

Characterization and Assessment of Groundwater Resources in a Complex Hydrological Basin of Central Greece (Kopaida basin) with the Joint Use of Hydrogeochemical Analysis, Multivariate Statistics and Stable Isotopes

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Received: 11 March 2017 / Accepted: 5 September 2017 / Published online: 9 September 2017
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Abstract Combined assessments from different methodologies, including hydrogeochemical analysis, multivariate statistics and stable isotopes, were used in order to characterize the groundwater resources of a heterogeneous aquifer system in central Greece and to evaluate the overall environmental regime. Results outlined the driving factors that chiefly control groundwater chemistry and delineated the major pathways of groundwater flow. Following the results of the combined assessments, hydrogeochemistry is influenced both by geogenic and anthropogenic factors including the geological substrate, intense agricultural activities and ongoing geochemical processes which impact the concentrations of redox sensitive agents like NO_3 , Fe, Mn and SO_4 . Stable isotope evaluations supplemented the above assessments by providing critical information for the hydrodynamics of the heterogeneous aquifer system. Evaporation is the main factor influencing the isotopic composition of water resources, in addition to the slow percolation rates of the thick unsaturated zone. Comparisons between $\delta^{18}\text{O}$ and δD values for surface and groundwater samples revealed an interaction among water systems through the developed karstic network and/or the riverbeds of higher permeabilities. Eventually, the integrated conceptual approach of diverse methodologies was applied successfully for the identification of hydrogeological and hydrogeochemical assessments in the case of Kopaida basin; evaluations were cross-confirmed and supplemented when needed, hence providing essential information for strategic planning and water resources management.

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Keywords Hydrogeochemistry · Groundwater · Stable isotopes · Multivariate statistics · Karstic aquifer · Kopaıda basin

1 Introduction

The hydrogeochemical signatures of groundwater resources are chiefly influenced by the characteristics of their catchment area. Several factors like climatic conditions, bedrock geology, soil properties and anthropogenic activities influence water flow and its overall quality status. The key processes that drive hydrogeochemistry and consequently water resources quality involve both geogenic and anthropogenic factors. The natural (geogenic) processes include redox transformations; complexation; ion exchange; dissolution and precipitation; rock-water interaction; intermixing of water bodies and others depending on the specific characteristics of the examined system(s) (Drever 1997; Schwartz and Zhang 2003). The human-driven (anthropogenic) processes include point and diffuse pollution sources mainly related to agricultural practices, industrial activities, urbanization, landfills, domestic effluents and aquifer over-exploitation (Appelo and Postma 2005). Similarly, water resources quantity is strongly affected by several factors, mostly referring to irrational anthropogenic practices and climate change impact, often enhanced by the major losses (seepage, evaporation, leakage, etc.) from water delivered to the agricultural sites for irrigation and the municipal sites for domestic use.

The assessment of the hydrogeochemical conditions along with the identification of the key processes affecting water resources' environmental regime is a prerequisite to facilitate water resources management plans, prevention and mitigation schemes and reclamation policies. Especially in environmentally vulnerable arid or semiarid Mediterranean areas which are expected to face adverse impacts in future due to climate change (Panagopoulos et al. 2016) the aforementioned requirements are of paramount importance. In principal, acquisition and interpretation of similar information is rather demanding and complex task, which requires multidisciplinary approaches of different perspectives and methodologies. Thus, evaluations should not only focus on individual effects and processes, but holistically, on their interactions and synergetic contribution.

Such an approach requires the combinational consideration of various methodologies, i.e., classic hydrogeochemical molar ratios (e.g., Kim et al. 2003; Zhu et al. 2007; Mandilaras et al. 2008; Barzegar et al. 2017); multivariate statistical techniques (e.g., Stamatis et al. 2006; Güler et al. 2012; Devic et al. 2014; Voutsis et al. 2015; Barzegar et al. 2016); joint hydrogeochemical evaluations (e.g., Stamatis and Voudouris 2003; Markovic et al. 2013; Tziritis et al. 2016) and stable environmental isotopes assessments (e.g., Mali and Urbanc 2009; Tziritis 2010; Dogramaci et al. 2012; Kanduč et al. 2012; Ozyurt et al. 2014). Considering the above, the present paper aims to provide an insight to the hydrogeochemical characterization of groundwater resources in a complex karstic aquifer system, through an integrated conception of different methodologies that include conventional hydrogeological and hydrological information, hydrogeochemical evaluations, multivariate statistical techniques and stable isotope analyses. Even though groundwater is the focal point of this research, special consideration has been given to surface water reserves of the area, due to the potential interactions with the groundwater.

The research aims to provide a methodological approach for the characterization of groundwater resources through joint assessments and different techniques which are widely used in hydrogeochemical research; in this sense, research outcomes are seeking to

demonstrate how these techniques can be used efficiently in order to deliver sound and robust assessments in complex hydrogeological environments, under variable external factors (e.g., heterogeneity of the water systems, contamination/enrichment sources, etc.). Finally, in respect to regional (Kopaida basin, central Greece) hydrogeochemistry and water governance, the results are expected to deliver critical information about the dominant groundwater recharge conditions, key hydrogeochemical processes affecting water systems, as well as their water quality status and flow-pathways of intermixing within the karstic substrate of Kopaida basin, which is regarded as a basin of high significance.

2 Study Area

Greece is strongly dependent on groundwater resources for its water supply. The main aquifers, in terms of significance, are developed within the carbonate rocks (karstic aquifers) with remarkable attributes in respect to their overall productivity and exploitation potential. During the last decades, there is an intensive use of groundwater resources, particularly in agricultural areas like Kopaida basin, which has established a negative water balance and led to critical environmental pressures, like the piezometric level decline and water quality deterioration (Tziritis 2008). Kopaida basin is a fertile plain area with intensive agricultural activities and is considered among the most productive basins of Greece with profound financial significance, due to its high product supply (mainly onions, potatoes and carrots) to Greek markets. It is located in Boeotia, central Greece, and covers approximately an area of 2000 km². It constitutes the downstream-end part of the Viotikos Kifissos River basin system (Fig. 1), consisting of at least three sequential heterogeneous karstic aquifer systems (Pagounis et al. 1994).

The natural VKR system flows across Kopaida from west to east, and finally discharges through a hydraulically interconnected artificial underground canal in the adjacent hydrological unit of Lake Yliki; the latter constitutes a subsidiary strategic water reserve

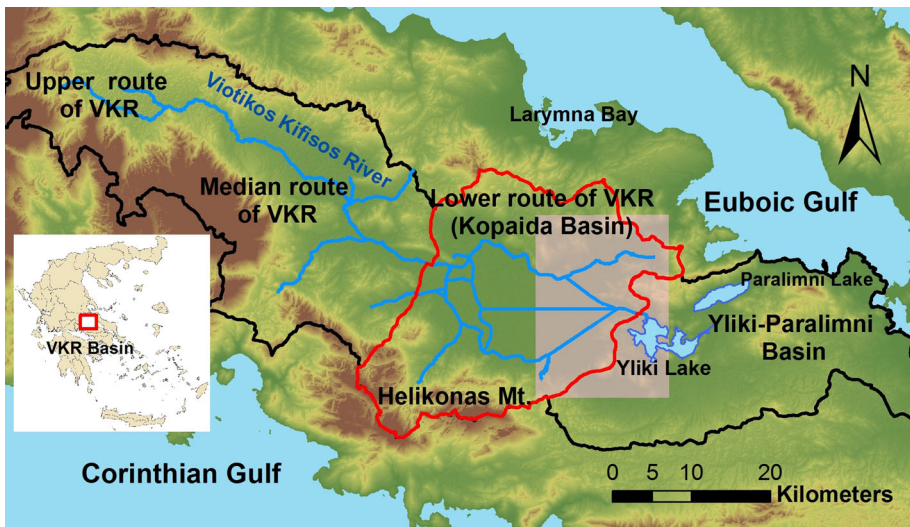


Fig. 1 Geographical setting of Viotikos Kifissos River (VKR) basin and its lower route (Kopaida basin). The red-shaded rectangle depicts the groundwater (GW) focal area, where more than 80% of abstraction wells are located

for capital Athens and is characterized as a “Habitat Directive Site” of NATURA 2000 (EC 1992). According to Pagounis et al. (1994) the water reserves of Lake Yliki are exclusively fed by the surface discharge of VKR and the ephemeral ditches of the surrounding catchment. The hydraulic interactions between the Lake and the aquifer systems are limited to the underground Lake discharge toward south-southeast (Pagounis et al. 1994; Tziritis 2008).

Within Kopaida basin VKR is fed by other natural streams (e.g., Melas, Erkina, etc.) without any hydraulic interaction with the aquifer systems, due to the impermeable nature and great thickness of the alluvial underlying formations along its route (Pagounis et al. 1994). The drainage network that runs Kopaida plain is rather extended, due to the development of multiple artificial irrigation channels. Paleogeographic evidences (Griffiths et al. 2002) indicate that Kopaida was formerly a tectonically controlled lake which progressively turned into a swamp and finally dried in the year 1930 (Allen 1986).

Bedrock geology (Pagounis et al. 1994; Allen 1986; Apostolikas 2007; Tziritis 2008) (Fig. 2) at the bottom of the strata mainly consists of a heterogeneous sequence

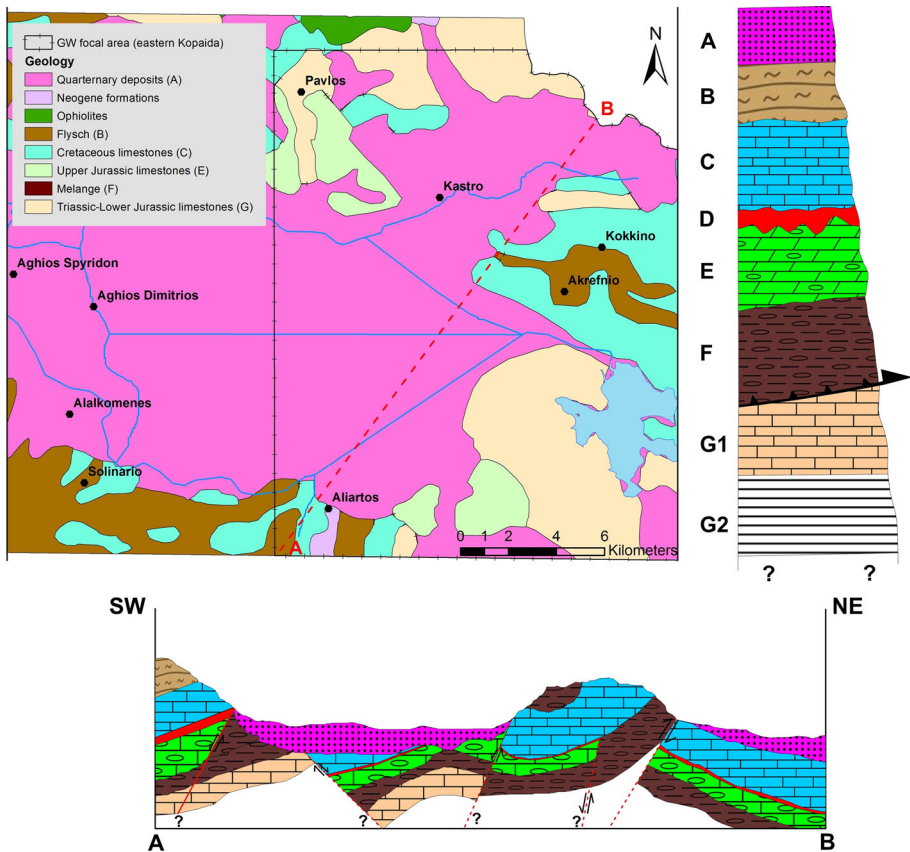


Fig. 2 Simplified geological map of eastern Kopaida basin (modified by Tziritis 2008) with the addition of a typical stratigraphic column for the GW focal area. Horizons D (Fe–Ni-rich laterites) and E (mélange) do not have surface occurrence on the map but do exist in the bedrock strata; ophiolites and Neogene formations appear only at the northern and southern extremities of the study area and practically are not part of its typical stratigraphic column

that includes Triassic to lower Jurassic limestones (G2) often containing intercalations of dolostones and dolomitic limestones (G1); accordingly follows a stratigraphical sequence of a tectonically driven metamorphic complex (mélange) of schists which include serpentized ophiolites in blocks and intercalations of limestones (F). Stratigraphy continues with a series of upper Jurassic bituminous limestones (E) and at their top is developed a paleo-karst surface filled by the chemically weathered material of the surrounding ultrabasic formations (ophiolites) that has been progressively altered into a Fe–Ni-rich lateritic horizon; finally, the upper bedrock sequence is completed with a highly karstified Cretaceous limestone (C) and the typical flysch (B). Post-Alpine formations have variable thickness, locally significant (central part of the plain) and are consisted of recent fluvial, lacustrine and terrestrial deposits (A). At the central part of the basin, the thickness of Quaternary and Neogene organic-rich formations is reported locally more than 500 m (Allen 1986). Due to the organic-rich sediments of the substrate, locally are developed strong reducing conditions and oxygen depletion.

The hydrogeological regime is controlled by the karstic network which drives the general groundwater flow from west to east; water depth from surface varies locally from few meters to ~ 150 m depending on substrate permeability (see Fig. 6) (Tziritis 2008). The main aquifer bodies in terms of water storage and yield are developed within the variable karstic formations but are often interconnected and may be considered as a unified heterogeneous system. Based on previously recorded data (Pagounis et al. 1994; Tziritis 2008), hydraulic conductivity (k) in productive aquifers ranges between 10^{-1} – 10^{-4} cm/sec and specific storage (S) between 0.08 and 0.039. The vast majority of boreholes (over 80%) in Kopaida basin are developed within the study area in the eastern part of the basin (eastern Kopaida, sub-basins of Kastro and Davlosi), shown in Fig. 3 as GW focal area. In this part, the alluvial thickness in the plain area is in general low and karstic aquifer can be exploited, as well as at the extremities of the plain where limestones outcrop. Discharge rates (Q) range from 50 to 120 m^3/h and reach up to 170 m^3/h for the most productive boreholes. Pumped volumes are used mainly for irrigation (about 90–95%) and the rest as drinking water resources for local communities. The transitional area between eastern Kopaida basin and Lake Yliki (Ptoon Mt.) is dominated by various katavothrae and sinkholes, frequently developed in surface but—in major—developed underground as a complex network that drives groundwater to sea (Euboic Gulf) where it is discharged by submerged springs.

3 Materials and Methods

3.1 Sampling and Analyses

Sampling was conducted in two campaigns (March–April and September–October); based on local climatic data (Tziritis 2008), the period of March–April is considered as the end of the wet hydrological period, while September–October as the end of the dry period.

Hence, sampling was intentionally carried out within these two periods, so as to deliver representative mean values for the entire hydrological year.

Totally 82 sites were sampled (Figs. 3, 4) of both surface (30) and groundwater (52). Surface water samples (S1–S30) included Lake Yliki, irrigation channels and natural river systems (Viotikos Kifissos, Melas and Erkina). Groundwater samples (G1–G52) were

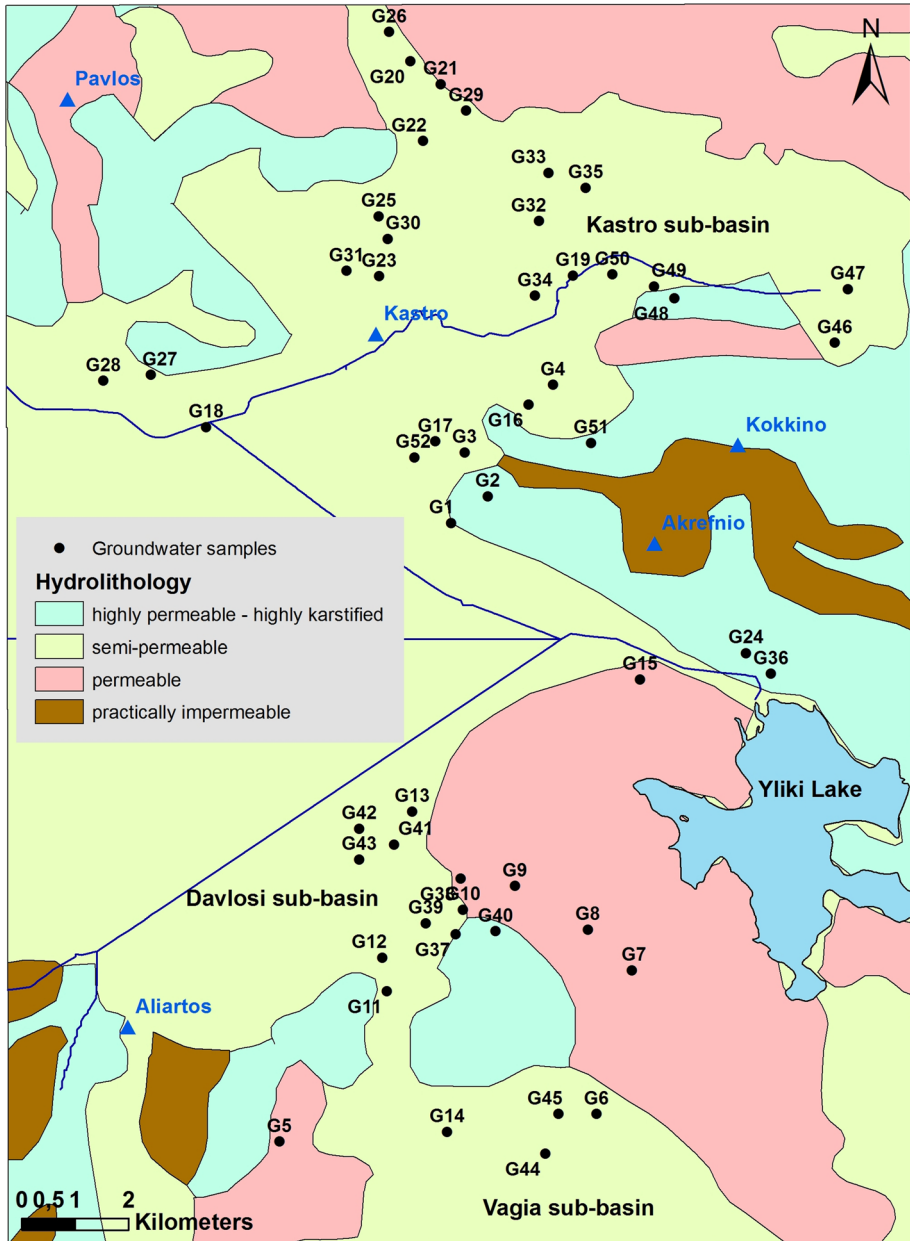


Fig. 3 Location of groundwater sampling sites at eastern Kopaida basin (GW focal area)

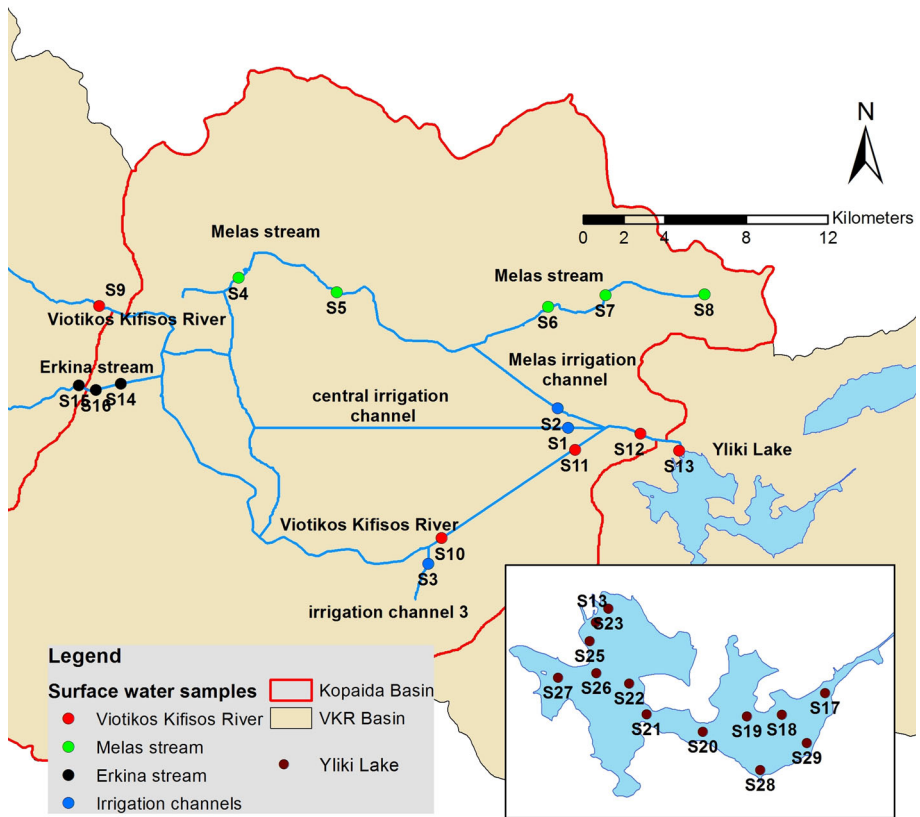


Fig. 4 Location of surface water sampling sites at Kopaida basin and Lake Yliki

collected from boreholes of the karstic aquifer, located in the GW focal area of eastern Kopaida basin. The parameters of pH and EC were measured in situ with portable equipment. Water samples were immediately filtered in the field through conventional 0.45 μm membrane filters and separated into two aliquots of 1 L and 50 mL, respectively. The smaller aliquot was acidified down to $\text{pH} \approx 2$ with HNO_3 in order to prevent metal precipitation and complexation and stored in new polyethylene bottles for cation analyses. Major ions were analyzed spectrophotometrically (Laboratory of Geochemistry, Athens University, Greece) except HCO_3^- that was determined by titration. Minor and trace elements were analyzed by ICP/MS (ACME analytical laboratories, Canada). In respect to isotopes, sampling followed the standard procedures of IAEA (2014); an aliquot of 50 mL was collected directly from the source and was double-capped to polyethylene air tight vials. Then, it was carefully stored and transported to the laboratory. Hydrogen and oxygen isotope composition (D/H and $^{18}\text{O}/^{16}\text{O}$) of water samples were analyzed in the Laboratory of Research Institute of Materials, Akita University, Japan. Sampled water was converted to hydrogen gas through reaction with zinc metal at 415 $^\circ\text{C}$. The D/H ratio was measured with the use of a mass spectrometer (MAT 250), while oxygen isotopic ratio was determined using the $\text{H}_2\text{O}-\text{CO}_2$ equilibrium technique. Isotopic ratios are expressed as delta (δ) notation in per mille (‰) relative to the reference Vienna Standard Mean Ocean Water (VSMOW). Results are shown in Appendices A and B.

Overall, samples were analyzed for 21 parameters including major and minor ions, trace elements, physicochemical parameters and stable isotopes. The average values of the two periods, as well as their descriptive statistics, are shown in Appendices A and B. Accuracy and precision of analyses was checked by duplicates for every five samples and revealed negligible systematic and random errors. Quality assurance of chemical analyses was tested through ion balance ratios which were found to be less than $\pm 10\%$ for nearly all samples; hence, results are within the acceptable margins for similar research assessments (Güler et al. 2002; Yaouti et al. 2009) and considered reliable.

3.2 Multivariate Statistical Analysis

Groundwater samples were statistically processed with R-mode factor analysis (FA) in order to comprehend the correlations and identify the most important factors contributing to the data structure. Factor analysis (FA) is a multivariate statistical technique which has been widely used in environmental sciences and hydrogeochemical research (e.g., Liu et al. 2003; Panda et al. 2006; Oyebogb et al. 2012; Kumar 2014; Tziritis et al. 2016). It involves linear combinations of variables through a correlation-focused approach and seeks to reproduce the inter-correlations among variables, in which the factors represent their common variance. The relationship among a number of observed quantitative variables is represented in terms of a few underlying, independent variables, called factors, which may not be directly measured or even measurable. In this study, the exact number of factors was extracted with the use of Kaiser's criterion (Kaiser 1958), according to which significant factors are considered those with eigenvalues above 1; hence, six factors were finally selected that explained 79.5% of total variance.

Prior to processing, initial data have been standardized through log-transformation and z-scores in order to eliminate the influence of different units between variables and acquire a normal or a log-normal distribution (Reimann et al. 2008). Variables who failed to meet that criterion were omitted from further data processing; finally, only 16 parameters compiled the correlation matrix that accounted for the degree of mutually shared variability between individual pairs of groundwater quality parameters. Consequently were extracted the eigenvalues and the factor loadings that identify the groups of variables, most highly correlated among them; factor loadings were optimized with Varimax rotation method (Kaiser 1958) in order to facilitate interpretation by providing simpler factor structure. The higher is the factor loading of a parameter the greater is its participation to the examined factor. As high factor loadings were considered those above 0.750, as medium ones those among 0.500 and 0.750 and as weak ones those among 0.400 and 0.500 (Panda et al. 2006).

4 Results

4.1 Physicochemical Parameters

Based on the analyses performed (see Appendices A and B), groundwater samples are nearly alkaline (pH median value = 7.8). Cationic composition is primarily affected by calcium, owed to the dissolution of the karstic substrate and the abundance of detritus carbonate grains and kankar concretions (hardpans) in soils. Calcium predominance is documented by its median value (92 mg/L) which exceeds the typical average value

(75 mg/L) for karstic catchments (Appelo and Postma 2005). Additionally, the cationic composition is also influenced by magnesium which is locally enriched as a result of the ultrabasic blocks of the substrate and the dedolomitization process of the Triassic dolostones. In respect to the anionic composition, groundwater is dominated by bicarbonates, mainly due to karstification processes; however, sulfates and nitrates have locally elevated concentrations and control anionic composition, as a result of the manmade and geogenic processes explained below.

Based on the electrical conductivity (EC) values that range from 330 to 1300 $\mu\text{S}/\text{cm}$ (median value = 685 $\mu\text{S}/\text{cm}$), it is assumed that the majority of groundwater samples (77%) exceed the threshold of 600 $\mu\text{S}/\text{cm}$ which indicates contamination with ions from non-carbonate sources in predominantly karstic basins (Krawczyk and Ford 2006).

Regarding surface waters, they are clearly alkaline (pH median values = 8.3) and their cationic composition is dominated by calcium and sodium; calcium is significantly lower (median value = 43 mg/L) compared with groundwater, while sodium is higher (median value = 38 mg/L), probably due to weathering of abundant Na-rich surface minerals, like Na-clays (e.g., montmorillonite) and Na-feldspars (e.g., albite). The anionic composition is solely controlled by bicarbonates (median value = 140 mg/L), while the remaining anions appear low values. Nitrates are in general low (median values = 6 mg/L), indicating that despite the intensive agricultural activities and the excessive use of nitrogen fertilizers, there is negligible contamination to surface water owed to surface runoff.

Viotikos Kifissos River is characterized upwards by waters which are rich in sodium and progressively across Kopaida plain are enriched in calcium and magnesium. Melas River is characterized by fresh waters for almost its entire route, apart from its latter parts which are clearly affected by transitional waters; the origin of upwards fresh water is Orchomenos springs which discharge a karstic massif at the western part of the basin and feed Melas River.

Lake Yliki is dominated by sodium and bicarbonates, probably as a result of the “natural softening” process in which Ca^{2+} is sorbed onto the clay mineral surfaces and Na^+ is released in solution (Appelo and Postma 2005; Younger 2007). Lake Yliki exhibits no remarkable deviations to the values of the analyzed/measured parameters. Nevertheless, calcium values are doubled compared to the rest in two of the samples (S18 and S25) denoting an impact of an external factor, like the excessive dissolution of the karstic substrate or ion exchange.

In respect to environmental perspective, surface water samples are in general in good quality; individual deviations from this trend include few elevated values of Cd in samples S1, S2, S6 and S12; based on geological evidences the substrate is free of Cd; hence, elevated concentrations should be attributed to anthropogenic factors like agricultural activities. Cadmium is likely to be an additive of the applied agrochemicals, a fact that explains its elevated concentrations mainly at the artificial irrigation channels which are the direct receptors of surface runoff, probably enriched in agrochemicals.

4.2 Multivariate Statistics

Multivariate factor analysis (FA) was used in order to exploit the potential processes (factors) that drive hydrogeochemical conditions of groundwater samples. The results shown in Table 1 indicate the existence of six main factors that explain 79.5% of total variance. The dominant factor (FA1) that affects groundwater hydrogeochemistry explains 20.1% of total variance and includes with strong positive loadings the parameters of Na and Cl, and with medium ones the parameters of EC, K and SO_4 . The second factor (FA2)

Table 1 Factor loadings and eigenvalues of the six extracted factors with the use of multivariate factor analyses

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Na	0.916	0	0	0	0	0	0.850
Cl	0.888	0	0	0	0	0	0.889
EC	0.740	-0.491	0	0	0	0	0.881
K	0.716	0	0	0	0	0	0.71
Si	0	-0.873	0	0	0	0	0.767
Mg	0	-0.812	0	0	0	0	0.827
HCO ₃	0	-0.796	0	0	0	0	0.794
Cr	0	0	-0.828	0	0	0	0.829
Mn	0	-0.430	0.688	0	0	0	0.801
NO ₃	0	0	-0.682	0	0.559	0	0.864
Ca	0	0	0	-0.814	0	0	0.785
pH	0	0	0	0.704	0	0	0.717
SO ₄	0.528	0	0	-0.572	0	0	0.809
Fe	0	0	0	0	-0.872	0	0.799
Zn	0	0	0	0	0	0.755	0.674
Cu	0	0	0	0	0	0.731	0.717
Eigenvalues	3.213	2.770	2.007	1.748	1.639	1.337	12.714
% Var	20.1	17.3	12.5	10.9	10.2	8.4	79.5

Values below 0.400 are regarded as zero for simplification

explains 17.3% of total variance and includes with strong negative loadings the parameters of Mg, HCO₃ and Si, and with medium negative ones Mn and EC. The third factor (FA3) explains 12.5% of total variance and includes Cr and NO₃ with negative loadings and Mn with a positive one, denoting their antithetic covariance. The fourth factor (FA4) explains 10.9% of total variance and includes Ca and SO₄ with negative loadings and pH with a positive one. The fifth factor (FA5) explains 10.2% of total variance and includes with antithetic loadings the parameters of NO₃ and Fe. Finally, the sixth factor (FA6) explains 8.4% of total variance including positive loadings for Zn, Cu and Cd.

4.3 Stable Isotopes

The $\delta^{18}\text{O}$ values of groundwater in the study area range from -3.3‰ to -8.5‰ with median value of -6.8‰ , while δD values range from -26.2‰ to -53.5‰ with median value of -43.9‰ ; compared with values from spring discharges (-7.4‰ and -45.4‰ , respectively) in other areas of central Greece (Dotsika et al. 2010a) the median values of $\delta^{18}\text{O}$ and δD in Kopaïda basin are relatively enriched. Isotopic composition is affected by local precipitation that recharges groundwater and is chiefly controlled by the regional water vapor transport trajectories over the continents and the average rainout history of the air masses (Dotsika et al. 2010a). However, secondary processes like infiltration conditions, preferential groundwater flux and water–rock interactions may alter the initial isotope values.

Regarding surface water samples, Lake Yliki has median values of -5.8‰ and -39.4‰ for $\delta^{18}\text{O}$ and δD , respectively); accordingly the drainage network (natural and artificial) has median values of -6.5‰ and -44.3‰ for $\delta^{18}\text{O}$ and δD , respectively.

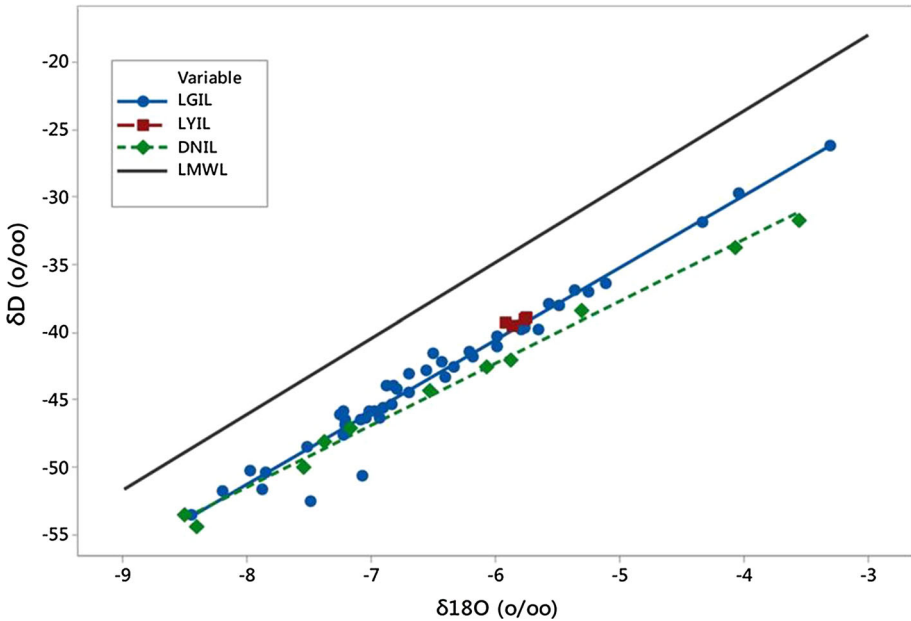


Fig. 5 $\delta^{18}\text{O}$ versus δD plots for groundwater samples (LGIL), Lake Yliki samples (LYIL) and drainage network samples (DNIL) with the addition of Local Meteoric Water Line (LMWL)

Based on the analytical results (Appendices A and B), the local isotopic lines for surface and groundwater samples are presented below (Fig. 5). The Local Surface Water Isotopic Line (LSIL) includes both natural (streams) and artificial (irrigation channels) drainage network; the Local Yliki Isotopic Line (LYIL) is estimated after omitting two samples considered as outliers and hence as non-representatives (at the pumping station with negligible circulation and right after the direct discharge of a local stream).

- Local Groundwater Isotopic Line (LGIL): $\delta\text{D} = 5.4 \delta^{18}\text{O} - 8.4$
- Local Surface Water Isotopic Line (LSIL): $\delta\text{D} = 4.7 \delta^{18}\text{O} - 13.6$
- Lake Yliki Isotopic Line (LYIL): $\delta\text{D} = 2.6 \delta^{18}\text{O} - 24.1$
- Drainage Network Isotopic Line (DNIL): $\delta\text{D} = 4.6 \delta^{18}\text{O} - 14.9$

5 Discussion

5.1 Hydrogeochemical Assessments

To have an insight into the processes that govern groundwater quality, the scatter diagrams of Ca versus HCO_3^- ; (Ca + Mg) versus ($\text{SO}_4 + \text{HCO}_3^-$); Ca versus SO_4 ; Na versus Cl have been plotted, where parameters are in meq/L. In the Ca versus HCO_3^- scatter diagram (Fig. 6), most of the samples fall near the 1:1 equiline, suggesting contribution from both weathering of carbonate and silicate minerals present in the geological formations (Datta and Tyagi 1996); however, some samples deviate significantly from the aforementioned equiline and clearly reflect the predominance of either silicate (e.g., G21, 23, 25, 42, 44 and 45) or carbonate weathering (e.g., G1, 4, 14, 30, 40 and 47), without any specific spatial

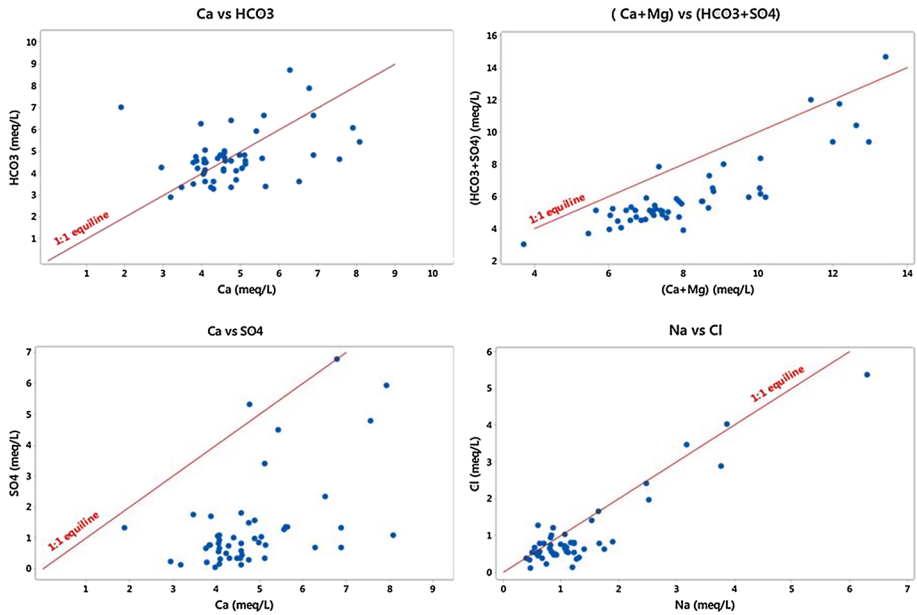


Fig. 6 Scatter diagrams of Ca versus HCO_3 , (Ca + Mg) versus ($\text{HCO}_3 + \text{SO}_4$), Ca versus SO_4 , and Na versus Cl for groundwater samples

pattern. Based on (Ca + Mg) versus ($\text{HCO}_3 + \text{SO}_4$) diagram, it is evident by the plotted samples that the prevailing process is the dissolution of carbonate minerals (calcite and dolomite) rather than silicates, a fact which is in compliance with rMg/Ca values that shows for nearly 80% of the groundwater samples ratios below 0.9, suggesting origin from dolostones or limestones (Mandel and Shiftan 1981; Demetriades 2010).

The presence of evaporitic minerals such as gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) or anhydrite (CaSO_4) and their impact on groundwater chemistry varies, depending on their spatial variability and local geological conditions. The increased content of Ca due to gypsum dissolution ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is related to a decrement in pH values and vice versa. The geochemical concept of this process is probably related to the common ion effect for Ca. As shown in the dissolution reaction of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Ca} + \text{SO}_4 + 2\text{H}_2\text{O}$), the products are composed of calcium and sulfates; a further increase in calcium's concentration due to karstic (calcite) dissolution will increase pH and subsequently direct the reaction toward the formation of CaSO_4 with a subsequent decrease in the overall concentrations of the products (Ca and SO_4). Hence, although pH would be expected to increase with Ca due to the impact of the calcareous substrate, the local presence of gypsum activates the common ion effect and causes a relative decrement. Another possible explanation could be the dissolution of evaporitic minerals (e.g., gypsum and halite) which are locally hosted in the soils; the solubility of gypsum is likely to be affected (increased) by the presence of aqueous saline solutions (e.g., presence of NaCl), while pH shows a relative decrease (Shukla et al. 2008), depending on solution temperature. The above-described process clearly affects the concentrations of Ca over SO_4 ; that is why it is generally addressed by their scatter diagram (Fig. 6) that Ca dominates over SO_4 , thus erroneously concluding to a different origin. Hence, in this case, it is evident that the joint use of methods for a common

objective may enhance the robustness of the assessment and amend any initial misleading interpretations.

The few individual elevated values of SO_4 are possibly owed to anthropogenic factors such as use of soil amendments (e.g., Na_2SO_4) and pyrite oxidation (pyrite is abundant locally due to past paleogeographic conditions) affected by the overall redox changes (Tziritis 2008); however, the potential effect from the dedolomitization process is also expected to contribute synergetically with the other factors, at least locally, to the elevated values of SO_4 .

In respect to Na versus Cl diagram (Fig. 6), it is evident that does not follow a linear (1:1) approach, at least for the majority of samples, suggesting that groundwater exploitation is induced by intermixing of multiple-sourced groundwaters of variable salinities along specific flow paths (Datta et al. 1996). In absence of any Cl-bearing mineral in the substrate, elevated Cl levels in groundwater may be additionally attributed to leaching of surface/subsurface salts and irrigation water return flow, likewise for the relatively higher values of Na, K, SO_4 and EC for the samples located at the southeastern part of the study area that depicts increased groundwater salinity.

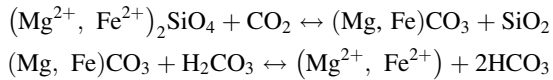
Regarding nitrate levels, as indicated by the analytical results it is evident a relative enrichment in groundwater; specifically, 21% ($n = 11$) of the samples are above the triggering value of 37 mg/L for alerting and 12% ($n = 6$) are above the maximum permissible value of 50 mg/L (EC 2000) for human consumption. The origin of NO_3 enrichment is related to the intense agricultural activities (excessive use of N-fertilizers), rather than sewage effluents and septic tanks; the latter is indicated by the negligible correlation ($r = +0.02$, p value = 0.908) between NO_3 and Cl, as well as between NO_3 , PO_4 , and HCO_3 which in the case of sewage or waste contamination shows a positive correlation (Tziritis 2009). Nevertheless, it should be noticed that locally elevated values of nitrates could occur due to the flushing of the manure from the scattered small farms, as well as due to the oxidation of lignitic lenses within the alluvial deposits (Tziritis 2010); however, their contribution is anticipated to be minor compared to fertilization.

Based on the results of the factor analyses (Table 1), the first factor (FA1), considered as dominant, is related to the increased groundwater salinity due to irrigation water return flows which enrich the concentrations of salts in the water bodies following surface and subsurface leaching (García-Garizábal and Causapé 2010; Barros et al. 2012). Calcium would be expected to join this factor due to its abundance in Kopaida's soils; however, the ion-exchange process with the clay minerals is likely a limiting factor and affects its overall concentration. Additionally, a supplementary component of groundwater salinity should be the connate groundwater at the southern parts of the basin, as well as the groundwater which is "trapped" at the greater depths (>120 m) due to the developed aquitards with limited or negligible recharge.

Magnesium enrichment in groundwater is attributed to two different sources, namely the weathering of ultrabasic formations and the dedolomitization of dolostones, which act jointly, but yet it is difficult to distinguish them and quantify their individual impact. However, a rough assessment of their contribution is performed by the (Ca + Mg) versus ($\text{HCO}_3 + \text{SO}_4$) plot (Fig. 6) and the $r\text{Mg}/\text{Ca}$ values which show that the dominant process in Mg enrichment is related to dolostones. Specifically, dedolomitization is referred as a

common geochemical process in similar environments (Szynkiewicz et al. 2012) in which the dissolution of gypsum and anhydrite leads to dolomite dissolution and replacement with calcite.

In addition, the impact of the ultrabasic blocks hosted in the schists of *mélange* is identified by FA2; the process is controlled by the slow dissolution of olivine which produces silica, bicarbonates and magnesium by the reaction(s):



Accordingly, FA2 identifies manganese influence, which is probably related to the dissolution of pyroxenes hosted on the matrix of ultrabasic blocks and, elevated EC values indicate that these waters are not fresh with limited or negligible recharge, leading to excess of dissolved contents.

Based on the geological evidences and the results of FA3, the Cr which is hosted in the matrix of the geological substrate undergoes redox transformations that impact groundwater; even though it is not documented by chemical analyses, it is regarded that the existing Cr concentrations should be in the hexavalent form, likewise reported in neighboring catchments (e.g., Tziritis et al. 2012) with similar geological characteristics. Alike with the study area, elevated Cr(VI) concentrations in groundwater have been reported in catchments with weathered products of ultramafic formations, these products are usually obtained from the oxidation of Cr(III), due to the catalytic action of Mn oxides (Eary and Rai 1997; Oze et al. 2007) such as pyrolusite (MnO_2). The covariance of Cr with NO_3 is probably not related to a common process, but is likely the result of their random coexistence in the plain areas of Kopaida basin, due to different processes. As a matter of fact, Cr dissolution from the stable Cr-bearing mineralogical phases (e.g., chromite) which are hosted in the parent ultrabasic rocks is a very slow process; on the contrast, the weathered products of these parent rocks contain unstable mineralogical phases (e.g., serpentinites) which favor dissolution and subsequent enrichment of Cr in soils and eventually in groundwater due to leaching. These weathered products are abundant in the plain areas as a result of surface runoff. Similarly, nitrate concentrations are elevated in plain areas due to the existing land-use activities (intensive agriculture) that favor excessive use of nitrogen fertilizers.

It should also be noticed that NO_3 concentrations are abruptly decreased locally, even between adjacent boreholes, which have significant deviations to their nitrates content. This phenomenon has been previously reported for the study area (Tziritis 2009) and is probably attributed to the locally developed anoxic conditions that favor the depletion of potential reductants like nitrates, with a simultaneous increase in the concentrations of Fe^{2+} and Mn^{2+} . As a result, groundwater is enriched in ferrous iron and depleted in nitrates, a fact that explains sufficiently the anomalies in NO_3 spatial distribution and is identified by FA5.

The impact of Zn and Cu which are reflected in FA 6 is possibly attributed to soil amendments and/or agrochemicals that contain impurities of the aforementioned metals. The contribution of Cd that was traced in surface water samples and is related with agrochemicals is probably negligible due to its limited mobility in groundwaters.

5.2 Hydrodynamic Characteristics and Isotopic Signatures

In order to identify the hydrodynamic characteristics of groundwater, the samples were classified according to their ionic composition (Frazee 1982; Voutsis et al. 2015). Results revealed the existence of eight major groups, which are shown in the Piper diagram of Fig. 7, and are described in Table 2; group B dominates with nearly half of the samples ($n = 30, 58\%$), followed by group C ($n = 8, 15\%$). The remaining groups include only few samples (groups A, D, E, F and G) and some individuals (groups A and H). The distribution of water groups in the GW focal area is shown in Fig. 8.

Water types A, B and F are the source waters in eastern Kopaıda basin. Group A waters are characterized as “fresh recharge waters” derived from precipitation and interaction with aquifer matrix, principally karst. Similarly, waters belonging to group B are enriched in magnesium and characterized as “fresh recharge waters” belonging to a solution mix between two end members (Ca–Mg) affected by limestone and dolomitic/ultrabasic formations. Similar to groups A and B may be considered the group type F, which reflects the recharge waters related to the direct impact from Mg-rich formations. The spatial distribution of these samples is chiefly over or near the outcrops of the bedrock, which

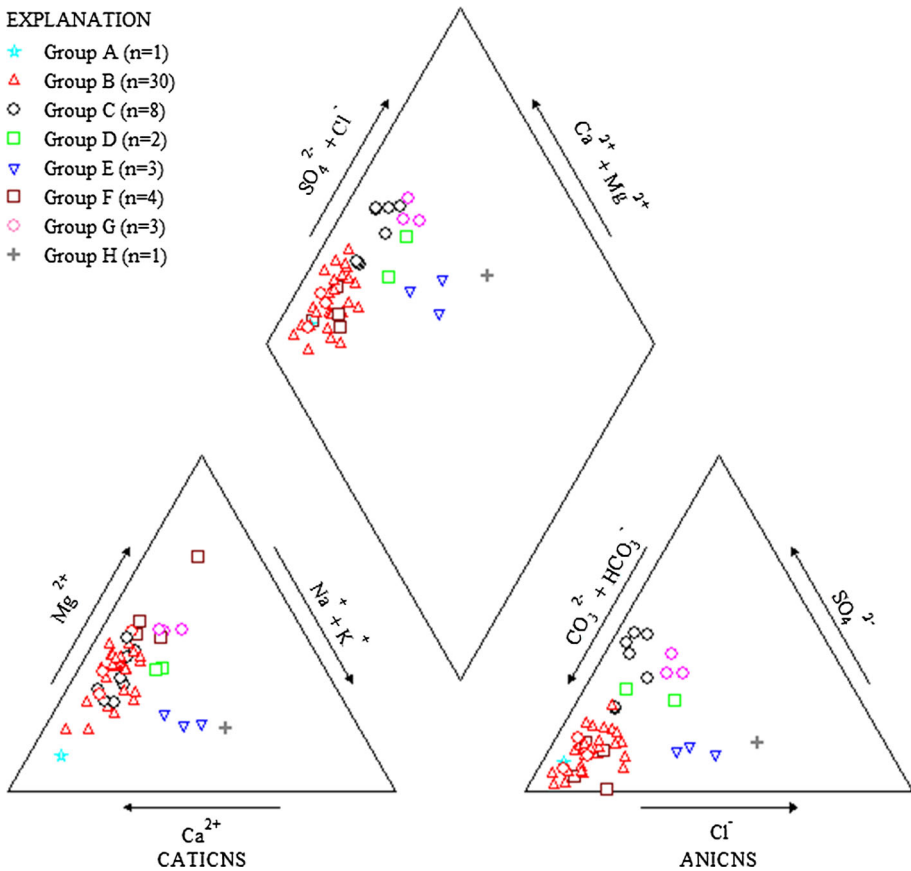


Fig. 7 Piper diagram for the groundwater samples of the study area

Table 2 Water types of groundwater samples and relative characterization, based on Frazee (1982) facies classification and modified by Voutsis et al. (2015)

Hydrochemical type	Samples	Group	Characterization
Ca–HCO ₃	1	A	Fresh recharge waters rich in Ca
Ca–Mg–HCO ₃	30	B	Fresh recharge waters rich in Ca
Ca–Mg–HCO ₃ –SO ₄ Ca–Mg–SO ₄ –HCO ₃	8	C	Transitional (intermediate) waters
Ca–Mg–Na–HCO ₃ –Cl–SO ₄ Ca–Mg–Na–HCO ₃ –SO ₄	2	D	Transitional (intermediate) waters
Ca–Na–Mg–Cl–HCO ₃ Ca–Na–Mg–HCO ₃ –Cl	3	E	Transitional (intermediate) waters
Mg–Ca–HCO ₃ Mg–HCO ₃	4	F	Fresh recharge waters rich in Mg
Mg–Ca–HCO ₃ –SO ₄ Mg–Ca–Na–HCO ₃ –SO ₄ –Cl Mg–Ca–SO ₄ –HCO ₃	3	G	Transitional (intermediate) waters
Na–Ca–Mg–Cl–HCO ₃	1	H	Relict seawater

practically relate them with direct recharge conditions and short residence time and water–rock interaction.

Groups C, D, E and G are characterized as “transitional (intermediate) waters” which according to Frazee (1982) and Voutsis et al. (2015) are evolving by geochemical reactions with aquifer matrix, or waters that changed their geochemical character by mixing with other geochemically distinct waters. Group C waters include the inherent geochemical characteristics of the dominant types (A and B) but are affected by secondary geochemical processes, like redox transformations, as denoted by the contribution of sulfates probably due to pyrite oxidation which is reported locally (Tziritis 2009). Group D is similar to group C but with profound contribution from sodium and chlorides; the two samples are spatially related and probably reflect the impact from irrigation water return flow or soil amendments (e.g., Na₂SO₄). Waters of Group E have higher ionic strength and greater contribution of sodium as a result of longer residence time, intermixing, different aquifer or unsaturated zone matrix or finally ongoing geochemical processes like ion exchange. Their spatial distribution is mainly located in areas of deep water table that justifies the profound impact of long residence time and water–rock interaction. Group G waters are similarly characterized as “transitional waters” but with no significant impact from magnesium, hence related to recharge water types like those of group F. Finally, the individual sample of group I based on Frazee (1982) classification may be theoretically regarded as a “relict” connate water sample, probably trapped during the diagenetic processes in a previous geological time; however, the salinization effect is possible to be supplemented also by irrigation water return flow due to the followed irrigation practices of the cultivated plain areas. In accordance with the above, samples of group E seem to be affected by the intermixing with more saline waters (e.g., similar to group H) and define a hypothetical intermixing plume along the boreholes G8, G16 and G49 at the southern of the basin (Vayia sub-basin).

In respect to isotopic signatures, the wide range of $\delta^{18}\text{O}$ groundwater values indicates the occurrence of a heterogeneous aquifer system in its lateral extent, possibly due to

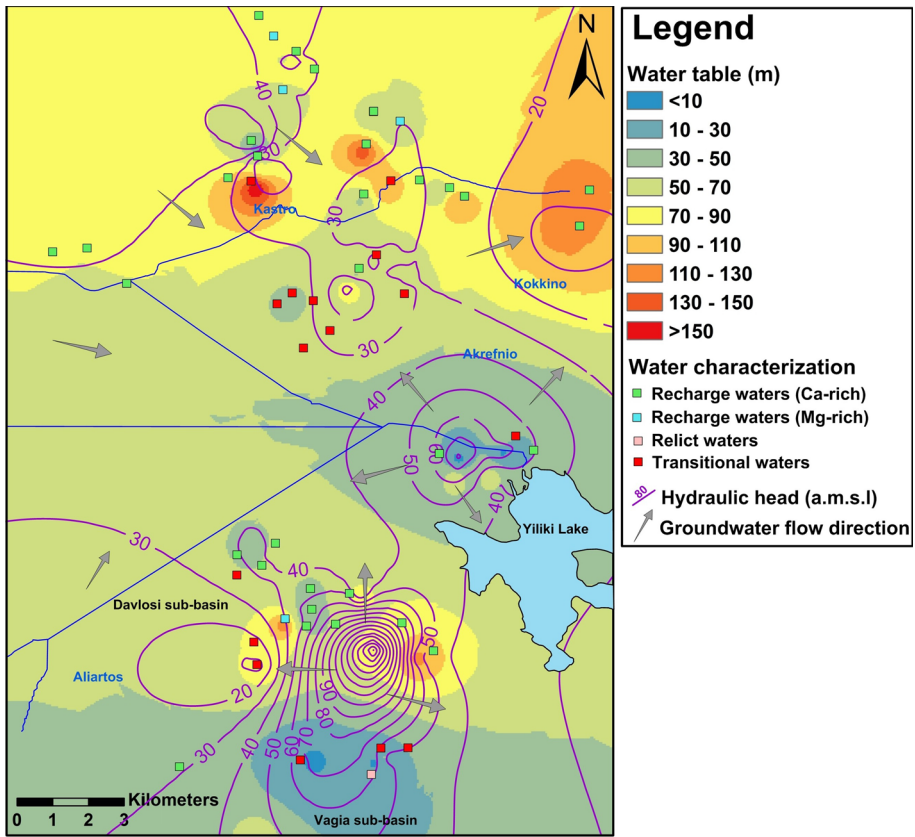


Fig. 8 Piezometric level of aquifer systems and groundwater follow in the study area, along with the hydrodynamic characterization of samples

complex stratigraphy and tectonics, a fact which is in accordance with the geological and hydrogeological setting of the area. Assuming as Local Meteoric Water Line (LMWL) of the study area ($\delta D = 5.6 \delta^{18}O - 1.2$) the one reported for central Greece by Dotsika et al. (2010a), it can be assessed that it is nearly parallel to LGIL (Fig. 5). However, a significant shift between LGIL and LMWL is noticed; this is likely attributed to the relative enrichment of $\delta^{18}O$ and δD that causes different deuterium excess (d-excess) values, as described in similar cases by Gat (2010). Deuterium excess is usually considered as a conservative property in the part of the atmospheric water cycle beginning with water vapor formation by evaporation to rainfall just below cloud level (Ciais and Jouzel 1994). Variations in 'd-excess' could arise due to varying temperature, relative humidity and wind speed at the sea surface where atmospheric moisture mainly originates, and from the admixture of recycled continental vapor (Dotsika et al. 2010b). Negrel et al. (2011) report that 'd-excess' values lower than 5 suggest significant evaporation of rainwater, leaving the residual groundwater with lower values and enriched $\delta^{18}O$. Based on the d-excess values of LWML, LGIL and LSWIL for the study area, it may be assumed that evaporation is a major factor for isotopic composition of water resources; however, it should be noted that also other factors seem to control isotope composition of meteoric water such as the altitude of the recharge area, the temperature of formation (different temperatures during

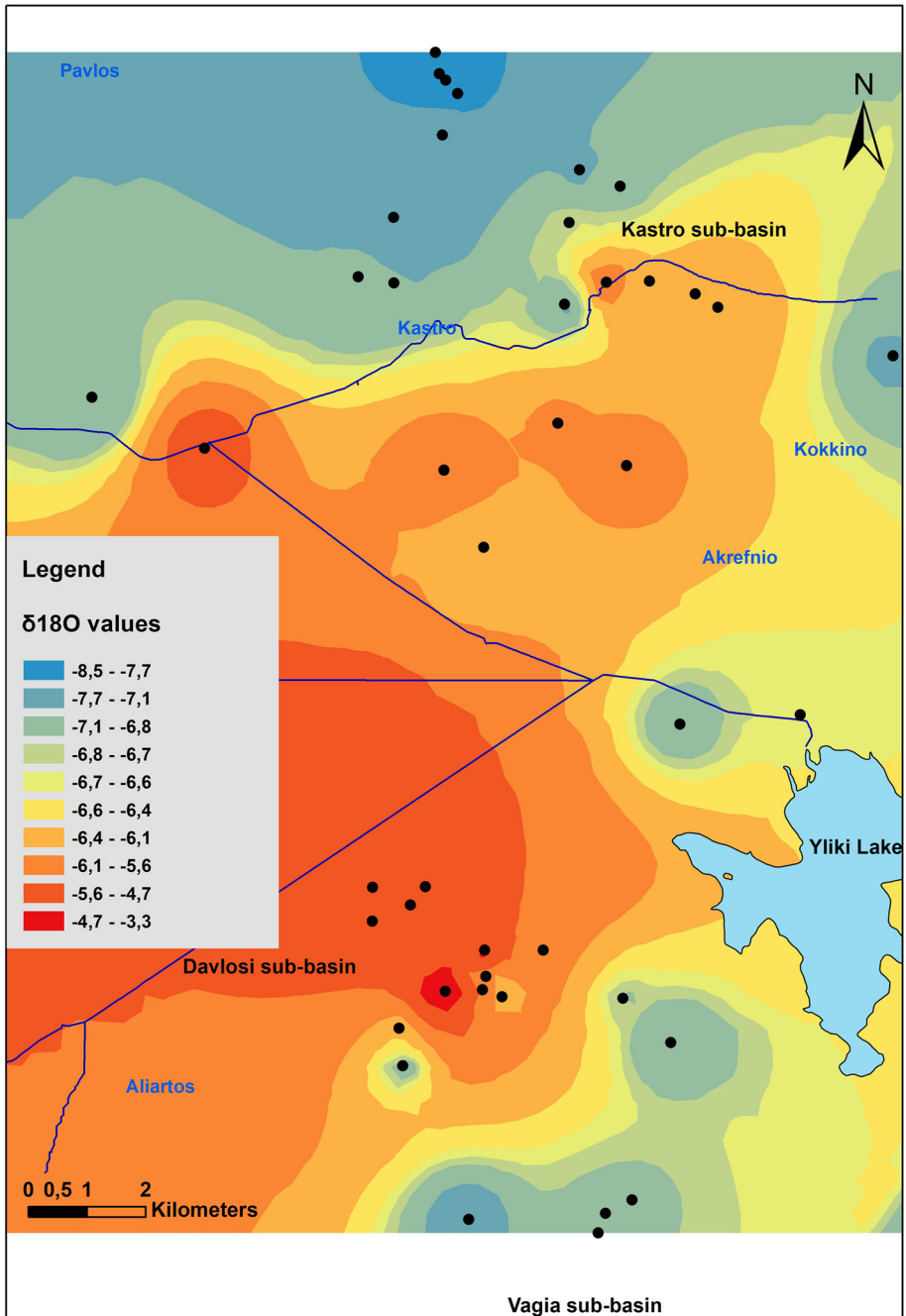


Fig. 9 Interpolation of $\delta^{18}\text{O}$ values for groundwater samples

winter and summer precipitation will involve different isotope fractionations), etc., as well as the slow percolation rates of the unsaturated soils that cause enrichment of $\delta^{18}\text{O}$ in groundwater.

As may be deduced by Fig. 5, LGIL and DNIL appear a relative identity for a range of values (e.g., $\delta^{18}\text{O} < -7\text{‰}$ and $\delta\text{D} < -45\text{‰}$) a possible intermixing between streams and groundwaters due to the developed hydraulic connection of the riverbeds with the aquifer systems, where alluvial thickness is low and/or karstic substrate is near surface; the shift between these two lines is probably attributed to the increased evaporation of surface waters. Based on the plot of Yliki samples which fall near and/or over the LGIL is assumed a possible hydraulic interaction through the extensively developed karstic network of sinkholes and katavothraes at the eastern part of the basin. In contrast, the hydraulic connection of the drainage network and Lake Yliki through the discharge of Viotikos Kifissos River, although existing, is not verified by the isotopic results. A possible explanation to this may be the decreased flow of Viotikos Kifissos River, especially during dry hydrological periods, compared with the significant evaporation rates of Yliki Lake.

In order to delineate the possible groundwater pathways in the GW focal area (Fig. 9), isotopic values of $\delta^{18}\text{O}$ were interpolated with the use of IDW algorithm through GIS software (ArcGIS 10.2). Interpolation classes were selected according to statistical criteria (geometric mean) which ensures representativeness and identification of real patterns instead of interpolation artifacts, if for example random classes were used (e.g., equal interval of -1‰). The spatial distribution of $\delta^{18}\text{O}$ values revealed two main aquifer recharge areas at the southern and at the northern parts of the basin. This assessment is in compliance with the findings of the hydrodynamic characterization of Table 2, as the northern part (NW of Kastro sub-basin) has been already delineated as a recharge area. Therefore, the initial assessment for the recharge areas is confirmed and validated by the joint use of two different methodologies. In contrast, at the southern part (Vayia sub-basin) even though the isotopic composition denotes groundwater recharge, the hydrogeochemical signatures based on Na, Cl and EC values reveal an ongoing salinization process. Increasing levels of Na, Cl and EC in groundwater with no significant change in $\delta^{18}\text{O}$ could possibly be attributed to leaching of surface/subsurface salts and irrigation water return flow, a fact which is highlighted by the results of multivariate statistical analysis.

The enriched isotopic values (-5.6 to -3.3‰) are located in the central part of the basin and their spatial extension follows the relief of the plain areas (Davlosi and Kastro sub-basins) which are consisted of high thickness Quaternary deposits with low hydraulic conductivity and limited percolation potential; thus, infiltration is achieved through low velocities. These conditions favor evaporation of precipitates during the percolation through soils. In addition to slow percolation rates, the isotopic enrichment for the central parts of the basin is also attributed to the recharge from the upward hydrogeological systems of Viotikos Kifissos River (median route). The recharge groundwaters of the median route are characterized by greater transient times which progressively lead to isotopic enrichment.

Individual “hot-spots” of rather enriched values compared to others are likely related to deeper aquifer systems and the prevalence of strong anoxic conditions followed by limited recharge and long residence times (e.g., Davlosi area), which are in compliance with the aforementioned hydrogeological, hydrogeochemical and multivariate statistical analysis. These groundwaters may be considered, under circumstances, as potential paleowaters that are characterized by isotopic enrichment and a smaller d-excess value. On the contrary, at the outcrops of the karstic substrate between Lake Yliki and Kopaida plain, where karstification favors direct infiltration with high velocities, the isotopic composition is relatively depleted and resembles this of meteoric water. Abrupt variations of isotopic values

between adjacent sampling points show the occurrence of steep hydrogeological boundaries. As a result, the aquifer system is rather heterogeneous in places, due to the development of aquitards which are attributed to the complicated stratigraphy and tectonics; practically, this heterogeneity develops locally isolated areas of different hydrogeological and hydrogeochemical conditions (e.g., SW of Davlosi and NW of Kastro sub-basins).

6 Conclusions

Joint assessments and compilation of variable data through different methodologies, including hydrogeological and hydrogeochemical evaluations, multivariate statistics and stable isotope analyses, provided significant information about the hydrogeochemistry and hydrodynamics of Kopaida basin, which can be summarized to the following:

- Hydrogeochemistry of groundwaters is affected both by the natural geological background and the impact of the extensive agricultural practices. Dominant geogenic factors include the karstic substrate and the occurrence of Fe–Ni-rich geological formations, including laterites and ultrabasic serpentized blocks; anthropogenic factors include the impact of irrigation water return flow and nitrogen excess due to the application of N-fertilizers and manure disposal. However, significant changes in the hydrogeochemical regime should be attributed to secondary redox processes, which create local areas of strong reducing conditions.
- Hydrogeochemistry of surface waters varies depending on the examined water bodies. In general, drainage network exhibits a relative enrichment in ions progressively along its route. Locally were identified relative enrichments in Zn and Cd, as a result of surface runoff which contains an excessive amount of agrochemicals. Lake Yliki exhibits normal values for natural surface waters, denoting negligible environmental pressure from the intense agricultural activities of the adjacent basin.
- Multivariate statistical analysis of groundwater samples confirmed the predominance of the aforementioned geogenic and anthropogenic factors. Factor analysis denoted the existence of supplementary geochemical processes affecting overall hydrogeochemical signatures, like redox reactions that favor anoxic conditions in accordance with NO_3 depletion and increment in Fe^{2+} , Mn^{2+} and SO_4 values. Additionally, the mobility and occurrence of Cr in groundwaters is chiefly driven by the catalytic action of MnO_2 hosted in soils and the overall redox conditions of the saturated zone.
- The hydrogeological information supplemented by the hydrogeochemical signatures of groundwater based on molar ratios and definition of hydrochemical water types revealed two main recharge areas. “Hot-spots” of possible formation waters were also identified and associated with deeper aquifers of limited recharge and residence time.
- Isotopic assessments supplemented the hydrogeochemical and statistical outcomes for groundwater and delineated the areas of recharge based on their relative isotopic depletion. The hydrodynamics of the complex aquifer system were identified by the definition of two main groundwater flux pathways; the first is related to direct infiltration and recharge with fresh water from the areas northern and southern of eastern Kopaida basin; the second is related with the hydraulic connection with the median route of VKR, which recharges Kopaida through its central parts, containing groundwater of long residence time, isotopic enrichment and probably elevated values of NO_3 .

- The wide range of $\delta^{18}\text{O}$ groundwater values indicates the occurrence of heterogeneous aquifer systems in their lateral extent, due to complex stratigraphy and tectonics. Comparison of $\delta^{18}\text{O}$ versus δD plots for all surface and groundwater water systems revealed a hydraulic interaction between them, through the developed karstic network and/or the riverbeds of higher permeabilities, whereas the low thickness of alluvial deposits occurs.

The integrated conceptual approach of diverse, yet cross-engaged, methodologies was applied successfully for the identification of hydrogeochemical and hydrodynamical assessments in the case of a heterogeneous karstic basin; evaluations were confirmed and supplemented when needed, hence providing critical information for strategic planning and overall water resources management for the area.

Appendix A: Chemical and Isotope Composition of Groundwater Samples

Sample	pH	EC μS/cm	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Si mg/L	Cl mg/L	NO ₃ mg/L	SO ₄ mg/L	PO ₄ mg/L
G1	7.9	960	151.5	54.0	1.6	43.6	7.5	29.4	65.5	229.5	0.5
G2	7	850	97.7	36.5	2.0	24.4	7.0	25.2	22.1	75.0	0.1
G3	7.5	700	69.4	36.5	1.7	40.2	5.8	21.9	4.0	84.0	0.2
G4	7	870	130.7	39.2	2.2	19.2	7.0	35.5	55.3	112.0	0.3
G5	7.6	580	95.3	15.4	0.8	16.9	10.5	7.8	24.8	13.4	0.1
G6	7.6	960	81.5	24.7	11.6	86.6	5.8	102.7	21.9	51.5	1.2
G7	7.6	510	86.3	20.7	1.3	20.6	5.5	17.1	27.9	15.3	0.7
G8	7.7	560	91.2	20.5	1.4	25.7	6.0	18.5	21.9	15.9	0.1
G9	7.6	610	75.5	22.7	2.4	29.2	6.1	12.8	37.9	31.6	0.1
G10	7.9	680	97.8	32.4	1.8	30.1	8.0	13.9	51.6	46.8	0.2
G11	7.5	720	102.5	27.1	2.4	28.0	8.4	18.5	20.6	164.0	0.1
G12	7.3	990	158.9	42.4	3.6	32.2	8.9	22.0	3.5	285.0	0.7
G13	8	820	111.4	56.5	2.3	9.0	8.2	13.2	5.1	61.0	0.1
G14	8.1	670	85.9	24.6	2.7	58.0	4.6	70.1	27.4	35.0	0.2
G15	7.9	610	81.3	35.4	1.2	19.7	9.5	18.0	64.6	26.4	0.4
G16	7.9	670	77.4	33.1	2.4	20.2	7.5	16.4	27.9	36.9	0.2
G17	8.2	1210	108.6	87.6	2.0	57.0	8.7	85.6	24.1	216.5	0.2
G18	7.9	680	91.8	39.2	1.7	24.9	6.9	19.9	27.7	38.9	0.4
G19	8.2	1300	95.4	90.2	1.8	72.9	8.2	123.6	7.3	256.0	0.2
G20	8.2	570	59.1	43.9	1.0	13.8	10.4	19.2	19.5	11.0	0.2
G21	8.1	600	81.4	40.3	1.5	28.1	7.8	28.4	16.6	31.5	0.2
G22	8.3	980	37.8	99.4	1.2	38.2	16.4	28.0	54.9	63.5	0.4
G23	7.9	830	91.6	51.1	1.4	26.9	6.9	28.8	39.4	87.0	0.3
G24	7.3	330	77.7	37.9	1.4	18.8	9.7	26.0	27.9	81.0	0.4
G25	7.8	650	99.7	42.7	1.4	19.0	11.1	19.4	32.8	40.5	0.3
G26	8.1	770	80.8	43.2	1.0	28.0	12.4	27.3	42.1	51.0	0.4
G27	7.9	690	113.1	27.1	1.7	13.1	6.8	18.0	29.7	64.0	0.2
G28	7.8	880	138.0	21.8	2.2	21.0	7.2	16.2	48.3	32.0	0.3

Sample	pH	EC μS/cm	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Si mg/L	Cl mg/L	NO ₃ mg/L	SO ₄ mg/L	PO ₄ mg/L
G29	8.1	600	81.7	38.3	1.4	11.2	6.6	19.0	14.6	7.0	0.4
G30	7.9	680	102.9	43.0	1.8	18.3	10.0	23.0	30.5	36.0	0.2
G31	8.1	560	91.6	34.7	1.1	10.4	6.5	12.0	19.0	5.0	0.3
G32	8	750	88.1	50.1	1.0	19.6	6.4	43.0	46.0	48.0	0.1
G33	8.2	590	82.1	37.7	0.8	12.2	6.5	24.0	27.4	14.0	0.1
G34	7.9	670	84.7	45.8	1.5	24.3	6.0	36.0	16.4	24.0	0.2
G35	8	700	76.7	50.0	1.1	18.7	6.8	33.0	37.6	37.0	0.2
G36	8.3	680	92.0	31.1	2.7	35.1	7.7	50.0	19.9	21.0	0.1
G37	7.5	800	138.0	38.6	2.2	22.6	10.6	27.0	77.5	63.0	0.2
G38	7.5	580	89.5	31.8	1.9	13.6	5.9	16.0	10.2	16.0	0.1
G39	7.8	830	79.6	58.6	2.8	37.7	11.9	59.0	3.5	2.0	0.1
G40	7.7	580	91.5	26.3	1.4	14.5	7.7	20.0	26.6	27.0	0.1
G41	7.4	720	112.4	42.2	2.0	14.0	7.9	18.0	6.2	64.0	1.1
G42	7.8	1000	125.8	81.5	4.6	24.3	14.3	23.0	3.1	32.0	0.2
G43	7.3	1090	136.1	80.6	4.3	25.2	15.5	24.0	2.7	326.0	0.2
G44	7.9	1130	95.2	32.4	7.7	145.0	6.5	191.0	19.9	71.0	0.1
G45	7.6	920	101.1	26.8	4.8	88.9	6.0	143.0	21.7	49.0	0.1
G46	7.7	680	162.0	23.7	1.3	13.6	5.4	45.0	12.0	52.3	0.8
G47	7.8	530	81.6	33.9	1.4	14.3	6.3	28.0	13.3	43.6	0.8
G48	7.6	610	81.2	38.6	1.5	16.1	6.9	28.0	15.9	38.9	0.2
G49	7.8	590	81.1	34.3	1.1	13.7	6.9	23.0	16.8	16.0	0.3
G50	7.7	620	96.8	43.9	1.6	16.1	9.8	26.0	27.0	43.0	0.5
G51	7.9	1220	112.4	89.8	1.9	53.0	8.5	86.0	24.8	271.0	0.1
G52	7.4	1160	126.5	63.7	2.2	67.2	7.7	117.0	7.5	169.0	0.2
Min	7.0	330	38	15	1	9	5	8	3	2	0.1
Max	8.3	1300	162	99	12	145	16	191	78	326	1
Median	7.8	685	92	38	2	23	7	25	23	43	0
SD	0.31	208.6	24.4	19.5	1.8	24.7	2.5	37.1	17.3	78.5	0.2
Sample	HCO ₃ mg/L	Cd μg/L	Cr μg/L	Cu μg/L	Fe μg/L	Mn μg/L	Ni μg/L	Pb μg/L	Zn μg/L	δ ¹⁸ O VSMOW	δ ² H
G1	282.0	1.0	2.0	2.0	3.0	8.0	4.0	<0.5	50.0	-6.6	-42.8
G2	250.0	<0.5	<0.5	3.0	2.0	5.0	1.0	<0.5	11.0	n/a	n/a
G3	205.0	<0.5	<0.5	4.0	3.0	14.0	<0.5	2.0	5.0	n/a	n/a
G4	220.0	<0.5	1.0	5.0	13.0	1.0	6.0	1.0	19.0	n/a	n/a
G5	277.0	<0.5	3.0	11.0	1.0	1.0	8.0	1.0	110.0	n/a	n/a
G6	253.0	<0.5	2.0	6.0	4.0	2.0	2.0	<0.5	12.0	-6.9	-43.9
G7	220.0	2.0	1.0	5.0	5.0	5.0	2.0	2.0	27.0	-7.2	-45.8
G8	250.0	<0.5	1.0	2.0	13.0	1.0	1.0	1.0	8.0	-6.9	-43.9
G9	273.0	1.0	1.0	6.0	3.0	37.0	1.0	<0.5	366.0	-7.2	-45.8
G10	224.0	1.0	2.0	5.0	6.0	3.0	1.0	1.0	8.0	-6.8	-45.4
G11	269.0	1.0	1.0	5.0	2.0	260.0	5.0	<0.5	64.0	-6.2	-41.8
G12	370.0	<0.5	2.0	1.0	550.0	380.0	1.0	<0.5	6.0	-6.4	-43.4
G13	284.0	<0.5	<0.5	2.0	3.0	750.0	6.0	1.0	15.0	-7.1	-46.3

Sample	HCO ₃ mg/L	Cd μg/L	Cr μg/L	Cu μg/L	Fe μg/L	Mn μg/L	Ni μg/L	Pb μg/L	Zn μg/L	δ ¹⁸ O VSMOW	δ ² H
G14	200.0	<0.5	5.0	2.0	24.0	1.0	1.0	1.0	37.0	-6.3	-42.5
G15	245.0	<0.5	6.0	2.0	<0.5	1.0	<0.5	<0.5	22.0	-5.3	-37.1
G16	278.0	<0.5	2.0	4.0	4.0	3.0	8.0	<0.5	57.0	-7.5	-48.5
G17	361.0	1.0	2.0	5.0	3.0	1.0	3.0	<0.5	13.0	-7.0	-45.8
G18	306.0	1.0	3.0	2.0	4.0	2.0	2.0	2.0	221.0	-6.0	-41.1
G19	391.0	2.0	1.0	2.0	20.0	24.0	2.0	<0.5	210.0	n/a	n/a
G20	260.0	3.0	5.0	6.0	8.0	1.0	1.0	1.0	142.0	-5.1	-36.4
G21	273.0	2.0	8.0	2.0	20.0	3.0	14.0	1.0	20.0	-5.7	-39.8
G22	428.0	6.0	33.0	2.0	2.0	1.0	1.0	<0.5	15.0	-8.4	-53.5
G23	287.0	2.0	5.0	4.0	6.0	3.0	2.0	<0.5	80.0	-7.1	-46.5
G24	256.0	<0.5	15.0	1.0	<0.5	<0.5	<0.5	<0.5	26.0	-8.2	-51.8
G25	295.0	<0.5	12.0	4.0	15.0	2.0	2.0	1.0	16.0	-8.0	-50.2
G26	241.0	<0.5	6.0	3.0	3.0	2.0	4.0	<0.5	20.0	-7.1	-50.6
G27	206.0	<0.5	<0.5	5.0	<0.5	2.0	<0.5	<0.5	17.0	-7.1	-46.5
G28	404.0	<0.5	2.0	2.0	4.0	1.0	1.0	<0.5	21.0	-7.2	-47.6
G29	307.0	1.0	9.0	4.0	158.0	1.0	0.0	<0.5	26.0	-7.5	-52.6
G30	277.0	1.0	6.0	7.0	51.0	4.0	1.0	<0.5	16.0	-7.9	-51.6
G31	301.0	<0.5	6.0	6.0	3.0	<0.5	<0.5	<0.5	20.0	n/a	n/a
G32	285.0	2.0	5.0	3.0	152.0	1.0	1.0	<0.5	31.0	-7.2	-47.6
G33	274.0	<0.5	4.0	11.0	151.0	<0.5	<0.5	<0.5	13.0	-7.9	-50.4
G34	205.0	2.0	6.0	2.0	129.0	4.0	2.0	<0.5	49.0	n/a	n/a
G35	290.0	2.0	4.0	6.0	147.0	1.0	<0.5	<0.5	48.0	-7.0	-45.8
G36	277.0	8.0	5.0	3.0	202.0	1.0	1.0	<0.5	63.0	-6.7	-43.0
G37	295.0	<0.5	5.0	11.0	30.0	2.0	1.0	2.0	56.0	-7.2	-46.9
G38	293.0	4.0	1.0	1.0	154.0	<0.5	<0.5	<0.5	10.0	-7.2	-46.4
G39	383.0	4.0	1.0	2.0	162.0	85.0	1.0	1.0	77.0	-6.9	-45.6
G40	254.0	2.0	3.0	2.0	235.0	1.0	<0.5	<0.5	274.0	-6.7	-44.4
G41	405.0	3.0	1.0	2.0	220.0	301.0	3.0	<0.5	12.0	-5.8	-39.8
G42	532.0	3.0	1.0	2.0	263.0	252.0	3.0	<0.5	13.0	-4.3	-31.8
G43	481.0	2.0	1.0	2.0	818.0	285.0	<0.5	<0.5	15.0	-3.3	-26.2
G44	205.0	<0.5	3.0	3.0	6.0	1.0	1.0	<0.5	20.0	-6.5	-41.6
G45	256.0	1.0	2.0	2.0	211.0	1.0	<0.5	<0.5	21.0	-5.6	-37.9
G46	331.0	42.0	16.0	5.0	245.0	6.0	6.0	1.0	424.0	-4.0	-29.7
G47	220.0	4.0	10.0	2.0	218.0	1.0	<0.5	1.0	61.0	-5.4	-36.8
G48	282.0	1.0	2.0	1.0	132.0	<0.5	<0.5	<0.5	8.0	-6.8	-43.9
G49	280.0	2.0	3.0	3.0	17.0	1.0	<0.5	<0.5	35.0	-6.9	-46.4
G50	272.0	1.0	7.0	2.0	184.0	4.0	1.0	<0.5	9.0	-7.3	-46.1
G51	348.0	1.0	2.0	4.0	5.0	1.0	3.0	<0.5	25.0	-6.8	-44.2
G52	381.0	1.0	1.0	2.0	236.0	72.0	1.0	<0.5	109.0	-6.0	-40.2
Min	200	<0.5	<0.5	1	<0.5	<0.5	<0.5	<0.5	5	-8.4	-53.5
Max	532	42	33	11	818	750	14	2	424	-3.3	-26.2
Median	278	2	3	3	17	2	2	1	21.5	-6.9	-45.4
SD	70.9	7.2	5.5	2.4	153	139	2.8	0.4	88.2	1.1	5.7

Appendix B: Chemical and Isotope Composition of Surface Water Samples

Sample	pH	EC μS/cm	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Si mg/L	Cl mg/L	NO ₃ mg/L	SO ₄ mg/L	HCO ₃ mg/L
S1	8.2	450	72.9	28.1	1.7	17.3	2.4	7.5	9.1	31.0	210.0
S2	8.2	415	50.6	23.2	1.3	11.8	1.9	8.6	9.3	23.2	185.0
S3	8.2	690	64.0	7.7	41.0	51.0	n/a	62.0	6.6	13.3	230.0
S4	8.2	540	52.5	16.7	0.9	19.5	3.0	3.1	15.1	9.3	223.0
S5	8.2	430	79.0	21.0	0.9	10.0	n/a	2.4	14.2	8.5	210.0
S6	8.1	460	66.7	22.7	1.1	12.1	4.7	11.9	5.8	32.0	228.0
S7	8.3	480	51.5	32.1	2.0	27.5	n/a	9.7	9.3	21.4	270.0
S8	8.3	370	28.0	22.8	2.6	53.0	n/a	16.2	7.1	33.0	162.0
S9	8.4	420	54.5	21.4	0.9	48.5	n/a	4.2	11.7	23.1	161.0
S10	8.2	370	43.0	15.3	2.4	35.5	n/a	9.2	7.3	36.6	110.0
S11	8.3	340	31.7	26.5	1.1	15.4	n/a	19.0	5.3	46.6	135.0
S12	8.4	370	47.0	24.9	1.6	47.0	1.4	10.5	8.4	40.1	202.0
S13	8.4	430	41.5	26.1	1.9	30.5	n/a	7.4	9.1	38.7	205.0
S14	8.1	510	85.9	12.1	2.5	12.1	n/a	11.0	6.2	23.9	253.0
S15	8.4	150	62.0	8.6	1.6	56.0	n/a	8.4	10.2	36.1	200.0
S16	8.1	530	59.0	13.0	2.9	31.0	5.2	6.2	12.0	36.6	220.0
S17	8.2	320	43.0	17.1	1.8	36.0	n/a	11.9	6.2	46.8	135.0
S18	8.1	310	76.0	17.6	1.9	40.0	n/a	11.7	4.9	50.4	131.0
S19	8.3	340	29.0	17.2	2.0	42.0	n/a	12.4	5.8	41.1	124.0
S20	8.4	310	33.0	18.1	1.8	38.0	n/a	11.9	5.3	40.5	130.0
S21	8.4	310	30.0	18.3	1.9	34.0	n/a	12.1	6.2	42.0	122.0
S22	8.4	330	29.0	16.9	1.9	41.0	n/a	12.1	5.8	41.6	124.0
S23	8.4	340	31.0	17.5	1.8	37.0	n/a	11.9	5.8	40.4	123.0
S24	8.5	300	32.0	19.0	1.9	40.0	n/a	12.8	5.3	41.9	124.0
S25	8.4	320	65.0	17.9	1.8	43.0	n/a	12.0	6.6	42.4	131.0
S26	8.4	320	31.0	16.2	1.9	48.0	n/a	12.7	4.9	41.5	145.0
S27	8.3	300	34.0	19.0	1.9	45.0	n/a	11.6	5.8	42.6	135.0
S28	8.3	310	35.0	18.8	1.9	53.0	n/a	10.9	4.9	41.8	130.0
S29	8.4	290	30.0	18.2	1.9	41.0	n/a	11.3	5.8	41.8	118.0
S30	8.3	300	32.5	23.0	1.7	12.1	1.7	17.0	6.2	44.2	113.0
Min	8.1	150	28	7.7	0.9	10	1.4	2.4	4.9	8.5	110
Max	8.5	690	85.9	32.1	41	56	5.2	62	15.1	50.4	270
Median	8.3	340	43	18	2	38	2	12	6	40	140
SD	0.12	120	18.3	5.9	9.5	14.8	1.5	13.1	3.0	11.9	50.3
Sample	Cd μg/L	Cr μg/L	Cu μg/L	Fe μg/L	Mn μg/L	Ni μg/L	Pb μg/L	Zn μg/L	δD VSMOW	δ ¹⁸ O	
S1	3.0	4.0	2.0	70.0	4.0	1.0	<0.5	19.0	-47.1	-7.2	
S2	4.0	2.0	3.0	75.0	2.0	2.0	1	26.0	-44.3	-6.5	

Sample	Cd μg/L	Cr μg/L	Cu μg/L	Fe μg/L	Mn μg/L	Ni μg/L	Pb μg/L	Zn μg/L	δD VSMOW	δ ¹⁸ O
S3	1.0	1.0	<0.5	79.0	150.0	7.0	<0.5	30.0	−38.3	−5.3
S4	1.0	4.0	<0.5	5.0	2.0	1.0	<0.5	19.5	−54.4	−8.4
S5	0.0	2.0	1.0	5.0	1.0	<0.5	<0.5	2.0	n/a	n/a
S6	3.0	3.0	1.0	74.0	3.0	2.0	<0.5	8.0	−42.0	−5.9
S7	1.0	7.0	1.0	15.0	46.0	3.0	<0.5	11.0	n/a	n/a
S8	1.0	<0.5	<0.5	7.0	1.0	5.0	<0.5	30.0	−31.8	−3.6
S9	<0.5	3.0	2.0	21.0	3.0	1.0	1	17.0	−50.0	−7.6
S10	<0.5	2.0	1.0	13.0	2.0	3.0	1	16.5	−48.2	−7.4
S11	<0.5	1.0	3.0	80.0	1.0	1.0	<0.5	37.0	−33.7	−4.1
S12	4.0	1.0	2.0	5.0	1.0	1.0	1	30.0	n/a	n/a
S13	1.0	2.0	1.0	9.0	1.0	2.0	<0.5	16.0	−42.6	−6.1
S14	2.0	1.0	1.0	219.0	38.0	1.0	<0.5	19.0	−53.6	−8.5
S15	2.0	2.0	<0.5	24.0	5.0	1.0	<0.5	30.0	n/a	n/a
S16	1.0	7.0	1.0	15.0	29.0	2.0	1	7.0	n/a	n/a
S17	<0.5	<0.5	1.0	5.0	4.0	<0.5	<0.5	18.0	n/a	n/a
S18	<0.5	2.0	1.0	5.0	1.0	<0.5	1	17.0	n/a	n/a
S19	<0.5	1.0	<0.5	0.0	1.0	<0.5	<0.5	20.0	−39.5	−5.9
S20	<0.5	0.0	<0.5	0.0	2.0	<0.5	<0.5	19.0	n/a	n/a
S21	<0.5	2.0	1.0	5.0	1.0	<0.5	<0.5	16.0	−39.0	−5.8
S22	<0.5	<0.5	1.0	<0.5	3.0	<0.5	<0.5	18.0	n/a	n/a
S23	1.0	<0.5	1.0	<0.5	1.0	<0.5	<0.5	12.0	n/a	n/a
S24	<0.5	<0.5	<0.5	2.0	1.0	<0.5	<0.5	18.0	−38.9	−5.8
S25	<0.5	<0.5	<0.5	1.0	3.0	1.0	1	18.0	n/a	n/a
S26	<0.5	2.0	1.0	5.0	2.0	<0.5	1	18.0	n/a	n/a
S27	<0.5	1.0	<0.5	<0.5	1.0	1.0	<0.5	17.0	−39.3	−5.9
S28	<0.5	1.0	2.0	5.0	1.0	1.0	1	18.0	−41.6	−5.9
S29	1.0	<0.5	1.0	<0.5	1.0	<0.5	<0.5	18.0	n/a	n/a
S30	2.0	3.0	2.0	5.0	2.0	11.0	<0.5	42.0	−41.1	−5.6
Min	<0.5	<0.5	1	<0.5	1	<0.5	<0.5	2	−54.4	−8.5
Max	4	7	3	219	150	11	1	42	−31.8	−3.6
Median	1	2	1	7	2	2	1	18	−41.6	−5.9
SD	1.2	1.9	0.7	58.6	36.6	3.1	0.0	9.5	6.8	1.5

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