



Hydrogeochemical baseline in a human-altered landscape of the central Pacific coast of Costa Rica

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Abstract Groundwater pollution in tropical and human-altered coastal landscapes is receiving novel attention due to decreasing in annual recharge as a consequence of recurrent droughts and overexploitation, whereby saline intrusion, point and diffuse source contamination, and water conflicts are common denominators. This study presents a detailed groundwater evaluation in a coastal aquifer within the central Pacific coast of Costa Rica. Three sampling campaigns including major ions, heavy metals, and fecal coliform

analyses were conducted between July 2013 and March 2014 across 17 wells within the alluvial and fissured units of the Jacó aquifer. The groundwater system is classified as mixed HCO_3^- - Ca^{2+} - Mg^{2+} type. Coliforms presence was found in two wells, nearby Mona Creek headwaters and near the coastal line. Heavy metal concentrations were below quantification limits in most of the wells; however, chromium concentrations up to 6.56 $\mu\text{g/L}$ were quantified within the coastal line and central portion of the alluvial aquifer in 20 out of the 48 samples. The spatial distribution of major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^-) exhibited an increasing trend towards the central portion of the alluvial aquifer,

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which may be potentially associated with the large unregulated urban expansion, invoking a need of a continuous water quality monitoring program in this touristic hot spot. This study provides useful information for other similar coastal aquifers in Central America, whereby increasing population growth and unregulated touristic, industrial, and agricultural activities are posing a truly challenge to ensure water security and sustainability parallel to the economic development in a changing climate.

Keywords Costa Rica · Human-altered tropical coastal aquifer · Hydrogeochemical processes · Water quality

Introduction

Coastal aquifers are an important water source for human development (Ferguson and Gleeson 2012; Michael et al. 2017). They represent a complex interface between oceanic and terrestrial aquatic ecosystems. The solute equilibrium between coastal freshwater aquifers, based on meteoric water recharge at high-elevation headwaters, and the oceanographic forcing is essential to sustain an important reaction zone, which is characterized by strong physical and chemical gradients (Vera et al. 2012). This reaction or mixing zone may strongly influence the oceanic cycling of trace elements and attenuate anthropogenic-related contaminants such as nutrients and trace metals (Moore 2010). However, in recent years, this equilibrium has been influenced by high freshwater abstraction due to increasing socio-economic activities (Dias et al. 2013; Isla 2013), causing seawater intrusion, a common denominator of coastal aquifers across the tropics (Petheram et al. 2008; Aris et al. 2010; Isa et al. 2012; Vera et al. 2012; Chandrasekar et al. 2014; Mangimbulude et al. 2016; Dieng et al. 2017; White and Kaplan 2017).

In the Pacific coast of Costa Rica, the development of large touristic projects coupled with an increasing demographic growth and extension of agriculture lands have increased the need for new water governance, particularly, in regions where current climate variability, and consequently water scarcity are affecting socio-economic assemblages (Kuzdas et al. 2014; Babcock et al. 2016). The increasing water demand for

agriculture, touristic, and drinking water activities in coastal aquifers along the Pacific coast of the country has resulted in the first cases of saline intrusion (i.e. movement of sea water into freshwater coastal aquifers) with electrical conductivities values reaching up to 16,200 $\mu\text{S}/\text{cm}$ (Arellano and Vargas 2011; Calderón et al. 2002; Arias-Salguero and Vargas 2003). This situation has recently invoked strong environmental awareness within local communities and stakeholders, considering that water supply is essential to support tourism and agriculture which are the main economic activities of the country (PEN 2015; Esquivel-Hernández et al. 2018). However, to our knowledge, detailed and continuous (i.e. monthly basis) hydrogeochemical monitoring are still absent in coastal aquifers in the country, a situation that clearly challenges decision making and effective water management.

This study presents the first comprehensive hydrogeochemical evaluation in the Jacó aquifer within the central Pacific coast of Costa Rica. The main objective was to establish a temporal and spatial groundwater baseline based on physical, chemical, and microbiological indicators. Spatial groundwater biogeochemical characteristics are presented and analysed in the light of the main hydrogeological units and land use. Our baseline seeks to evaluate pollution levels, to prioritize the allocation for water quality monitoring as well as to shed light on potential regulation of future tourism, residential, and commercial development in the region. Likewise, this study provides useful information for other similar coastal aquifers in Central America, whereby increasing population growth and unregulated activities coupled with El Niño-Southern Oscillation (ENSO)-related droughts (Sánchez-Murillo et al. 2016) are posing a truly challenge to ensure water security and sustainability.

Study area

Geographical and Climate generalities

Jacó aquifer is located in the central Pacific coast of Costa Rica (Fig. 1), between 9°N and 84°W with an elevation gradient from 0 to 820 m. The region is characterized by two distinct seasons: dry (December to April) and wet (May to November) seasons. Average annual rainfall is 3000 mm with a mean

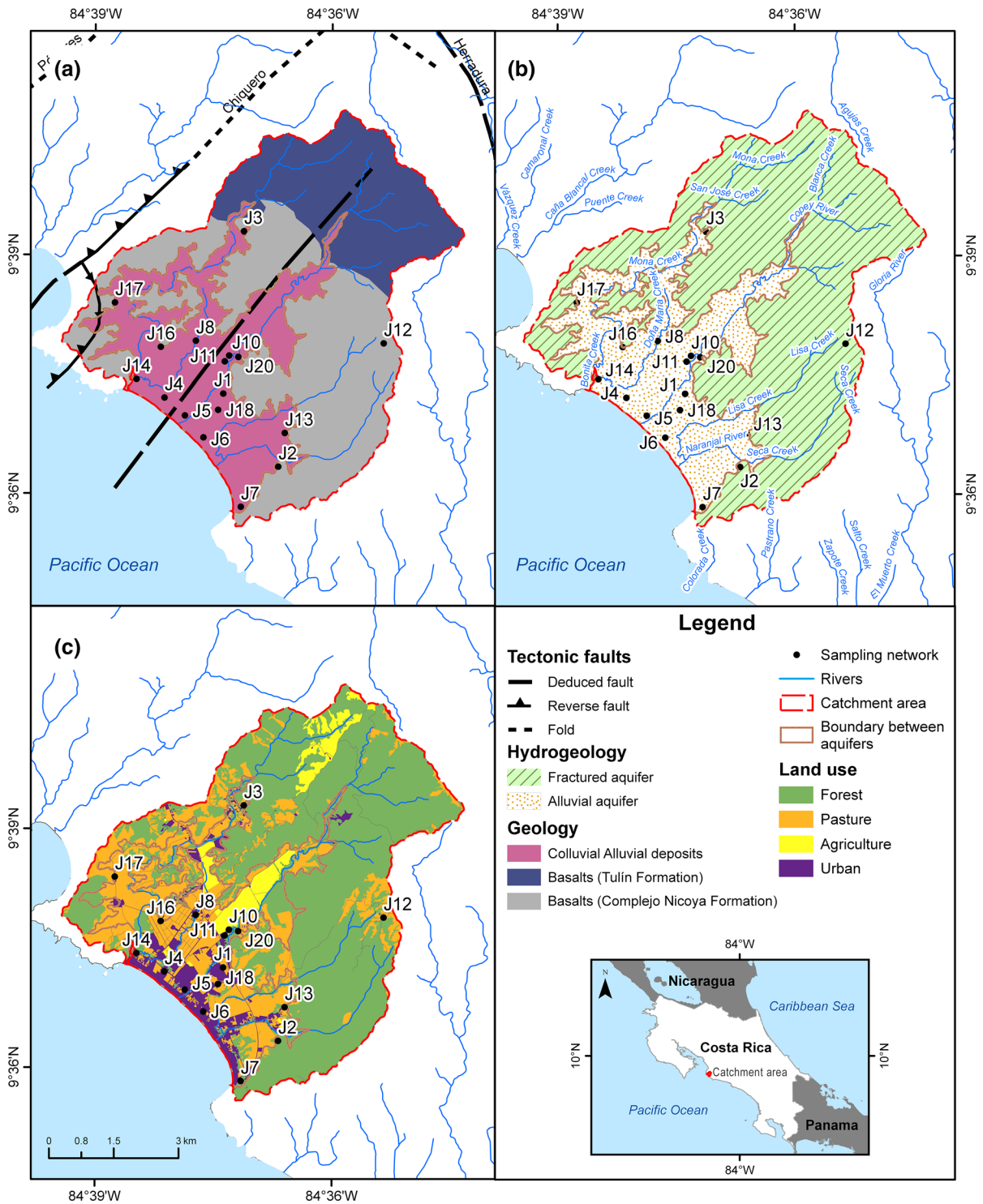


Fig. 1 Jacó aquifer including sampling sites, **a** geology, **b** hydrogeology, and **c** land use

annual temperature and relative humidity of 27 °C and 85%, respectively (Municipalidad de Garabito 2007). Jacó aquifer covers an area of 48 km², including the three small river basins of Mona, Copey, and Naranjal.

The district of Jacó is a touristic hot spot with a population of approximately 22,800 inhabitants (INEC 2011). Drinking water sources are mainly composed of headwater springs and shallow lowland wells. Groundwater is the main source during the dry season. The alluvial origin, shallow water table (up to 5 m depth in the coastal lowlands), and high groundwater consumption turn Jacó aquifer in a highly susceptible and vulnerable system for saline intrusion, fecal coliform bacteria presence, and rapid transport of other pollutants from septic tanks and latrines. In this region, 87% of the houses use septic tanks, while 10% use latrines, resulting in high risk of nitrate and chloride infiltration to the shallow aquifer (Arias-Salguero and Vargas 2003).

Geological setting and hydrogeology

The aquifer is comprised of unconsolidated Quaternary deposits from terrestrial and marine origin (Fig. 1a). Terrestrial deposits come from alluvial and co-alluvial materials (i.e. sandy and clay-loam-type deposits) mainly due to rock weathering at the headwaters. Marine deposits (i.e. sandy- and loam-type materials) are found at the coastal confluence of Mona, Copey, and Naranjal rivers. The formation at the headwaters is associated with very old and weathered basaltic rocks of the Nicoya Complex (Arias 1996; Arias-Salguero 2002) and to younger basaltic fractured rocks of the Tulín formation (Arias-Salguero and Vargas 2003). The aquifer is divided into two main units including an alluvial unit with an area of 15 km² located at the lowlands, and a fractured unit located in the headwaters. The alluvial unit of the aquifer is shallow, unconfined, with non-consolidated deposits of sand, loam, and gravel at the lowlands. On average, the water level is between 0 and 5 m below the surface (Agudelo 2005). The fractured unit is unconfined and composed of basalts with a lateral flow contribution of groundwater to the alluvial aquifer (Fig. 1b). Groundwater levels indicate that there is just one aquifer in the area (Gómez-Cruz et al. 2019). However, in the central part of the plain, whereby the fractured rocks underlie the alluvial unit, there is also evidence of spouting in wells reaching the basaltic

formation due to different permeability conditions or to the fact that deeper wells reached different equipotential lines (Gómez-Cruz et al. 2019). In the area, water recharge is mainly due to localized infiltration (Agudelo 2005).

Land use

Land use categorization is shown in Fig. 1c. In the alluvial unit, 20% is destined to urban use (i.e. tourism-related activities), 22% is forest cover, 49% is pasture, and 9% is dedicated to farming activities. In the fissured unit, 79% corresponds to forest area, 16% to pasture, 3% to farming, and only 1% to urban development (Orozco 2015).

Materials and methods

Sampling campaigns and hydrochemical analyses

Water samples were collected from 17 wells (Fig. 1a) during three samples campaigns (July 2013, November 2013, and March 2014). Wells were located in private and public areas; a detailed description is presented in Table S1. Prior sample collection, all the wells were purged for 10 min to avoid potential stagnant water in the pipe system. Water samples were collected in high-density polyethylene bottles previously washed with HCl 3% m/v and de-ionized water. Samples for microbiological analysis were collected in non-reusable sterile containers. Water samples were stored at 4 °C and delivered within 24 h after collection from the Laboratory of Chemical Analysis and the Laboratory of Microbial Biotechnology at Universidad Nacional, Costa Rica. Water temperature, pH, electrical conductivity (EC), and turbidity were measured in situ using a pre-calibrated hand-held multi-parameter probe WTW Multi 3430 (Weilheim, Germany). Hardness and alkalinity were determined by titration using EDTA and sulphuric acid standard solutions, respectively. Total dissolved solids (TDS) were determined by the gravimetric method at 180 °C. Ion chromatography (Dionex ICS-90, CA, USA) was used to analyse soluble bromide, chloride, fluoride, nitrate, sulphate, and phosphate. Atomic absorption spectrometry (Perkin Elmer AAnalyst 800, CT, USA) was used to analyse all metals. Calcium, magnesium, sodium, potassium, iron, zinc, manganese, and copper

were determined using an air–acetylene flame, while graphite furnace with Zeeman effect allowed the analysis of lead, cadmium, nickel, and chromium. Mercury concentration was analysed using the cold vapour atomic absorption technique (Perkin Elmer MHS 15, CT, USA) with NaBH₄ as reducing reagent. Finally, total coliform, fecal coliform, and *Escherichia coli* were determined by the multiple tube fermentation procedure. Physico-chemical and microbiological analyses were carried out following the procedures of the Standard Methods for the Examination of Water and Wastewater (Rice et al. 2012).

Quality control and data analysis

Field multi-parameters and laboratory instruments were calibrated using certified standard materials. Procedural blanks, calibrations, and recovery standards were performed in each batch of analysis. In addition, charge-balance error (CBE) was calculated as follows:

$$\%CBE = \frac{|\sum_{EqAnions} - \sum_{EqCations}|}{|\sum_{EqAnions} + \sum_{EqCations}|} \times 100 \quad (1)$$

where $\sum_{EqAnions}$ and $\sum_{EqCations}$ are the equivalent sum of the major anions and cations, expressed in meq/L, respectively (Freeze and Cherry 1979). Among all samples, CBE was consistently below 5% (Table S2). The quantification limit (QL) of each analytical technique was determined using Miller and Miller (2010) approach.

Descriptive statistics of values below QL were calculated using robust regression on order statistics (ROS) method (Helsel 2011). Parameters with more than 80% of values below QL were not included for the subsequent statistical analysis. Analysis of similarities (ANOSIM) was used to test changes in water composition among sampling campaigns. Kendall's tau correlation coefficient and principal component analyses (PCA) were applied to further identify common parameters that are influencing wells chemical composition. Satisfactory data adequacy for the PCA was tested using the Kaiser–Meyer–Olkin (KMO > 0.75) and the Bartlett's sphericity tests ($p < 0.01$). Additionally, wells were grouped using the hierarchical cluster analysis with Ward (1963) method of association and squared Euclidean distance as a measure of similarity. Data below QL were

transformed to tied ranks before performing multivariate analysis. Statistical tests were carried out in R 3.5.0 (R Core Team 2018). Piper (1944) diagram and $[Mg^{+2}]/[Ca^{+2}]$, $[Na^{+}]/[Cl^{-}]$ and $[HCO_3^{-}]/[Cl^{-}]$ ratios were calculated for the two aquifer units. To analyse the influence of precipitation, rock–water interaction, and evaporation processes in the groundwater geochemical evolution, a Gibbs (1970) analysis was conducted. This analysis is based on the comparison of salinity (express as TDS) and the concentration of major cations ($[Na^{+}]/[Na^{+} + Ca^{2+}]$) and anions ($[Cl^{-}]/[Cl^{-} + HCO_3^{-}]$). Spatial representations were carried out using ArcGIS® software by Esri (CA, USA).

Results and Discussion

Physico-chemical properties and major ions

The summary of the physical, chemical, and microbiological parameters within the Jacó aquifer is presented in Table 1. Groundwater was slightly alkaline (pH values ranged from 6.70 to 8.20), suggesting transport processes through different layers of calcareous materials (Abboud 2018). The latter was also supported by the high concentration of bicarbonate in all the water samples, which ranged from 144.3 mg/L to 353.9 mg/L with an average of 242.0 mg/L. Bicarbonate concentration was considerably high compared to other anions (i.e. sulphate and chloride). Average values of EC and TDS were 360 μ S/cm and 255 mg/L, respectively. The moderate EC values are a clear indication of negligible saline intrusion within this aquifer. However, wells closer to the coast and to the central area of the alluvial aquifer showed a tendency of greater EC and TDS than the rest of the aquifer system. Nevertheless, both parameters presented maximum values below 1500 μ S/cm and 1000 mg/L, respectively, which are within freshwater standards (Chandrasekar et al. 2014; Abboud 2018). Average total hardness was 184.0 mg/L CaCO₃ and ranged from 88.9 to 281.7 mg/L CaCO₃. Groundwater was classified as “hard” (150–300 mg/L CaCO₃) in more than 80% of the samples, while the rest were classified as “moderately hard” (75–150 mg/L CaCO₃) (Abboud 2018), the latter clearly represented by high Ca²⁺ and Mg²⁺ concentrations (Li et al. 2018).

Table 1 Summary of the physical, chemical, and microbiological groundwater characteristics within the Jacó aquifer

Parameter	Units	Mean	SD	Minimum	Maximum	CR ^c	WHO ^d
Temperature	°C	28.1	1.4	25.1	31.5	–	–
pH	–	7.40	0.36	6.70	8.20	6.0–8.0	6.5–9.5
Conductivity	µS/cm	360	114	141	550	400	–
TDS	mg/L	255	49	148	365	1000	1000
Hardness	mg/L CaCO ₃	184.0	45.9	88.9	281.7	400	–
Ca ²⁺	mg/L	41.14	11.50	18.89	65.79	100	–
Mg ²⁺	mg/L	17.76	5.95	8.56	29.33	50	–
Na ⁺	mg/L	12.74	9.13	3.07	40.76	200	200
K ⁺	mg/L	1.568	2.014	0.176	10.896	10	–
Fluoride ^a	mg/L	0.104	0.038	< 0.06	0.211	0.7	1.5
Bicarbonate	mg/L	242.0	61.5	114.3	353.9	–	–
Bromide ^b	mg/L	–	–	–	< 0.45	–	–
Chloride	mg/L	5.534	4.713	1.040	15.764	250	250
Nitrate ^a	mg/L	2.331	5.292	< 0.4	26.92	50	50
Phosphate ^b	mg/L	–	–	–	< 0.6	–	–
Sulphate	mg/L	6.087	5.818	0.892	23.226	250	500
Cu ^b	mg/L	–	–	–	< 0.3	2	2
Fe ^b	mg/L	–	–	< 0.2	0.587	0.3	–
Mn ^b	mg/L	–	–	< 0.2	1.501	0.5	0.4
Zn ^b	mg/L	–	–	< 0.1	0.267	3	3
Cd ^b	µg/L	–	–	–	< 0.45	3	3
Cr ^a	µg/L	3.208	1.126	< 3	6.557	50	50
Ni ^b	µg/L	–	–	–	< 10	20	70
Pb ^b	µg/L	–	–	–	< 10	10	10
Hg ^b	µg/L	–	–	–	< 0.48	1	6
Total coliform	MPN/100 mL	–	–	ND	23	–	–
Fecal coliform	MPN/100 mL	–	–	ND	13	–	0
<i>Escherichia coli</i>	MPN/100 mL	–	–	ND	13	0	0

SD standard deviation, MPN most probable number, TDS total dissolved solids

^aEstimated using the ROS method

^b> 80% of the data below the quantification limit

^cCosta Rican legislation for drinking water

^dStandards of the World Health Organization

Cations concentration abundance followed: Ca²⁺ > Mg²⁺ > Na⁺ > K⁺ (based on average values and meq/L). Average Ca²⁺ and Mg²⁺ concentrations per well ranged from 21.29 to 58.81 mg/L, and from 9.61 to 13.50 mg/L, respectively. Ca²⁺ and Mg²⁺ dominance is likely related to the rock–water interactions in presence of calcite and dolomite (Zhang et al. 2018). The spatial distribution of these two cations exhibited an increasing trend towards the coastal zone and the central section of the study area (Fig. 2a, b), whereby groundwater pumping is consistently high throughout the year. Average Na⁺ and K⁺ values ranged from 5.65 to 37.10 mg/L, and from 0.28 to 6.29 mg/L, respectively. Sites near the coast (J6, J14 and J18) presented the highest average concentrations for both cations. However, wells J4 and J5, located in the

central section of the alluvial aquifer, and also close to the coast, remained low and similar to the wells located at the headwaters (Fig. 2c, d). In general, distant to the ocean and anthropogenic activities are likely key drivers of the aquifer hydrochemistry.

The dominance order of major anions was as follows: HCO₃[−] > SO₄^{2−} > Cl[−] > NO₃[−]. Bicarbonate concentration ranged from 114.3 to 353.9 mg/L, with an average of 242.0 mg/L (Fig. 3a). Bicarbonate was the predominant anion, and its spatial distribution showed an increasing trend in the alluvial aquifer and near the coastal zone (Fig. 3a). According to the Chebotarev (1955) sequence, groundwater recharge processes within the Jacó aquifer may be considered rapid with short residence times, due to the alluvial unconsolidated materials with calcareous composition

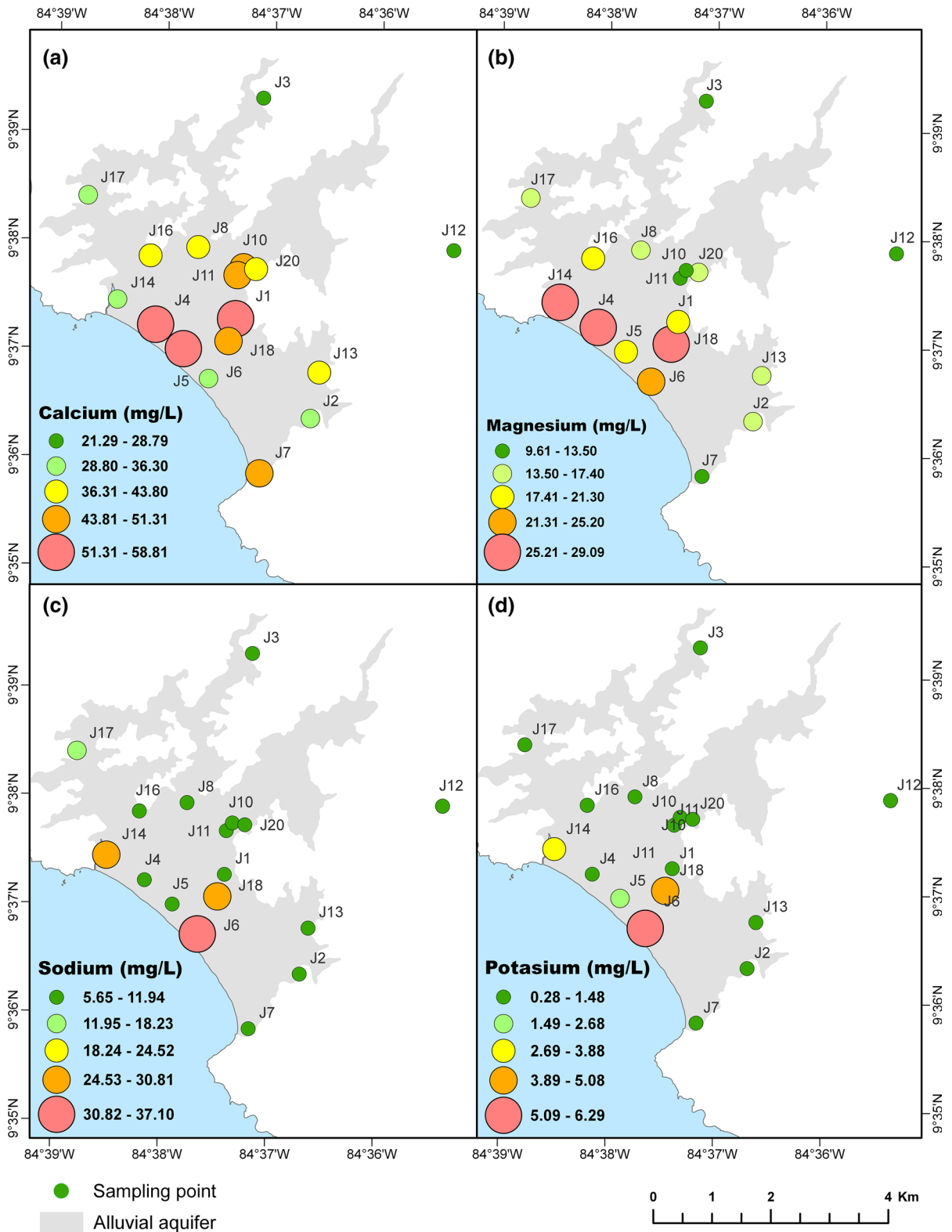


Fig. 2 Average concentration of major cations within the Jacó aquifer: **a** Ca^{2+} , **b** Mg^{2+} , **c** Na^+ , and **d** K^+

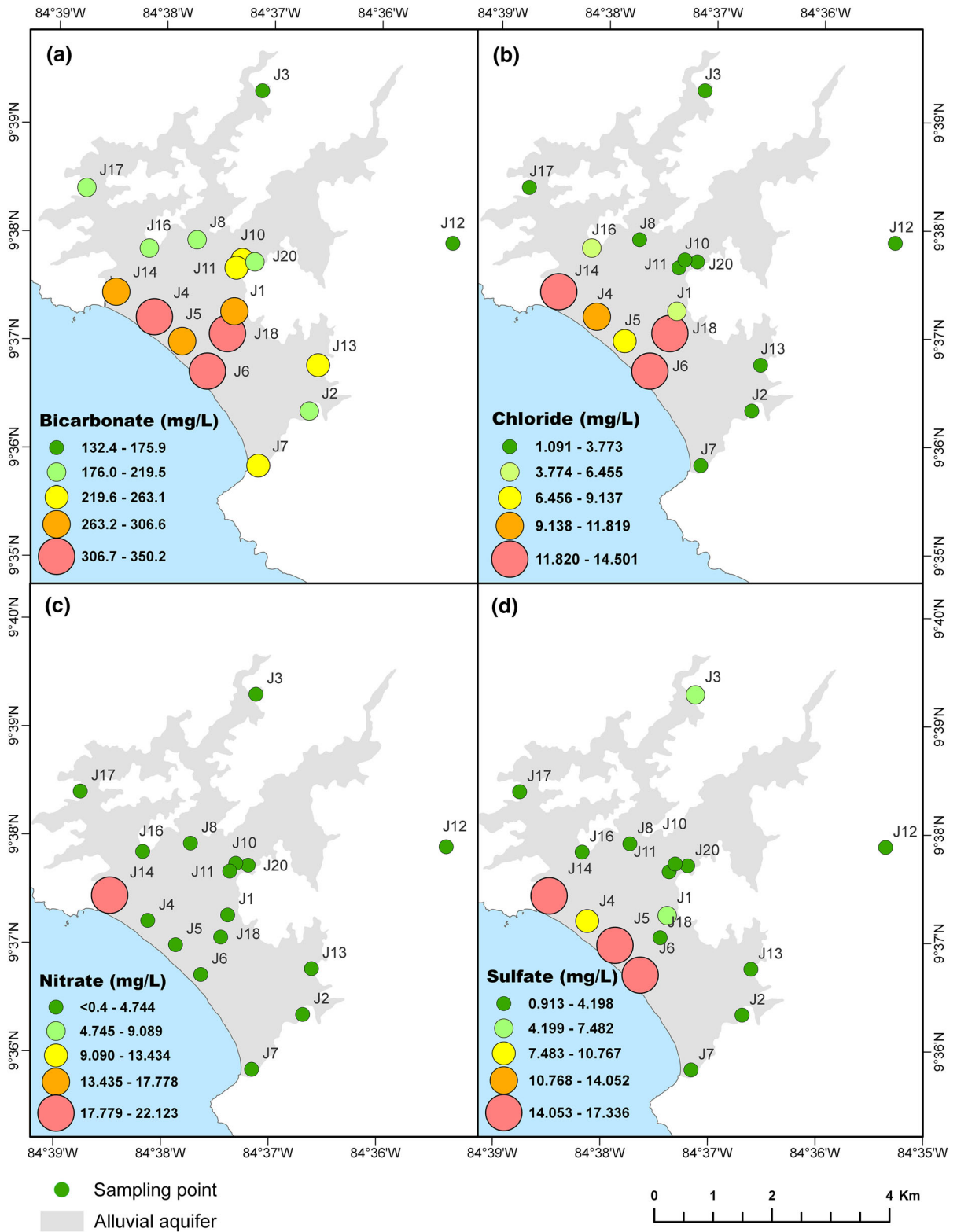


Fig. 3 Average concentration of major anions within the Jacó aquifer: **a** bicarbonate, **b** chloride, **c** nitrate, and **d** sulphate

of the aquifer (Agudelo 2005; Khairy and Janardhana 2014; Yidana et al. 2018). Sulphate and chloride were found in similar concentrations, ranging from 0.89 to 23.23 mg/L, and from 1.04 to 15.76 mg/L, respectively (Fig. 3b, d). Sulphate and chloride are usually related to dissolution processes of gypsum and halite, anthropogenic pollution, atmospheric deposition, and the influence of ancient seawater entrapped into sediments (Singaraja et al. 2014). Chloride can be also used as a salinity tracer due to its conservative properties (Souid et al. 2018). In the other hand, nitrate average concentration was 2.33 mg/L. Nitrate concentration usually does not exceed 10 mg/L. However, an average concentration almost ten times greater (22.12 mg/L) was found in sample site J14 (Fig. 3c). In general, sites with the high EC, TDS, and bicarbonate content also presented the highest sulphate and chloride concentrations. Bicarbonate concentration appears to be linked with the calcareous composition of the alluvial unconsolidated materials, whereas the increasing solute trend may be related to the extensive use of septic tanks and latrines in the study area. For instance, anomalous high nitrate concentrations might be related to inadequate septic tanks infrastructure, facilitating infiltrations near production wells (Madrigal-Solís et al. 2019; Mena-Rivera and Quirós-Vega 2018; Mtoni et al. 2013). This seems to be the case of site J14, a particularly shallow well in the study area, where the high $[\text{NO}_3^-]/[\text{Cl}^-]$ ratio (0.87) could indicate fecal contamination (Custodio and Llamas 2001). However, isotopic analyses are still needed to defragment origin and potential sources.

Minor ions, trace metals, and microbiological data

Fluoride concentrations ranged from < 0.06 to 0.21 mg/L. Low fluoride contents are often related to the low solubility in presence of high Ca^{2+} content (Custodio and Llamas 2001). Bromide and phosphate were reported below their respective QL (Table 1). Similarly, metals such as Cu, Fe, Mn, and Zn were mainly reported below the QL (Fig. S1). Site J18 consistently resulted in levels above the QL for Mn and Fe. No direct point sources were detected to explain this pattern. However, the presence of Mn and Fe in groundwater has been previously related to several groundwater processes including weathering and increasing solubility under reducing conditions

(Kshetrimayum and Hegeu 2016; Oyem et al. 2015; Palmucci et al. 2016; Weng et al. 2007), even in aquifers with fluvial to marine geology facies (Carrertero and Kruse 2015) similar to the study area. However, more analyses are needed to better understand Fe and Mn dynamics in this specific site.

Trace metals (Cd, Cr, Hg, Ni and Pb) were evaluated to test the potential contamination of the aquifer through lixiviation from a landfill nearby or other activities. Overall, trace metal concentrations were found below the QLs except for chromium. This metal reported values up to 6.56 $\mu\text{g/L}$ in 20 out of the 48 samples (Fig. S1). Although no direct anthropogenic sources were identified, wells with chromium presence were found in one site in the fractured aquifer (J12), in three samples near the coast (J6, J7 and J14), and in six samples in the central area of the alluvial aquifer (J2, J8, J10, J11, J12, J20). Pipes corrosion, in addition to metallurgic and lubricant-oil-type wastewaters that are commonly discharged to the streams, may be responsible for this trend (Chen et al. 2019; Edokpayi et al. 2018; Lu et al. 2016). Although the values were below the WHO standards, a more detailed analysis of unregulated and untreated discharge is required to provide a more concise trace element assessment.

Total coliforms, fecal coliform, and *Escherichia coli* were not found in most of the wells, except for the sample sites J3 and J14. Site J14 exhibited the maximum concentration of both sites with values of 23 MPN/100 mL for total coliform, and 13 MPN/100 mL for fecal coliform and *E. coli*. In both cases, the concentrations reported are above the water quality standards for drinking water and could be related to point sources of pollution, particularly from septic tanks lixiviation nearby well depression cones (Ngasala, Masten, and Phanikumar 2019; Norat-Ramírez et al. 2019).

Correlation and cluster analysis

Kendall's tau correlation coefficients are given in Table 2. Strong positive correlations were obtained for bicarbonate-EC ($\tau = 0.849$), bicarbonate-TDS ($\tau = 0.718$), and Mg^{2+} -TDS ($\tau = 0.795$); which suggest that there is a significant contribution of bicarbonate and Mg^{2+} to the TDS content. This contribution is likely due to rock–water interaction processes. Around 18 significant and moderate

Table 2 Kendall's tau correlation coefficients of the physico-chemical parameters within the Jacó aquifer

	Temperature	pH	Conductivity	TDS	Hardness	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	F ⁻	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Cr
Temperature	1														
pH	0.277	1													
Conductivity	0.508	0.429	1												
TDS	0.491	0.255	0.620	1											
Hardness	0.363	0.263	0.565	0.521	1										
Ca ²⁺	0.348	0.202	0.554	0.324	0.496	1									
K ⁺	0.441	0.378	0.507	0.419	0.256	0.223	1								
Mg ²⁺	0.487	0.211	0.609	0.795	0.480	0.261	0.411	1							
Na ⁺	0.331	0.243	0.436	0.602	0.303	0.079	0.390	0.535	1						
F ⁻	0.197	0.082	0.270	0.294	0.210	0.270	0.160	0.259	0.215	1					
HCO ₃ ⁻	0.527	0.396	0.849	0.718	0.628	0.567	0.454	0.641	0.465	0.306	1				
Cl ⁻	0.496	0.283	0.521	0.600	0.418	0.197	0.496	0.683	0.505	0.147	0.480	1			
NO ₃ ⁻	0.002	0.164	0.085	0.057	0.027	0.097	0.129	0.042	0.030	0.041	0.089	0.063	1		
SO ₄ ²⁻	0.282	0.290	0.300	0.228	0.229	0.130	0.278	0.323	0.246	0.062	0.230	0.505	0.286	1	
Cr	- 0.126	0.023	- 0.068	- 0.145	- 0.121	- 0.035	- 0.051	- 0.204	- 0.156	- 0.030	- 0.091	0.039	0.265	- 0.094	1

Bold values *p* < 0.05

correlations were identified ($0.7 > \tau > 0.5$) including Mg^{2+} -EC, Mg^{2+} -bicarbonate, Mg^{2+} -chloride, Ca^{2+} -bicarbonate, and hardness-bicarbonate. Low ($0.5 > \tau > 0.3$) and weak ($0.3 > \tau$) positive correlations were observed in 26 and 28 associations, respectively. Interestingly, a low significant correlation between Ca^{2+} - Mg^{2+} ($\tau = 0.261$) was determined, suggesting a different origin (geological versus marine, for example). Finally, 24 out of the 30 non-significant correlations involved nitrate and chromium. The latter may indicate a potential similar anthropogenic origin (Chandrasekar et al. 2014; Saldarriaga-Noreña et al. 2014).

Cluster analysis determined four general groups at $(D_{link}/D_{max}) \times 100 < 40$ (Fig. 4). The first group was constituted by four sample sites (J18, J4, J5 and J1), and the second cluster grouped just two sites (J14 and J6). In general, these six wells are located in the central area of the aquifer and near the coast. In this area, land cover is characterized by urban use, where water abstraction is used to supply touristic and commercial activities. The third cluster includes nine wells (J20, J8, J2, J11, J10, J7, J16, J13 and J17), which are spatially distributed in the middle area of the catchment but within the alluvial aquifer. These wells are less influenced by the urban land use in comparison to the previous clusters. Cluster number four is only

formed by two wells (J3 and J12). The site J12 is within the fractured aquifer, and the J3 in the boundary line between the two aquifers.

Hydrogeochemical relations

Figure 5 shows a Piper diagram for water composition classification into seven categories depending on its relative ion abundances. Bicarbonate was the predominant ion in all the water samples within the anion domain, which supports the hypothesis that groundwater residence time is short in agreement with the aquifer geology (i.e. sandy soils in the alluvial deposits). However, wells within the cluster 2 exhibited lower bicarbonate contents. Overall, Ca^{2+} and Mg^{2+} dominance within the cation domain categorized the groundwater system as HCO_3^- - Ca^{2+} - Mg^{2+} type. This classification, along with low EC values, is typical of non-polluted freshwaters (Mtoni et al. 2013).

The ratios of anions and cations as well as the TDS values for the Gibbs analysis are given in Table S3. Although the water residence time is assumed as relative short, Gibbs’s characterization indicated a rock–water-type interaction (i.e. rock mineralization) as the main mechanism controlling the aquifer hydrochemistry (Abboud 2018).

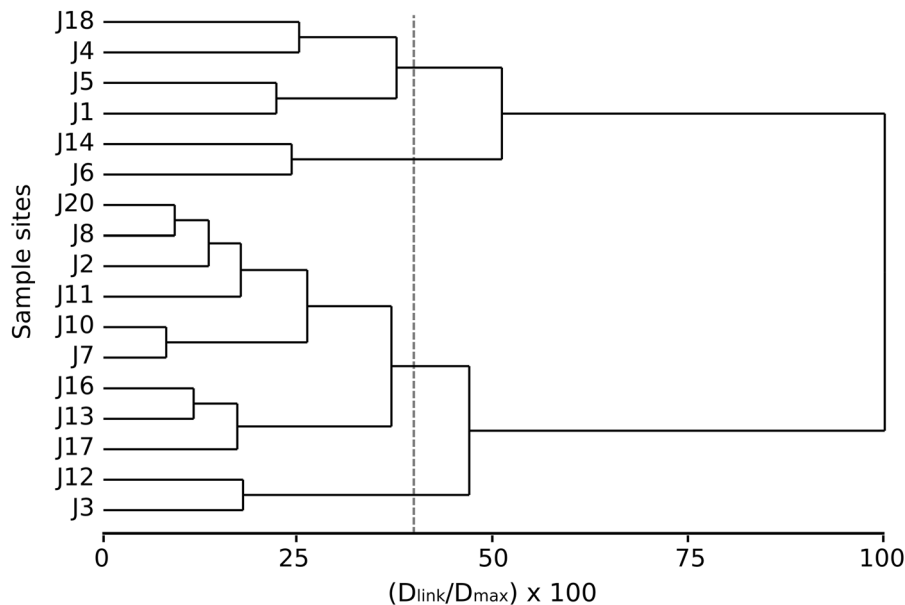


Fig. 4 Dendrogram showing wells grouping using hierarchical cluster analysis within the Jacó aquifer. Cluster 1 (J18, J4, J5 and J1), cluster 2 (J14 and J6), cluster 3 (J20, J8, J2, J11, J10, J7, J16, J13 and J17), and cluster 4 (J3 and J12)

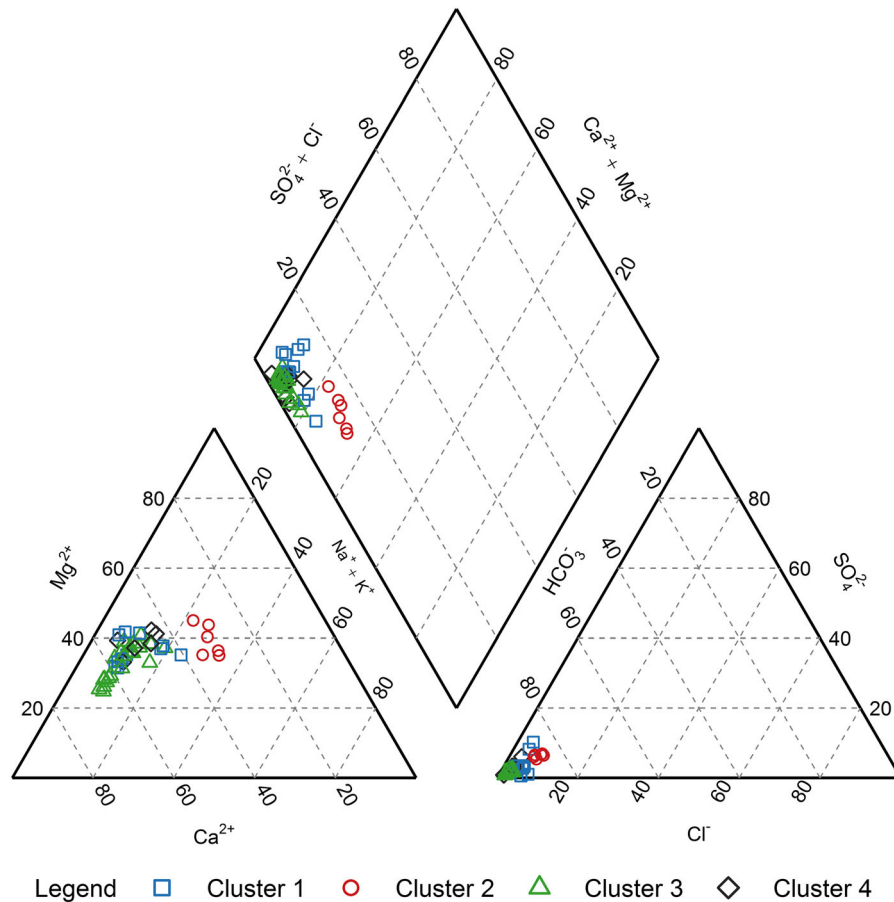


Fig. 5 Piper diagram of the groundwater samples within the Jacó aquifer

Figure 6 shows several ionic relations that can be used to better understand the hydrogeological processes within the aquifer considering the type of mineral and the rock–water interactions (Mtoni et al. 2013; Zhang et al. 2018). $[\text{Mg}^{2+} + \text{Ca}^{2+}]$ versus $[\text{SO}_4^{2-} + \text{HCO}_3^-]$ presented a nearly linear relationship with a 1:1 ratio (Fig. 6a). These values indicate that calcite, dolomite, and/or gypsum are likely the dominant minerals in the aquifer (Pazand et al. 2018). $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratios ranged from 0.38 to 1.48, with an average of 0.74 (Fig. 6b). Values of this ratio are usually associated with dissolution of silicates (< 0.5), calcites (between 0.5 and 1), and dolomites (> 1) (Zhang et al. 2018). In general, calcite strongly affects water composition in the aquifer. Wells of cluster 2 (J14 and J6) are more likely influenced by dolomites. $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratios near 1 are typical of freshwaters, in contrast to saline waters where ratios are greater than 5 (Mtoni et al. 2013; Pazand et al. 2018).

Based on $[\text{Na}^+]/[\text{Cl}^-]$ ratio (Fig. 6c), no saline intrusion was detected in the aquifer (values ranged from 1.06 to 10.67). This relation is equal or below 0.86 in aquifers with saline intrusion (Rachid et al. 2017; Motevalli et al. 2018). Finally, $[\text{HCO}_3^-]/[\text{Cl}^-]$ ratios were above 10 (Fig. 6d), which correspond again to continental freshwater without saline intrusion. Ratios below 2 are found in aquifers with saline intrusion (Mtoni et al. 2013; Motevalli et al. 2018). Although conclusive evidence of saline intrusion was not detected, the ion spatial increasing trend towards the central portion of the aquifer and near the coast should be carefully analysed with a more detailed temporal evolution of the hydrogeochemical signals.

Principal component analysis

PCA results are presented in Table 3. The analysis included only those components with eigenvalues

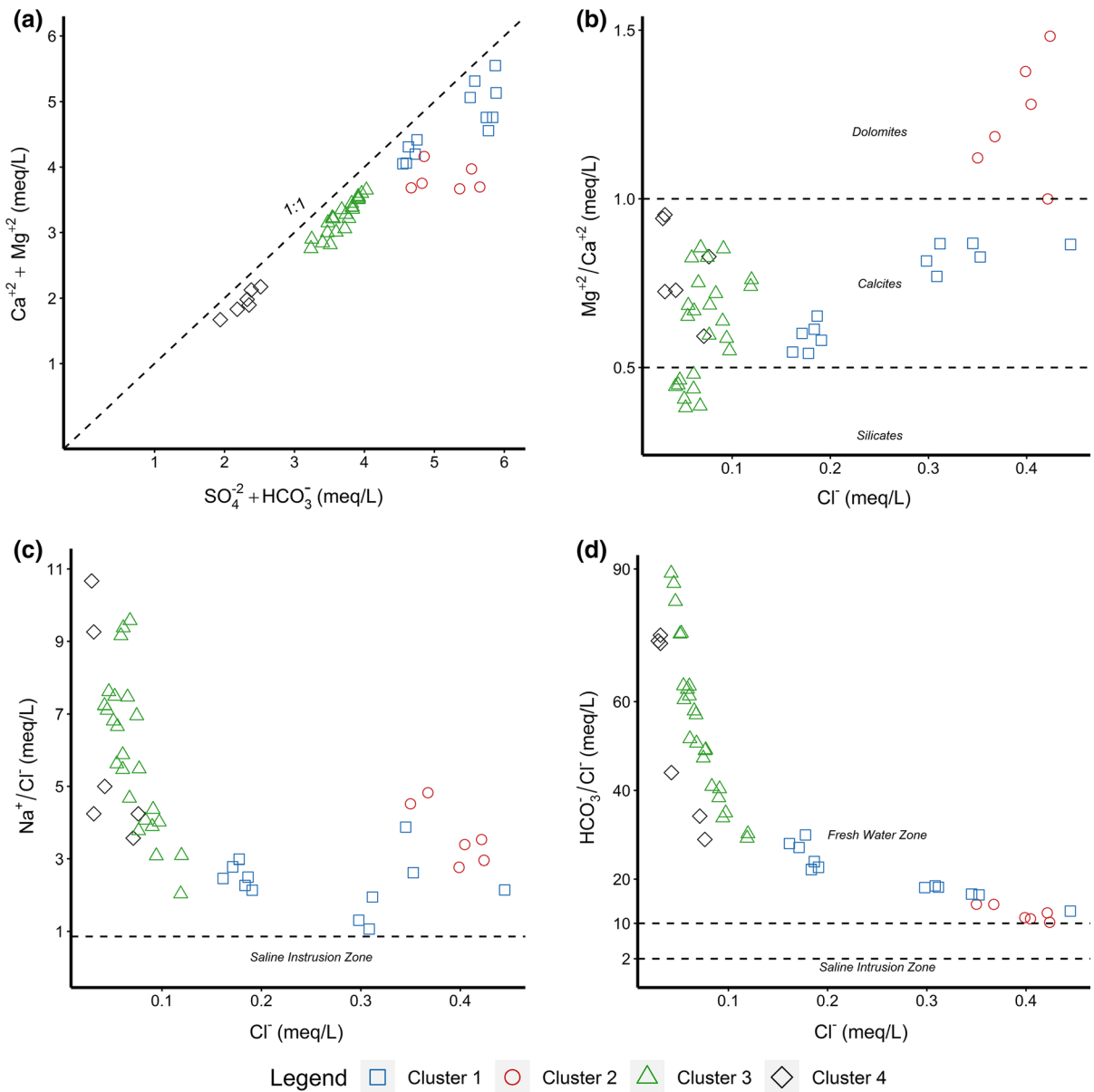


Fig. 6 Hydrogeochemical relations of the groundwater samples within the Jacó aquifer: **a** $[Ca^{2+} + Mg^{2+}]$ versus $[SO_4^{2-} + HCO_3^-]$, **b** $[Mg^{2+}]/[Ca^{2+}]$ versus $[Cl^-]$, **c** $[Na^+]/[Cl^-]$ versus $[Cl^-]$, and **d** $[HCO_3^-]/[Cl^-]$ versus $[Cl^-]$

greater than 1 (Yeomans and Golder 1982), which explained 74.9% of the total variance. PC1 represented 48.0% of the variance and highlighted the importance of some parameters such as TDS, Mg^{2+} , bicarbonate, hardness, sodium, and chloride. This component represented the parameters which are strongly influencing the aquifers hydrogeochemistry (e.g. Mg^{2+} and bicarbonate). PC1 also highlighted TDS, sodium, and chloride which are indicators of

saline intrusion (Seddique et al. 2019; Souid et al. 2018). However, no conclusive evidence of this process was found. In PC2, 14.7% of the variance was explained with significant contributions for Ca^{2+} , pH, and sulphate. PC2 denoted processes likely related to minerals weathering such calcites and dolomites (Ansari and Umar 2019; Pazand et al. 2018). Finally, PC3 explained 12.2% of the variance with negative contributions for nitrate and chromium. This may be

Table 3 Principal component analysis results within the Jacó aquifer

Parameter	PC1	PC2	PC3
pH	− 0.231	− 0.343	− 0.132
TDS	− 0.372	0.143	− 0.017
Hardness	− 0.275	0.294	− 0.072
Ca ²⁺	− 0.206	0.443	− 0.358
K ⁺	− 0.270	− 0.258	0.281
Mg ²⁺	− 0.373	0.060	0.078
Na ⁺	− 0.305	− 0.322	0.198
F [−]	− 0.172	0.288	− 0.186
HCO ₃ [−]	− 0.370	0.212	− 0.056
Cl [−]	− 0.373	− 0.146	0.118
NO ₃ [−]	− 0.043	− 0.260	− 0.662
SO ₄ [−]	− 0.265	− 0.332	− 0.145
Cr	0.090	− 0.281	− 0.460
Eigenvalue	6.245	1.914	1.591
% Total variance	48.0	14.7	12.2
% Cumulative	48.0	62.7	74.9

associated with the impact of anthropogenic activities in detrimental of the water quality; as mentioned before, nitrate and chromium were significantly correlated and are usually anthropogenic pollution indicators (Chen et al. 2019; Modibo and Xueyu 2018).

Water quality and broader management implications

Results were compared to the drinking water standards established in the Costa Rican legislation (MINSAs 2015) and the World Health Organization (2011) (Table 1). In particular cases (i.e. parameter and well), the results exceed the standards, but overall, there is a high degree of compliance with the regulations. Well J14 is one of the sites that did not meet the standards. Microbiological contamination, above the recommended limits, the highest concentration of nitrate, and the presence of chromium in concentrations up to 4.90 µg/L were found in this site. In addition, site J18 also presented values of Mn and Fe which were above the recommendations. Only site J3 reported microbial contamination in the three sampling campaigns. Overall, the wells located in the fractured aquifer presented better physico-chemical water quality. Of

particular attention is the spatial distribution of chromium concentration. Even though, these values are not considered harmful for human health, potential sources of pollution and long-term exposure effects should be evaluated in the near future.

Water composition did not change throughout the three sampling campaigns ($R = 0.055$, $p = 0.05$), which suggest that there was not seasonal influence in the water quality. The lack of long-term monitoring networks regarding water quality and abstraction, undoubtedly, limits temporal analysis. On this regard, authorities should establish monitoring programs including critical parameters that are not normally determined at operational levels, such as nitrate, metals, or emerging pollutants. In addition, the implementation of adequate wastewater, urban planning, and land management are the most urgent challenges that local authorities are facing to ensure sustainable development, not only in the district of Jacó, but also at national and regional scales.

Conclusions

Water within the alluvial and fractured aquifers can be classified as mixed HCO₃[−]–Ca²⁺–Mg²⁺ type with short residence time. The main process influencing its composition is rock–water interaction processes with minerals such as dolomite and calcite.

Despite the increase in socio-economic activities in the study area, and consequently, the increase in groundwater abstraction, groundwater characteristics are generally suitable for human consumption. Several wells should be closely monitored since particular parameters exceeded the standards for drinking water. This was the case of well J3 which presented microbiological contamination, well J14 with high nitrate concentration, and well J18 where Fe and Mn were found exceeding the regulations. Further assessments of presence and origin of chromium must be conducted in a near future. Our data determined that saline intrusion is not an issue within the aquifer. However, there was a clear increase in the concentration of major anions and cations towards the central and coastal regions of the aquifer. These results are in agreement with Gómez-Cruz et al. (2019) that highlighted the hydrogeological vulnerability of the alluvial aquifer. Therefore, integrated water resources

management is necessary to ensure water security in the future.

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Author Contributions R.S-G., L.M-R., A.F-S and H.M-S designed the study. R.S-G performed the experiments and data analysis with significant contribution of L.M-R and R.S-M. All the authors contributed to write the manuscript.

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