Hydrochemical Characteristics of Mid-Low Sections of North Patagonia Rivers, Argentina

Camilo Vélez-Agudelo, Daniel E. Martínez, Orlando M. Quiroz-Londoño, and Marcela A. Espinosa

Abstract The chemical composition of water in the mid-low sections of the three main rivers of Patagonia (Colorado, Negro and Chubut rivers) is an important proxy for the understanding of the water cycle in the region. River water samplings were done in summer and winter campaigns at Colorado (15 sites), Negro (18 sites) and Chubut (17 sites). Hydrochemical variables: pH, conductivity, salinity, and ion concentrations were measured. The data processing included regular hydrochemical diagrams, multivariate statistical analysis and saturation indexes calculation. The three rivers have two different sections: one inland section having the continental hydrochemical fingerprint and an estuarine section, with a markedly seawater mixing effect. Most water samples of the inland sites belong to the Mg^{2+}–Ca^{2+}–HCO_3^- type in the Negro and Chubut rivers and to the Ca^{2+}–SO_4^{2-} type in the Colorado River. In contrast, the prevailing hydrochemical facies was the Na–Cl type at estuarine sites. In general, rock weathering was the main hydrogeochemical process controlling chemistry composition of rivers, being the dissolution of gypsum, carbonate and silicate minerals the primary contributors. The inland section has a different composition for each river, which is related to differences in the rock-composition at the sources and chemical reactions during downstream flow. The Colorado River also showed the highest average values in salinity, conductivity and dissolved ions. Basin geology and brackish discharges from Curacó River during the high rainfall season contributed to explain the ionic concentration in Colorado River, in particular the excess of calcium and sulfate.

Keywords Major ions · River · Hydrochemistry · Patagonia

C. Vélez-Agudelo · D. E. Martínez (✉) · O. M. Quiroz-Londoño · M. A. Espinosa
Instituto de Geología de Costas y del Cuaternario, Universidad Nacional de Mar del Plata/CIC,
CC 722 7600 Mar del Plata, Argentina
e-mail: demarti@mdp.edu.ar

Instituto de Investigaciones Marinas y Costeras, CONICET, Universidad Nacional de Mar del Plata, Mar del Plata, Argentina

© The Author(s), under exclusive license to Springer Nature Switzerland AG 2021

A. I. Torres and V. A. Campodonico (eds.), *Environmental Assessment of Patagonia's Water Resources*, Environmental Earth Sciences,
https://doi.org/10.1007/978-3-030-89676-8_7

1 Introduction

Climatic change and human pressures increasingly stress the water resources worldwide (WWAP 2019). The challenge is greater in semiarid and arid areas, not only due to the predominant water scarcity but also to the increased vulnerability of their aquatic ecosystems (Huang et al. 2017; Wu et al. 2013). In these regions, the supply of easily accessible freshwater resources is found in dryland rivers, having their headwaters in areas of higher elevation. These fluvial environments are heterogeneous and complex systems whose hydrological dynamic occur on a small spatial and temporal scale (Davies et al. 2016). The chemical composition of surface waters in dryland rivers is characterized by the strong interaction between factors such as basin geology, hydroclimatic regimen, groundwater inputs, and biological activities (Sheldon and Fellows 2010). At a local scale, external factors such as soil erosion and the discharge of domestic and agricultural sewage also strongly affect the chemical balance of fluvial waters.

Hydrogeochemical studies are recognized as powerful tools to insight the processes and interactions that determine the composition and evolution of river systems (Hem et al. 1990; Hua et al. 2020; Jiang et al. 2020). The hydrochemical composition of rivers is indicative of the predominating processes of the drainage area and its linked environmental conditions are applied since the pioneer work of Gibbs (1970). In a broad sense, such studies enable to analyze the water–sediment interactions (ion exchange, dissolution–precipitation), to establish possible water mixtures (seawater intrusion, contribution from different aquifers), and to define sources and contamination processes (Carol and Kruse 2012; Li et al. 2019). Although hydrochemical studies have been effectively and widely applied to the assessment of surface water quality around the world, their potential in management matters remains still overlooked in Patagonia.

Compared with other continental landmass of the Southern Hemisphere, the Patagonia steppe has characteristics that make it unique in the region. In geological terms, this ancient basement is characterized by a varied lithology, structure and age (Coronato et al. 2008). This vast territory is also crossed by several dryland rivers, recording in the chemistry of its waters the effects on the environmental differences in the regional gradient. Among the eight main fluvial systems, Colorado, Negro and Chubut rivers account for about 78% of the drainage basin of Argentine Patagonia (Pasquini and Depetris 2007). These rivers support most of the economic, social and cultural activities of the region since they are the only available and stable water source for the surrounding communities. However, the rivers are currently threatened by moderate to intense human impacts because unsustainable agricultural practices, oil extraction and transportation, the expansion of urban areas, salinization of soils, use of agrochemicals and sewage effluents insufficiently treated of domestic and industrial activities (Abrameto et al. 2017; Brunet et al. 2005; Isla et al. 2015).

Up to now the hydrochemical studies of Patagonia rivers are either scarce or based only in a few samples, so further investigations are required (Brunet et al. 2005; Depetris 1980; Depetris et al. 2005; Gaiero et al. 2003). As the Colorado, Negro and

Chubut rivers flow through a large semiarid to arid region, these fluvial systems are strategically crucial to support both, biodiversity conservation and sustainable use of water resource from northern Patagonia. Hence, it is essential to have a comprehensive and extensive analysis of the hydrochemistry processes that take place in this arid region in order to develop suitable and efficient management strategies of their water resources.

In this context, a hydrochemical survey performed at several sampling points in the mid-low sections of the Colorado, Negro and Chubut rivers during summer and winter seasons is presented. The specific research questions intended to be addressed by the current study include: (i) What are the general hydrochemical characteristics of rivers? (ii) Are there spatial and temporal variations in the chemical composition among rivers? (iii) What are the main dominant processes controlling the hydrogeochemistry on a local scale? The main goal is to characterize the water composition and to analyze environmental factors that constrain the evolution of each river water composition.

2 Regional Setting and Previous Studies

Patagonia is the southernmost portion of Argentina (Fig. 1) representing about a third part of the country's territory. In this vast and diverse region, the Andes Cordillera plays an essential role in controlling the climate (Coronato et al. 2008). The moist air coming from the Pacific Ocean is lifted as it moves over the mountain range, producing heavy rainfalls on the western side. When the westerlies winds reach the eastern side of Patagonia, they become warmer and drier and the precipitation decreases abruptly (Paruelo et al. 2007). This strong west-east rainfall gradient creates two climatic and phytogeographic units: Andean Patagonia to the west and extra-Andean plateau drylands extending eastwards. A wet-temperate forest characterizes the first (about 700 mm year^{-1}), while a dry to semiarid climate (200 mm year^{-1} or less) prevails over the plateau. This last region is a large and heterogeneous environment that represents more than 60% of Patagonia region (Coronato et al. 2017; Depetris et al. 2005).

In addition to its aridity, the plateau drylands show a winter-summer thermal amplitude ranging from 5 to 16 °C, a highly evaporative condition and the intensity and persistence of the westerly winds exert a strong influence on the erosive processes that affect the extra-Andean region (Garreaud et al. 2013; Mazzoni and Vázquez 2009).

The geology of the Patagonia plateau (Fig. 2) exhibits a diverse lithology usually dominated by basalts, andesites, rhyolites and the well-known occurrence of pebbles or *rodados patagónicos* i.e. rounded rock fragments generated by erosion during water transport (Gaitán et al. 2020; Zambrano and Urien 1970). Tectonic, volcanism and past glaciations shaped diverse landforms, including elevated tablelands, hilly ranges, terraced levels, dune fields and fluvioglacial valleys that descend in elevation from the Andean sector towards the Atlantic coast (Hernández et al. 2008).

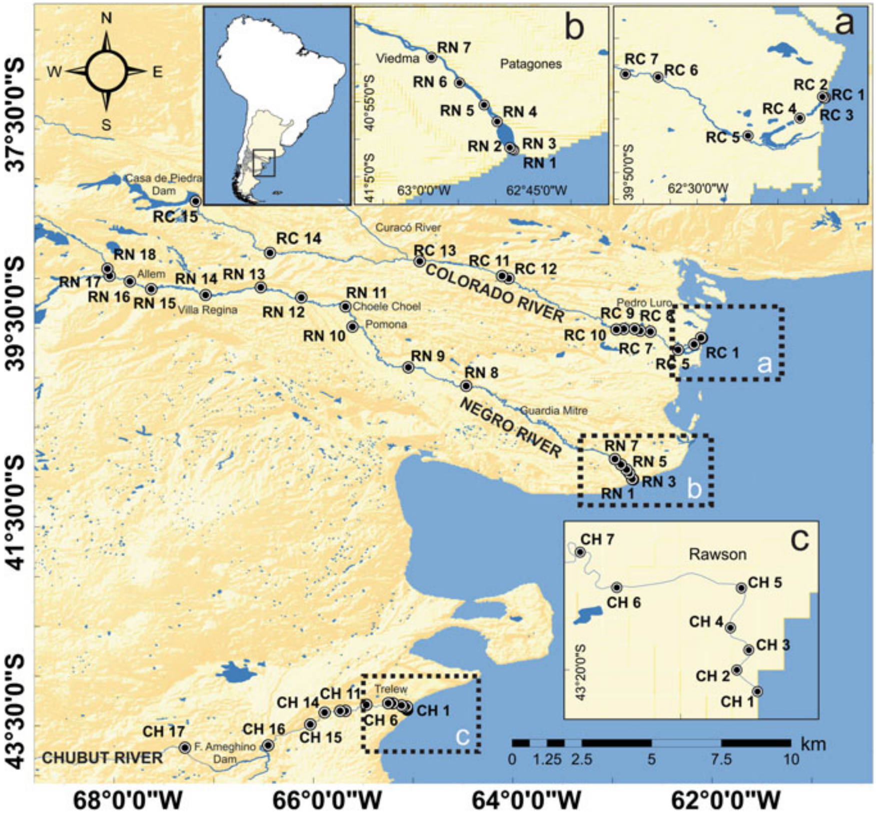

Fig. 1 Map of north Patagonia showing the location of sampling sites at the Colorado, Negro and Chubut rivers

The Colorado, Negro and Chubut rivers cross the northern Patagonia through wide fluvial valleys characterized by high cliffs. These watercourses originate on the eastern slope of the Andes and flow in a NW–SE direction until they reach the South Atlantic Ocean. As these rivers run through the arid tableland eastward, they gradually acquire allochthonous conditions and become more meandering, allowing the development of highly diverse riparian zones which are dynamic on a spatial and temporal scale (Paruelo et al. 2007).

While the Negro and Chubut rivers show a pluvio-nival regime due to the rainfall and snowfall contributions at the headwaters, the Colorado River is fed mostly by snowmelt (Coronato et al. 2008). It should be noted that the Atlantic Ocean exerts a moderate effect in temperature and precipitation in some areas of northeastern Patagonia (Gaitán et al. 2020).

The Negro River starts from the confluence of the Limay and Neuquén rivers at 635 km from the coast. This river displays a mean annual discharge of 900 $m^3\ s^{-1}$ (1951–2012), the greatest flow of Patagonia. Discharges of the Colorado

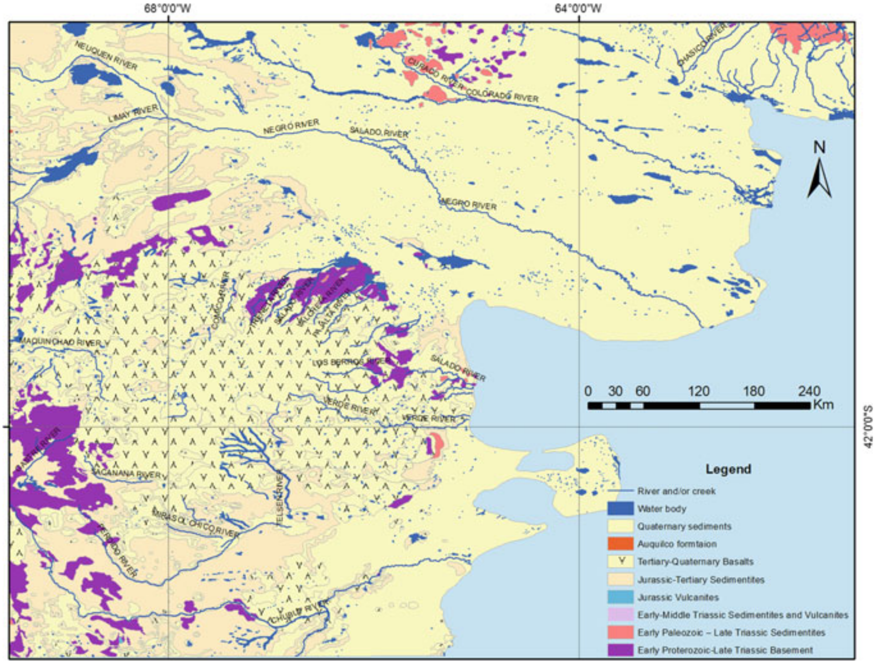

Fig. 2 Geological map of the study area

and Chubut rivers are about 155 m^3 s^{-1} (1940–2016) and 48 m^3 s^{-1} (1943–2016), respectively. At the Colorado River, the increase in discharge takes place at the end of the southern winter (due to snowmelt), reaching its highest values in spring and gradually decreasing towards the end of summer (Fig. 3). Meanwhile, the Negro and Chubut rivers show two peaks of flood discharges: one during the autumn and winter rainfalls and another one in spring due to snowmelt in the Andes (Pasquini et al. 2005; Romero and González 2016).

Climatic factors and the construction of several dams in the middle basins, have caused a downward trend of discharges at these rivers (Barros et al. 2015). Dams provide hydroelectric generation, land irrigation and water supply for human consumption at a provincial and national scale.

3 Materials and Methods

3.1 *Sample Collection and Chemical Analysis*

Fifty sampling sites were selected at the lower and middle basins from Colorado (15), Negro (18) and Chubut (17) rivers, covering a broad environmental gradient

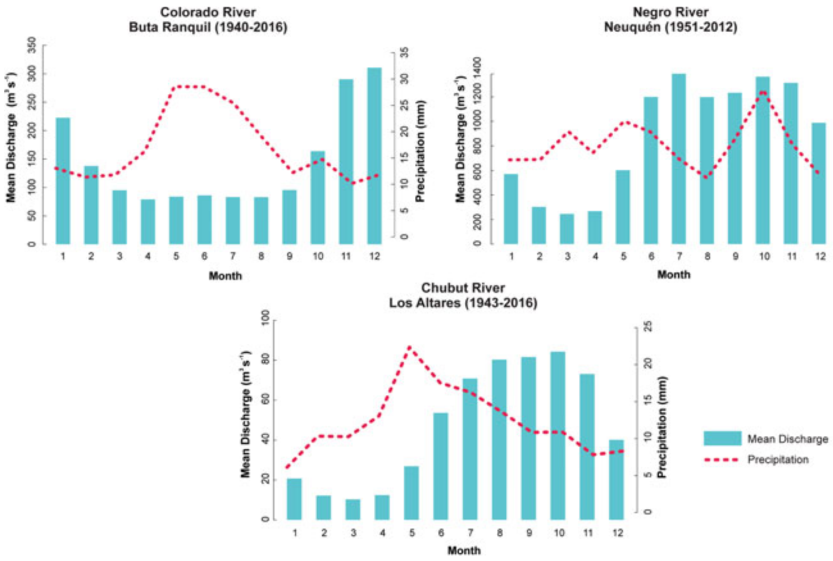

Fig. 3 Hydrographs showing the average discharges and precipitation of the north Patagonian rivers. Database of Colorado and Chubut rivers was taken from the National Water Information System of Argentina. Hydrological information of Negro River was modified from Romero and González (2016)

and fluvial morphology (Fig. 1). In addition, these sampling sites also were selected on the basis of some land-use activities characterizing each rivers section: intensive irrigation agriculture, livestock farms, mining and urban areas. In each site, physical and chemical variables of surface water were measured twice (during summer and winter) between the 2014 and 2015. It was not possible to measure in field and collect samples during austral winter in sites close to the outlet (RC1, RC2, RC3 and RC4) of the Colorado River, because diversion towards the main channel of the river, to prevent flooding, caused the complete dry up of the northern branch of the delta.

A Horiba U-10 water quality analyser was used to measure in situ pH, salinity (‰), conductivity (μS cm^{-1}), and water temperature (ºC). Major ions (HCO_3^-, Cl^-, SO_4^{-2}, NO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+}), and additional chemical variables as total hardness and silica (SiO_2) were analysed in the laboratory according to standardized methods (APHA 1998) including the corresponding detection limits (DL): chloride following Mhor method (DL 0.1 mg L^{-1}), sulfate by turbidimetry (DL 1 mg L^{-1}), calcium (DL 0.5 mg L^{-1}) and magnesium (DL 1 mg L^{-1}) by complexometric titrations with EDTA, sodium (DL 0.2 mg L^{-1}) and potassium (DL 0.1 mg L^{-1}) by flame spectrometry, bicarbonate (DL 0.5 mg L^{-1}) by potentiometric titrations, total silica by means of silico-molybdate method (DL 0.2 mg L^{-1}) and nitrate by a spectrophotometer Hach DREL 2800 method (DL 0.5 mg L^{-1}).

Water samples were collected in polypropylene bottles and kept refrigerated until the laboratory analysis. For nitrate analysis, water samples were preserved by acidification with HCl at $pH < 2$. Electroneutrality balances were done in order to check the quality of the results, and in all the cases the error was below 10%, being below 5% in about 90% of the samples.

3.2 Preprocessing Data and Numerical Methods

The seasonal variation (winter–summer) of the physical and chemical variables was explored using beanplot analysis (Kampstra 2015). This graphical technique is an alternative way to compare univariate data into each river and among rivers. Furthermore, Kruskal-Wallis test followed up by Dunn's test were applied to identify significant differences among rivers. Principal Component Analysis (PCA) based on a correlation matrix was undertaken to reduce dimensionality of the whole dataset and identify meaningful variables that influence the chemical signature of surface waters in rivers. Prior to this analysis, environmental data (except for the pH) were log-transformed (log + 1) due to their skewed distribution. In order to eliminate the effect of tides both, the descriptive and ordination analyses, were conducted with the complete data set (50 sites) and without the estuarine sites (38 sites).

Major ion composition was analysed from typical diagrams such as the Gibbs diagram (Gibbs 1970) and Piper-Hill diagrams (Piper 1944). Ionic ratios of major elements were used to analyse the relative concentration of the different ions and their interaction, as well as to determine the types of hydro-geochemical processes controlling the chemical composition of rivers. Moreover, the chemical processes explaining the hydrochemical evolution were treated with the support of the PHREEQC code (Parkhurst and Appelo 1999). All descriptive and ordination analyses were performed with the statistical software R version 3.2.2 (R Development Core Team 2015), using additional packages such as "vegan" version 2.3-0 (Oksanen et al. 2015), and "beanplot" version 1.2 (Kampstra 2015).

4 Results

4.1 General and Seasonal Variability

Statistical analysis results of physical and chemical variables measured in the study area are presented in Tables 1, 2 and 3. Although only one sampling is not enough to characterize the seasonal behavior of a river, the availability of many sampling sites allows performing a comparison on the distribution of values comparing summer against winter campaigns.

The hydrochemical analyses provided a clear distinction among the middle basin sites and those located at the estuarine sites of the rivers (Fig. 4). Surface water temperature exhibited the same seasonal pattern in the three rivers. Although this

Table 1 Statistical summary of physical and chemical variables measured in summer (complete data set)

	Chubut River					Colorado River					Negro River				
	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV
pH	8.7	9.1	9.4	0.2	2.4	7.4	8.4	9.4	0.7	8.1	7.5	8.8	9.6	0.5	5.1
Conductivity (mS cm^{-1})	0.2	3.8	26.8	8.3	215.5	0.1	4.2	20.1	6.3	151.4	0.1	1.5	10.2	3.0	204.3
Temperature (ºC)	17.0	19.1	20.8	1.4	7.1	20.0	22.7	27.5	2.1	9.1	20.9	22.0	25.0	0.9	4.3
Salinity (‰)	0.0	2.2	16.5	5.1	232.3	0.5	2.3	12.1	3.8	163.9	0.0	0.7	5.6	1.7	233.8
Hardness (mg L^{-1})	141.3	501.0	2104.0	609.6	121.7	395.0	822.6	2110.0	607.0	73.8	93.5	300.9	1256.0	311.5	103.5
SiO_2 (mg L^{-1})	3.2	12.4	22.2	5.3	42.6	6.6	11.6	23.2	5.0	43.3	4.8	14.1	40.7	10.2	72.3
HCO_3^- (mg L^{-1})	23.0	168.3	278.0	56.1	33.3	113.6	233.6	387.0	87.7	37.6	55.6	123.3	248.5	51.8	42.0
Cl^- (mg L^{-1})	25.5	1113.7	8630.0	2429.2	218.1	148.0	994.1	5065.0	1752.8	176.3	18.2	432.0	2471.0	832.9	192.8
SO_4^{2-} (mg L^{-1})	18.0	155.1	960.0	296.2	191.0	225.0	559.3	1770.0	517.0	92.4	13.0	55.0	224.0	55.2	100.4
NO_3^- (mg L^{-1})	0.3	2.3	5.3	1.7	75.8	0.3	2.5	10.4	2.8	112.4	0.3	2.8	10.9	2.4	86.7
Ca^{2+} (mg L^{-1})	5.0	105.2	700.0	216.8	206.1	75.0	166.3	780.0	190.1	114.3	2.0	36.0	208.0	65.4	181.7
Mg^{2+} (mg L^{-1})	26.0	57.2	187.0	40.9	71.6	38.4	97.7	343.0	79.2	81.1	16.8	50.6	176.0	38.9	76.8
Na^+ (mg L^{-1})	6.0	564.6	4800.0	1311.8	232.3	87.0	536.9	2650.0	905.3	168.6	2.0	211.4	1200.0	412.1	194.9

(continued)

Table 1 (continued)

	Chubut River					Colorado River					Negro River				
	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV
K^+ (mg L^{-1})	0.6	7.4	66.0	16.1	218.2	1.0	55.4	600.0	155.0	279.5	0.3	7.3	55.0	14.3	195.4

Min minimum, *Max* maximum, *SD* standard deviation, *CV* coefficient of variation (%)

Table 2 Statistical summary of physical and chemical variables measured in winter (complete data set)

	Chubut River					Colorado River					Negro River				
	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV
pH	7.6	9.2	10.4	0.6	6.6	7.6	8.4	8.9	0.4	4.6	7.5	8.0	8.8	0.4	4.8
Conductivity (mS cm^{-1})	0.2	0.8	6.4	1.6	192.2	1.4	1.9	2.1	0.3	13.5	0.1	3.7	28.3	8.4	230.3
Temperature (ºC)	5.8	8.0	10.0	1.2	15.6	5.1	7.3	10.8	1.9	25.4	6.5	8.6	9.4	0.7	8.0
Salinity (‰)	0.0	0.4	3.3	0.9	219.3	0.6	0.8	0.9	0.1	15.1	0.0	2.1	17.1	5.0	242.2
Hardness (mg L^{-1})	97.5	160.1	474.0	96.7	60.4	417.0	622.7	1000.0	205.7	33.0	99.0	660.9	6513.0	1509.2	228.4
SiO_2 (mg L^{-1})	9.0	14.6	34.8	5.8	39.5	2.6	6.3	10.0	2.7	42.2	2.0	3.6	6.9	1.2	34.0
HCO_3^- (mg L^{-1})	99.4	189.0	298.0	57.8	30.6	106.0	151.4	220.0	36.0	23.8	60.6	97.2	212.1	35.5	36.5
Cl^- (mg L^{-1})	10.9	210.3	1418.0	371.9	176.8	183.0	285.0	337.0	53.6	18.8	17.2	924.4	9406.0	2440.8	264.0
SO_4^{2-} (mg L^{-1})	21.0	43.2	124.0	29.3	67.7	228.0	461.8	670.0	142.7	30.9	17.0	260.4	1770.0	504.9	193.9
NO_3^- (mg L^{-1})	0.1	4.1	22.5	5.7	139.5	0.5	4.0	8.5	3.0	73.9	0.5	6.1	14.1	4.2	68.4
Ca^{2+} (mg L^{-1})	2.0	9.8	32.0	8.8	89.1	70.0	115.9	182.0	32.9	28.4	6.0	85.2	574.0	160.9	189.0
Mg^{2+} (mg L^{-1})	19.2	32.9	94.5	18.7	57.0	22.0	80.0	160.8	53.9	67.4	15.6	107.5	1323.1	304.0	282.8
Na^+ (mg L^{-1})	12.0	136.3	800.0	210.4	154.4	50.0	177.8	370.0	95.4	53.7	7.0	485.3	4400.0	1204.3	248.1

(continued)

Table 2 (continued)

	Chubut River					Colorado River					Negro River				
	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV	Min	Mean	Max	SD	CV
K^+ (mg L^{-1})	0.6	5.4	30.0	7.9	146.1	2.8	4.7	8.5	2.2	45.6	0.2	20.5	220.0	57.1	278.4

Min minimum, Max maximum, *SD* standard deviation, *CV* coefficient of variation (%)

Table 3 Results of the Kruskal–Wallis test and the Dunn's multiple comparisons test among rivers in relation to the physical and chemical variables measured in the inland sites

	Kruskal–Wallis Test		Dunn's Test		
	H	*p* value	CH–RC	CH–RN	RC–RN
pH	27.5	***	***	***	ns
Conductivity (mS cm^{-1})	46.1	***	***	**	***
Temperature (°C)	7.7	*	*	**	ns
Salinity (‰)	60	***	***	ns	***
Hardness (mg L^{-1})	46	***	***	ns	***
SiO_2 (mg L^{-1})	17.9	***	*	*	ns
HCO_3^- (mg L^{-1})	29.5	***	***	ns	***
Cl^- (mg L^{-1})	40.5	***	***	ns	***
SO_4^{2-} (mg L^{-1})	47	***	***	ns	***
NO_3^- (mg L^{-1})	5.6	ns	ns	*	ns
Ca^{2+} (mg L^{-1})	46.3	***	***	ns	***
Mg^{2+} (mg L^{-1})	24.9	***	***	ns	***
Na^+ (mg L^{-1})	44.4	***	***	ns	***
K^+ (mg L^{-1})	31.3	***	***	ns	***

CH Chubut river, *RC* Colorado river, *RN* Negro River
ns non-significant, *p*, significance level: * $p \leq 0.05$; ** $p \leq 0.01$; *** $p \leq 0.001$

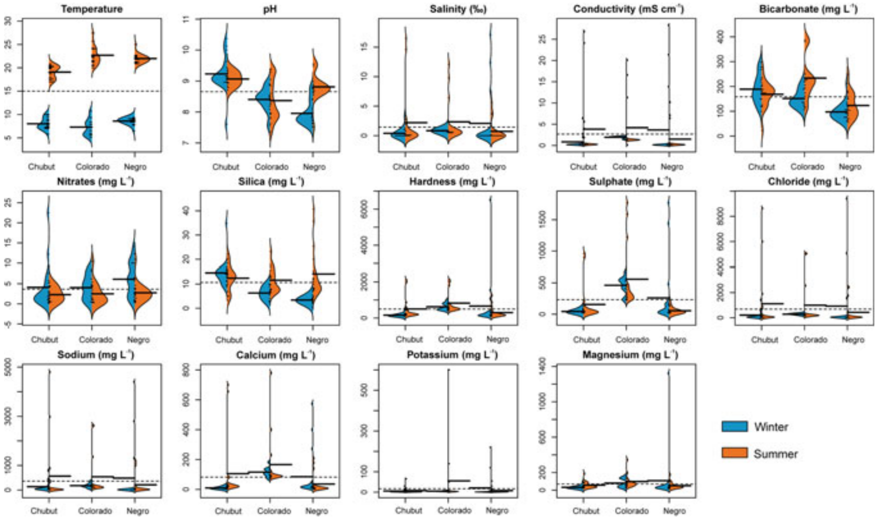

Fig. 4 Beanplots of physical and hydrochemical variables measured in the Colorado, Negro and Chubut rivers. The dotted line is the overall mean for each variable, while the solid line indicates the mean value in each season

variable showed similar values in the three rivers during winter, the mean temperature of the Chubut River during summer was statistically lower compared to those recorded in the other rivers. Salinity, conductivity, total hardness and the water ionic concentration increase as rivers flow towards the outlet. According to the pH values, the surface water of rivers ranged from slightly basic to basic with an average value of about 8.6. The Chubut River had the highest average pH value (9.1 ± 0.4) ($p = 1 \times 10^{-6}$), whereas the Colorado and Negro rivers showed similar average pH values (8.3 ± 0.5). However, the Negro River exhibited a significant seasonal difference in pH values ($p > 0.05$), with an average of 8.6 in summer and 7.8 in winter. In both seasons, this river also showed the highest pH values in the outlet sampling sites (RN1, RN2 and RN3).

The analysis excluding the samples belonging to the estuarine zone of the rivers allows a better observation of the seasonality in the variable's behavior (Fig. 5). The Colorado River showed the highest values of salinity, conductivity, total hardness and major ionic content. These variables also had a significant seasonal behavior in this river with higher concentrations in winter than in summer ($p = 0.04$). According to the hardness scheme (Durfor and Becker 1964), the Negro and Chubut rivers were categorized as hard waters (average total hardness of 180.8 mg L^{-1} and 164.9 mg L^{-1}, respectively), while the Colorado River was considered as very hard water (average total hardness of 576.1 mg L^{-1}). Comparatively, the Negro River had the lowest average concentrations of bicarbonate irrespective of the season (123.3 mg L^{-1} in summer and 97.2 mg L^{-1} in winter). In Colorado and Negro rivers the concentrations of this variable increased in summer and decreased in winter, but this seasonal trend

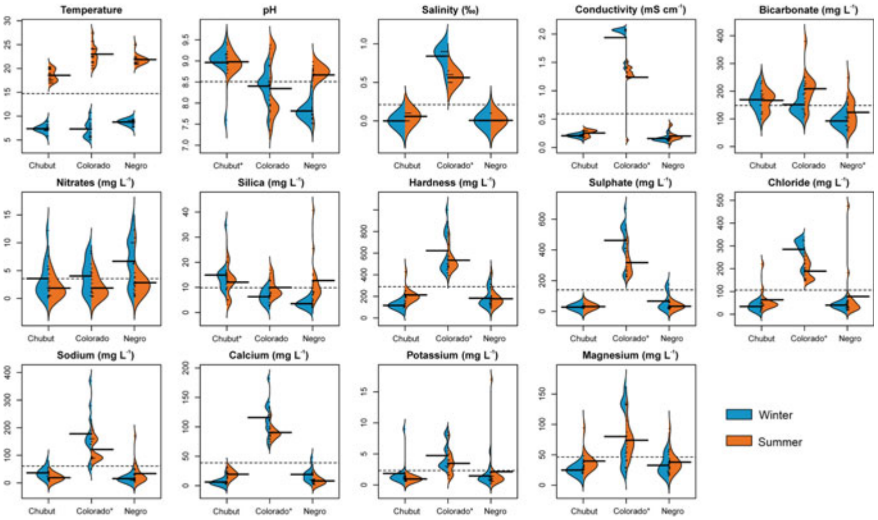

Fig. 5 Beanplots of physical and hydrochemical variables measured in inland areas (without estuarine sites). Asterisk (*) denotes the river that shows significant differences ($\alpha = 0.05$) based on Kruskal–Wallis and Dunn post hoc statistical tests

was only significant in the Colorado River ($p = 0.03$). Such seasonal pattern in the bicarbonate concentrations of the Colorado River was shown as inversely related to the behavior of major dissolved ions in the same river.

Nitrate concentrations varied from 0.3 mg L^{-1} to 8.5 mg L^{-1} in the Colorado River, from 0.3 mg L^{-1} to 14.1 mg L^{-1} in the Negro River and from 0.1 mg L^{-1} to 12.2 mg L^{-1} in the Chubut River. As for this variable, the statistical analyses did not show significant differences among rivers ($p = 0.06$). Although an apparent seasonal pattern in nitrate content in the three rivers occurs, with high mean values in winter and low concentrations in summer, the Kruskal–Wallis test indicated that these seasonal variations of nitrate were significant only in the Negro River ($p = 0.02$). Finally, the Chubut River showed high silica content with average values of 14.9 mg L^{-1} and 12.1 mg L^{-1} in winter and summer, respectively. Meanwhile, the Colorado and Negro rivers showed a slightly seasonal trend for this variable, with high values in summer and low values in winter.

The first two components of the PCA ordination explained 64.9% and 70.8% of the total variation in the summer and winter complete data, respectively (Fig. 6a, b). In both cases, the first axis explains the greatest amount of variation describing

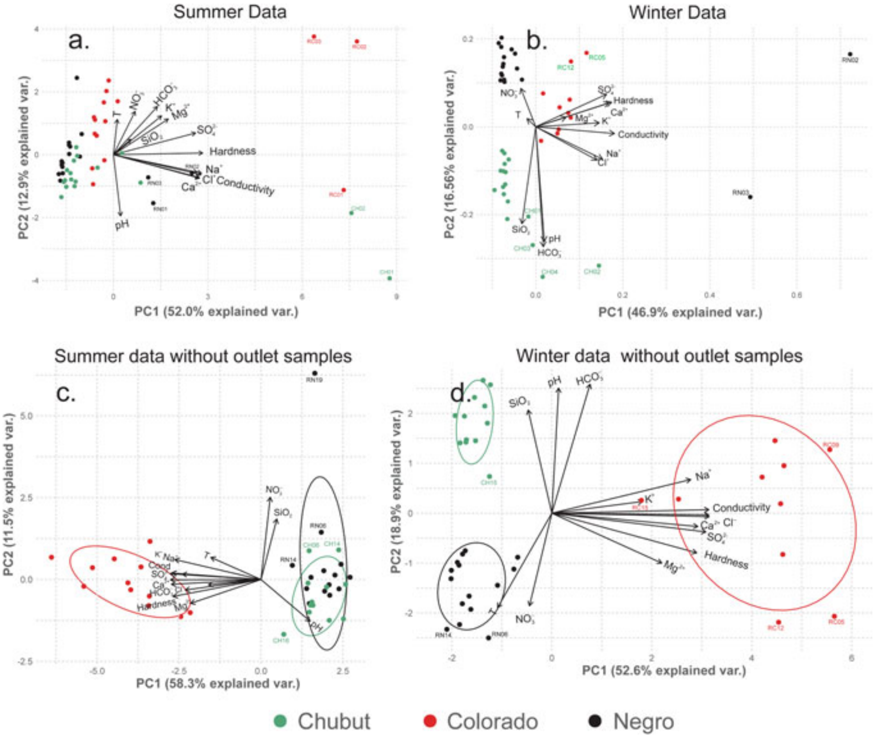

Fig. 6 Principal component analysis of physical and chemical data (summer and winter) with all sampling sites and without outlet sites

an ionic gradient that is highly correlated with conductivity, salinity, hardness, Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, Mg^{2+} and K^+.

Considering only the freshwater sites of the three rivers (without the outlet sampling sites), the PCA showed that the first two axes capture up to 69.8% and 71.5% of the total variance in summer and winter data, respectively (Figs. 6c, d). However, seasonal differences regarding the ordination of data occurs as it can be observed from the figures. In summer data (Fig. 6c), the first axis was highly correlated with conductivity, salinity, total hardness, HCO_3^-, Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, Mg^{2+} and K^+. Sites from the Colorado River showed a strong linear relationship with this component.

The second component was mainly associated with pH and SiO_2 as well as with the sampling sites of the Negro and Chubut rivers. Except for HCO_3^-, the first component of the winter data (Fig. 6d) was also related to conductivity, salinity, total hardness and major ions. Likewise, this ionic gradient was also associated with the sampling sites of the Colorado River. The second axis was mainly associated with pH, SiO_2, NO_3^- and HCO_3^-. Sites from the Chubut River were positively correlated with pH, SiO_2 and HCO_3^-, while the group of the Negro River sites exhibited moderate and direct correlation with NO_3^-.

4.2 Rivers Hydrogeochemistry

The samples taken in the Colorado, Negro and Chubut rivers have been plotted in Gibbs' diagrams (Fig. 7) (Gibbs 1970) in order to identify dominating processes in the determination of the composition of surface waters.

In Fig. 7 it is possible to observe that no water samples plot in the area assigned to precipitation dominance. Most of the samples are in the zone of water–rock interaction domain and displacing along a line parallel to the x axis, out of the fields described by Gibbs (1970). Samples from the Colorado River are disposed along to the zone indicated as corresponding to evaporation processes. Other samples from the three rivers are also towards the extreme of the evaporation zone, but they are those corresponding to the rivers' estuaries, being the result of seawater mixing.

The major ion composition of the three rivers was represented in two Piper diagrams, separating winter and summer samplings (Fig. 8). The Chubut River water is of the Mg^{2+}–Ca^{2+}–HCO_3^- type, evolving towards Na–Cl waters. The Colorado River belongs to the Ca^{2+}–SO_4^{2-} hydrochemical facies (Back 1960) with a Na–Cl–SO_4^{2-} member, close to seawater composition. The Negro River is mostly of the Mg^{2+}–Ca^{2+}–HCO_3^- type in summer, and divided into Mg^{2+}–Ca^{2+}–HCO_3^- and Mg^{2+}–Ca^{2+}–SO_4^{2-} types in winter, with a Na–Cl extreme member. In all the cases, the Na–Cl members correspond to the samples closer to the rivers' outlets to the Atlantic Ocean.

Cross sections representing the dissolved ion contents from the outlets towards inland show a strong increase of the anions Cl^- and SO_4^{-2} (Fig. 9a) and all the cations, but mostly Na^+ (Fig. 9b). At the continental area the contents of the different

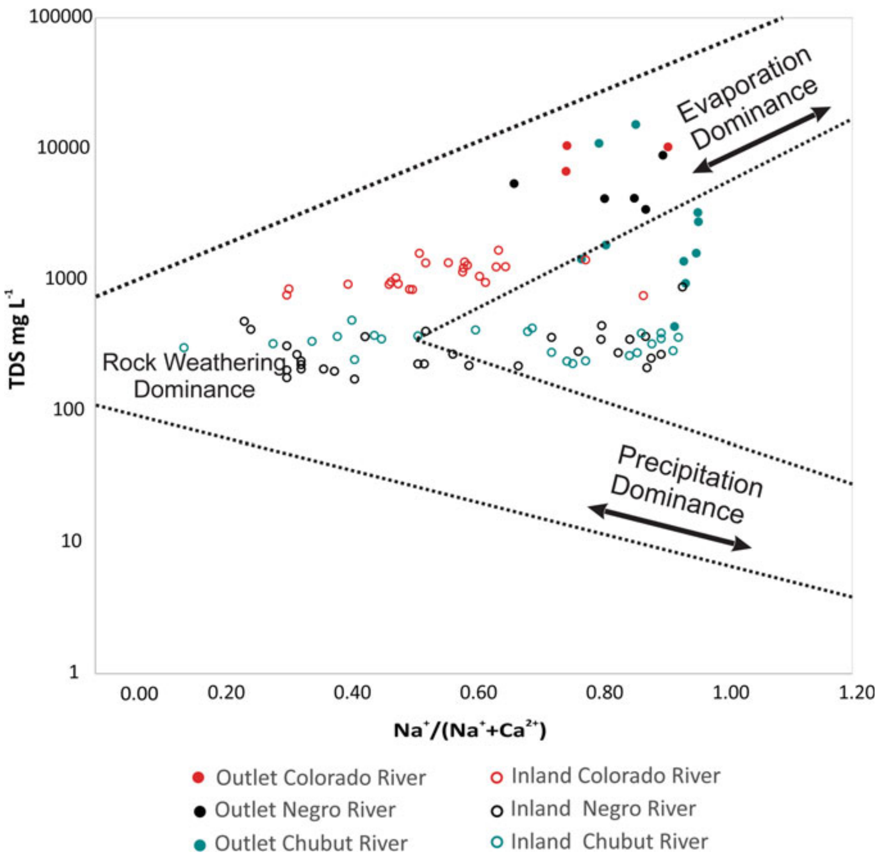

Fig. 7 Gibbs diagram showing major processes controlling surface water chemistry in the Colorado, Negro and Chubut rivers

ions are quite homogeneous, with an observable SO_4^{-2}, Cl^-, Na^+ and Ca^{+2} increase in the Colorado River, downstream point RC13.

The Piper diagram (Fig. 8), and the distribution of ion concentrations along the course, allows to differentiate a typical river section and an estuarine section for each river. The estuarine section can be defined by the point where the chloride and sodium contents increase several times compared to the previous site, resulting in Na–Cl water types.

The quite homogeneous composition of river waters upstream the estuarine zones (Figs. 8 and 9) indicates few changes regarding the water entering from the source areas. It is strengthened by the absence of significant tributaries in the considered river sections, with the exception of the occasional discharge of the Curacó River in the Colorado River. The hydrochemical fingerprint of each river shown in the Piper diagrams can be related to the rock source interaction through ionic ratios, their graphical representation and the equilibria against dominating minerals.

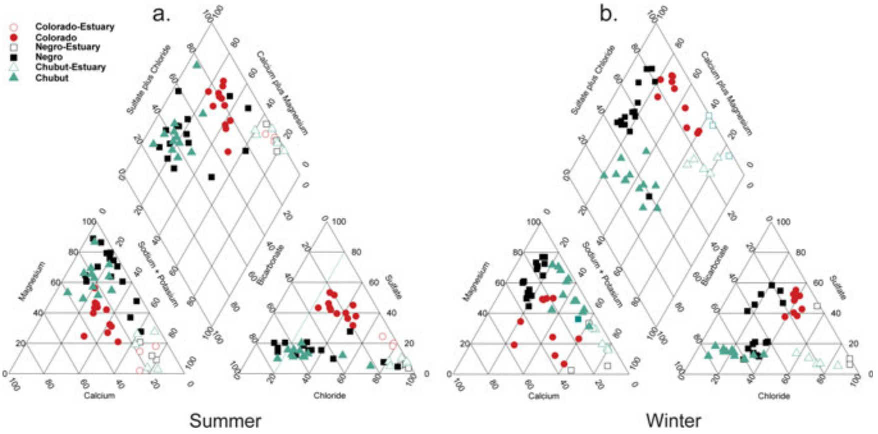

Fig. 8 Piper diagrams for summer **a** and winter **b** sampling periods

In order to have a first approximation of the rock source for the dissolved ions, HCO_3^-/SiO_2 ratios can be used as indicative of the main source of dissolved carbon species. If the mentioned ratio is >10 carbonate weathering is the assumed source, while if the ratio is < 5 it is considered to be a consequence of silicate weathering. All the samples explain their HCO_3^- sources by carbonate weathering, with the exception of samples RC05, RCH17 with rations assigned to silicate weathering.

Saturation indexes (SI) calculated using PHRREQC (Parkhurst and Appelo 1999) showed that 50% of the samples have a $SI_{calcite}$ between −0.5 and 0.5, which is considered the equilibrium fringe. About 25% of the samples are subsatutared in calcite, being mostly samples of the Negro River, and the other 25% is supersaturated, mostly in a low degree (IS < 1). High supersaturation (values up to 10) is observed in samples belonging to the estuary of the Chubut River.

$IS_{dolomite}$ shows equilibrium for 25% of the samples, and a similar proportion of sub-saturated samples. Dolomite supersaturated is observed in about 50% of the samples. IS_{gypsum} indicates subsaturation in all cases.

The Na^+/Cl^- ratio is often used to identify processes involving saline intrusions in arid and semiarid regions (Yang et al. 2016). In general, if the Na^+/Cl^- relationship is about 1 it is assumed that sodium comes mostly from halite dissolution. Figure 10a shows that almost all water samples belonging to inland sites in the studied Patagonia rivers not only showed a low Na^+/Cl^- ratio but also were plotted along the line 1:1. This means that, regardless of the season, the dissolution of halite is the main source of Na^+ in the freshwater sites of rivers. Moreover, samples at the estuarine sections are represented above this line, corresponding to a Na^+/Cl^- value of 0.86, typical of seawater.

The dissolution of carbonates (calcite and dolomite) and sulphate (gypsum) minerals are the dominant hydrogeochemical processes occurring in surface waters of rivers if the ratio $Ca^{2+}+Mg^{2+}$ against $HCO_3^-+SO_4^{2-}$ is close to 1 (Li et al. 2016). As it can be seen from Fig. 10b, most water samples of the Negro and Chubut rivers

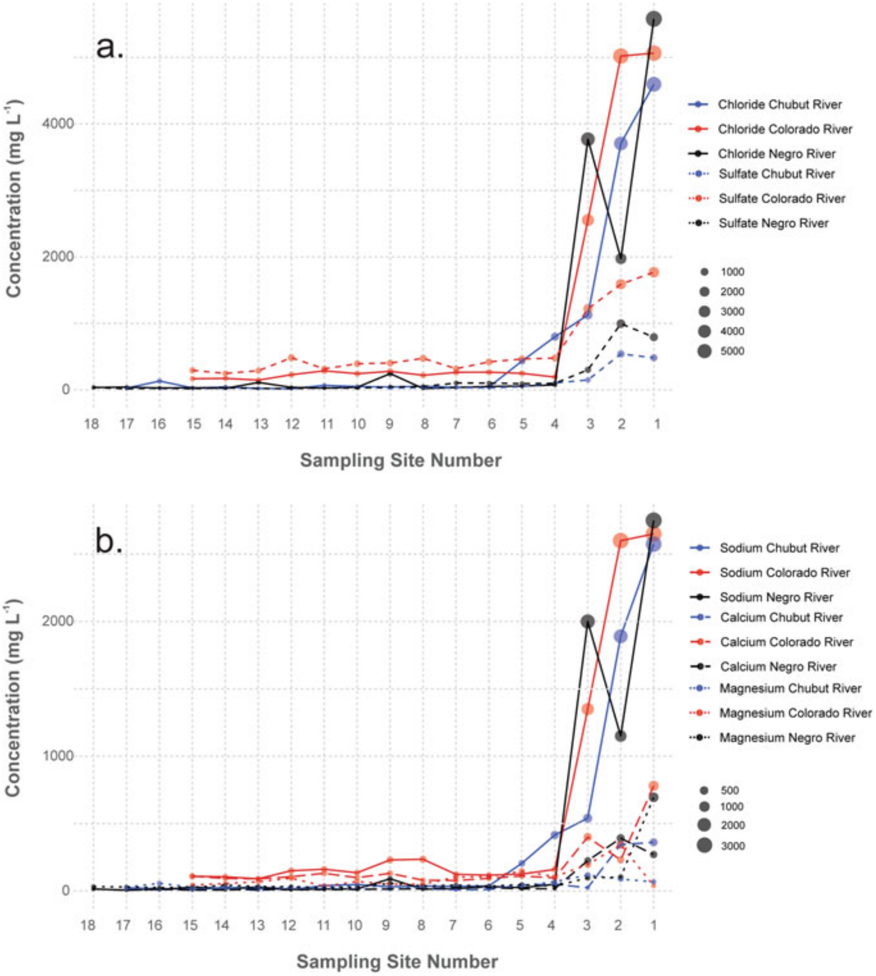

Fig. 9 Average winter-summer contents from river discharge at the inland towards the Ocean (point 1) **a** for anions chloride and sulfate, and **b** cations sodium, calcium and magnesium

showed low ratios and fall close to the line. Meanwhile, samples of the Colorado River were plotted above or below the 1:1 line. These trends suggest that the weathering of carbonate, silica and sulphate rocks is the main controlling factor of the chemical composition of Patagonia rivers. Dedolomitazion processes of the *rodados patagónicos*, which cover most of the surface of these basins, were identified in previous studies (Baumann et al. 2019).

Similarly, there is a linear relationship between Ca^{2+} and $SO_4{}^{2-}$ when the dissolution of gypsum is the main source of these ions. However, water samples should be plotted along the 1:1 line if Ca^{2+} and $SO_4{}^{2-}$ originate from the dissolution of gypsum. Figure 10c shows that most inland water samples of the Negro and Chubut

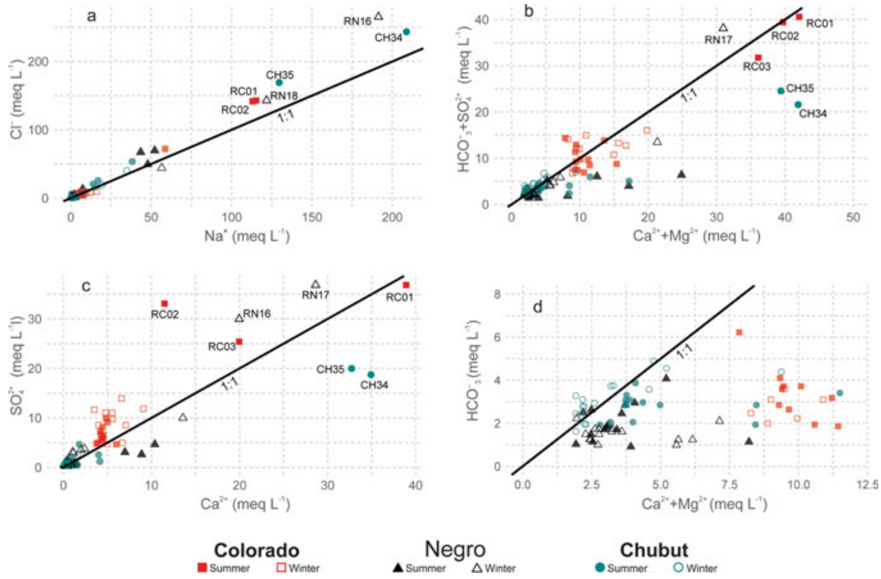

Fig. 10 Major ion ratios

rivers fall on the lower limit of the line, but the ionic ratio do not show a linear relationship, indicating that the dissolution of gypsum is not the main source of $SO_4{}^{2-}$ in these rivers. Meanwhile, the water samples of the Colorado River deviate from the expected 1:1 line, displaying an excess of $SO_4{}^{2-}$ over Ca^{2+}.

When the dissolution of dolomite and calcite controls the concentration of Ca^{2+}, Mg^{2+} and $HCO_3{}^{-}$, water samples should plot between the 1:1 line of the diagram. Figure 9d showed that most samples of the Negro and Chubut rivers were cluster below the 1:1 line, displaying a slightly excess of Ca^{2+} and Mg^{2+}. This fit of the $HCO_3{}^{-}$ against $Ca^{2+} + Mg^{2+}$ contents to the 1:1 line likely can result from the mentioned dolomite dissolution, which is a typical consequence of the previously mentioned dedolomitazion process (Baumann et al. 2019), taking place at those basins. On the other hand, most water samples of the Colorado River were plotted to the right of the 1:1 line indicating an excess of Ca^{2+} and Mg^{2+} over $HCO_3{}^{-}$ (Fig. 10d). This suggests that the dissolution of gypsum or silicates (anorthite and calcium montmorillonite), besides dolomite, may be the main sources of Ca^{2+} and Mg^{2+} in the Colorado River.

The minimum, maximum and average values of calcite saturation indexes for each river are shown in Table 4. Clear differences are observed between Negro River, on a side, and Colorado and Chubut rivers on the other side, which are expressing the differences in the main constraints for each water chemistry. Despite in average the three rivers are in the range of ±0.5 $SI_{calcite}$, which can be indicating equilibrium dominating conditions, the negative average value for the Negro River is the result

Table 4 Calcite saturation indexes minimum, maximum and average values for each river, calculated with PHREEQC software (Parkhurst and Appelo 1999)

River	Minimun	Maximin	Average
Colorado	−0.161	1.070	0.529
Negro	−0.978	0.817	−0.549
Chubut	−0.083	1.240	0.385

of waters that are always subsaturated in calcite, with the only exception of the site RN01 which is affected by seawater in the river outlet.

Samples of the other two rivers are dominated by slightly supersaturated values. It can be a consequence of the analytical error, 0.5 of uncertainty in pH measurement implies 0.5 units of $SI_{calcite}$ (Appelo and Postma 1993). However, the dominance of low positive values should be interpreted as indicative of an overlapping of processes with different reaction kinetics, capable of producing the observed values. Typically, the gypsum dissolution increases the Ca^{+2} contents and leads calcite to precipitate, but this precipitation is kinetically slower that the gypsum dissolution (Appelo and Postma 1993).

5 Discussion

The physical and chemical variables measured in this study show clear differences in the Colorado, Negro and Chubut rivers, reflecting contrasting environmental conditions and external pressures across their watersheds. Of main river fluvial systems that flows through the plateau steppe, the Colorado River has the highest conductivity due to the geological features of its basin and the sporadic inputs of brackish water from the Curacó River, which in turn has connections with ENSO events (Gaiero et al. 2003; Isla and Toldo 2013). During periods of either high precipitation or snowmelt runoff from the Andean Mountains, the salinized waters accumulated in a variety of inland saline wetlands of the Curacó River are discharged into the Colorado River. This behavior also explains the Ca^{2+}-$SO_4{}^{2-}$ dominating water type, because the headwaters of the river are located at the Andes at southern Mendoza province, where the Auquilco Formation is outcropping (Nullo et al. 2005; Weaver 1931). These marine sequences belong to the Lotena Group in the Neuquén Basin, and lithologically they are evaporites composed mainly by thick banks of gypsum and anhydrite, stratified, sometimes laminated or nodular (Narciso et al. 2004). In addition, the upper and middle valley of the river is characterized by Holocene lacustrine deposits containing evaporite minerals rich in sulfate sodium (Folguera et al. 2015). The erosion of these materials mostly by the wind effect can also play a pivotal role on the supply of sulfate to the river, explaining the sulfate excess over calcium (Fig. 7c) in waters of the Colorado River. On the other hand, the inter-annual hydrological dynamics clearly explain the seasonal variability of conductivity, salinity, total hardness, and dissolved ions in the Colorado River. Ionic concentration decreases in summer when the highest flows occur, and increases in winter due to the decrease in the river flow. Recently, some studies indicate a significant decrease in the flow of the Colorado River since 2010, leading to a critical increase in the concentration of dissolved ions in the river (COIRCO 2017). These recent changes in the water quality affect the functioning of the river aquatic ecosystem, and have a strong impact on the productive, economic and social development of the region (Lurman et al. 2007).

Due to the recorded pH ranges, it can be stated that bicarbonate is the carbon species dominating the dissolved inorganic carbon in the rivers. Lithology, river discharge, temperature fluctuation, and biogeochemical processes play a pivotal role controlling the spatial and temporal trends of inorganic carbon content in most natural waters (Cai et al. 2008). A study conducted by Brunet et al. (2005) shows that the Colorado, Negro and Chubut rivers show the highest values of inorganic carbon compared with other Patagonia rivers. They argue that the occurrence of lakes and dams in the upper and middle basins seem to enhance the exchanges between river waters and atmospheric CO_2. In the same way, the low concentrations of bicarbonate recorded in the Negro River are likely linked with its high discharge, which is about ten and twenty times greater than that of the Colorado and Chubut rivers, respectively. This trend is consistent with previous studies indicating that the inverse correlation between the inorganic carbon content and river discharge is due to a simple dilution effect controlled by the precipitation and evaporation balance in the drainage basin (Cai et al. 2016; He and Xu 2018).

Negro and Chubut rivers are both of the Mg^{2+}–Ca^{2+}–HCO_3^- water type, but the HCO_3/SiO_2 ratio indicates some differences in the composition origin. The points located upstream of the Chubut River have a ratio >10, indicating that the water source is the weathering of silicates, basaltic and andesitic rocks at the headwaters. On the other hand, the composition of the Negro River probably has the same rock source composition, but the dams located upstream of the study section favor the silica precipitation lowering the HCO_3/SiO_2 ratio. In both rivers, water is equilibrated with calcite along the courses, being the reaction controlling the dissolved ion contents. The $SI_{calcite}$ values in Table 4 reflect the importance of the higher discharge of the Negro River, diluting the solution and sustaining the slightly undersaturated conditions. The lower discharge of the Chubut River put the $SI_{calcite}$ values in equilibrium values, according to the chemical reactivity of the *rodados patagónicos* (Baumann et al. 2019). On the other hand, Colorado River $SI_{calcite}$ is mostly supersaturated due to the mentioned discharge of Ca^{+2} from gypsum dissolution and the slower kinetic of calcite precipitation.

It is worth mentioning that the Colorado and Negro rivers show a noticeable seasonal variation in the bicarbonate concentration, with average values higher in summer, when the river flows are also higher, than in winter. This fluctuation might be partially explained by the annual thermal regime rather than due to variations in river flows. Biological respiration and decomposition processes of aquatic organisms tend to be higher as the water warms up in summer months, which increases the bicarbonate levels in the water (Cole 2013). Moreover, high salinity in the Colorado River during winter involves the increase of Ca^{+2}. As a consequence of the Ca^{+2}

increase the ionic activity product of Ca^{+2} and HCO_3^- equals the calcite equilibrium constant, resulting in calcite precipitation which controls the dissolved total inorganic carbon. In the Chubut River this temporal pattern in the bicarbonate concentrations is not clearly observed.

The concentration of nitrates in the analysed rivers indicates anthropogenic inputs and nutrient-enrichment in some extent, but for now the nitrate values are less than 13 mg L^{-1}, which is the maximum level allowed for protection and development of aquatic biological communities (CWQG 2012). The analysis seems to reveal that the Negro River has a moderate relationship with the nitrate content, particularly in winter when the river discharge is the lowest. It should be highlighted that the Negro River basin is the most extended hydrographic system of Patagonia, and is considered one of the most important agricultural and processing areas of Argentina. As a consequence, this river receives a large amount of sediments and agrochemicals such as fertilizers and pesticides (Isla et al. 2010; Miglioranza et al. 2013). In fact, some studies already indicate a strong trend of nitrate increasing towards the Lower Valley of the Negro River which are caused mainly by industrial inputs, sewage treatment plants discharge and agrochemicals runoff from Guardia Mitre, Zanjon Oyuela, Viedma and Carmen de Patagones (Abrameto et al. 2017). These results provide critical information indicating the need to develop a holistic and integrated approach in order to improve the monitoring programs in the river since nitrate pollution is one the major threats in arid/semiarid aquatic ecosystems worldwide (Cook et al. 2010).

6 Conclusions

The hydrochemical characteristics of the northern Patagonia rivers are a consequence of the weathering of silicate volcanic rocks located at the headwaters in the Andes, but strongly modified and conditioned by processes taking place during runoff in the extra-Andean zone. HCO_3^-/SiO_2 indexes indicate how the main processes move from silicate dissolution to carbonates equilibrium downflow and the important control of hydrological features in the different composition of rivers. Being carbonates equilibrium a dominant constraint, due to widespread distribution of the carbonatic cement of the *rodados patagónicos*, calcite saturation index variations are indicators of the other processes explaining variations among rivers. Moreover, the effect of seawater mixing is the main hydrochemical constraint at estuarine outlet sections. Discharge of the Negro River is several times higher than the others, and the dilution effect leads to unsaturated values and a Mg^{2+}–Ca^{2+}–HCO_3^- water type. In the case of the Chubut River, the water type is the same, but the lower discharge allows to sustain the calcite equilibrium along the studied section. On the other side, the Colorado River waters are of the Ca^{2+}–SO_4^{2-} type due to contributions of gypsum dissolution in the Upper Basin and by irregular brackish discharges from the Curacó River. This discharge of high Ca^{2+} contents, and the differences into reactions kinetic, results in slight carbonate supersaturation. Then, the effect of amount of discharge and specific contributors establish the main hydrochemical differences at the inland area. Close to the outlet, estuarine behavior has been observed at the three rivers, and the chemical composition becomes of the Na–Cl type, and Cl^- contents indicate a seawater mixing proportion of about 25%. Significant seasonal differences were only observed with higher values in summer in the case of the pH of the Negro River, salinity in the Colorado River, Cl^- in Negro and Colorado rivers. These variations can be related to higher surface water evaporation during summer. Although it is preliminary, the hydrochemical information achieved from this study will be useful to understand the predominating processes that underlie the chemical composition in north Patagonia rivers. Revealing the main ion sources and the primarily controlling factors are key topics for developing effective management strategies of water resources in arid and semiarid regions like Patagonia.

Acknowledgements The authors wish to acknowledge F. Isla, R. Fayó, J. Bedmar and M. Taglioretti for their assistance with field sampling, and G. Bernava for hydrochemical analysis. This study was funded by the Agencia Nacional de Promoción Científica y Tecnológica ANPCyT (grant number PICT 1146/16).

References

Abrameto M, Torres M, Ruffini G (2017) Nutrients distributions in an estuary of the Argentine coast. WIT Trans Ecol Environ 216:277–283

APHA, American Public Health Association. (1998) Standard methods for the examination of water and wastewater. Water Environment Federation, Washington

Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. Balkema, The Netherlands

Back W (1960) Hydrochemical facies and ground-water flow patterns in Northern Atlantic Coastal Plain. AAPG Bull 44:1244–1245

Barros VR, Boninsegna JA, Camilloni IA, Chidiak M, Magrín GO, Rusticucci M (2015) Climate change in Argentina: trends, projections, impacts and adaptation. Wiley Interdisciplinary Reviews. Clim Chang 6:151–169

Baumann GO, Vital M, Glok-Galli M, Grondona S, Massone H, Martinez DE (2019) Hydrogeochemical modeling and dedolomitization processes in the Patagonian Boulders and Patagonia Formation in the eastern Patagonia, Argentina. Environ Earth Sci 78:1–16

Brunet F, Gaiero D, Probst J, Depetris PJ, Gauthier Lafaye F, Stille P (2005) $\delta 13C$ tracing of dissolved inorganic carbon sources in Patagonian rivers (Argentina). Hydrol Process 19:3321–3344

Cai W-J, Guo X, Chen C-TA, Dai M, Zhang L, Zhai W, Lohrenz SE, Yin K, Harrison PJ, Wang Y (2008) A comparative overview of weathering intensity and HCO_3^- flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers. Cont Shelf Res 28:1538–1549

Cai Y, Shim M, Guo L, Shiller A (2016) Floodplain influence on carbon speciation and fluxes from the lower Pearl River, Mississippi. Geochim Cosmochim Acta 186:189–206

Carol ES, Kruse EE (2012) Hydrochemical characterization of the water resources in the coastal environments of the outer Río de la Plata Estuary, Argentina. J South Am Earth Sci 37:113–121

COIRCO, Comité Interjurisdiccional del Río Colorado (2017) Análisis estadístico de los parámetros fisicoquímicos, metales y metaloides. Estación piloto "Buta Ranquil". Universidad Nacional del Sur, Argentina (in Spanish)

Cole JJ (2013) The carbon cycle: with a brief introduction to global biogeochemistry. In: Weathers KC, Strayer DL, Likens GE (eds) Fundamentals of ecosystem science. Academic Press, New York, pp 109–135

Cook PL, Aldridge K, Lamontagne S, Brookes J (2010) Retention of nitrogen, phosphorus and silicon in a large semi-arid riverine lake system. Biogeochemistry 99:49–63

Coronato A, Coronato F, Mazzoni E, Vázquez M (2008) The physical geography of Patagonia and Tierra del Fuego. Dev Quat Sci 11:13–55

Coronato A, Mazzoni E, Vázquez M, Coronato F (2017) Patagonia. Una síntesis de su geografía física. Ediciones Universidad Nacional de la Patagonia Austral, Santa Cruz, Argentina (in Spanish)

CWQG, Canadian Water Quality Guidelines for the Protection of Aquatic Life (2012) Nitrate Ion. Canadian Council of Ministers of the Environment, Winnipeg

Davies J, Barchiesi S, Ogali CJ, Welling R, Dalton J, Laban P (2016) Water in drylands: adapting to scarcity through integrated management. IUCN, Gland, Switzerland

Depetris PJ (1980) Hydrochemical aspects of the Negro river, Patagonia, Argentina. Earth Surf Process 5:181–186

Depetris PJ, Gaiero DM, Probst JL, Hartmann J, Kempe S (2005) Biogeochemical output and typology of rivers draining Patagonia's Atlantic seaboard. J Coast Res 21:835–844

Durfor CN, Becker E (1964) Public water supplies of the 100 largest cities in the United States. US Government Printing Office, Washington

Folguera A, Etcheverría M, Zárate M, Miranda F, Faroux A, Getino P (2015) Hoja Geológica 3963-I, Río Colorado. Provincias de La Pampa, Buenos Aires y Río Negro. Instituto de Geología y Recursos Minerales, Servicio Geológico Minero Argentino, Buenos Aires (in Spanish)

Gaiero DM, Probst J, Depetris PJ, Bidart SM, Leleyter L (2003) Iron and other transition metals in Patagonian riverborne and windborne materials: geochemical control and transport to the southern South Atlantic Ocean. Geochim Cosmochim Acta 67:3603–3623

Gaitán JJ, Bran DE, Oliva GE (2020) Patagonian Desert. In: Goldstein M, DellaSala D (eds) Encyclopedia of the world's biomes. Elsevier, pp 163–180

Garreaud R, Lopez P, Minvielle M, Rojas M (2013) Large-scale control on the Patagonian climate. J Clim 26:215–230

Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170:1088–1090

He S, Xu YJ (2018) Freshwater-saltwater mixing effects on dissolved carbon and CO_2 outgassing of a coastal river entering the northern Gulf of Mexico. Est Coast 41:734–750

Hem JD, Demayo A, Smith RA (1990) Hydrogeochemistry of rivers and lakes. In: Wolman MG, Rigss HC (eds) The geology of North America. Geological Society of America, USA, pp 189–231

Hernández MA, González N, Hernández L (2008) Late cenozoic geohydrology of extra-Andean Patagonia, Argentina. Dev Quat Sci 11:497–509

Hua K, Xiao J, Li S, Li Z (2020) Analysis of hydrochemical characteristics and their controlling factors in the Fen River of China. Sustain Cities Soc 52:101827

Huang J, Li Y, Fu C, Chen F, Fu Q, Dai A, Shinoda M, Ma Z, Guo W, Li W, Zhang L, Liu Y, Yu H, He Y, Xie Y, Guan X, Ji M, Lin L, Wang S, Yan H, Wang G (2017) Dryland climate change: recent progress and challenges. Rev Geophys 55:719–778

Isla F, Espinosa M, Rubio B, Escandell A, Gerpe M, Miglioranza K, Rey D, Vilas F (2015) Avulsion at a drift-dominated mesotidal estuary: the Chubut River outlet, Patagonia, Argentina. J Hydrol 529:632–639

Isla F, Miglioranza K, Ondarza P, Shimabukuro V, Menone M, Espinosa M, Quiroz Londoño M, Ferrante A, Aizpún J, Moreno V (2010) Sediment and pollutant distribution along the Negro River: Patagonia, Argentina. Int J River Basin Manag 8:319–330

Isla F, Toldo E (2013) ENSO impacts on Atlantic watersheds of South America. Quat Environ Geosci 4:34–41

Jiang Y, Gui H, Yu H, Wang M, Fang H, Wang C, Fang H, Chen C, Zhang Y, Huang Y (2020) Hydrochemical characteristics and water quality evaluation of rivers in different regions of cities: a case study of Suzhou city in northern Anhui Province, China. Water 12:950

Kampstra P (2015) Beanplot: visualization via beanplots. R package version 1.2. https://cran.r-project.org/package=beanplot. Accessed 15 June 2020

Li P, Zhang Y, Yang N, Jing L, Yu P (2016) Major ion chemistry and quality assessment of groundwater in and around a mountainous tourist town of China. Expos Health 8:239–252

Li Z, Xiao J, Evaristo J, Li Z (2019) Spatiotemporal variations in the hydrochemical characteristics and controlling factors of streamflow and groundwater in the Wei River of China. Environ Pollut 254:113006

Lurman D, Aragón M, Sánchez R, Ancía V (2007) Variables a considerar para una estimación de las pérdidas económicas por causa de la salinización del río Colorado y su cuantificación. CORFO-INTA 1:1–11 (in Spanish)

Mazzoni E, Vázquez M (2009) Desertification in Patagonia. In: Latrubesse E (ed) Geomorphology of natural and human-induced disasters in South America. Elsevier, Amsterdarm, pp 351–377. https://doi.org/10.1016/S0928-2025(08)10017-7

Miglioranza KS, Gonzalez M, Ondarza PM, Shimabukuro VM, Isla FI, Fillmann G, Aizpún J, Moreno VJ (2013) Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Río Negro basin. Sci Total Environ 452:275–285

Narciso V, Santamaría G, Zanettini J (2004) Hoja Geológica 3769-I, Barrancas. Provincias de Mendoza y Neuquén. Instituto de Geología y Recursos Minerales, Servicio Geológico Minero Argentino, Buenos Aires (in Spanish)

Nullo FE, Stephens G, Combina A, Dimieri L, Baldauf P, Bouza P, Zanettini JC, Leanza HA (2005) Hoja Geológica 3569-III/3572-IV Malargüe, provincia de Mendoza. Servicio Geológico Minero Argentino. Instituto de Geología y Recursos Minerales, Buenos Aires (in Spanish)

Oksanen J, Blanchet FG, Kindt R, Legendre P, Minchin PR, O'Hara RB, Simpson GL, Solymos P, Stevens MMH, Wagner H (2015) Vegan: community ecology package. R package version 2.3-0. https://cran.r-project.org/package=vegan. Accessed 16 June 2020

Parkhurst DL, Appelo C (1999) User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resour Invest Rep 99–312

Paruelo JM, Jobbágy EG, Oesterheld M, Golluscio RA, Aguiar MR (2007) The grasslands and steppes of Patagonia and the Río de la Plata plains. In: Veblen T, Young K, Orme A (eds) The physical geography of South America. Oxford University Press, New York, pp 232–248

Pasquini AI, Depetris PJ (2007) Discharge trends and flow dynamics of South American rivers draining the southern Atlantic seaboard: an overview. J Hydrol 333:385–399

Pasquini AI, Depetris PJ, Gaiero DM, Probst J-L (2005) Material sources, chemical weathering, and physical denudation in the Chubut River basin (Patagonia, Argentina): implications for Andean rivers. J Geol 113:451–469

Piper AM (1944) A graphic procedure in the geochemical interpretation of water analyses. Eos, Tran Am Geophys Union 25:914–928

R Development Core Team R (2015) Language and environmental for statistical computing. R Foundation for Statistical Computing: Viena, Austria. www.r-project.org. Accessed 15 June 2020

Romero P, González M (2016) Relación entre caudales y precipitación en algunas cuencas de la Patagonia norte. Rev Geol Apl Ingen Ambiente 36:7–13 (in Spanish)

Sheldon F, Fellows CS (2010) Water quality in two Australian dryland rivers: spatial and temporal variability and the role of flow. Mar Fresh Res 61:864–874

Stiff HAJ (1951) The interpretation of chemical water analysis by means of patterns. J Pet Technol 3:15–13

Weaver CE (1931) Paleontology of the Jurassic and Cretaceous of west central Argentina. University of Washington press, Seattle

Wu G, Li L, Ahmad S, Chen X, Pan X (2013) A dynamic model for vulnerability assessment of regional water resources in arid areas: a case study of Bayingolin, China. Water Resour Manage 27:3085–3101

WWAP, World Water Assessment Programme (2019) The United Nations world water development report 2019: leaving no one behind. UNESCO, Paris

Yang Q, Li Z, Ma H, Wang L, Martín JD (2016) Identification of the hydrogeochemical processes and assessment of groundwater quality using classic integrated geochemical methods in the Southeastern part of Ordos basin, China. Environ Pollut 218:879–888

Zambrano J, Urien C (1970) Geological outline of the basins in Southern Argentina and their continuation off the Atlantic shore. J Geophys Res 75:1363–1396