitization processes

The high (Ca + Mg)/HCO₃ ratio (> 0.5) can be attributed to the depletion of water samples in bicarbonates due to dedolomitization processes triggered by (Eberts and George, 2000): 1) dissolution reactions with carbonate minerals and gypsum, or/and 2) sulphuric acid neutralization, which involves dissolution of carbonate minerals with sulphuric acid generated by the oxidation of pyrite.

All samples showed a Ca/(Ca + SO₄) ratio higher than 0.5, indicating that the calcium source was probably not gypsum (Hounslow, 1995). Moreover, gypsum presence in the Neogene sediments of the deltaic plain is not reported by other researchers (Katsikatos and Migiros, 1982). Thus, a dedolomitization model due to gypsum cannot explain the bicarbonate depletion.

Sulphide minerals, mainly pyrite, have been observed in the amphibolites, schists and prasinites of the metamorphic ophiolites (Katsikatos and Migiros, 1982). Therefore, dedolomitization due to pyrite oxidation was a possible source of bicarbonate depletion. On a plot of (Ca + Mg) vs (SO₄ + 0.5HCO₃), the dedolomitization reaction yields a straight line with slope 1 (Fig. 10a). The groundwater samples

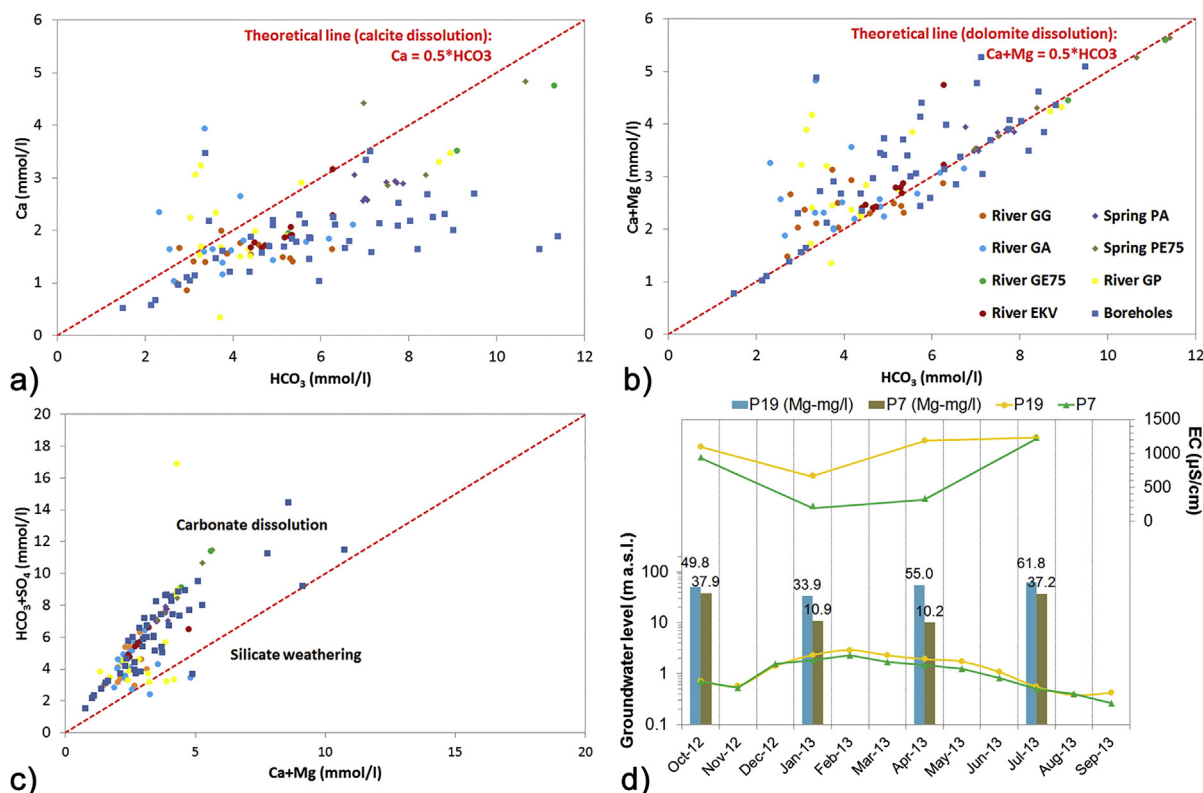


Fig. 9. Scatter plot of a) Ca vs HCO₃, b) Ca + Mg vs HCO₃, and c) HCO₃ + SO₄ vs Ca + Mg, and d) temporal variation of groundwater level, EC and magnesium concentration (vertical bar chart) in two groundwater sampling sites of the study area.

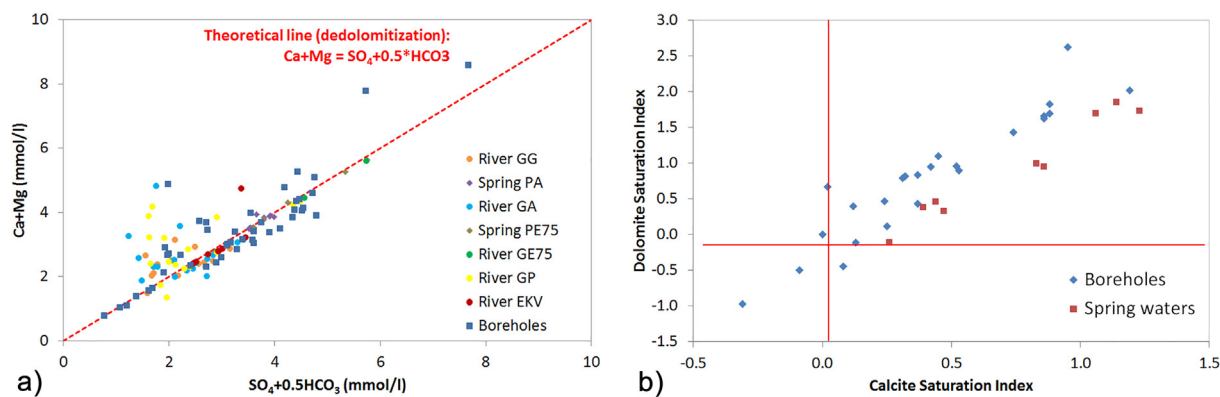


Fig. 10. Scatter plots of a) Ca + Mg vs SO₄ + 0.5HCO₃, and b) Dolomite SI vs Calcite SI of water samples from the study area.

plotted close to the dedolomitization line. However, during a dedolomitization process, the (Ca + Mg)/SO₄ ratio is expected to be close to unity and the saturation indices, with respect to calcite and dolomite to show saturation and undersaturation, accordingly (Hounslow, 1995). Most of the samples showed a (Ca + Mg)/SO₄ ratio higher than 5 and supersaturation with respect to dolomite ($SI_{dolomite} > 0$), indicating that dedolomitization is not likely to occur (Fig. 10b). The samples that exhibited undersaturation with respect to dolomite ($SI_{dolomite} < 0$) showed ratios of (Ca + Mg)/SO₄ away from 1, so such a process cannot explain the decreased bicarbonate values in the water samples.

The presence of sulphates in the water samples was examined by calculating the SO₄/Cl ratio. A marine origin of sulphates is indicated by a ratio of 0.05 (as mmol/l) (Hem, 1985). Most samples showed an excess of SO₄ (SO₄/Cl above 0.05 mmol/l) compared to the composition of sea water, so non-marine sources were considered, such as dedolomitization or agricultural activities. As discussed earlier, it is not likely that dedolomitization processes are taking place in the region, so agricultural activities are considered an additional source of SO₄. On the contrary, samples in the northern part of the deltaic plain (e.g. P10, P13) that showed SO₄/Cl below 0.05 mmol/l, could be due to removal of SO₄ or supply of non-marine Cl, e.g. from the brackish deeper aquifer.

4.6. Multivariate statistical analysis

The results of PCA revealed that the contribution of the first five components (component #1, component #2, component #3, component #4 and component #5) was 34.5%, 14.5%, 10.3%, 9.5% and 8.1%, respectively, accounting for approximately 77% of the total geochemical variance (Table 8 of supplementary material). The loadings of the Varimax rotated component matrix for the five-component model are presented in Fig. 11, where evidently the first factor was generally more correlated with the variables than the second and third.

Component #1 exhibited high loadings for EC, Na, K, Cl, and Mg, which are derived from saline sources, either from seawater influence or evaporation or interaction with saline components of the deeper aquifer. Hence, component #1 was interpreted as the “salinity” factor.

Component #2 was defined as the “water-silicate rocks interaction” factor because of the high loadings of Fe, Zn and the moderate loadings of Mn. This factor was associated with the dissolution of silicate minerals bearing these trace elements. The geological setting of the plain is partly composed of metamorphic formations (e.g. shales and ophiolites) hosting silicate minerals such as pyroxenes, feldspars, mica, olivine and pyrite (Katsikatsos and Migiros, 1982). Although silicate weathering is a very slow process, it seems to be important in places.

Component #3 was interpreted as the “hardness” factor because of its moderate positive loadings in Ca and HCO₃, which can be associated with calcite dissolution. The presence of carbonate formations in the study area supports the current interpretation. The weak correlation

with Na can be explained by the occurrence of cation exchange processes, as discussed earlier.

Component #4 was interpreted as “nitrogen pollution” since NO₃, showed the highest loading. To further investigate nitrogen pollution, PCA was applied only to groundwater samples. The results of the second PCA showed the nitrogen pollution factor exhibited even higher loadings in NO₃ (0.720) and Mn (−0.788), indicating a stronger negative correlation between the two elements, which could support the occurrence of denitrification processes. Under anaerobic (hypoxic-anoxic) conditions bacteria remove oxygen from nitrate (denitrification) to produce N₂ (gas) and also from manganese and iron oxides, thereby increasing the concentration of dissolved manganese and iron in groundwater and a decrease in nitrates (Güler et al., 2012; Kendall, 1998).

To explore the possible occurrence of denitrification, the relationship between NO₃ and Mn was investigated. The surface water and the spring water samples retained very low and constant Mn concentrations indicating that denitrification is not prevalent. The groundwater samples showed the highest Mn concentrations with a trend of increase relative to decreasing nitrate concentrations. There was no correlation between nitrates and iron. However, the measured iron concentration refers to the total dissolved iron and not to Fe²⁺ which is released during a denitrification process. Therefore, it was assumed that denitrification is occurring at a limited extent; however, additional measurements (e.g. Fe²⁺, dissolved oxygen, N-isotopes) are required to confirm the occurrence of the denitrification process. The increased dissolved manganese concentrations in most boreholes can originate from minerals, such as pyrolusite, but no such minerals have been identified in the region based on the literature review of the geological setting.

Component #5 is interpreted by high loadings of SO₄ and Mn, that could be attributed either to dedolomitization processes or to increased agricultural input. Dedolomitization was not confirmed from the correlations between the hydrochemical variables, as discussed earlier, so agricultural influence should be considered as additional source of SO₄ and Mn enrichment. Manganese fertilizer (MnSO₄) is mainly used as feed additive and catalyst of synthesizing chlorophyll for plants and is easily soluble in water. Therefore, component #5 can be defined as the “non-N-related artificial fertilizers” factor.

During the PCA procedure scores for each water sample, which represent the influence of each factor on the samples, were calculated (Fig. 11). In the northern part of the plain, sampling sites P10 and P13 showed the highest scores on component #1 indicating that they are characterized by high salinity content. These sampling sites were characterized by a Na-Cl water type. Sampling sites P3, P4, P7, P10 and P19 showed the highest positive scores on component #2, suggesting Fe, Zn and Mn enrichment from water-rock interaction. The highest positive scores for component #3, which reflects high content in Ca, Na and HCO₃, were observed outside and inside the deltaic plain (P13,

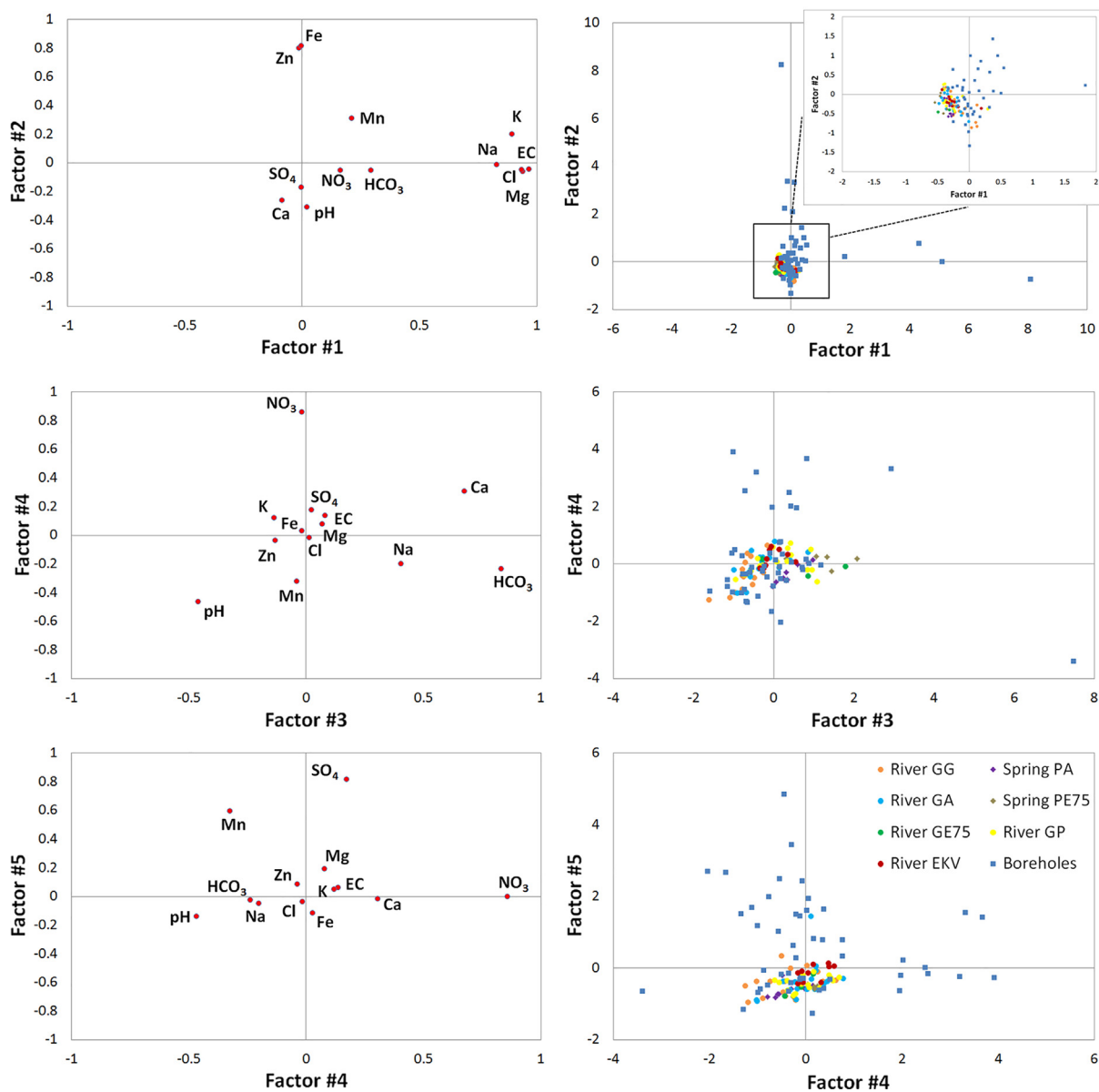


Fig. 11. Loadings for rotated component matrix (rotation method: Varimax with Kaiser normalization) of PCA (left) and scores (right).

P15, GE75, PE75, GP and PA), which showed the highest concentrations in calcium and sodium, and were characterized by a Ca-HCO₃ or a Na-HCO₃ water type. The P13 sampling site showed two water types during the sampling campaigns (Na-HCO₃ and Na-Cl), which justifies the high scores on component #1 and component #3. The P2, P3, P10, P11 and P15 sampling sites showed the highest scores on component #4, indicating that they are enriched in nitrates due to agricultural activities and domestic effluents. Many samples (P4, P7, P10, P12, P15, P18, P19, P22) exhibited high positive scores on component #5, suggesting that the application of non-N-related artificial fertilizers are contaminating the aquifer.

4.7. Comparison with river deltas worldwide

During the last years, numerous studies and monitoring networks have reported the occurrence of contaminants, especially of nitrate and chloride ions, in river water and groundwater of deltaic plains. The European Environmental Agency (EEA) has launched in 2015 an interactive map that shows the mean annual concentration of nitrates observed in river monitoring stations and reported by EEA member

countries via WISE (Water quality in transitional, coastal and marine waters) database. The nitrate concentration values of 2012 referring to the major river deltas in Europe were derived from this database, so to compare them with the results of the current study. In addition, a literature review of case studies concerning shallow aquifers hosted in river deltas worldwide and impacted by anthropogenic activities was performed, to identify differences between the aquifers, including the shallow aquifer examined in this paper. The review included only studies which applied multivariate statistical techniques to identify hydrogeochemical processes and factors to define the groundwater quality. The ranges (minimum and maximum values) and the mean concentrations of nitrate as NO₃, chloride, as well as the PCA findings reported for aquifers hosted in deltaic environments, including the current study, are summarized in Table 1.

According to EEA (2015), NO₃ concentrations in European Rivers flowing in a deltaic environment exhibit a range of mean annual values from ~0 to 16 mg/l, without exceeding the threshold value of 50 mg/l set for water intended for human consumption (Directive 98/83/EC). Pinios River showed low nitrate concentrations (mean NO₃ = 3.0 mg/l), indicating that the nitrogen load in the river is relatively low.

Table 1

Mean concentration of nitrate and chloride ions, with mean and max values (in parentheses), where available, and PCA findings in river deltas.

Location	Cl (mg/l)	NO ₃ (mg/l)	PCA factors	References
<i>Surface water</i>				
Danube River delta (Romania)	–	6.8	–	EEA (2015)
Rhone River delta (France)	–	5.9	–	EEA (2015)
Llobregat River delta (Spain)	–	15.6	–	EEA (2015)
Neretva River delta (Croatia)	–	2.6	–	EEA (2015)
Hollands Diep (estuary of the Rhine and Meuse River) (Netherlands)	–	10.9	–	EEA (2015)
Mekong river Delta (Vietnam)	–	– (0.66–1.89)	Soil erosion, wastewater treatment plants, domestic wastewaters, agricultural pollution, industrial pollution	Phung et al. (2015)
Pinios River delta (Greece)	27.8 (3.9–226)	3.0 (0.0–7.9)	–	Current study
<i>Groundwater</i>				
Cauvery River delta (India)	– (24.9–1387)– (355–845)	–	Seawater intrusion, water-soil/rock interaction, ion exchange processes, agricultural pollution, natural salinization	Jayakumar and Siraz (1997), Venkatramanan et al. (2013)
Western Niger Delta (Nigeria)	70.2 (28.1–234)	–	Seawater intrusion, water-soil/rock interaction, vehicular and petroleum refining activities, pyrite dissolution	Olobaniyi and Owoyemi (2006)
Eastern Niger delta (Nigeria)	161 (12–710)	12.8 (0.0–45)	Seawater intrusion, water–rock interaction, agricultural pollution, domestic and hazardous wastes disposal, industrial pollution	Amadi et al. (2012)
Tarsus River delta (Turkey)	67.8 (6.1–433)	11.1 (0.4–201)	Water-rock interaction, agricultural pollution, seawater intrusion, evaporate dissolution, natural origin of heavy metals, industrial pollution	Güler et al. (2012)
Nile River delta (Egypt)	790 (7–12186)	12.34 (0.3–118)	Seawater intrusion, mineral dissolution, domestic waste disposal, agricultural pollution, calcium and phosphate fertilizers application	Masoud (2014)
Niger River delta (Nigeria)	19.2 (2.9–54.8)	1.1 (0.0–8.7)	Water-rock interaction, ion exchange processes, domestic wastes disposal, nitrogen pollution	Okiongbo and Douglas (2015)
Pinios River delta (Greece)	169 (5.3–3190)	6.2 (0.0–31.8)	Sea water intrusion, interaction with brackish aquifer, water-rock interaction, agricultural pollution, domestic effluents, calcite dissolution, non-N-related artificial fertilizers application	Current study

However, the temporal variation of nitrate concentration (~ 0 – 7.9 mg/l) shows that the river receives different nitrogen loads throughout the year and thus the nitrate concentration in the river may vary.

Nitrate concentrations in shallow aquifers hosted in deltaic environments exhibit a wide range of values ranging from ~ 0 to 201 mg/l as NO₃. The higher concentrations were reported for the Eastern Niger River delta in Nigeria and Nile River delta in Egypt, due to agricultural activities and wastewater leakages (Amadi et al., 2012; Masoud, 2014). In the latter, nitrate concentrations locally exceeded 50 mg/l due to the intensive application of manure and chemical fertilizers and to insufficient sewage facilities (Masoud, 2014). The extent of nitrogen pollution in the groundwater of the Pinios River deltaic plain is relatively low (mean NO₃ = 6.2 mg/l) compared to other case studies.

Chloride concentrations of groundwater in river deltas range between 2.9 and 12186 mg/l. Masoud (2014) reported extremely high chloride concentrations in the Nile River delta due to intensive seawater influence, especially at the mouth of the river, making the groundwater unsuitable even for irrigation purposes. In the Cauvery River delta, the high chloride values (> 1000 mg/l) in the coastal area are attributed to over-pumping in the pre-monsoon period and to the tidal phenomena during the monsoon period, which activate the penetration of seawater into the groundwater system through seepage (Jayakumar and Siraz, 1997). In the Tarsus River delta (Güler et al., 2012) and in the Nile River delta (Masoud, 2014) the salinization of the aquifer was due to seawater intrusion and mineral dissolution (evaporites). In the Pinios River delta, seawater intrusion is limited at the mouth area and the high chloride concentrations (> 1000 mg/l) observed in the northern part of the plain are attributed to the interaction with the brackish deeper aquifer.

In most hydrogeochemical studies carried out in deltaic areas, the factors controlling groundwater chemistry are similar to the ones identified in the present study, i.e. water-rock interaction, seawater intrusion and nitrogen pollution. In most case studies (e.g. Amadi et al., 2012; Güler et al., 2012; Olobaniyi and Owoyemi, 2006) mineral dissolution (e.g. calcite, silicates, gypsum) and ion exchange processes are reported as the main processes releasing major ions, such as Ca, Mg, Na,

K and HCO₃, in the groundwater. In the Nile River delta (Masoud, 2014), the high calcium and phosphate concentrations were attributed to the application of calcium and phosphate fertilizers for agricultural purposes. By applying PCA techniques, groundwater salinity has been shown to be not always related to over-pumping (El Arabi et al., 2013; Masoud, 2014), but also to natural factors, such as storm surges and high tidal events (Jayakumar and Siraz, 1997; Olobaniyi and Owoyemi, 2006), or to the interaction with deeper aquifers of higher salinity (current study). Moreover, the spatial distribution of the factor scores extracted from PCA has shown that nitrate pollution originated not only from agricultural activities, but also from wastewater treatment plants, septic systems and urban wastes (e.g. Masoud, 2014; Phung et al., 2015). By using PCA techniques, the presence of high SO₄ concentrations in the groundwater of the Western Niger Delta has been attributed to the dissolution of minerals, such as pyrite, and to contamination by petroleum refinery wastes and heavy vehicular activities (Olobaniyi and Owoyemi, 2006). Moreover, heavy metal pollution has been attributed to natural background (e.g. chromium minerals), but also to the release of wastes from chemical industries and petroleum hydrocarbon storage facilities, and the disposal of hazardous wastes, such as batteries, electronics and machine scraps (e.g. Amadi et al., 2012; Güler et al., 2012).

5. Conclusions

This work presents a regional hydrogeochemical study of the deltaic plain of River Pinios (central Greece), an evaluation of the water quality status and the identification of the main geochemical processes controlling water hydrochemistry and its spatial evolution. The river is primarily recharged by groundwater influxes from the surrounding mountains and secondarily by precipitation and the shallow aquifer inside the deltaic plain.

The results of the Water Quality Index classification showed that spring water and river water in the deltaic plain are characterized by high quality rankings. In the river mouth area, the water quality degradation was mostly attributed to limited seawater intrusion, which

classifies most of the mouth area water samples into the “Moderate” water quality class.

Calcite and dolomite dissolution, cation exchange processes and silicate weathering control the groundwater chemistry. Locally high concentrations of Na and Cl were attributed to the interaction of the shallow aquifer with a deeper brackish aquifer, especially in the northern part of the delta. Agricultural activities and point sources of contamination introduce N-pollutants into the subsurface through leaching. This deterioration was reflected in the Water Quality Index, as most of the samples from that area were classified as of “Good” to “Poor” water quality.

Five factors explained 77% of the total variance in the water quality. Component #1 was the “salinity” factor due to seawater influence, evaporation and interaction with saline components of the deeper aquifer. Component #2 was the “water-silicate rocks interaction” factor and related to the dissolution of silicate minerals bearing Fe, Zn and Mn. Component #3 was the “hardness” factor and was associated with calcite dissolution and cation exchange processes. Component #4 was the “nitrogen pollution” factor, whereas component #5 was interpreted as the “non-N-related artificial fertilizers” factor.

The results showed that the water quality was good, compared to other river deltas worldwide, but river and groundwater were susceptible to contamination, especially from agricultural practices and point sources of nitrogen pollution. These findings can be used by stakeholders in the application of strategies for the sustainable management of the water resources in the deltaic plain.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhydrol.2018.03.067>.

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