DOI: 10.24850/j-tyca-14-02-08

Articles

Temporal and spatial changes in surface water chemistry in a Mediterranean river of central Chile: The case of the Mataquito river (~35°S)

Cambios temporales y espaciales en la química del agua superficial en un río mediterráneo de Chile central: el caso del río Mataquito (~35°S)

Juan A. Placencia[1]
Patricio Torres-Ramírez[2]
José Ortiz-Riquero[3]
Rodolfo Jerez-Ruiz[4]

[1]Department of Environmental Chemistry, Faculty of Sciences, Universidad Católica de la Santísima Concepción, Concepción, Chile, jplacencia@ucsc.cl

[2]Centro Regional de Estudios Ambientales (CREA), Universidad Católica de la Santísima Concepción, Concepción, Chile, ptorres@ucsc.cl

[3]Sustainability and External Affairs Management, Sustainability and External Affairs Management, Corporación Nacional del Cobre (CODELCO Chile), Andean Division, Santiago, Chile, jorti028@codelco.cl

[4]Centro Regional de Estudios Ambientales (CREA), Universidad Católica de la Santísima Concepción, Concepción, Chile, rjerez@ucsc.cl

Corresponding author: Juan A. Placencia, jplacencia@ucsc.cl

Abstract

Spatial and temporal changes in water chemistry were evaluated using surface water extracted from a Mediterranean river basin, i.e., The Mataquito River, central Chile. The processes that control water chemistry dynamics in the basin were determined by assessing the relationship between hydrologic events (rainfall, river flow, runoff rates), physical-chemistry properties, and major ion concentrations/distributions along the river. During the rainy period, major ion levels were controlled predominantly by weathering (rainfall). During the dry period, seawater intrusion was the main factor controlling water chemistry. Unusually high chlorine and sulfate concentrations suggested anthropogenic sources of the ions entering the basin. Thus, pollution from industrial and agricultural activities in the basin might be quantitatively important and should be considered in future studies of this area.

Keywords: Mediterranean River, hydrologic regimes, water chemistry, weathering, pollution, central Chile.

Resumen

Se evaluaron los cambios espaciales y temporales en la química del agua superficial de un río Mediterráneo, *i.e.*, río Mataquito, Chile central. Los procesos que controlan la dinámica de la química del agua en la cuenca se determinaron evaluando la relación entre los eventos hidrológicos (lluvia, caudal del río, tasas de escorrentía), propiedades fisicoquímicas y la concentración/distribución de iones principales a lo largo del río. Durante el periodo lluvioso, los niveles de iones principales fueron controlados de modo predominante por la meteorización (lluvia). Durante el periodo seco, la intrusión de agua de mar fue el principal factor de control de la química del agua en el área de estudio. Concentraciones inusualmente altas de cloro y sulfato sugirieren fuentes antrópicas de iones que ingresan a la cuenca. Por lo tanto, la contaminación por actividades industriales y agrícolas en la cuenca podría ser cuantitativamente importante y debería considerarse en futuros estudios de esta área.

Palabras clave: río Mediterráneo, regímenes hidrológicos, química del agua, meteorización, contaminación, Chile central.

Received: 07/07/2020

Accepted: 15/10/2021

Introduction

Rivers make important impacts regionally, continentally, and globally. However, riverine effects are especially significant for continental shelf regions that receive freshwater inputs, as these affect coastal circulation dynamics and the distribution of organisms (*e.g*., Dávila, Figueroa, & Müller, 2002; Nash & Moum, 2005; Palmer *et al*., 2008; Saldías, Sobarzo, Largier, Moffat, & Letelier, 2012; Saldías *et al*., 2016; Dessandier *et al*., 2016). The world's largest rivers provide approximately 40 % of the freshwater input into the oceans. Moreover, rivers carry important amounts of suspended solids and dissolved solutes, major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, CO_3^{2-}), carbon species, organic and inorganic matter, and dissolved silicon (H_4SiO_4) from the continents to coastal marine ecosystems (*e.g*., Humborg, Ittekkot, Cociasu, & Bodungen, 1997; Dagg, Benner, Lohrenz, & Lawrence, 2004; Chase, Strutton, & Hales, 2007; Frings, Clymans, Fontorbe, De-La-Rocha, & Conley, 2016; Saldías *et al*., 2016).

Several authors have studied riverine chemistry on global/regional scales (e.g., Gibbs, 1970; Chen, Wang, Xia, & Zhang, 2002; Li, Chetelat, Yue, Zhao, & Liu, 2014a; Li, Lu, & Bush, 2014b; Armengol, Manzano, Bea, & Martínez, 2017; Mapoma *et al*., 2017). These authors have focused on two main areas: 1) the origins of elements and processes that determine the temporal and spatial distributions of ions, nutrients, organic carbon, and pH in various water bodies in order to understand dissolved inputs in coastal areas (dominated by rivers), and 2) whether or not the waters comply with standards for potable water, irrigation, and industrial uses. Other researchers have studied water quality variability with respect to changes in land use, finding some relationships between temporal or spatial variations in water quality and land use (*e.g.*, Singh, Malik, & Sinha, 2005; Zampella, Procopio, Lathrop, & Dow, 2007; Bahar, Ohmori, & Yamamuro, 2008; Vrebos, Beauchard, & Meire, 2017). Many other studies have indicated that major ions or other chemical characteristics of rivers are influenced directly or indirectly by human activities, i.e., mining, industry, and effluents from large cities (*e.g.*, Mulk, Azizullah, Korai, & Khattak, 2015).

Mediterranean rivers are characterized by being influenced by seasonal patterns of rainfall and temperature. Typically, with most rainfall during winter and high river flow, is followed by dry summers with slight or no rainfalls and low river flow (*e.g.*, Bonada & Resh, 2013). The intensity of these hydrological events affects the composition and distribution of dissolved chemical substances, as well as water quality. Moreover, human-driven disturbances can also significantly affect the chemical composition of water (*e.g.*, Benabdelkader, Taleb, Probst, Belaidi, & Probst, 2018; Hanna *et al.*, 2018). On this basis, the Mataquito River is a very good scenario to study the effects of hydrological and anthropogenic factors on the water chemistry, because this Mediterranean river has been used for multiple anthropogenic activities: agricultural irrigation, hydropower, industry, and as a receptor of pulp mill and urban discharges, among others (*e.g.*, Pizarro, Vergara, Rodríguez, Sanhueza, & Castro, 2010; Torres-Ramírez, Ortiz, Figueroa, Jerez, & Arcos, 2017).

The Mataquito River basin is located in central Chile (between ~34ºS and 35ºS), which has a Mediterranean climate, characterized by rainfalls in winter months followed by dry summers with slight or no rainfalls (Torres-Ramírez *et al*., 2017). The river has a surface area of >6,000 km^2 (Pizarro *et al*., 2010; Figure 1). The Mataquito sedimentary basin is composed mostly of clays, limestones, and volcanic ash, with lithic fragments in some areas (*e.g*., Belmar & Morata, 2005; Muñoz *et al.,* 2007). Landscape use is ~0.17 % agricultural, 0.06 % for livestock, and 0.03 % for forestry (Pizarro *et al*., 2010). The Mataquito is a coastal river that begins at the confluence of the Teno and Lontué rivers. After running its course for 95 km, the river discharges into the Pacific Ocean. The hydrological regime is strongly influenced by the seasons, with peak flows during the rainy winter (July-August, >150 m^{3}s^{-1}), minimum flows in summer (January-March, <20 m^{3}s^{-1}), and medium flows in spring (100 m^{3}s^{-1}) due to melting glaciers (www.dga.cl). Given the seasonal patterns of precipitation and river runoff at this latitude, we expected the amount of dissolved and particulate matter transported to the coastal marine ecosystem to exhibit important seasonal variability.

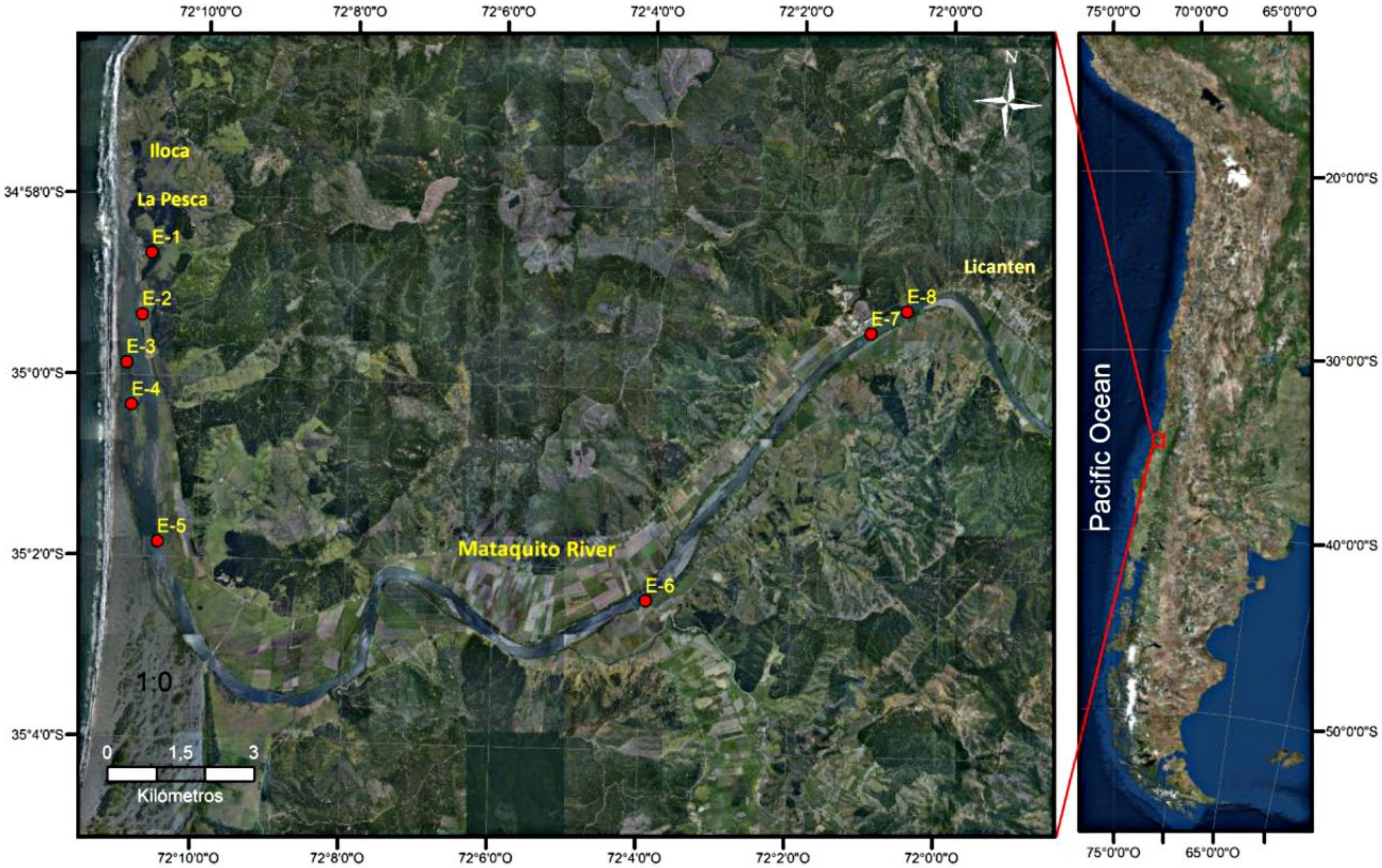


Figure 1. Sampling stations along the Mataquito River (~35°S), central Chile.

The main objectives of this study are: (1) to identify the sources of chemical elements in a Mediterranean river, and (2) to reveal the controlling hydrological processes that influence the surface water chemistry changes along the river. We hypothesize that the water chemistry depends on the hydrological regime along the river. Therefore, we predict that the chemical elements sources are mainly controlled by rock weathering processes, due to precipitation and surface runoff. On the other hand, the seawater intrusion and anthropogenic activities can be important factors that control the water chemistry in the Mataquito river.

Materials and methods

Surface water samples were collected from eight sites along the Mataquito River (Figure 1) between June 2007 and November 2008, during the last week of each month. Temperature, pH, total dissolved solids (TDS) and conductivity (EC) were directly determined on the field using portable device (YSI model 556 MPS). Water samples were collected separately at each sampling site using high density polyethylene bottles. Samples were taken to the laboratory and stored at 4°C until analysis. Dissolved cations of sodium, aluminum, iron, potassium, magnesium, and calcium were analyzed by Atomic Absorption Spectrometry (AAnalyst 200, Perkin Elmer). The concentration of chloride, sulfate, bicarbonate and Total suspended solids (TSS) were determined by applying the method 4500-

Cl^-, 4500-SO_4-C, 2320-B and 2540-D, respectively, according to Standard methods for the examination of water and wastewater (Greenberg, Clesceri, & Eaton, 1995). For the quality control, blanks, standard dissolutions, and certified reference materials were used in all analyses. Recovery percent values for the chemical elements ranged between 90 and 110 %.

The discharge and precipitation dataset (June 2007-November 2008) was acquired from Dirección General de Aguas Chile (DGA) (www.dga.cl). Monthly surface runoff for the Mataquito basin was obtained using the GES-DISC Interactive Online Visualization And aNalysis Infrastructure (Giovanni) as part of NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC) (Acker & Leptoukh, 2007).

Physical-chemical parameters were identified using principal component analysis (PCA) and then were correlated to determine which are responsible for the observed spatial and temporal variances (*e.g.*, Orrego, Marshall-Adams, Barra, Chiang, & Gavilan, 2009). Additionally, Spearman's product moment correlation analysis was used to elucidate the relationship between chemical characteristics and water discharge and precipitation. Significance was based on a 95 % confidence level and was classified as positive or negative according to the gradient of the regression relationship.

Results

Average river discharge from 2007 to 2008 showed a general pattern of variation characterized by high flow rates between June and December 2007, and between June and November 2008 (Figure 2a). In 2007, maximum discharges occurred in August and November due to heavy rainfall and declined gradually as the rain decreased (Figure 2a). In 2008, peak discharges occurred in May, June, and August, due to heavy rainfall, but although precipitation increased through November 2008, flow rates did not achieve maximum values (Figure 2a). Minimum flow rates were detected between January and April 2008, as a consequence of rapidly decreasing precipitation (Figure 2a). Surface runoff peaked in October 2007 (4×10^{-6} kg m^{-2} s^{-1}) and September-October 2008 (2.1×10^{-5} – 3.0×10^{-5} kg m^{-2} s^{-1}), both rainy periods (Figure 2a). Throughout the sampling period, variations in electric conductivity (EC) seemed to follow discharge variations (Figure 2a, b). EC ranged from 158.95 to 39,761 µS cm^{-1}. The lowest EC values fluctuated between 12,000 and 200 µS cm^{-1} during peak discharges along the river course.

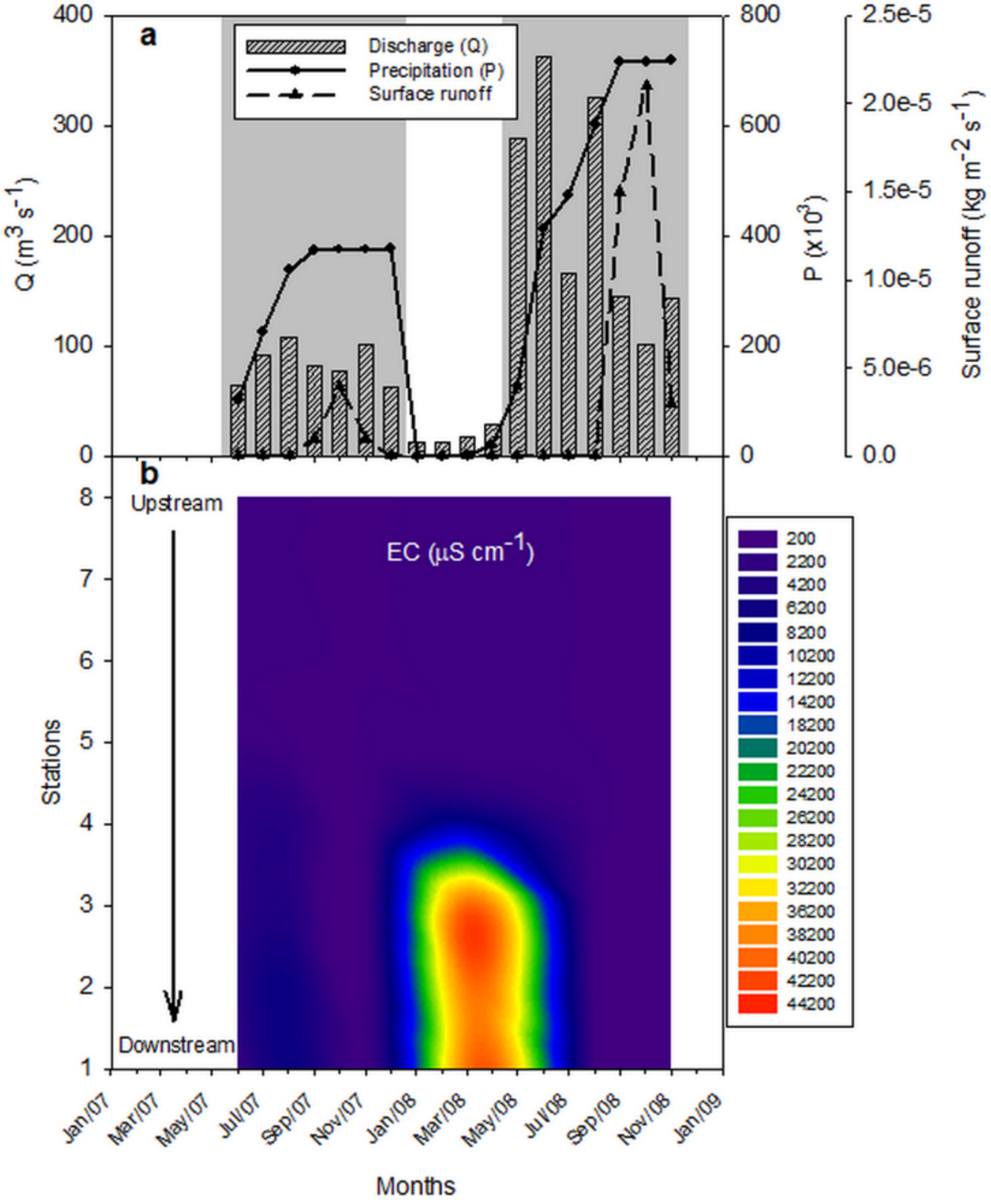


Figure 2. Temporal variations of (a) monthly discharge, surface runoff, and precipitation; and (b) conductivity along the Mataquito River. Discharge and precipitation levels were obtained from the database of

Dirección General de Aguas Chile (DGA, see www.dga.cl). Analyses and visualizations of surface runoff data were produced with the Giovanni online data system, developed and maintained by the NASA GES DISC (Acker & Leptoukh, 2007).

In contrast, the highest EC values (>15 000–44 000 µS cm^{-1}) occurred during the dry, warm period (January-April 2008, see also Figure 3a).

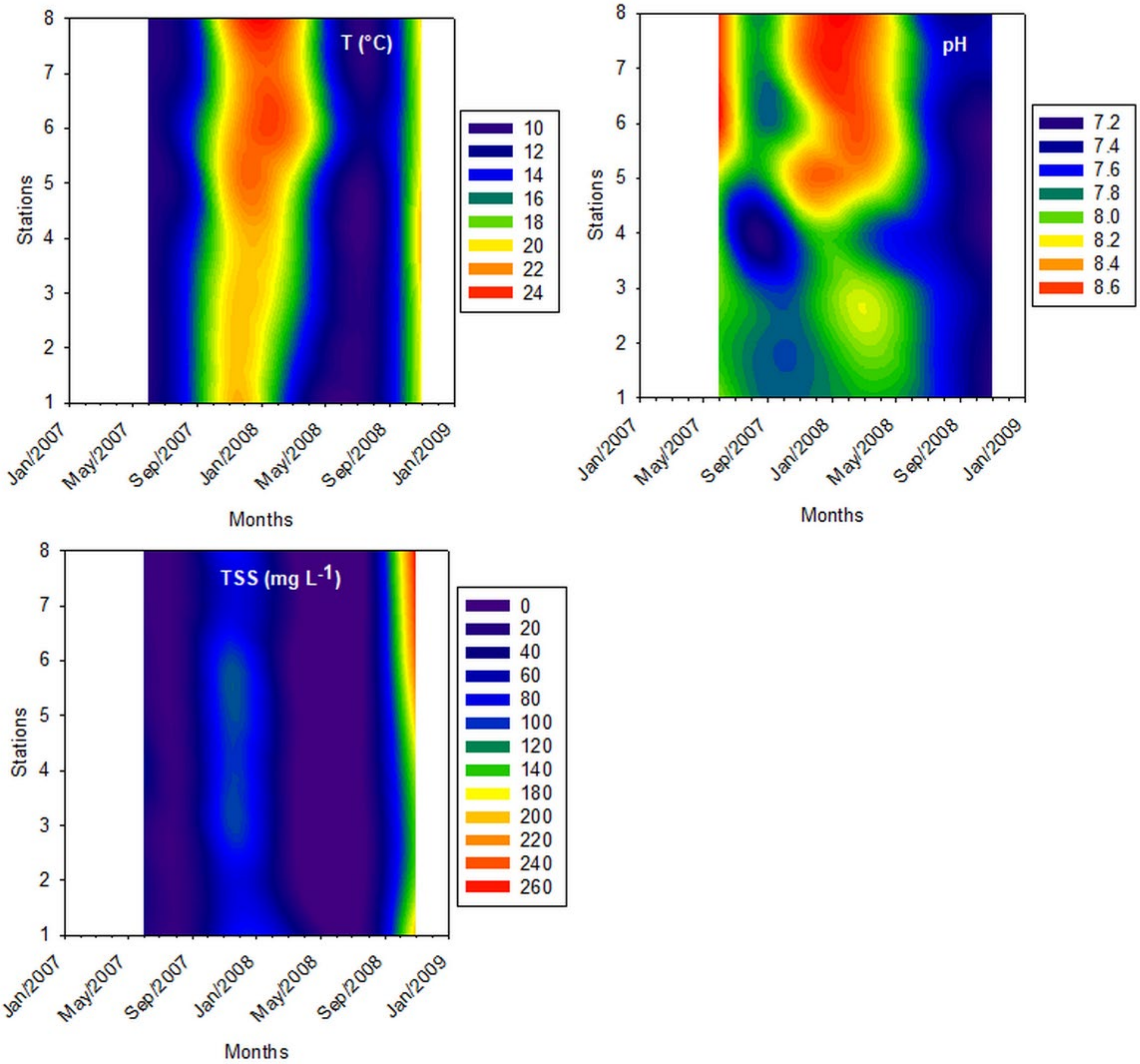


Figure 3. Temporal variations of (a) temperature, (b) pH, and (c) total suspended solids (TSS) along the Mataquito River.

Throughout the time series, variations in water temperature, pH, and total suspended solids (TSS) showed similar patterns. All seemed to follow the discharge fluctuations (Figure 3a-c). Surface river water temperatures were highest in November 2007 and 2008 (~22º - 24ºC, Figure 3a) and lowest during high-discharges periods (~14º - 10ºC, Figure 3a).

Water in the Mataquito River is neutral and mildly alkaline. The pH fluctuated between 7.07 and 8.67, with the most alkaline values observed in June 2007 and March 2008, at field sampling sites E8 to E5 (Figure 3b). TSS concentrations ranged from 5.0 to 266.5 mg L^{-1}. TSS levels were 21 mg L^{-1} (June 2007), 5 mg L^{-1} (August 2007), 86 mg L^{-1} (November 2007), 20 mg L^{-1} (March 2008), 12 mg L^{-1} (August 2008), and 204 mg L^{-1} (November 2008). TSS concentrations in August and November 2008 were >50 % higher than in 2007.

Figure 4 (a-f) shows the relationship between major ion concentrations (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}) and conductivity parameters during the 2007-2008 time series for the Mataquito River. Ion contents were positively and significantly correlated with conductivity throughout the sampling area and period, but with relatively low coefficients (Cl^-: $r^2 = 0.62$; SO_4^{2-}: $r^2 = 0.67$; Na^+: $r^2 = 0.82$; K^+: $r^2 = 0.58$; Mg^{2+}: $r^2 = 0.67$; Ca^{2+}: $r^2 = 0.69$).

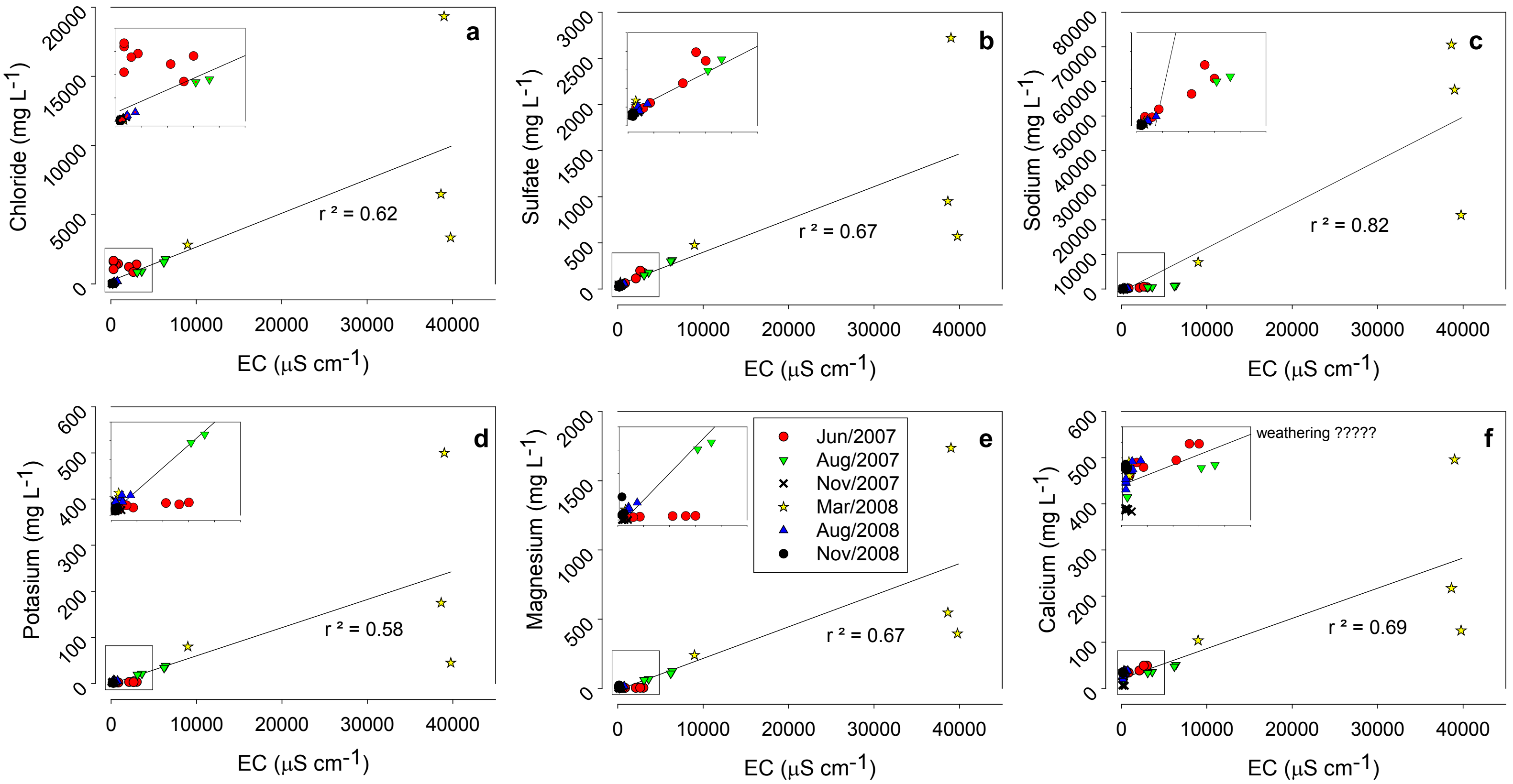


Figure 4. Linear regression between electrical conductivity (EC) and major ion concentrations: (a) chloride, (b) sulfate, (c) sodium, (d) potassium, (e) magnesium, and (f) calcium.

Chloride and sulfate concentrations were higher than expected in June 2007 in the samples (Figure 4a-b). However, sodium, potassium, and magnesium levels were lowest in June 2007 (Figure 4c-e). On the other hand, calcium levels were enhanced during rainy periods (August-November 2007/2008) at almost all sites along the Mataquito River

(Figure 4f). Seawater intrusion was very clearly indicated by all ions during the dry period (March 2008), and high ion concentrations and conductivity were found at the first three sampling sites closest to the river mouth (Figure 4a-f).

Figure 5 shows the relationship between total dissolved solids (TDS) and the $Na^+/(Na^+ + Ca^{2+})$ ratio (cation ratio) during the 2007-2008 time series along the Mataquito River. TDS and cation ratio in surface waters fluctuated between 106.5 and 109755.4 mg L^{-1}, and 0.06 and 1.00, respectively (Figure 5). High values of TDS and cation ratio were observed at the downstream sampling sites between June 2007 and August 2008. March 2008 exhibited the highest values (TDS: 6020.6-26639.8 mg L^{-1}, cation ratio: 0.99-1.00, stations E1-E4), followed by August 2007 (TDS: 2070.3-4281.3 mg L-1, cation ratio: 0.93-0.95, stations E1-E4), June 2007 (TDS: 397.6-2014.0 mg L-1, cation ratio: 0.71-0.93, stations E1-E5), August 2008 (TDS: 258.6-504.1 mg L-1, cation ratio: 0.93-0.95, stations E1-E4) and November 2007 (TDS: 267.0 mg L-1, cation ratio: 0.90, station E1) (Figure 5).

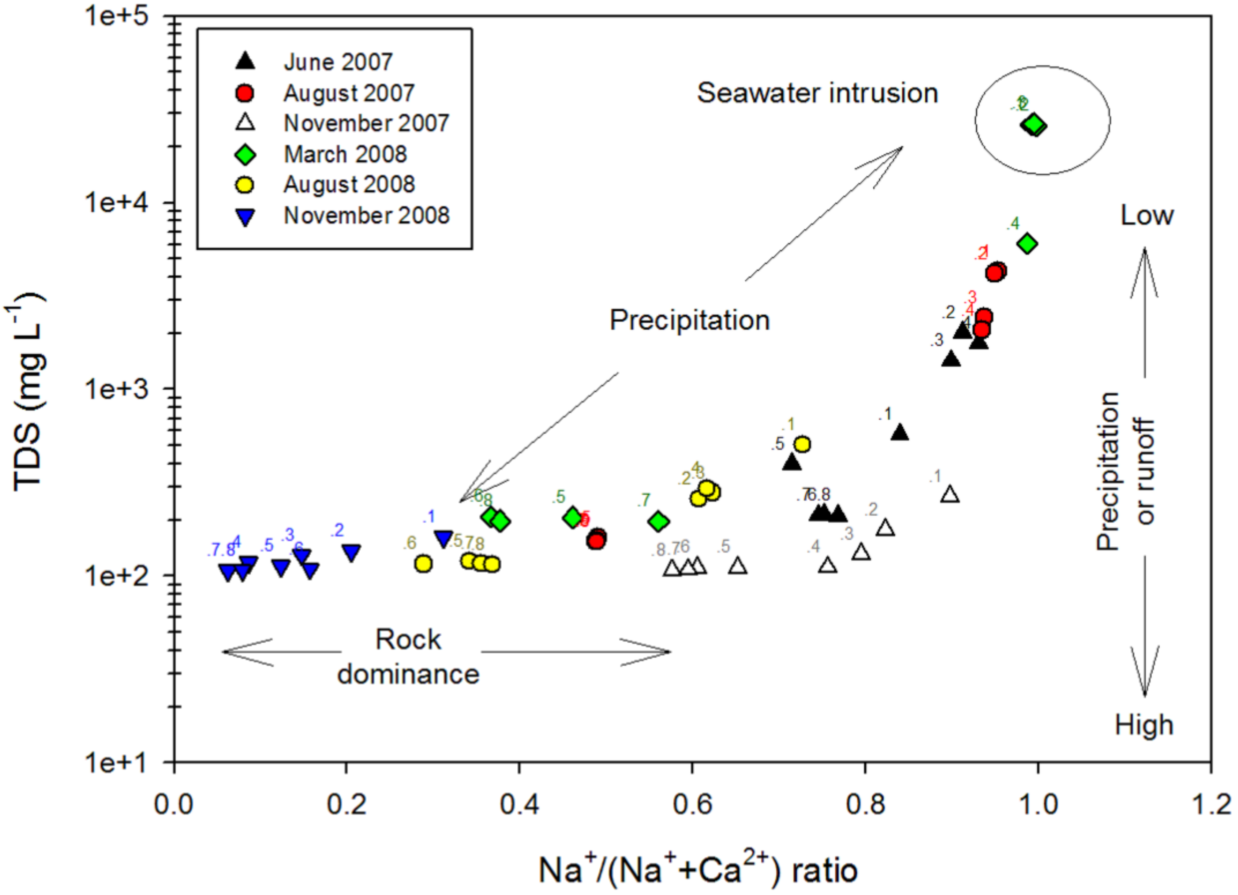


Figure 5. Variations in the weight ratio of $Na^+/(Na^++Ca^{2+})$ as a function of the total dissolved solid (TDS) contents of the Mataquito River surface waters (Modified from Torres-Ramírez *et al*., 2017).

In November 2008, relatively low TDS values were observed in along river (106.5-161.17 mg L-1, stations E1-E8), whereas cation ratio increased at the downstream sites (0.06-0.31, Figure 5). A similar contrast in TDS and cation ratio was observed between June 2007 and

August 2008, at upstream sampling sites (Figure 5). Samples from stations: E6-E8 (June 2007), E5-E8 (August 2007, March 2008, and August 2008) and E2-E8 (November 2007), showed low and relatively constant TDS values (107.0-212.7 mg L-1), while cation ratio increased between 0.29 and 0.82 (Figure 5).

The relative proportions of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}; Figure 6a) appeared distinct in terms of cation amounts and rainfall patterns for the Mataquito River (see Figure 2a). In June 2007, Na^+ + K^+ ranged from 70 to 90 %. In contrast, Ca^{2+} and Mg^{2+} were <10 % at all sampling sites (Figure 6a). In August 2007, at the first four sampling sites (E1-E4), Na^+ + K^+ was almost 90 %, Mg^{2+} was 10 %, and Ca^{2+} was 0 %. However, the upstream sites (E5-E8) showed 45 % Na^+ + K^+, 15 % Mg^{2+}, and 40 % Ca^{2+} (Figure 6a). The pattern observed in November 2007 was similar to that of June 2007, when Na^+ and K^+ were the predominant ions (~65-90 %; Figure 6a). The driest season (March 2008) showed clear evidence of a significant influence from seawater intrusion. The chemical composition was 100 % Na^+ and K^+ at the downstream sampling sites (E1-E4), and ~50 % of Na^+ + K^+ and Ca^{2+} at the upstream sites (E5-E8) (Figure 6a).

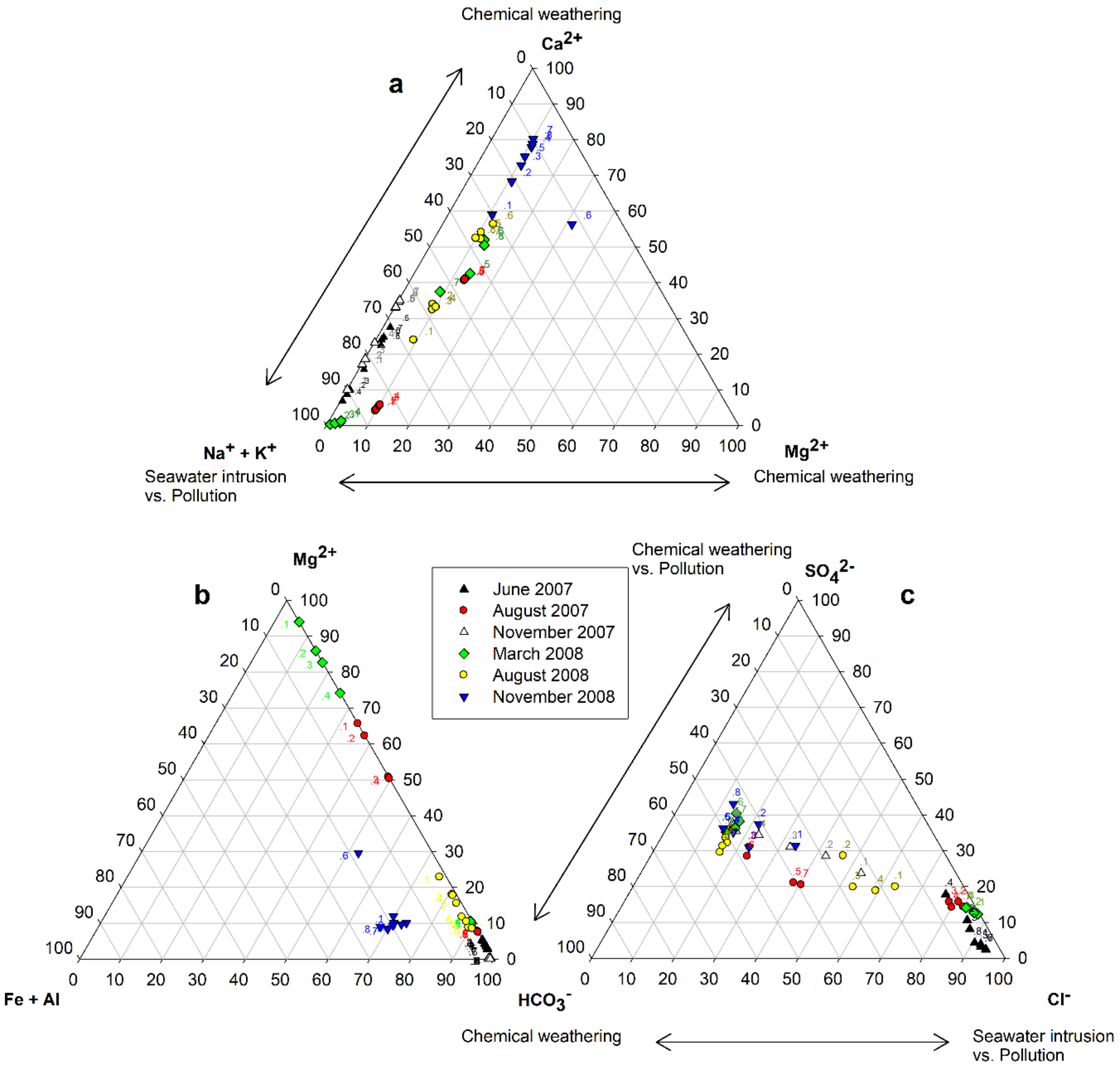


Figure 6. Ternary diagrams for: (a) the major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}), (b) Mg^{2+}, Fe+Al, and HCO_3^-, and (c) HCO_3^-, Cl^-, and SO_4^{2-} in the Mataquito River from June 2007 to November 2008.

In November 2008, the water's surface chemistry exhibited a heterogeneous ion composition along the river course, with a predominance of Na^+ and K^+ downstream and Ca^{2+} upstream. Ca^{2+} ranged between 50 and 80 % at all sampling sites, increasing towards the upstream sites. The other cations ($Na^+ + K^+$, Mg^{2+}) did not exceed 40 % (Figure 6a).

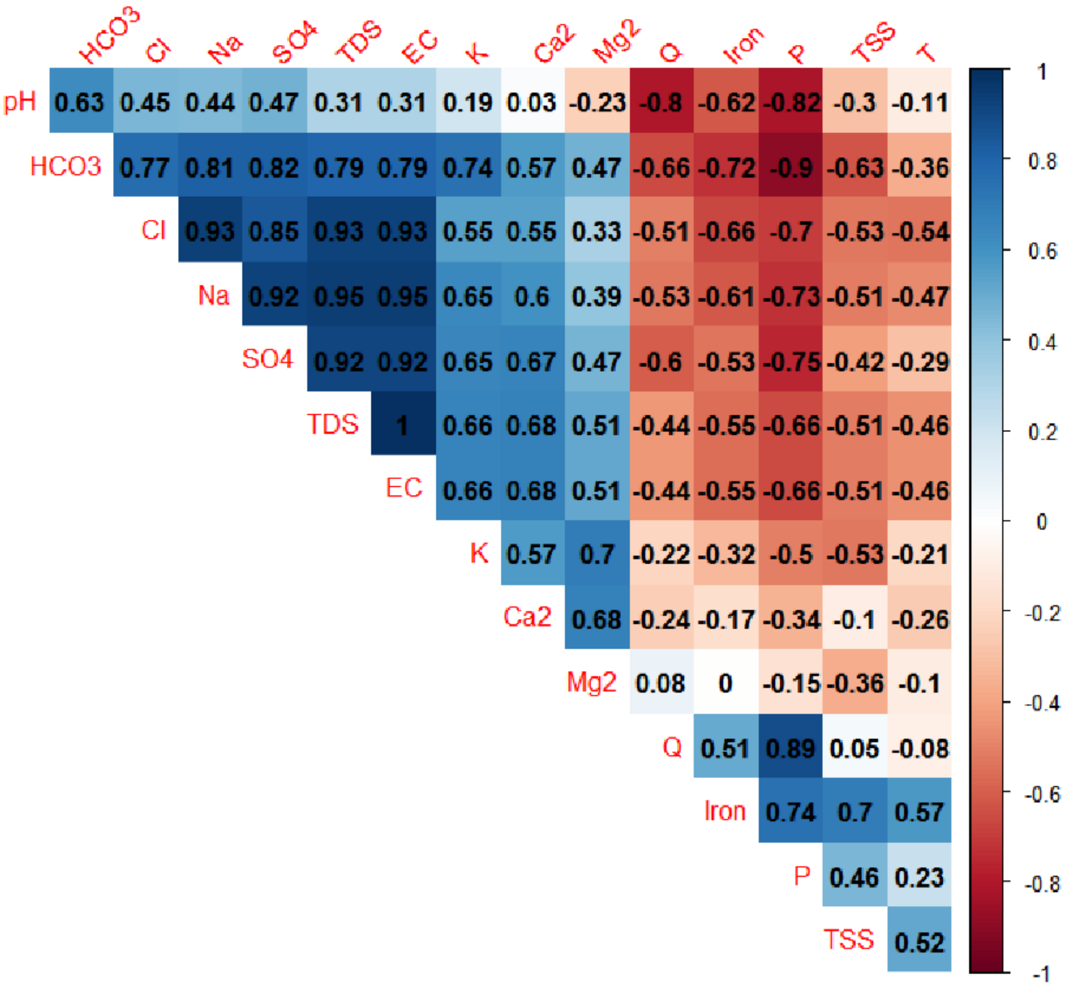
Figure 6b shows the relationship between the relative proportions of Fe+Al, Mg^{2+}, and HCO_3^-. The contents of Fe+Al, Mg^{2+}, and HCO_3^- in the surface waters of the Mataquito River varied widely along the time series (Figure 6b). Bicarbonate was almost 100 % in June 2007, unlike the other cations, but during the remaining months, bicarbonate levels dropped to <10 %, and the percent of Mg^{2+} increased (>90 %). Fe+Al did not exceed 5 %. In November 2008, Fe+Al increased significantly to >20 % at all sampling sites (Figure 6b), in agreement with the high rainfall and runoff detected during this time period (see Figure 2a).

In order to determine the contributions from natural processes (i.e., chemical weathering) versus pollution (i.e., industrial, and domestic effluents) to the hydrochemistry of the Mataquito River, we plotted changes in the proportions of three anions: HCO_3^-, SO_4^{2-}, and Cl^- (Figure 6c). In June 2007, Cl^- was between 70 and 90 %, whereas $SO_4^{2-}$and HCO_3^- were <20 % and <10 %, respectively (Figure 6c). In August 2007, the four downstream sampling sites (E1-E4) displayed almost 80 % Cl^-, 15 % HCO_3^-, and 5 % SO_4^{2-}. On the contrary, the upstream sites (E5-E8) showed 20-40 % Cl^-, 40-50 % HCO_3^-, and 20-30 % SO_4^{2-} (Figure 6c). In

November 2007, Cl^- declined to ~30-60 % at the four downstream sites (E1-E4), whereas $HCO_3^-$and SO_4^{2-} both increased (20 and 50 %, respectively, Figure 6c). A significant influence from seawater incursions was apparent during the driest season (March 2008), with >80 % Cl^- at the downstream sites (E1-E4), similar to Na^+ and K^+ (see Figure 6a). Upstream (E5-E8), the Cl^- distribution was 15 %, HCO_3^- was ~50 %, and SO_4^{2-} was 35 % (Figure 6c).

In November 2008, the surface water chemistry was slightly predominated by HCO_3^- and SO_4^{2-} upstream and Cl^- downstream. HCO_3^- ranged between 35 and 50 %, and SO_4^{2-} was between 30 and 40 %, increasing farther upstream. Cl^- did not exceed 25 %, and only station E1 exceeded 30 % (Figure 6c).

Figure 7 shows Spearman's correlation coefficients between discharge (Q), precipitation (P), and the physical-chemical parameters. Discharge (Q) had a positive significant correlation with precipitation (P), but negative significant correlations with temperature, EC, Ph, TDS, Cl-, HCO_3^-, and SO_4^{2-}. Moreover, Q had a negative but non-significant correlation with TSS and the other major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}; Figure 7). Precipitation (P) had significant negative correlations with EC, Ph, TDS, and the major ions, but positive correlations with TSS and iron (Figure 7).



	HCO3	Cl	Na	SO4	TDS	EC	K	Ca2	Mg2	Q	Iron	P	TSS	T
pH	0.63	0.45	0.44	0.47	0.31	0.31	0.19	0.03	-0.23	-0.8	-0.62	-0.82	-0.3	-0.11
HCO3		0.77	0.81	0.82	0.79	0.79	0.74	0.57	0.47	-0.66	-0.72	-0.9	-0.63	-0.36
Cl			0.93	0.85	0.93	0.93	0.55	0.55	0.33	-0.51	-0.66	-0.7	-0.53	-0.54
Na				0.92	0.95	0.95	0.65	0.6	0.39	-0.53	-0.61	-0.73	-0.51	-0.47
SO4					0.92	0.92	0.65	0.67	0.47	-0.6	-0.53	-0.75	-0.42	-0.29
TDS						1	0.66	0.68	0.51	-0.44	-0.55	-0.66	-0.51	-0.46
EC							0.66	0.68	0.51	-0.44	-0.55	-0.66	-0.51	-0.46
K								0.57	0.7	-0.22	-0.32	-0.5	-0.53	-0.21
Ca2									0.68	-0.24	-0.17	-0.34	-0.1	-0.26
Mg2										0.08	0	-0.15	-0.36	-0.1
Q											0.51	0.89	0.05	-0.08
Iron												0.74	0.7	0.57
P													0.46	0.23
TSS														0.52

Figure 7. Spearman's correlation coefficients between discharge (Q) and precipitation (P) and the physical-chemical parameters. Color bars represent strength of correlation.

According to the principal component analysis (PCA), three principal components (PC1, PC2, PC3) with eigenvalues >1 explained ~89 % of the total variance (Table 1). PC1 explained 55.1 % of the total variance, which was highly influenced by EC, TDS, three anions (Cl^-, HCO_3^-, SO_4^{-2}), and four cations (Na^+, K^+, Mg^{+2}, Ca^{+2}) (Figure 8). Moreover, these variables were directly related to seawater intrusion, except at sampling sites E5-E8 in June 2007. Unexpectedly, Na^+ and Cl^- levels were highest at these sites in this month.

Table 1. Loading factor matrix, eigenvalues, variance, and cumulative variance for the PCA of environmental data in the Mataquito River.

Variables	Component 1	Component 2	Component 3	Component 4
Q	-0.433	0.299	**0.780**	-0.059
P	-0.590	**0.716**	0.321	-0.023
Temperature	-0.127	0.361	**-0.806**	-0.072
EC	**0.896**	0.153	-0.012	-0.399
Ph	0.268	**-0.754**	-0.410	0.107
TSS	-0.283	**0.819**	-0.437	0.082
TDS	**0.896**	0.153	-0.012	-0.399
Cl^-	**0.944**	0.196	0.080	0.232
HCO_3^-	**0.813**	-0.424	-0.021	0.006
SO_4^{2-}	**0.947**	0.239	0.069	0.180
Na^+	**0.887**	0.217	0.006	-0.261
K^+	**0.921**	0.275	0.082	0.236
Mg^{2+}	**0.935**	0.278	0.069	0.171
Ca^{2+}	**0.943**	0.280	0.075	0.136
Iron	-0.340	**0.822**	-0.273	0.020
Eigenvalues	8.3	3.2	1.8	0.6
Variance (%)	55.1	21.7	12.2	4.0
Cumulative variance(%)	55.2	76.8	89.0	93.0

PCA loadings >0.70 are shown in bold.

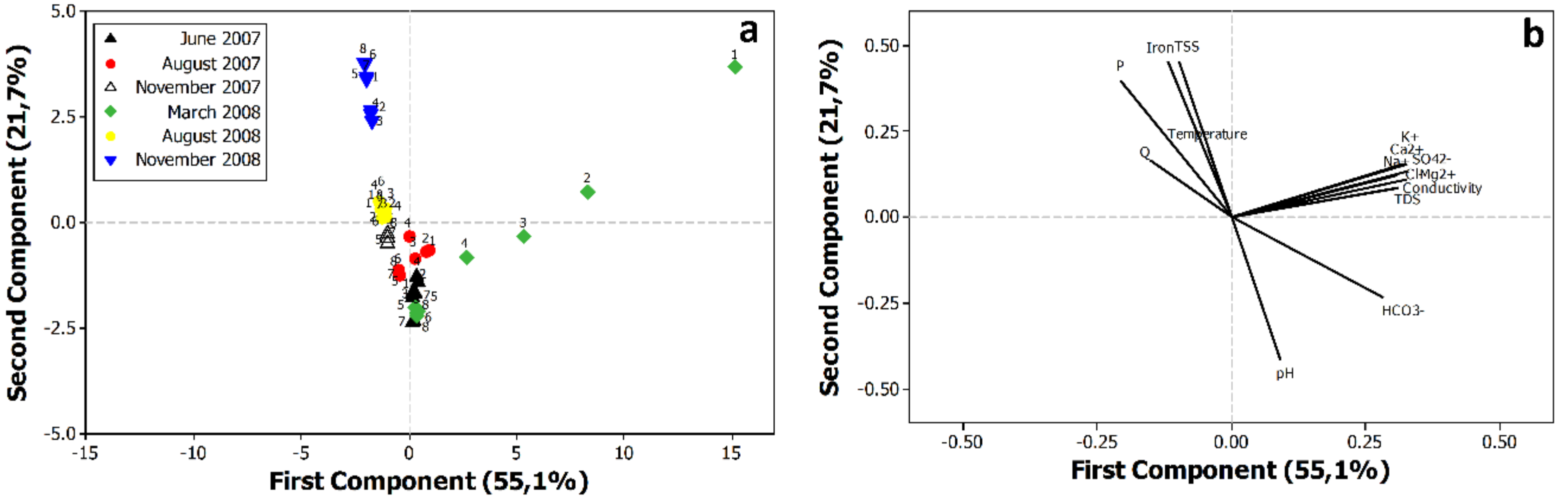


Figure 8. Factors and scores of the physical-chemical variables for the sampling sites during the 2007-2008 time series for the two first principal components.

PC2 explained 21.7 % of the total variance, characterized by P, pH, TSS, and iron. PC3 explained only 12.2 % of the total variance and was closely tied to water discharge (Q) and temperature (see Figure 8).

Discussion

Dissolved and particulate matter in river surface waters is strongly influenced by hydroclimate dynamics (*e.g.*, Rubio-Álvarez & McPhee, 2010; Urrutia *et al*., 2011; Saldías *et al*., 2016; Godin, Macdonald, Kuzyk, Goñi, & Stern, 2017); lithology, type and relative abundance of minerals (*e.g*., Muñoz *et al*., 2007; McClain & Maher, 2016); intensity of weathering processes (*e.g.*, Chen *et al*., 2002; Li *et al*., 2014a; Li *et al*., 2014b), and anthropogenic alterations (*e.g*., Xia, Yang, Wang, & Meng, 2005; Pizarro *et al.,* 2010; Potot *et al*., 2012; Vrebos *et al*., 2017).

The physical-chemical properties of the Mataquito River are closely associated with the seasonal hydrologic regime, i.e., rainfall, surface runoff, flow rates (Figure 2 and Figure 3), as occurs in other rivers with seasonal dynamics in central Chile (*e.g*., Debels, Figueroa, Urrutia, Barra, & Niell, 2005; Rubio-Álvarez & McPhee, 2010; Muñoz *et al*., 2016). However, seawater intrusions might control the chemistry of the Mataquito River upstream during dry conditions (March 2008) in response to decreased river discharge during this period (*e.g*., Gong & Shen, 2011; Gong, Shen, & Jia, 2013). Apparent pollution upstream was observed in June 2007. High percentages of sodium, chloride, and sulfate, found upstream in June 2007, suggest that conductivity is largely controlled by the release of these ions from industrial/agricultural activities and/or natural fluctuations within the basin. It can be difficult to differentiate between anthropogenic and natural sources of these ions. Nonetheless, several authors have reported that high levels of chlorine, sulfate, and sodium (amongst other parameters) indicate pollution and suggest that chloride is derived mainly from industrial and domestic effluents, whereas sulfate comes from air pollution and/or agricultural activities (*e.g.,* Chen *et al*., 2002; Singh *et al*., 2005; Huang, Sillanpää, Gjessing, & Vogt, 2009; Mulk *et al*., 2015).

The general processes controlling the chemistry of the Mataquito River were summarized in the Gibb's model plot (see Figure 5). Seasonally, the potential sources of the chemical elements varied widely at all sampling sites. In June 2007, a period with moderate precipitation and discharges (see Figure 2a), as reflected in the TDS vs. $Na^+/(Na^+ + Ca^{2+})$ ratio, the effects of precipitation increased steadily from down- to upstream (Figure 5). Although precipitation/discharge was significant in August 2007 (see Figure 2a), its influence (as well as that of weathering) on ion distribution was only observed at the four most upstream sampling sites. Downstream, the seawater influence was observed in a high-conductivity and high-cation ratio (Figure 5). In November 2007, the hydrological scenario was almost the same as before (Figure 2a), but the TDS/cation relationship showed a predominance of soil/rock weathering processes brought on by high precipitation, surface runoff, and discharge at all sampling sites (Figure 5). In March 2008, the hydrological scenario deviated completely from the rest of the time series. Seawater contributions were very clear downstream during the dry season (sampling sites E4-E1; see also Figure 2b) and sodium was the dominant ion, as at the other sampling sites (see Figure 4a-f). Upstream, the relationship showed a dominance of rock weathering processes controlled by river flow (Figure 5). High rainfall in August 2008 showed a distinct hydrological pattern from the previous year's (see Figure 2a). The low TDS/high calcium ratio indicated that derivate processes of rainfall (e.g., chemical weathering) were predominantly responsible for the surface water chemistry along the course of the Mataquito River. In fact, in November 2008, the peak precipitation levels and minimum TDS and cation ratios suggested predominantly rock sources due to weathering, due to high runoff (see also Figure 2a). This factor could also be seen in the high suspended particulate material concentrations along the Mataquito River during this period (see Figure 3c).

The ternary plots analysis of this time series suggests that surface water chemistry upstream in the Mataquito River is mainly determined by rainfall and runoff processes. Consequently, the combination of these processes might increase Ca^{2+}, Mg^{2+}, and HCO_3^- relative to Na^+, K^+, and Cl^- due to erosion and rock weathering reactions, mainly during wet months (*e.g.*, Chen *et al*., 2002; Meybeck, 2003; Huang *et al*., 2009). The relative dominance of Ca^{2+}, Mg^{2+}, and HCO_3^- during rainy periods might indicate carbonate weathering and/or dissolution of CO_2 gas (*e.g.*, Singh *et al*., 2005; Singh *et al*., 2008; Zhang, Kang, Wang, Li, & Xu, 2008; Huang *et al*., 2009). However, increased Fe+Al levels during the period of greatest precipitation and surface runoff rates (August-November 2008) suggest that the chemistry of the Mataquito River can also be influenced by silicate mineral weathering (*e.g*., Li *et al.,* 2014a; Mapoma *et al*., 2017).

The combination of several factors (e.g., heavy precipitation, high discharges, unusually high iron and TSS concentrations, warm temperatures from August-November 2008) revealed what may be the greatest weathering rates in the Mataquito basin. On the other hand, the effects of seawater intrusion (downstream, March 2008) and pollution (upstream, June 2007) are reflected in the highest percentages of sodium and chlorine.

Conclusions

This study reveals how, together, natural (precipitation, runoff, river flow, seawater intrusion) and anthropogenic (industrial/agricultural activities) factors may have modified the surface water chemistry in a Mediterranean river, i.e., Mataquito River. Important changes occurred in the water chemistry of the Mataquito River from 2007-2008, due to significant fluctuations between rainy and dry periods. During the wet months, heavy rainfall increased the input of major ions, mainly via rock weathering processes. However, during the dry period, seawater intrusion controlled the water chemistry in almost all the study area. The highest concentrations of chlorine and sulfate were found in areas associated with industrial and agricultural activities in the basin, suggesting that pollution was quantitatively important, a factor which should be considered in future studies in the area.

Acknowledgments

Authors thank Teresa Aguayo for their help in analyses in the Biotecmar Laboratories at UCSC, and the Environmental Management Office of Arauco y Constitución S.A. for providing the information presented in this study. JAP thanks the Research Office at UCSC.

References

Acker, J. G., & Leptoukh, G. (2007). Online analysis enhances use of NASA Earth Science Data. *Eos, Transactions American Geophysical Union*, 88(2), 14. Recovered from https://doi.org/10.1029/2007EO020003

Armengol, S., Manzano, M., Bea, S. A., & Martínez, S. (2017). Identifying and quantifying geochemical and mixing processes in the Matanza-Riachuelo Aquifer System, Argentina. *Science of the Total Environment*, 599-600, 1417-1432. Recovered from https://doi.org/10.1016/j.scitotenv.2017.05.046

Bahar, M. M., Ohmori, H., & Yamamuro, M. (2008). Relationship between river water quality and land use in a small river basin running through the urbanizing area of Central Japan. *Limnology*, 9, 19-26. Recovered from https://doi.org/10.1007/s10201-007-0227-z

Benabdelkader, A., Taleb, A., Probst, J. L., Belaidi, N., & Probst, A. (2018). Anthropogenic contribution and influencing factors on metal features in fluvial sediments from a semi-arid Mediterranean river basin (Tafna River, Algeria): A multi-indices approach. *Science of the Total Environment*, 626, 899-914. Recovered from https://doi.org/10.1016/j.scitotenv.2018.01.107

Belmar, M., & Morata, D. (2005). Nature and P-T-t constraints of very low-grade metamorphism in the Triassic-Jurassic basins, Coastal Range, central Chile. *Revista Geológica de Chile*, 32(2), 189-205. Recovered from https://doi.org/10.4067/S0716-02082005000200002

Bonada, N., & Resh, V. H. (2013). Mediterranean-climate streams and rivers: Geographically separated but ecologically comparable freshwater systems. *Hydrobiologia*, 719, 1-29. Recovered from https://doi.org/10.1007/s10750-013-1634-2

Chase, Z., Strutton, P. G., & Hales, B. (2007). Iron links river runoff and shelf width to phytoplankton biomass along the U.S. West Coast. *Geophysical Research Letters*, 34(4). Recovered from https://doi.org/10.1029/2006GL028069

Chen, J., Wang, F., Xia, X., & Zhang, L. (2002). Major element chemistry of the Changjiang (Yangtze River). *Chemical Geology*, 187(3-4), 231-255. Recovered from https://doi.org/10.1016/S0009-2541(02)00032-3

Dagg, M., Benner, R., Lohrenz, S., & Lawrence, D. (2004). Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: Plume processes. *Continental Shelf Research*, 24(7-8), 833-858. Recovered from https://doi.org/10.1016/j.csr.2004.02.003

Dávila, P. M., Figueroa, D., & Müller, E. (2002). Freshwater input into the coastal ocean and its relation with the salinity distribution off austral Chile (35-55°S). *Continental Shelf Research*, 22(3), 521-534. Recovered from https://doi.org/10.1016/S0278-4343(01)00072-3

Debels, P., Figueroa, R., Urrutia, R., Barra, R., & Niell, X. (2005). Evaluation of water quality in the Chillán River (Central Chile) using physicochemical parameters and a modified Water Quality Index. *Environmental Monitoring and Assessment*, 110, 301-322. Recovered from https://doi.org/10.1007/s10661-005-8064-1

Dessandier, P. A., Bonnin, J., Kim, J. H., Bichon, S., Deflandre, B., Grémare, A., & Sinninghe-Damsté, J. S. (2016). Impact of organic matter source and quality on living benthic foraminiferal distribution on a river-dominated continental margin: A study of the Portuguese margin. *Journal of Geophysical Research: Biogeosciences*, 121(6), 1689-1714. Recovered from https://doi.org/10.1002/2015JG003231

Frings, P. J., Clymans, W., Fontorbe, G., De-La-Rocha, C. L., & Conley, D. J. (2016). The continental Si cycle and its impact on the ocean Si isotope budget. *Chemical Geology*, 425, 12-36. Recovered from https://doi.org/10.1016/j.chemgeo.2016.01.020

Gibbs, R. J. (1970). Mechanisms controlling world water chemistry. *Science*, 170(3962), 1088-1090. DOI: 10.1126/science.170.3962.1088

Godin, P., Macdonald, R. W., Kuzyk, Z. Z. A., Goñi, M. A., & Stern, G. A. (2017). Organic matter compositions of rivers draining into Hudson Bay: Present-day trends and potential as recorders of future climate change. *Journal of Geophysical Research: Biogeosciences*, 122(7), 1848-1869. Recovered from https://doi.org/10.1002/2016JG003569

Gong, W., & Shen, J. (2011). The response of salt intrusion to changes in river discharge and tidal mixing during the dry season in the Modaomen Estuary, China. *Continental Shelf Research*, 31(7-8), 769-788. DOI: 10.1016/j.csr.2011.01.011

Gong, W., Shen, J., & Jia, L. (2013). Salt intrusion during the dry season in the Huangmaohai Estuary, Pearl River Delta, China. Journal of Marine Systems. Recovered from https://doi.org/10.1016/j.jmarsys.2012.11.006

Greenberg, A. E., Clesceri, L. S., & Eaton, A. D. (1995). *Standard methods for the examination of water and wastewater* (18th ed.). Washington, DC, USA: American Public Health Association.

Hanna, N., Lartiges, B., Kazpard, V., Maatouk, E., Amacha, N., Sassine, S., & El-Samrani, A. (2018). Hydrogeochemical processes in a small Eastern Mediterranean karst watershed (Nahr Ibrahim, Lebanon). *Aquatic Geochemistry*, 24, 325-344. Recovered from https://doi.org/10.1007/s10498-018-9346-x

Huang, X., Sillanpää, M., Gjessing, E. T., & Vogt, R. D. (2009). Water quality in the Tibetan Plateau: Major ions and trace elements in the headwaters of four major Asian rivers. *Science of the Total Environment*, 407(24), 6242-6254. Recovered from https://doi.org/10.1016/j.scitotenv.2009.09.001

Humborg, C., Ittekkot, V., Cociasu, A., & Bodungen, B. V. (1997). Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature*, 386, 385-388. Recovered from https://doi.org/10.1038/386385a0

Li, S. L., Chetelat, B., Yue, F., Zhao, Z., & Liu, C. Q. (2014a). Chemical weathering processes in the Yalong River draining the eastern Tibetan Plateau, China. *Journal of Asian Earth Sciences*, 88, 74-84. Recovered from https://doi.org/10.1016/j.jseaes.2014.03.011

Li, S., Lu, X. X., & Bush, R. T. (2014b). Chemical weathering and CO2 consumption in the Lower Mekong River. *Science of the Total Environment*, 472, 162-177. Recovered from https://doi.org/10.1016/j.scitotenv.2013.11.027

McClain, C. N., & Maher, K. (2016). Chromium fluxes and speciation in ultramafic catchments and global rivers. *Chemical Geology*, 426, 135-157. Recovered from https://doi.org/10.1016/j.chemgeo.2016.01.021

Mapoma, H. W. T., Xie, X., Liu, Y., Zhu, Y., Kawaye, F. P., & Kayira, T. M. (2017). Hydrochemistry and quality of groundwater in alluvial aquifer of Karonga, Malawi. *Environmental Earth Sciences*, 76. Recovered from https://doi.org/10.1007/s12665-017-6653-2

Meybeck, M. (2003). Global occurrence of major elements in rivers. In: *Treatise on geochemistry*. Recovered from https://doi.org/10.1016/B0-08-043751-6/05164-1

Mulk, S., Azizullah, A., Korai, A. L., & Khattak, M. N. K. (2015). Impact of marble industry effluents on water and sediment quality of Barandu River in Buner District, Pakistan. *Environmental Monitoring and Assessme*nt, 187. Recovered from https://doi.org/10.1007/s10661-014-4221-8

Muñoz, A. A., González-Reyes, A., Lara, A., Sauchyn, D., Christie, D., Puchi, P., Urrutia-Jalabert, R., Toledo-Guerrero, I., Aguilera-Betti, I., Mundo, I., Sheppard, P. R., Stahle, D., Villalba, R., Szejner, P., LeQuesne, C., & Vanstone, J. (2016). Streamflow variability in the Chilean Temperate-Mediterranean climate transition (35°S–42°S) during the last 400 years inferred from tree-ring records. *Climate Dynamics*, 47, 4051-4066. Recovered from https://doi.org/10.1007/s00382-016-3068-9

Muñoz, J. F., Fernández, B., Varas, E., Pastén, P., Gómez, D., Rengifo, P.,…, & Jofré, J. C. (2007). Chilean water resources. *Geological Society Special Publication*. Recovered from https://doi.org/10.1144/goch.8

Nash, J. D., & Moum, J. N. (2005). River plumes as a source of large-amplitude internal waves in the coastal ocean. *Nature*, 437, 400-403. Recovered from https://doi.org/10.1038/nature03936

Orrego, R., Marshall-Adams, S., Barra, R., Chiang, G., & Gavilan, J. F. (2009). Patterns of fish community composition along a river affected by agricultural and urban disturbance in south-central Chile. *Hydrobiologia*, 620, 35-46. Recovered from https://doi.org/10.1007/s10750-008-9613-8

Palmer, M. A., Reidy-Liermann, C. A., Nilsson, C., Flörke, M., Alcamo, J., Lake, P. S., & Bond, N. (2008). Climate change and the world's river basins: Anticipating management options. *Frontiers in Ecology and the Environment*, 6(2), 81-89. Recovered from https://doi.org/10.1890/060148

Pizarro, J., Vergara, P. M., Rodríguez, J. A., Sanhueza, P. A., & Castro, S. A. (2010). Nutrients dynamics in the main river basins of the centre-southern region of Chile. *Journal of Hazardous Materials*, 175(1-3), 608-613. Recovered from https://doi.org/10.1016/j.jhazmat.2009.10.048

Potot, C., Féraud, G., Schärer, U., Barats, A., Durrieu, G., Le Poupon, C.,…, & Simler, R. (2012). Groundwater and river baseline quality using major, trace elements, organic carbon and Sr-Pb-O isotopes in a Mediterranean catchment: The case of the Lower Var Valley (south-eastern France). *Journal of Hydrology*, 472-473, 126-147. Recovered from https://doi.org/10.1016/j.jhydrol.2012.09.023

Rubio-Álvarez, E., & McPhee, J. (2010). Patterns of spatial and temporal variability in streamflow records in south central Chile in the period 1952-2003. *Water Resources Research*, 46(5). Recovered from https://doi.org/10.1029/2009WR007982

Saldías, G. S., Sobarzo, M., Largier, J., Moffat, C., & Letelier, R. (2012). Seasonal variability of turbid river plumes off central Chile based on high-resolution MODIS imagery. *Remote Sensing of Environment*, 123, 220-233. Recovered from https://doi.org/10.1016/j.rse.2012.03.010

Saldías, G. S., Largier, J. L., Mendes, R., Pérez-Santos, I., Vargas, C. A., & Sobarzo, M. (2016). Satellite-measured interannual variability of turbid river plumes off central-southern Chile: Spatial patterns and the influence of climate variability. *Progress in Oceanography*, 146, 212-222. Recovered from https://doi.org/10.1016/j.pocean.2016.07.007

Singh, A. K., Mondal, G. C., Kumar, S., Singh, T. B., Tewary, B. K., & Sinha, A. (2008). Major ion chemistry, weathering processes and water quality assessment in upper catchment of Damodar River basin, India. *Environmental Geology*, 54, 745-758. Recovered from https://doi.org/10.1007/s00254-007-0860-1

Singh, K. P., Malik, A., & Sinha, S. (2005). Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques - A case study. *Analytica Chimica Acta*, 538(1-2), 355-374. Recovered from https://doi.org/10.1016/j.aca.2005.02.006

Torres-Ramírez, P., Ortiz, J., Figueroa, S., Jerez, R., & Arcos, D. (2017). Characterization of the coastal wetland Mataquito, Curico province, Maule region. In: *The Ecology and Natural History of Chilean Saltmarshes*. Recovered from https://doi.org/10.1007/978-3-319-63877-5_8

Urrutia, R. B., Lara, A., Villalba, R., Christie, D. A., Le-Quesne, C., & Cuq, A. (2011). Multicentury tree ring reconstruction of annual streamflow for the Maule River watershed in south central Chile. *Water Resources Research*, 47(6). Recovered from https://doi.org/10.1029/2010WR009562

Vrebos, D., Beauchard, O., & Meire, P. (2017). The impact of land use and spatial mediated processes on the water quality in a river system. *Science of the Total Environment*, 601-602, 365-373. Recovered from https://doi.org/10.1016/j.scitotenv.2017.05.217

Xia, X., Yang, Z., Wang, R., & Meng, L. (2005). Contamination of oxygen-consuming organics in the Yellow River of China. *Environmental Monitoring and Assessment*, 110, 185-202. Recovered from https://doi.org/10.1007/s10661-005-7863-8

Zampella, R. A., Procopio, N. A., Lathrop, R. G., & Dow, C. L. (2007). Relationship of land-use/land-cover patterns and surface-water quality in the Mullica River basin. *Journal of the American Water Resources Association*, 43(3), 594-604. Recovered from https://doi.org/10.1111/j.1752-1688.2007.00045.x

Zhang, Q., Kang, S., Wang, F., Li, C., & Xu, Y. (2008). Major ion geochemistry of Nam Co lake and its sources, Tibetan Plateau. *Aquatic Geochemistry*, 14, 321-336. Recovered from https://doi.org/10.1007/s10498-008-9039-y