

# A Hydrological and Biogeochemical Appraisal of Patagonia's Río Gallegos



Pedro J. Depetris, Diego M. Gaiero, and Nicolás J. Cosentino

**Abstract** The Gallegos is the southernmost river of continental Patagonia. It has the smallest drainage basin of all the main rivers in the region. Moderate atmospheric precipitations ( $\sim 500 \text{ mm y}^{-1}$  in the uppermost catchments) determine discharge maxima in austral winter (rainfall/snowfall) and spring (snowmelt), delivering  $\sim 0.573 \text{ km}^3 \text{ y}^{-1}$  of freshwater (i.e.  $\sim 57 \text{ L m}^2 \text{ y}^{-1}$ ) into an ample estuary in the SW Atlantic Ocean. The Gallegos stands out among the remaining Patagonian rivers for its connection ( $\sim 18$ -month significant squared coherency) with the Southern Annular Mode, and due to its biogeochemistry, which appears affected by groundwater and debris, both associated to some degree with Eocene bituminous coal beds. The relevant factors seem to be: (a) the marked prevalence of  $\text{NO}_3^-$ -N among nutrients (N:P = 50:1–60:1); (b) the mean DOC concentration ( $\sim 500 \mu\text{mol L}^{-1}$ ), higher than all remaining Patagonian rivers (mean of  $\sim 300 \mu\text{mol L}^{-1}$ ), and linked to river discharge; (c) high DIC, correlated with high  $\text{pCO}_2$  (probably groundwater-supplied); (d) mean POC/PN molar ratio of  $\sim 8:1$  (the highest in Patagonia's rivers), leading to infer a terrigenous source with some planktonic contribution. High DOC concentrations ( $\sim 1000 \mu\text{mol L}^{-1}$ ) are associated with low  $\delta^{13}\text{C}_{\text{DIC}}$  ( $\sim -11$  per mil), probably controlled by carbonate dissolution. Mean TOC in the Gallegos River is  $\sim 700 \mu\text{mol L}^{-1}$ , 70% of which is accounted for by DOC.

---

P. J. Depetris (✉)

Academia Nacional de Ciencias, Córdoba, Argentina

e-mail: [pedro.depetris@anc-argentina.org.ar](mailto:pedro.depetris@anc-argentina.org.ar)

D. M. Gaiero

Escuela de Geología, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Córdoba, Argentina

Centro de Investigaciones en Ciencias de la Tierra, Consejo Nacional de Investigaciones Científicas y Técnicas y Universidad Nacional de Córdoba, Córdoba, Argentina

N. J. Cosentino

Instituto de Geografía, Facultad de Historia, Geografía y Ciencia Política, Pontificia Universidad Católica de Chile, Santiago, Chile

Núcleo Milenio Paleoclima, Santiago, Chile

**Keywords** Hydrology · Biogeochemistry · Organic components · Nutrients · DOC · River sediments

## 1 Introduction

Without taking into account the main rivers draining the island of Tierra del Fuego (i.e. Grande, San Martín, Cullen, Chico, Fuego, and Ewan), the Gallegos is the Patagonia's southernmost river. It owes its name to Blasco Gallegos, a member of Ferdinand Magellan's expedition, which sailed the southern seas in the sixteenth century.

In terms of drainage basin area, the east-flowing Gallegos River is the smallest Patagonian river, ranking behind the Coyle (or Coig) River, its neighbor to the north. However, the Gallegos stands out among other Patagonian rivers due to a harmonic connection with the Southern Annular Mode (SAM), and to the presence in its drainage basin of subbituminous/bituminous coal-bearing beds of presumed Eocene age (i.e. 51°32' S, 72°19' W, Río Turbio Fm.). This chapter seeks primarily to explore a set of characteristics, probing into the impact which, apparently, they force on the main hydrological and biogeochemical features of the Gallegos River.

### 1.1 Geographic Characteristics

The binational Gallegos River (Fig. 1) drainage basin (51°17'–52°09' S, 68°56'–72°22' W), along with the less noticeable Chico River (i.e. inflowing from the south-east, with which the Gallegos shares the wide Atlantic estuary), drain the southernmost portion of Argentina's Santa Cruz Province as well as a portion of Chile's Región de Magallanes y de la Antártica Chilena. It has a drainage basin area of ~9554 km<sup>2</sup> (SSRH 2002). Climate in the region is temperate-cold; mean annual temperature is ~6 °C. Annual atmospheric precipitations (i.e. rain and snowfall) reach ~500 mm in the upper catchments and ~300 mm in the central and eastern reaches. Atmospheric precipitations are concentrated in (austral) autumn and winter. Relative humidity in July (austral winter) reaches 80% in the entire drainage basin, and oscillates between 60 and 70% in January (in the western and eastern regions), and between 50 and 60% in the central area. Strong western and southwestern winds sweep the region, affecting evapotranspiration. High river flow occurs between August and November, triggered by high atmospheric precipitations occurring in the wintertime, and snow/ice melt for the duration of springtime.

The Turbio River (i.e. Spanish for turbid, murky) is the main **headwater** tributary. It flows initially to the south, bordered by the Andes (to the west) and the Cordillera Chica to the north and east. Several Chilean rivers join the main stem in the upper and middle stretch (e.g. Rubens, Penitente, and El Zurdo rivers). The Gallegos is 300 km



**Fig. 1** Southernmost portion of Argentina's Santa Cruz Province, at the southern extreme of continental Patagonia. The city of Río Gallegos is the provincial capital. The map is framed between  $\sim 50^\circ$  to  $\sim 53^\circ$  S, and  $\sim 69^\circ$  to  $\sim 73^\circ$  W. Yacimientos Río Turbio situates the coal mine operation. Gauging stations: **A** Puente Blanco; **B** Toma de Agua

long; the lower 45 km are impacted by large oceanic tides, which reach variations of up to 13 m at the estuary.

In the western region, the Andean Cordillera exhibits a decreasing altitude towards the south. The dominant forest is typical of the Strait of Magellan region, where *guindo* (*Nothofagus betuloides*) predominates among deciduous species, as well as *lenga* (*Nothofagus pumilio*) and *ñire* (*Nothofagus antartica*), among the perennial trees. A steppe of low bushes and grasses prevail in the extra-Andean eastern slope. Most representative soils belong in the mollisols order.

The geology of Gallego's upper catchments is dominated by Pliocene-Recent basaltic rocks and glacial and glacial/fluvial sediments with a predominant basaltic mineral signature, and Quaternary sediments of varied grain-size. Water samples from the Gallegos River exhibited a mean  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of  $0.704863 \pm 0.000129$ , which is slightly higher than the mean composition found in local basaltic rocks ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.703267 \pm 0.000091$ ) (Brunet et al. 2005 and references therein).

The Río Turbio coal deposit, currently mined ( $51^\circ 32' \text{ S}$ ,  $72^\circ 19' \text{ W}$ ) (Río Tubio Fm., Eocene), is deemed an extension of the Loreto Fm. (i.e. Magellan Basin). Its reserves are estimated in 750 million tons of low-sulfur subbituminous-bituminous coal (e.g. Brooks et al. 2006).

## 1.2 Methodology

The field and laboratory techniques employed to analyze river water and sediment samples obtained during the European Commission-funded PARAT Project (Contract CII\*-CT94-0030) were described in Depetris et al. (2005).

The hydrological information was obtained from the data base operated by Argentina's *Secretaría de Infraestructura y Política Hídrica*,<sup>1</sup> and processed with standard statistical software.

Natural periodicities of multi-decadal river flow time series were evaluated by auto spectral analysis, while possible controlling factors of river discharge were analyzed through cross-spectral analysis. To improve the signal-to-noise ratio of the spectrum, the Blackman-Tukey method was used, based on dividing the time series into eight segments with 50% overlap (Blackman and Tukey 1958; Welch 1967). Prior to spectral analysis, all series were detrended based on a least-squares linear fit to the data.

## 2 Hydrological Features

Constrained by the Andean mountainous chain, the shallow Turbio River (i.e. with sources at 51°20' S, Dorotea mountain range) is the main tributary in the uppermost headwaters of the Gallegos River drainage basin (Díaz et al. 2016). To the best of our knowledge, there are no extended and continuous discharge records along its course. In the Gallegos, the uppermost gauging station with a recent continuous record is located at Puente Blanco (51°53'39" S, 71°35'46.6" W),<sup>2</sup> about 190 km **upstream** the estuary.

Figure 2 shows a markedly asymmetrical statistical discharge distribution that fits to a log-normal model (Chi-square = 8.72, d.f. = 2;  $p < 0.01$ ). The geometric mean  $\pm$  standard deviation is  $19.1 \pm 2.35 \text{ m}^3 \text{ s}^{-1}$  (1993–2021), whereas the arithmetic mean discharge is  $28.2 \text{ m}^3 \text{ s}^{-1}$  for the same period. Earlier discharge measurements for 1993–2000 exhibited a higher mean discharge:  $34.2 \text{ m}^3 \text{ s}^{-1}$ . The estimated runoff<sup>3</sup> at Puente Blanco is  $\sim 160 \text{ mm y}^{-1}$  and the specific water yield is  $\sim 140 \text{ L m}^2 \text{ y}^{-1}$ .

Figure 3 shows the synthetic hydrograph of Gallegos River at Puente Blanco gauging station. Maximum discharge is coherent with maximum rainfall/snowfall (Jul.–Aug.) and with snow-ice spring melting (Sep.–Oct.).

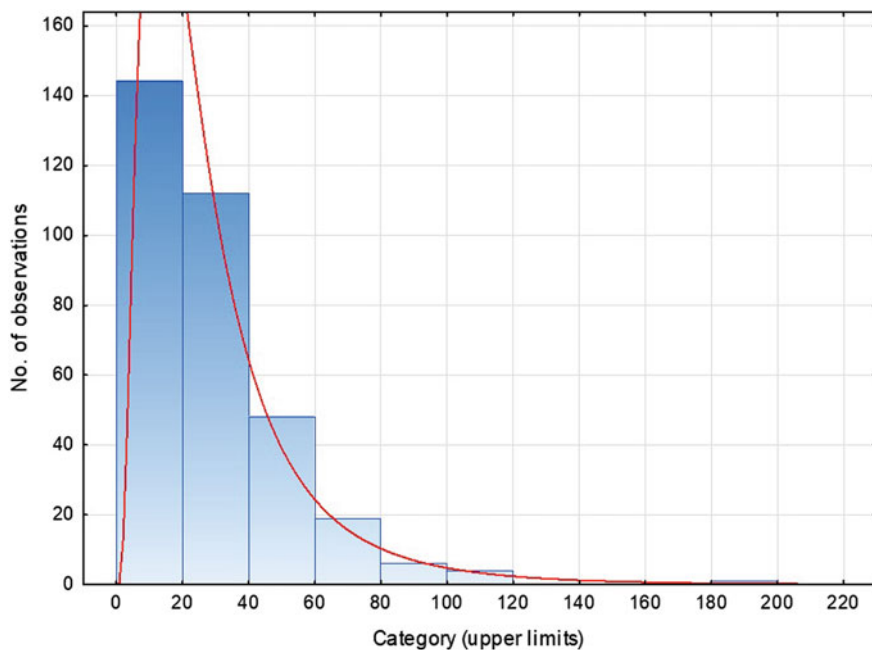
The graph in Fig. 4 shows the Gallegos discharge time series as well as the corresponding deseasonalized data series (1993–2020) determined for the upper reaches. Discharge data (Q) stripped from its seasonal components (i.e. deseasonalized) shows a significant ( $p < 0.05$ ) negative trend: its mean annual discharge has decreased about  $15 \text{ m}^3 \text{ s}^{-1}$  over the last  $\sim 27$  years, whereas its mean deseasonalized discharge has reached about  $-8.3 \text{ m}^3 \text{ s}^{-1}$  during the same period (i.e.  $\sim 40\%$  of its current geometric mean discharge).

River discharge is generally influenced by cyclic trends and changing atmospheric circulation patterns, such as **El Niño-Southern Oscillation (ENSO)** (e.g. Yang et al.

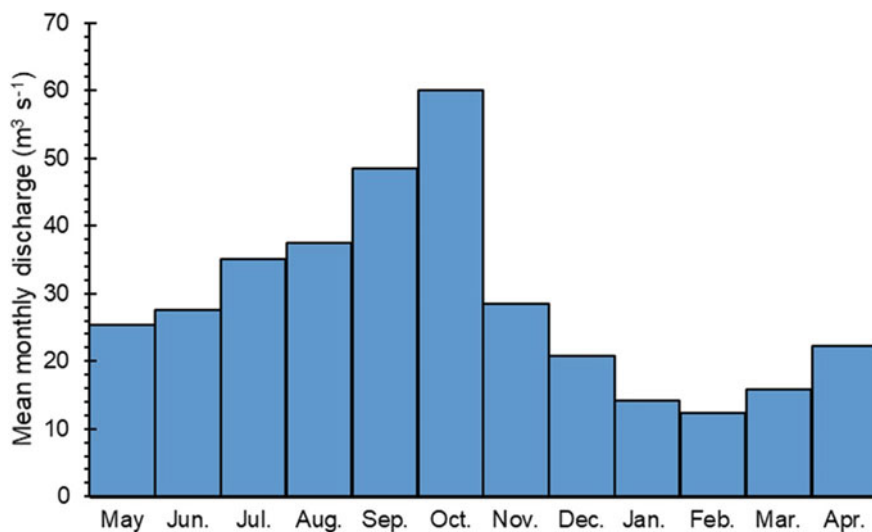
<sup>1</sup> <http://bdhi.hidricosargentina.gob.ar>.

<sup>2</sup> <https://snih.hidricosargentina.gob.ar/>.

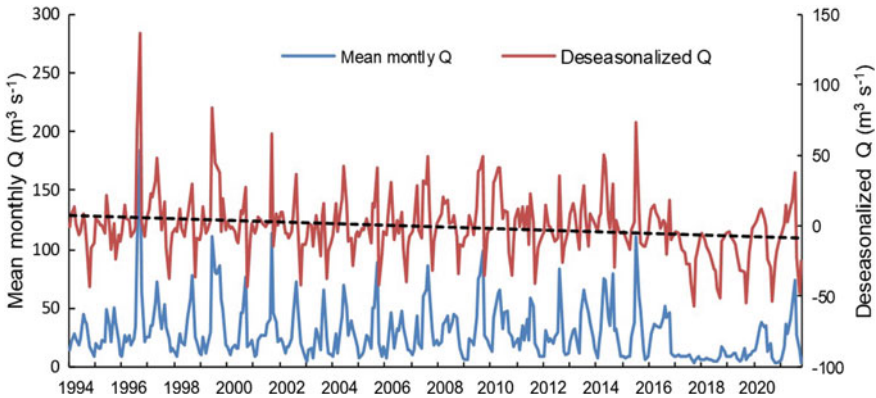
<sup>3</sup> Also known as overland flow.



**Fig. 2** Log-normal distribution of instantaneous discharges ( $N = 166$ ) of Gallegos River, measured at Puente Blanco gauging station (3.02.1993–29.01.2021)



**Fig. 3** Gallegos River synthetic hydrograph determined at the upstream Puente Blanco gauging station (station 2818). Highest discharges in the upper reaches ( $\sim 60 \text{ m}^3 \text{ s}^{-1}$ ) are controlled by snow/ice melt (i.e. spring)



**Fig. 4** The Gallegos River at Puente Blanco. The graph shows the mean monthly discharge, along with the corresponding deseasonalized Q time series (1993–2020). The slope of the regression line ( $y = -0.0486x + 7.8587$ ) is significantly different from zero ( $p < 0.05$ )

2018) or the Southern Annular Mode (SAM)<sup>4</sup> (e.g. Marshall 2003; Gillett et al. 2006). As a climate driver, the SAM affects southern latitudes (i.e. south of  $\sim 50^{\circ}$ – $60^{\circ}$  S). When in positive phase, the westerly wind belt driving the Antarctic Circumpolar Current intensifies and contracts towards Antarctica. In its negative phase, SAM expands towards the Equator. The negative phase will usually be more frequent if coincidental with El Niño events.

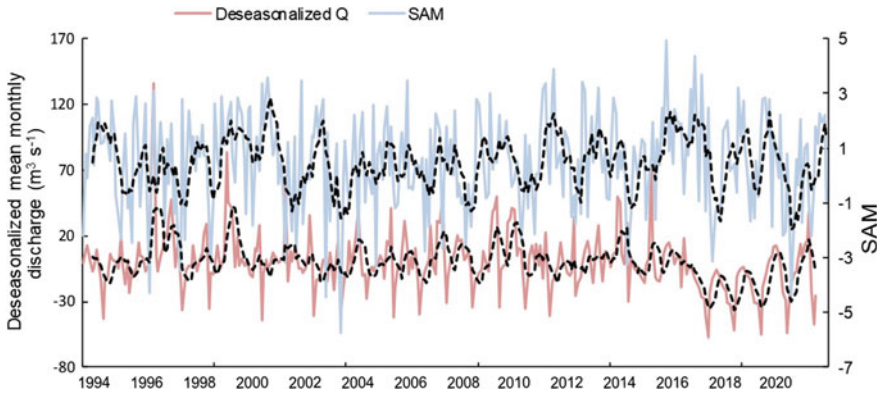
Contrasting with Patagonia,—where the impact of SAM is insufficiently known—its effect on Australian climate has been thoroughly researched<sup>5</sup> (e.g. Hendon et al. 2007). It refers to the (non-seasonal) N–S displacement of westerlies that almost constantly blow in the mid- to high-latitudes of the southern hemisphere. The time frame separating positive and negative events is fairly random, usually ranging between a week and a few months. The effect that the SAM has on rainfall varies greatly depending on season and region.

Figure 5 compares, for the period 1994–2020, the variability of SAM with the deseasonalized Gallegos River time series. A cursory inspection of the graph shows that some—but not all—positive or negative SAM departures coincide with corresponding positive or negative departures in the deseasonalized discharge time series. Clearly, both series do not exhibit a significant correlation and, hence, it is not possible to infer a consistent effect of SAM on precipitations by means of parametric statistics.

Spectrum analysis is related with the exploration of cyclical patterns of data, and may prove fruitful in the exploration of deseasonalized Gallegos discharges and SAM variability. The aim of the analysis is to decompose a complex time series with cyclical components into a few underlying sinusoidal functions of particular wavelengths. Performing spectrum analysis on a time series allows to identify the

<sup>4</sup> SAM is also known as the Antarctic Oscillation (AAO). It is defined as a low-pressure belt surrounding Antarctica.

<sup>5</sup> <http://www.bom.gov.au/climate/sam/>.



**Fig. 5** Comparison of SAM and Gallegos River mean monthly deseasonalized discharge series (at Puente Blanco). Some positive (negative) SAM departures are coherent with positive (negative) deseasonalized discharges. Broken lines are fitted moving averages (period = 5)

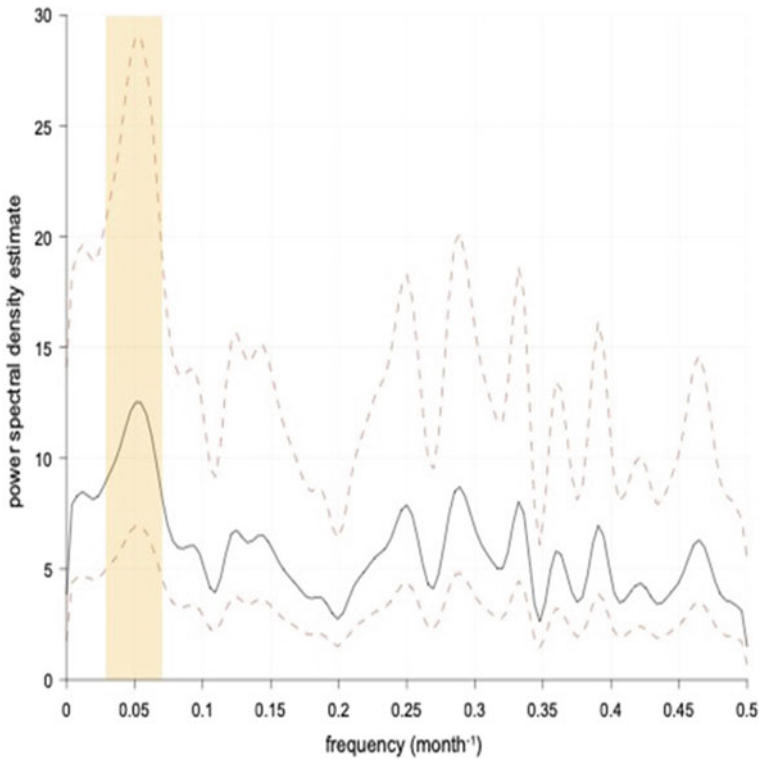
wave lengths and importance of underlying cyclical components. As a result, a few recurring cycles of different lengths in the time series may become evident, which at first looked like random noise (e.g. Figure 5).

Fourier harmonic analysis is helpful in exploring the relationship that is likely to exist between both time series in the 1994–2020-time interval. The first step was to explore the harmonic characteristics of SAM by means of its auto spectral analysis (Fig. 6). The power spectral density is high and significant ( $p < 0.05$ ) in the neighborhood of the 20-month period. This is a key feature when probing into the coherency with Gallegos' deseasonalized discharge.

Cross-spectrum analysis is an expansion of the auto spectral analysis to the simultaneous analysis of two series. The purpose of cross-spectrum analysis is to uncover the correlations between two series at different frequencies. The result is the squared coherency, which can be interpreted similarly to the squared correlation coefficient (i.e. the coherency value is the squared correlation between the cyclical components in the two series at the respective frequency).

Fourier's square coherency was employed to analyze the association existing between SAM and the Gallegos River deseasonalized discharge time series for the interval 1994–2020. Figure 7 shows the square coherence spectrum between both variables. A significant ( $p < 0.05$ ) peak is identifiable for the ~18-months period. It is coincidental with the peak identified in SAM's auto spectral analysis, meaning that in the Gallegos' discharge time series, there are recurring hydrological features, stripped from the seasonal component, which correlate with SAM, with ~18 months' time periodicity (i.e. ~0.05 frequency).

As mentioned above, the time frame separating SAM's positive and negative events is quite random, and it may reach high-frequency values, which may range

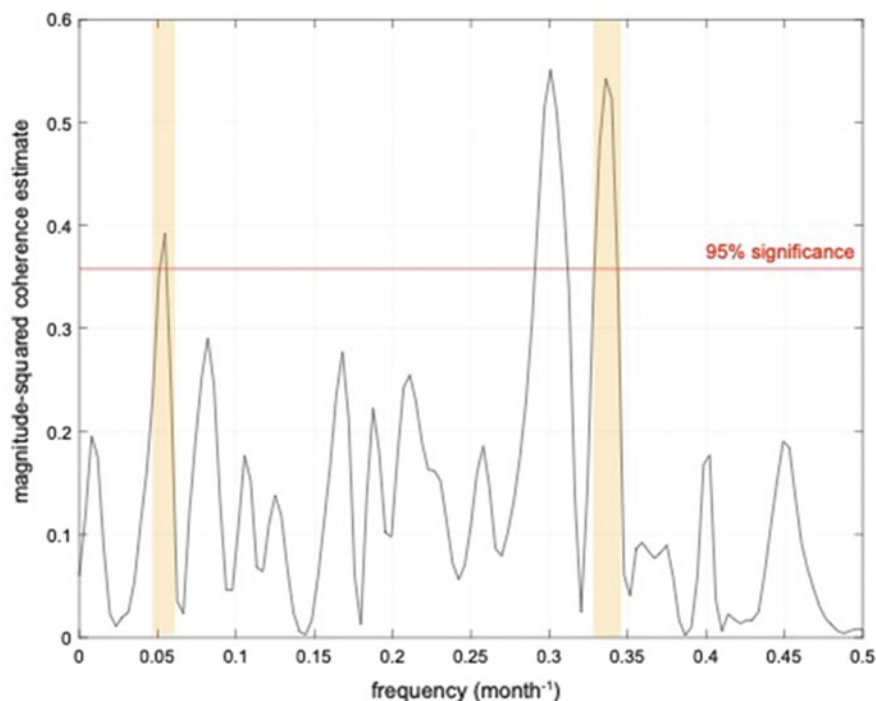


**Fig. 6** The auto spectral analysis of SAM shows a 95%-significant periodicity of ~20 months (light brown box). The power spectral density best estimate is shown in black, while the 95%-confidence interval is shown in dashed red lines

between a week and a few months. It might occur, then, that both variables are associated with short-period or high-frequency (i.e. ~0.33–0.34) deseasonalized hydrological events. It may be a seasonal-like signal that persists in deseasonalized data. It is difficult, however, to assign a physical meaning to the 2.9–3.0-month period peak observable in Fig. 7.

The Gallegos' water discharge shows a significant flow variation, at Toma de Agua, near the city of Río Gallegos (Fig. 8). The geometric mean discharge  $\pm$  standard deviation =  $15.5 \pm 1.71 \text{ m}^3 \text{ s}^{-1}$ . The river flow displays a decrease (i.e. with respect to Puente Blanco), replicated in the hydrograph, that can be attributed to several causes, including strong evapotranspiration and the consumptive use of the resource. The current mean (arithmetic) discharge at Toma de Agua is  $18.2 \text{ m}^3 \text{ s}^{-1}$  (2016–2020); the specific water yield at the Gallegos' mouth is  $57 \text{ L m}^2 \text{ y}^{-1}$ .

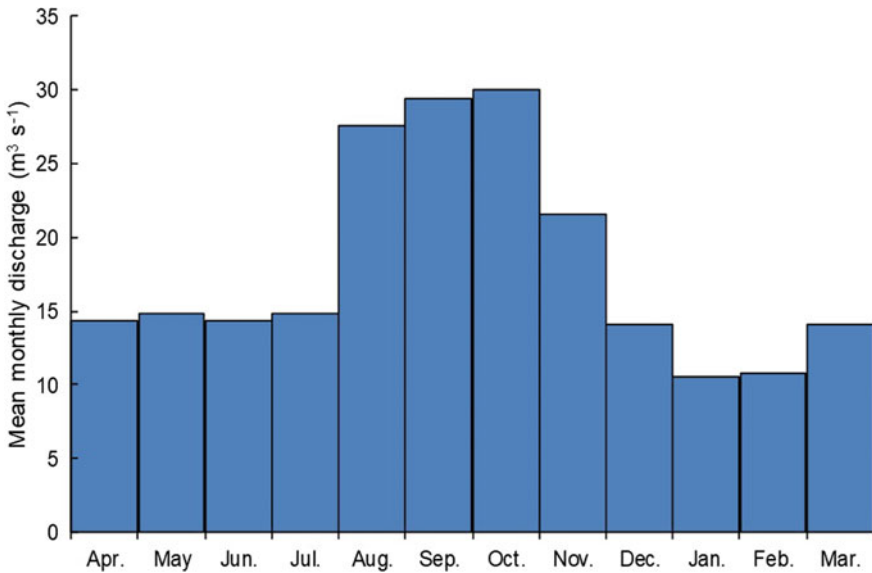




**Fig. 7** Gallegos River at Puente Blanco. The squared coherence calculated with Fourier harmonic analysis shows the relationship between the time series of SAM and deseasonalized Q, with two 95%-significant periodicities of 2.9–3.0 and ~18 months (light brown boxes), that also show strong relative peaks in the cross power spectral density estimate (not shown). The 95% significance level for the magnitude-squared coherence estimates was computed using a bootstrap method

### 3 Biogeochemical Evaluation

The Gallegos' main physicochemical parameters portray an Andean river subjected to a **weathering-limited denudation** (Carson and Kirkby 1972), basically governed by physical processes, with chemical weathering playing a subordinate role. The geochemical aspects of the Gallegos River were surveyed by the PARAT Project, between September 1985 and April 1998. The main physicochemical characteristics can be summarized as follows: pH frequently drops below neutrality ( $7.07 \pm 0.54$ ), and water conductivity is low ( $112.2 \pm 4.67 \mu\text{S cm}^{-1}$ ), with  $\Sigma\text{Z}^+$  (i.e.  $\Sigma\text{Z}^+ = 2\text{Ca}^{2+} + 2\text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ ) fitting in the medium dilute category ( $0.75 > \Sigma\text{Z}^+ > 1.5 \text{ meq L}^{-1}$ ) (Meybeck 2005). The most frequent order of decreasing abundance among cations is  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ , whereas among anions is  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . Lee et al. (2013) investigated a set of southern Patagonian rivers, including one sample from the Gallegos. Recent studies have shown that glacial sediments (Quaternary), prevailing in the drainage basin, regulate the material contribution to



**Fig. 8** Gallegos River mean synthetic hydrograph (2016–2020) determined near the estuary, at Toma de Agua (station 2838). High discharges are determined by winter precipitations (August) and snow/ice melt (September–October)

the dissolved and particulate load, balancing the output between silicates, evaporitic and carbonate rocks (Gaiero et al. submitted).

### 3.1 Dissolved Components

Nutrients are chemical elements essential for the development of plant and animal life. In oceans, rivers and lakes, nutrients are needed for the growth of algae that form the basis of an intricate food web sustaining the entire aquatic ecosystem. Nitrogen and phosphorous are the most conspicuous nutrients in rivers and lakes, whereas silicon and several other micronutrients also play a role in primary biological production.

Nitrogen is released during organic matter decomposition, largely as ammonium ( $\text{NH}_4^+$ ). It can be adsorbed onto negatively charged organic coatings on soil particles or clay mineral surfaces. Ammonium is also taken up by algae or plants, or converted to nitrite ( $\text{NO}_2^-$ ) through nitrification, which is oxidized further to nitrate ( $\text{NO}_3^-$ ), a process usually catalyzed by bacteria. Nitrate is soluble and it is not retained in soils. Consequently,  $\text{NO}_3^-$  supplied by rainwater, or derived from the oxidation of soil organic matter and animal wastes, will wash out of sediment or regolith/soils into rivers.

In natural waters, dissolved inorganic phosphorous (DIP) exists largely as a number of dissociation products of  $\text{H}_3\text{PO}_4$ . Phosphorous is usually retained in soils (e.g. by adsorption onto soil particles) or regolith. Phosphate is usually in sediments as insoluble  $\text{FePO}_4$  (i.e. under reducing conditions) and, therefore, DIP can be returned to the water column associated with Fe(III) reduction to Fe(II). Phosphorous may be supplied, as well, by the dissolution/hydrolysis of phosphate minerals, such as the apatite group (i.e.  $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$ ).

The Gallegos River showed a wide-ranging concentration variability in  $\text{NO}_3^- - \text{N}$ . Between Sep. 1995 and Apr. 1998 the river was sampled sporadically at the Güer Aike site (i.e. near the outfall into the estuary). During the sampling period, high and low concentrations fluctuated 100-fold, between  $\sim 92$  and  $0.97 \mu\text{mol L}^{-1}$ , whereas  $\text{NO}_2^- - \text{N}$  exhibited, as expected, much lower concentrations ( $12.80$ – $1.16 \mu\text{mol L}^{-1}$ ) during the same period. The markedly low concentrations of DIP ( $1.69$ – $0.02 \mu\text{mol L}^{-1}$ ) reflected the meager DIP supply received either from point or non-point sources. Hence, the approximate N:P dissolved ratio in the Gallegos apparently remained in the 50:1–60:1 range throughout the hydrological year, regardless of the water flow level. The high  $\text{NO}_3^- - \text{N}$  concentrations and the resulting, equally high N:P ratio, can only be explained by the contribution of groundwater, which dissolved phases may be supplied by coal-bearing beds and mudstones, containing nitrogen but only traces of phosphorous.<sup>6</sup> It must be added that, in comparison with the remaining Patagonian Rivers, the Gallegos is the river that showed the highest nitrogen concentrations in the set (Depetris et al. 2005).

Table 1 shows the concentrations of several chemical variables (i.e. also sampled at Güer Aike) of significance in biogeochemical reactions. Silicon, also a nutrient, is used—for example—by diatoms and radiolarian to build their exoskeletons and hence, also plays a significant biogeochemical role. The mean silicon oxide ( $\text{SiO}_2$ ) concentration found was  $243.2 \mu\text{mol L}^{-1}$  (i.e.  $14.6 \text{ mg L}^{-1}$ ) and also exhibited a constrained variability (i.e. the coefficient of variation is  $\sim 10\%$ ). Silicon originates solely from weathering reactions, and its inherently low concentrations may be modulated further by biological consumption.

Figure 9 shows the variability of dissolved organic carbon (DOC) and  $\delta^{13}\text{C}_{\text{DIC}}$  against Gallegos River discharge. In contrast with other examples, where DOC is diluted by swelling river flow, DOC concentrations in the Gallegos increase significantly, thus suggesting an allochthonous source for the dissolved organic carbon: a four-fold increase in discharge, from  $20$  to  $80 \text{ m}^3 \text{ s}^{-1}$ , generates an almost three-fold increase in DOC concentration.

In contrast,  $\delta^{13}\text{C}_{\text{DIC}}$  decreases with increasing discharge and DOC. The latter could contribute to decrease  $\delta^{13}\text{C}_{\text{DIC}}$ , as shown for the St. Lawrence River (Barth and Veizer 1999). Moreover, high discharge determines a more negative  $\delta^{13}\text{C}_{\text{DIC}}$ , which could mean a change in the supplying source.

DIC concentrations in fresh water bodies are controlled by lithology, water temperature, flow variations, and biogeochemical processes (e.g. organic matter oxidation).

---

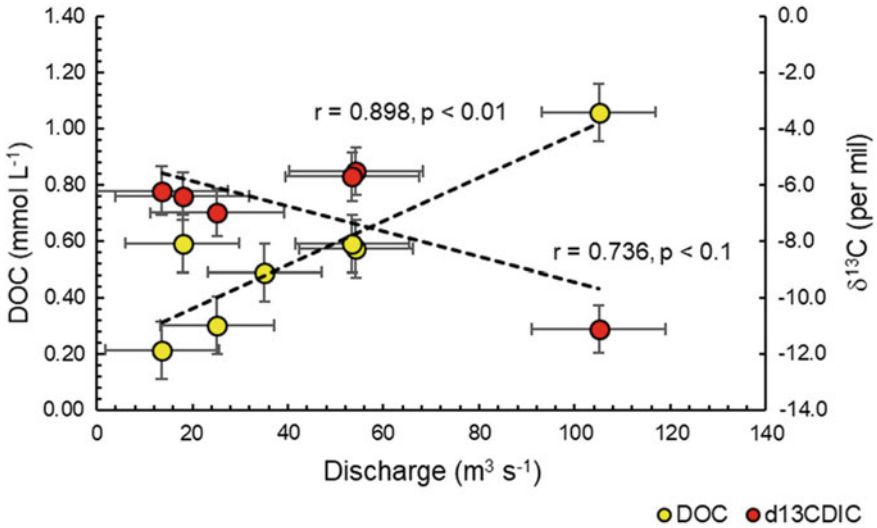
<sup>6</sup> Río Turbio subbituminous-bituminous coal (geometric) mean composition on a dry, ash-free basis, is  $\sim 56.6\%$  carbon,  $\sim 0.97\%$  nitrogen,  $\sim 0.68\%$  sulphur, and  $\sim 0.02\%$  phosphorous (Brooks et al. 2006).

**Table 1** Dissolved biogeochemical parameters determined in the Gallegos River at Güter Aike

Date	pH	Q (m <sup>3</sup> s <sup>-1</sup> )	TDS (mg L <sup>-1</sup> )	SiO <sub>2</sub> (μmol L <sup>-1</sup> )	Fe <sub>diss.</sub> (μmol L <sup>-1</sup> )	DOC (mmol L <sup>-1</sup> )	DIC (mmol L <sup>-1</sup> )	pCO <sub>2</sub> (μatm)	δ <sup>13</sup> C <sub>pDIC</sub> (per mil)
Sep. 1995	6.96	105	98.3	185	n.d	1.06	1.10	6907	-11.1
May 1996	6.90	54	76.4	266	0.23	0.57	0.85	6395	n.d
Sep. 1996	6.65	53	80.4	258	0.23	0.59	1.23	13,051	-5.5
Dec. 1996	7.44	14	106.1	248	0.09	0.22	1.00	2299	-5.7
Dec. 1997	6.41	18	85.5	252	0.27	0.59	1.47	18,427	-6.2
Apr. 1998	8.05	25	137.3	261	0.17	0.30	1.25	763	-6.4
G.M	<b>7.05</b>	<b>35</b>	<b>95.4</b>	<b>243.2</b>	<b>0.19</b>	<b>0.49</b>	<b>1.13</b>	<b>5153</b>	<b>-7.0</b>

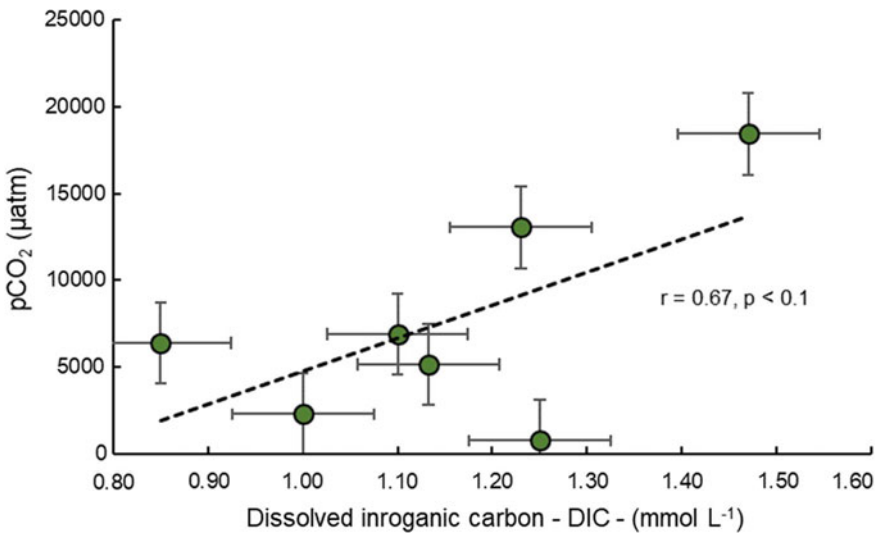
G.M. geometric mean

n.d. not determined



**Fig. 9** Scatter graph showing DOC and  $\delta^{13}\text{C}_{\text{DIC}}$  variation as a function of Gallegos River discharge. Significant correlations support a cause-effect relationship between the variables and river flow. Error bars are the standard error of the mean. Data from Brunet et al. (2005)

Brunet et al. (2005) studied the provenance of dissolved inorganic carbon (DIC) in Patagonian rivers. Their data, included in Fig. 10, points to an interesting aspect.

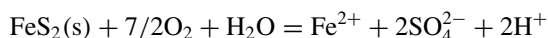


**Fig. 10** Variability of DIC and  $\text{pCO}_2$  in the Gallegos River. Error bars are the standard error of the mean. Data from Brunet et al. (2005)

One feature in which the Gallegos diverges from most Patagonian rivers is that a significant proportion of DIC is accounted for by  $\text{H}_2\text{CO}_3$  (i.e. high  $\text{pCO}_2$ ). Hence, high DIC may be linked to a significant groundwater supply or to waters circulating under snow/ice, in the mountainous upper reaches.

Iron is an indispensable micronutrient of **phytoplankton**. Iron plays an important role in many biological processes such as nitrogen assimilation,  $\text{N}_2$  fixation, photosynthetic and respiratory electron transport, and porphyrin biosynthesis. Consequently, the regulation effects of Fe should be considered besides nitrogen and phosphorus when dealing with the processes of river and lake **eutrophication**. There are several sources of Fe, including the above mentioned reduction of Fe(III) to Fe(II). Among them, pyrite ( $\text{FeS}_2$ ) is the most common sulfide mineral on the Earth's surface, and it plays an important part in geochemistry, as well as in biology and environmental processes. The maximum  $\text{SO}_4^{2-}$  concentration that can be attained by sulfide oxidation in surface waters saturated with  $\text{O}_2$  is  $\sim 400 \mu\text{eq L}^{-1}$  although subglacial waters may increase three-fold this concentration (Tranter 2005).

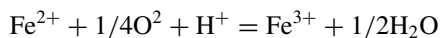
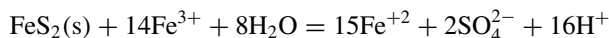
The Río Turbio coal has a mean of  $0.3 \pm 0.31\%$  pyritic sulfur, and  $0.5 \pm 0.23\%$  organic sulfur (Brooks et al. 2006). When exposed to air, pyrite is oxidized, whether by natural processes or anthropogenic activities, forming sulfuric acid in the presence of humidity (e.g. Campos dos Santos et al. 2016):



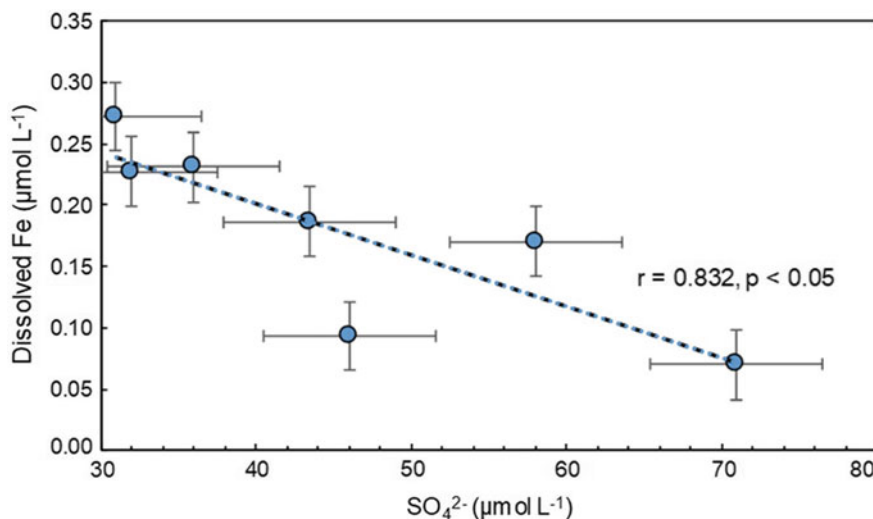
Stumm and Morgan (1996) described the following reactions:  $\text{Fe}^{2+}$  endures oxygenation to  $\text{Fe}^{3+}$ , which is subsequently hydrolyzed to  $\text{Fe}(\text{OH})_3(\text{s})$ , liberating more acidity and coating mineral grains in the streambed.



Pyrite can reduce  $\text{Fe}^{3+}$  and  $\text{FeS}_2(\text{s})$  is again oxidized. Acidity is released along with additional  $\text{Fe}^{2+}$ , which can again reenter the reaction cycle and drive it further:



This set of reactions can explain Fig. 11, where increasing  $\text{SO}_4^{2-}$  concentrations are accompanied by decreasing Fe concentrations due to a series of feedback chemical mechanisms—described above—which tend to precipitate  $\text{Fe}_3(\text{OH})_3(\text{s})$ , removing Fe from the solution.



**Fig. 11** Decreasing concentrations trends of  $\text{SO}_4^{2-}$  and Fe in the Gallegos River. See text for explanations. Error bars are the standard error of the mean

### 3.2 Particulate Organic Constituents

Particulate organic debris transported by rivers supplies important information on a series of important biogeochemical processes taking place within drainage basins. Depetris et al. (2005) have probed into the biogeochemical typology and output of all the main Patagonian rivers and the information collated in that particular project for the Gallegos Rivers is examined here in more detail. Figure 12 shows an illustrating image of a typical sample of the dark Gallegos' bed load sediment.

Table 2 shows mean values and fluxes, expressed in molar masses, as determined in the Gallegos River within the framework of the PARAT Project. The geometric mean of total suspended solids (TSS) was  $25 \text{ mg L}^{-1}$ , whereas its concentrations varied between  $5$  and  $60 \text{ mg L}^{-1}$  during the period of sampling. Between 6.5 and 9% of TSS was accounted for by organic matter.

It is clear from Table 2 that most of the carbon transported in suspension by the river was organic, in as much the difference between the mean total particulate carbon (PC) and the mean organic fraction (POC) is about  $120 \text{ mol L}^{-1}$  (~35%). Such proportion of the particulate phases is probably accounted for by carbonates, which have been identified as significant in the carbon-bearing Río Turbio beds (Brooks et al. 2006).

The concentration of POC (Table 2) is among the noteworthy concentrations in Patagonian rivers and the Gallegos' mean concentration is only exceeded by the Deseado and Chico rivers, with mean POC concentrations in the neighborhood of  $380 \text{ µmol L}^{-1}$ . The nearby Coyle River, draining marshes and peat bogs, showed a mean POC concentration of  $\sim 50 \text{ µmol L}^{-1}$  (Depetris et al. 2005).



**Fig. 12** Image of a typical bed sediment sample of the Gallegos River collected at a point bar. The mostly silt and sand grain-size sample includes large coal fragments (i.e. ~0.5–1.0 cm)

**Table 2** Gallegos River organic particulate matter: means and fluxes

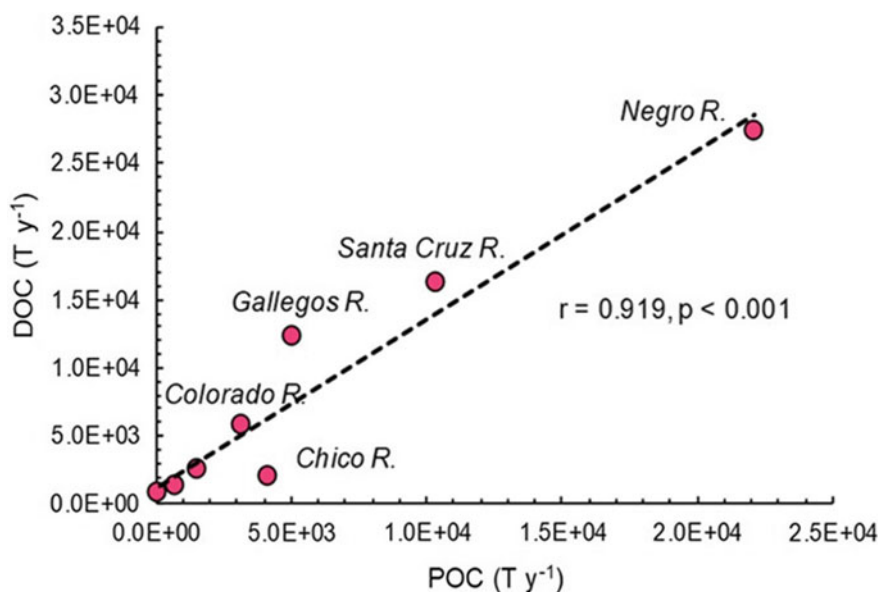
Variables	G.M. ( $\mu\text{mol L}^{-1}$ )	Mass ( $\text{Kmol y}^{-1}$ )	Yield ( $\text{mol km}^{-2} \text{y}^{-1}$ )
PC	332	10.5	1.10
POC	215	6.8	0.71
PN	28	0.9	0.09
DOC	491	15.5	1.62

G.M. geometric mean

C/N ratios in the range 4:1–10:1 are typically from marine (i.e. phytoplankton) sources, whereas higher ratios are to be expected to come from a terrestrial source because vascular plants from land-dwelling sources tend to have C/N ratios greater than 20. The mean POC/PN molar ratio in the Gallegos River is ~8:1, which leads to interpret a terrigenous source with some planktonic contribution. The Gallegos has the largest mean POC/PN ratio of all the Patagonian rivers, most of which point to a dominating autochthonous source (i.e. 4:1–5:1) (Depetris et al. 2005). It is worthwhile to highlight the significance of DOC over all the other forms of carbon (i.e. mean DOC/POC  $\approx$  2.3), which stands out among all the other Patagonian water bodies. The largest rivers in Patagonia (e.g. Negro, Santa Cruz, Chubut) exhibit DOC/POC < 2.0 (Depetris et al. 2005).

The world average total organic carbon (i.e. TOC = DOC + POC) concentrations in rivers fluctuates in the range of 730–880  $\mu\text{mol L}^{-1}$ . On a global scale, the mean concentrations of DOC and POC are 400–480  $\mu\text{mol L}^{-1}$  and 330–400  $\mu\text{mol L}^{-1}$ , respectively (Perdue and Ritchie 2005). In the Gallegos, mean TOC is 706  $\mu\text{mol L}^{-1}$ , below the global range. On the other hand, average DOC concentration in the





**Fig. 13** Mass transport rates of POC and DOC in Patagonian rivers. The Negro and Santa Cruz have the highest discharges in Patagonia's riverine set (Depetris et al. 2005)

Gallegos is somewhat higher than the most frequent global values. Mean POC, in contrast, is lower.

Patagonian rivers export to the SW Atlantic Ocean about  $47.4 \text{ Gg y}^{-1}$  of POC and about  $67.8 \text{ Gg y}^{-1}$  of DOC. The Gallegos River supplies about 11% of POC and about 18% of DOC supplied to the Patagonian coastal zone. Figure 13 shows the high covariance of both transport rates as well as the significance of high discharge (Depetris et al. 2005). Clearly, the relevance of both, the Negro and Santa Cruz rivers, is mainly determined by their high discharge, even though the Gallegos River exhibits higher organic carbon concentrations.

## 4 Final Observations

The Gallegos is the southernmost river of continental Patagonia. It delivers  $\sim 0.573 \text{ km}^3 \text{ y}^{-1}$  of freshwater into an ample estuary in the SW Atlantic Ocean. The water specific yield at the mouth is  $57 \text{ L m}^2 \text{ y}^{-1}$  and discharge peaks occur in August due to (austral) winter precipitations, and in September–October owing to snow/ice-melt occurring in the southern spring. Annual atmospheric precipitations are moderate and climate change is seemingly affecting the Gallegos River mean discharge: deseasonalized discharge data shows a significant ( $p < 0.05$ ) negative trend. Its mean monthly discharge has decreased  $\sim 15 \text{ m}^3 \text{ s}^{-1}$  over the last  $\sim 27$  years,

whereas its deseasonalized monthly discharge also shows a significant decrease of about  $-8.3 \text{ m}^3 \text{ s}^{-1}$  during the same period (i.e.  $\sim 40\%$  of its current mean discharge).

The Gallegos River discharge time series at Puente Blanco appears to be connected with the southern atmospheric pressure variability. Fourier harmonic analysis shows that the deseasonalized flow series is coherent with the SAM (a.k.a. Antarctic Oscillation, AAO) with significant peaks at 18 and 3 months. It is interesting to point out that the negative discharge trend exhibited by Gallegos' discharge trend does not appear to be associated with SAM's variability although there is a significant coherency between both variables.

Nutrients do not reach high concentrations in the Gallegos, as it happens in most Patagonian rivers. Several factors, however, suggest that the coal-bearing beds, which are being mined at Río Turbio, play a significant role in supplying dissolved and particulate matter to the river, thus affecting its biogeochemical characteristics.

Nitrogen, which is the factor limiting biological productivity in most Patagonian water bodies, is the most conspicuous nutrient in the Gallegos River.  $\text{NO}_3^-$ -N may reach almost  $100 \mu\text{mol L}^{-1}$  and the N:P ratio may be in the 50:1–60:1 range. This is an indication that dissolved nitrogen is likely supplied by N-rich groundwater, in contact with coal strata or with organic-rich mudstones. Likewise, the Gallegos has the highest DOC concentrations in Patagonian waters (e.g. mean concentrations of  $500 \mu\text{mol L}^{-1}$ ), which tend to increase with increasing discharge and shows an inverse relationship with  $\delta^{13}\text{C}$  (i.e.  $\delta^{13}\text{C}$  is possibly connected with the alkalinity supplied by carbonate dissolution). Additionally, DIC is significantly correlated with  $\text{pCO}_2$ , which concentration is possibly governed by groundwater. All these aspects reinforce the scenario of Río Turbio coal as a factor to consider in the riverine biogeochemistry.

Another interesting aspect is the dynamics of  $\text{SO}_4^{2-}$ . Río Turbio's is a low-sulfur bituminous coal but, according to Brooks et al. (2006), it has some pyritic sulfur (i.e. 0.1–0.8%) and organic sulfur (i.e. 0.3–0.8%). The opposite correlation of  $\text{SO}_4^{2-}$  with dissolved Fe, is probably governed by the precipitation of (oxy)hydroxides and further suggests the partial significance of a coal-related source for dissolved phases of biogeochemical meaning.

The mean POC/PN molar ratio in the Gallegos River (i.e.  $\sim 8:1$ ), is the highest C/N in Patagonia's riverine TSS, most of which exhibit a prevailing autochthonous source (i.e.  $\sim 4:1$ – $5:1$ ) (Depetris et al. 2005). This feature leads to infer for the Gallegos a phytoplankton source with some terrigenous contribution.

Mean TOC in the Gallegos River is  $\sim 700 \mu\text{mol L}^{-1}$ . This figure falls in the lower end of the riverine TOC global scenario (Perdue and Ritchie 2005). The DOC/POC mean ratio is  $\sim 2.3$ , because DOC supplies  $\sim 70\%$  of TOC and its mean concentration in the Gallegos is higher than the most frequent DOC concentrations, on a global basis (e.g. Perdue and Ritchie 2005). This further supports the image that the coal-bearing beds supplies, likely via groundwater, the important DOC concentrations exhibited by the Gallegos River.

Patagonian rivers export to the SW Atlantic Ocean  $\sim 115 \text{ Gg y}^{-1}$  of TOC, with an average DOC/POC ratio 1.4:1. The Gallegos River supplies about 11% of POC and about 18% of the DOC contributed by rivers to the Patagonian coastal zone (Depetris et al. 2005).

## References

- Barth JAC, Veizer J (1999) Carbon cycle in the St Lawrence aquatic ecosystem at Cornwall (Ontario), Canada: seasonal and spatial variations. *Chem Geol* 159:107–128
- Blackman RB, Tukey JW (1958) The measurement of power spectra from the point of view of communications engineering—part I. *Bell Syst Tech J* 37:185–282
- Brooks WE, Finkelman RB, Willett JC, Torres IE (2006) World quality inventory: Argentina. In: Karlens AW, Tewalt SJ, Bragg LJ, Finkelman RB (eds) *World coal quality inventory: South America*. US Geological Survey, Washington DC, pp 27–47
- Brunet F, Gaiero D, Probst J-L, Depetris PJ, Gauthier, Lafaye F, Stille P (2005)  $^{13}\text{C}$  tracing of dissolved inorganic carbon sources in Patagonian rivers (Argentina). *Hydrol Proc* 19:3321–3344
- Campos Dos Santos E, De Mendonça Silva JC, Anderson Duarte H (2016) Pyrite oxidation mechanism by oxygen in aqueous medium. *J Phys Chem C* 120(5):2760–2768
- Carson MA, Kirkby NJ (1972) *Hillslope form and processes*. University Press, Cambridge
- Depetris PJ, Gaiero DM, Probst J-L, Hartmann J, Kempe S (2005) Biogeochemical output and typology of rivers draining Patagonia's Atlantic seaboard. *J Coast Res* 21(4):835–844
- Díaz B, Monserrat MC, Tiberi PE, Mardewald G, Hofmann C, Caparrós L, Mattenet F, Zerpa D, Billoni SL, Martínez L (2016) Surface–water hydrology of the Río Gallegos watershed (South of Santa Cruz province, Argentina). *Techn Report-UNPA* 8(3):136–161 (in Spanish)
- Gillett NP, Kell TD, Jones PD (2006) Regional climate impacts of the Southern Annular Mode. *Geophys Res Lett* 33:1–4
- Hendon HH, Thompson DWJ, Wheeler MC (2007) Australian rainfall and surface temperature variations associated with the Southern Hemisphere Annular Mode. *J Clim* 20:2452–2467
- Lee B, Han Y, Huh Y, Lundstrom C, Siame LL, Lee JI, Park B-K, Aster, team. (2013) Chemical and physical weathering in south Patagonia rivers: a combined Sr-U-Be isotope approach. *Geochim Cosmochim Acta* 101:173–190
- Marshall GJ (2003) Trends in the Southern Annular Mode from observations and reanalyses. *J Clim* 16:4134–4143
- Meybeck M (2005) Global occurrence of major elements in rivers. In: Drever JI (ed) *Surface and groundwater, weathering and soils*. Elsevier, Amsterdam, pp 207–223
- Perdue EM, Ritchie JD (2005) Dissolved organic matter in freshwaters. In: Drever JI (ed) *Surface and groundwater, weathering and soils*. Elsevier, Amsterdam, pp 273–318
- SSRH (2002) *Acta digital de los recursos hídricos superficiales de la República Argentina*, CD-Rom, Buenos Aires (in Spanish)
- Stumm W, Morgan JJ (1996) *Aquatic chemistry. Chemical equilibria and rates in natural waters*. Wiley-Interscience, New York
- Tranter M (2005) Geochemical weathering in glacial and proglacial environments. In: Drever JI (ed) *Surface and groundwater, weathering and soils*. Elsevier, Amsterdam, pp 189–205
- Welch P (1967) The use of fast Fourier transform for the estimation of power spectra: a method based on time averaging over short, modified periodograms. *IEEE Trans Audio Electroacoust* 15(2):70–73
- Yang S, Li Z, Yu J-Y, Hu X, Dong W, He S (2018) El Niño–Southern Oscillation and its impact in the changing climate. *Ntl Sci Rev* 5(6):840–857