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Dynamics of Macronutrients in the San Jorge Gulf During Spring and Summer




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ABSTRACT. Following designation of San Jorge Gulf (SJG) as a priority for marine conservation by the Argentine scientific community, it was included in the "Pampa Azul" government initiative. As a contribution to this initiative, we analyzed macronutrient distribution and its relationship to the stratification and primary producer biomass in the water column during austral summer 2014 and spring 2016. In addition, we determined dissolved oxygen, chlorophyll concentrations, and pH. During both seasons in the central and northern gulf, strong stratification separated nutrient-poor, oxygenated surface waters from nutrient-rich, less-oxygenated deep waters. Thermal stratification was correlated to nutrient concentrations. Oxygen decreased up to 60% in bottom waters, although hypoxic conditions were not found. Nitrate limited primary production in surface waters. A tidal front near the gulf's mouth in the south and wind-forced upwelling in the southwestern coastal zone naturally fertilized the waters. Although there is no information on the precise amount of nutrients each source contributes to the SJG, a shortcut in the path toward resource conservation could be directed through the processes associated with water column stratification because it determines the availability of surface nutrients to primary producers.

INTRODUCTION

San Jorge Gulf (SJG) is the largest gulf on the Argentine coast. With a maximum depth of 110 m in the central region, it covers 39,340 km^2 (Fernández et al., 2005, 2007). No rivers drain into the SJG, and the annual rainfall is less than 200 mm yr^{-1}. The greatest winds, southwesterlies, occur in spring and summer. The amplitude of semidiurnal tides can reach 6 m. The gulf receives water from the Argentinean continental shelf, which is influenced by Magallanes Strait water (Fernández et al., 2005). In the southern part of the SJG's mouth, a tidal front supplies the gulf with nutrient-rich waters (Rivas and Pisoni, 2010), while in the coastal zone a thermohaline front is seasonally observed (Fernández et al., 2005). The phytoplankton growth pattern in the gulf is typical of temperate regions, where diatoms dominate in winter and dinoflagellates in summer (Akselman, 1996). Additionally, there are numerous bays, creeks, and small islands in the north. This great diversity of environments makes the SJG one of the most productive areas in Argentina, providing a wide variety of marine mammals and birds with places for resting, mating, breeding, and feeding (Yorio, 2001).

Fishing for crustaceans such as the Patagonian grenadier (*Pleoticus muelleri,* Bate 1888) and the Argentine hake (*Merluccius hubbsi,* Marini 1933), among others, is important to the region's economy (Góngora et al., 2012). However, crude oil extraction in the SJG is the region's main economic engine, representing almost 50% of the Argentinean crude oil total. Oil industry activities can have deleterious effects on the region's ecosystems, principally through spills associated with petroleum transportation in the SJG and along Argentina's coast (Commendatore et al., 2000). In 2007, an oil spill—approximately 300 m^3—was identified in front of Córdova Creek in the central region of the SJG. Unfortunately, the oil reached the coastline and caused irreparable damage along 4 km (Parada, 2008; Poleschi et al., 2008). Analysis of sediment samples taken in the intertidal zone indicated high concentrations of aliphatic and aromatic compounds (Marta Commendatore, CESIMAR, *pers. comm.*, February 6, 2018). Signs of that spill, such as weathered oil on intertidal hard-bottom substrates, remain today (Marta Commendatore, CESIMAR, *pers. comm.* February 6, 2018).

Akselman (1996) suggested that water column stratification in the SJG influences nutrient distribution and availability for primary producers. Supporting this hypothesis, Krock et al. (2015) observed low surface concentrations of nutrients in this region during autumn and high concentrations of inorganic nutrients at depths below 50 m. During the same cruise, a higher macronutrient surface concentration was reported in the northern gulf (Paparazzo et al., 2017) where tides ruptured the stratification. Fernández et al. (2005) found seasonal variations in the chemical and physical conditions of sediment and bottom waters in the SJG. Fernández et al. (2007) determined that while dissolved oxygen levels were within the normal range for oxygenated shelf environments, low oxygen values indicated hypoxic conditions in the south-central part of the gulf.

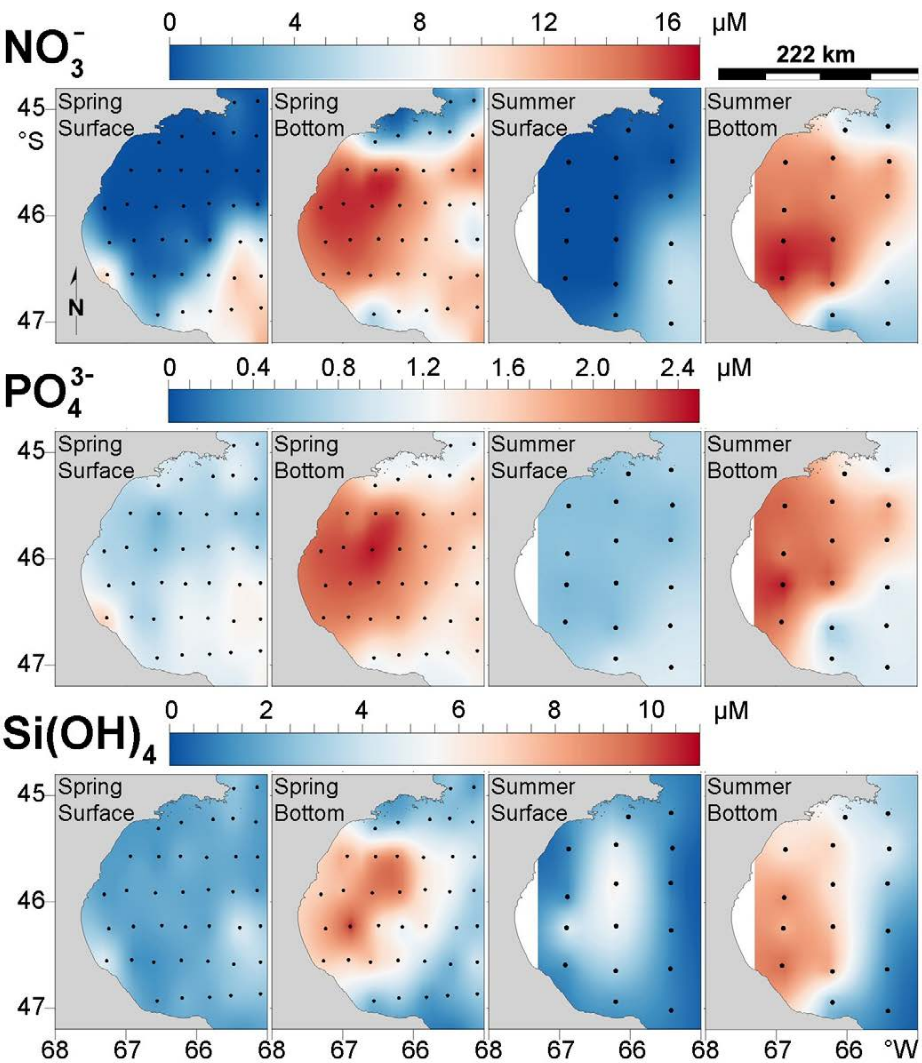

FIGURE 1. Macronutrient concentration at surface and bottom during spring and summer in San Jorge Gulf. Black dots indicate the sampling stations conducted during two cruises in spring 2016 and summer 2014.

To conserve biodiversity and natural resources, the northern zone of the SJG was protected by a national law (No. 26446) that created the Inter-Jurisdictional Coastal Marine Park "Patagonia Austral," the first marine park in Argentina (Yorio, 2001). In addition, the SJG was identified as a priority strategic area (hotspot) by Argentina's scientific community within the framework of the political science and technology national program for marine conservation "Pampa Azul," funded by the federal government. Subsequently, a bilateral cooperation agreement was signed between Argentina's Ministry of Science, Technology, and Innovation (MINCyT acronym in Spanish) and Québec University at Rimouski, Canada, and its Institute de Sciences de la Mer. Scientific research in the gulf thus began when R/V *Coriolis II* arrived in February 2014 to conduct physical, chemical, biological, and geological studies. Our contribution to these studies is the description of the nitrate, phosphate, and silicic acid dynamic of the SJG during spring and summer, showing how macronutrient concentrations are related to physical (stratification) and biological (biomass of primary producers) processes.

MATERIALS AND METHODS

Samples and data for this study were collected in the SJG (Figure 1) during austral summer (February 2014) at 16 sampling stations from R/V *Coriolis II* (ISMER-UQAR, Canada) and during austral spring (November 2016) at 39 sampling stations from R/V *Puerto Deseado* (CONICET, Argentina). Fewer sites were sampled during the initial summer campaign due to the numerous activities planned for the cruise and time limitations. To expand the study area and obtain more detailed information, 22 stations were added in spring 2016. Water samples from the CTD casts were only taken at representative depths, depending on vertical distribution of water column properties such as salinity, temperature, and maximum fluorescence.

Sampling and Measurements

Seawater samples were collected at each station at the surface, at the maximum fluorescence depth, immediately below the pycnocline, and near the bottom using a rosette system equipped with 12 Niskin bottles of 12 L each. Temperature, salinity, density, fluorescence, and depth profiles were obtained in situ using a Sea-Bird SBE-9 CTD. During the first cruise, dissolved oxygen (DO) concentrations were immediately analyzed on board using Winkler's automatic potentiometer titrations for all samples. In addition, pH was measured using a Yokogawa probe. On board the ship, 500 mL seawater samples were filtered for chlorophyll-*a* (Chl-*a*) analysis through GF/F filters and stored at −80°C. Seawater samples were stored at −20°C until analyzed. In the laboratory, Chl-*a* was extracted in 90% acetone and measured by fluorometry according to Strickland and Parsons (1972). Macronutrient concentrations such as nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and silicic acid ($Si(OH)_4$) were measured by colorimetric methods using an autoanalyzer (Skalar Analytical® V.B., 2005a,b,c). In addition, given the impossibility of using the colorimetric technique on board, and storage being problematic, we did not measure ammonium concentration. Given the low NO_2^- concentrations, $NO_2^- + NO_3^-$ will be referenced as NO_3^- in all cases here. Furthermore, the N/P ratio was estimated as $(NO_2^- + NO_3^-)/(PO_4^{3-})$. The precision and accuracy of the analytical procedures to determine nutrient concentrations were tested in the IOCC-JAMSTEC 2015 Inter-Laboratory calibration exercise for certified reference material for nutrients in seawater.

Physical Approximation

Profiles were collected at each station to quantify the stability of the water column analysis of vertical density. Stations that showed differences in water column density higher than 0.25 kg m^{-3} were identified as stratified and the number 1 was assigned. The stations where density variation was lower than 0.25 kg m^{-3} were identified as not stratified, and the number 0 was assigned. In addition, in those stations where the difference in density exceeded the threshold value and a pronounced change was not evident (the vertical profile shows that the density increases uniformly with depth), the value 0.5 was assigned. The contours of this new variable, which we used to describe the stability found in the data from the summer expedition, coincide with the quantification of the stability performed with the maximum Brunt-Väisälä frequency.

RESULTS

Nutrient Distribution

Over a broad area of the SJG, we observed a strong difference between surface and bottom nutrient concentrations (Figure 1). During both seasons, nutrient concentrations in north-central and coastal gulf surface waters ($NO_3^- \sim 0$ µM; $PO_4^{3-} \sim 0.7$ µM; $Si(OH)_4 \sim 1.4$ µM) were lower than those in bottom waters ($NO_3^- \sim 14$ µM; $PO_4^{3-} \sim 2.0$ µM; $Si(OH)_4 \sim 8.0$ µM). An increasing gradient in nutrient surface concentrations toward the southeast was observed, with the highest values recorded in the southern gulf ($NO_3^- \sim 10$ µM; $PO_4^{3-} \sim 1.2$ µM; $Si(OH)_4 \sim 1.0$ µM). In addition, we observed high nutrient concentrations but no stratification in a small coastal area situated in the southwestern gulf. This wind-driven upwelling was documented only in the spring sampling. It was not detected during summer under low-wind conditions, but fewer stations were made in the area during summer.

Dissolved Oxygen, pH, and N/P Ratio in the Water Column

DO concentration was measured only during the summer expedition. In contrast to nutrients, DO showed a pronounced decrease with depth in the water column (Figure 2). On the surface (up to 40 m) it ranged between 7.0 mg L^{-1} and 9.4 mg L^{-1}, decreasing to 4.8 mg L^{-1} at 80 m depth. No hypoxic conditions (<4.3 mg L^{-1}; Demaison and Moore, 1980) were found. In addition, DO correlated positively and significantly ($p < 0.05$) with the nutrient concentrations ($DO/NO_3^- = 0.850$; $DO/PO_4^{3-} = 0.835$; $DO/Si(OH)_4 = 0.798$; $n = 62$ in each case). The pH values presented a distribution pattern similar to DO decreasing from 8.3 in the upper layer to 7.5 in the deepest zones.

In spring and summer, the N/P ratio was less than 16 throughout the gulf (Figure 3). During both expeditions, this

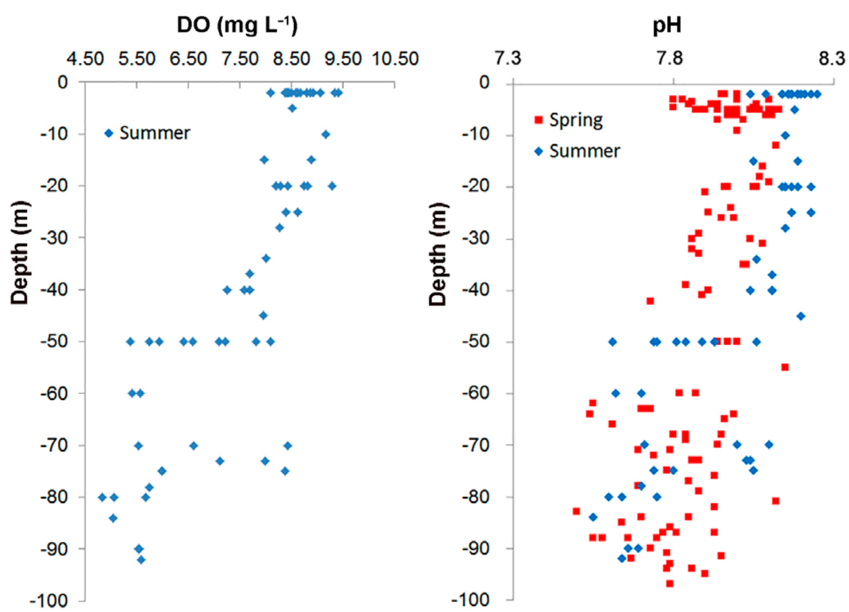

FIGURE 2. Concentrations of dissolved oxygen (DO) and pH in the water column during spring and summer in San Jorge Gulf.

relationship was greater at depth than on the surface. Low values (<1) coincident with the stratified sites and high Chl-*a* concentrations were observed (see next section). Sites with high N/P values were located near the southern and northern extremes of the mouth. Although the N/P ratio was higher in bottom water than in surface water, it overlapped in the stations where strong stratification in the water column was not observed. During both seasons, the N/P ratio exhibited latitudinal variation in deep water with a north-south gradient, and was more evident in the mouth area. Moreover, a longitudinal west-to-east gradient was observed from the coastal zone toward the mouth of the gulf (not shown).

DISCUSSION

As our data indicate, strong stratification and the absence of primary producers can result in the high nutrient concentrations observed at depth. These nutrients come from a variety of sources that favor a decrease in DO: organic matter remineralization, detritus from the surface layer, a tidal front, and organic-rich sediment that reaches deeper waters.

Influence of Stratification on Concentrations of Macronutrients

In the SJG, the superficial heat flux tends to stratify the water column from mid-September to the end of March. However, the strong and persistent westerly winds (monthly average >18 km h^{-1}) and intense tidal currents (50 cm s^{-1}; see Carbajal et al., 2018, in this issue) provide enough energy to mix the surface and bottom layers. The sudden change in topography in some surrounding areas such as the edge of the southern sector and the turbulence generated by the friction with the bottom are also sufficient to homogenize the entire water column (Rivas and Pisoni, 2010). On the southern coast, intense winds can lead to upwelling that also mixes the water column.

Based on this dynamic, a model that simulates the degree of stratification in a binary form may be appropriate for the SJG. In our spring data, the gulf exhibited a large stratified area (Figure 4) that included the center and northwest coast. In addition, three non-stratified areas were identified where the water column was well mixed from the surface to the seafloor: a tidal front close to the mouth in the southern region, an upwelling region along the southwest coast, and a possible tidal mixing area along the northern tip. In summer, the stratified area was larger than in spring but included a similar geographic region (Figure 4). Mixing of the water column in the southern region may be strongly associated with the presence of the tidal front and the entry of waters from the Argentine continental shelf, which is also affected by waters coming from the Strait of Magellan (Fernández et al., 2005). The tidal front is marked by a thermal gradient in spring and summer (Rivas and Pisoni, 2010; Glembocki et al., 2015) and occurs in the southeast sector near Cabo Blanco (Acha et al., 2004; Paparazzo et al., 2010).

In a large section of the SJG, as well as in the Southwest Atlantic Ocean, the NO_3^- concentration limits primary productivity in the euphotic layer. In this environment, phytoplankton blooms occur in spring and summer, and NO_3^- consumption exceeds production, decreasing the concentration in the upper layer (Garcia et al., 2008; Paparazzo et al., 2010, 2017). On the sea surface, primary producers consume nutrients, while regeneration and decomposition processes occur near the bottom. As a result, the availability of nutrients for the primary producers is closely related to water column stability during spring and summer. Consequently, in the stratified sector of the SJG, we found the surface and bottom waters were separated by a marked pycnocline, with greatly reduced surface nutrient concentrations and

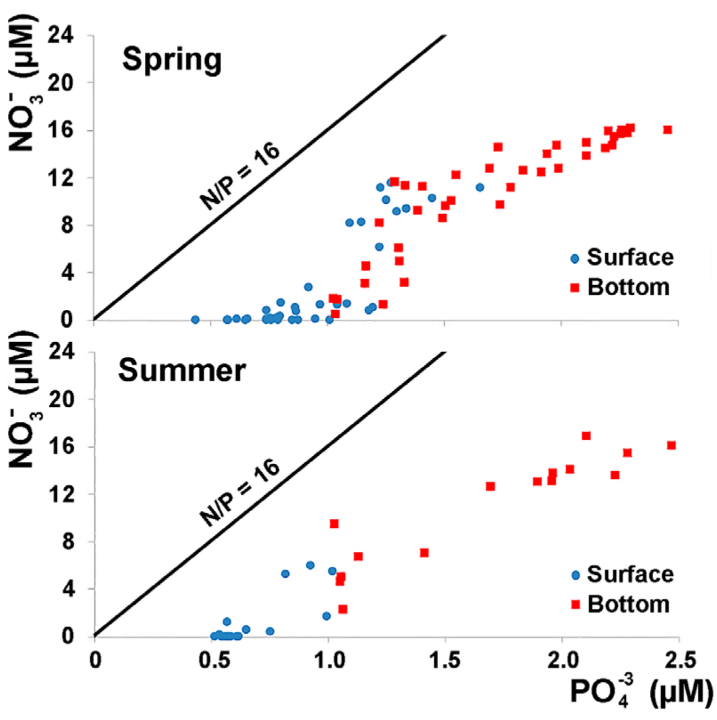

FIGURE 3. NO_3^-/PO_4^{3-} ratio from surface and bottom during spring and summer in San Jorge Gulf.

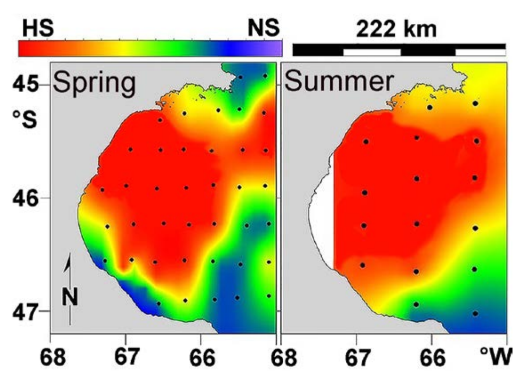

FIGURE 4. Stability of the water column during spring and summer in San Jorge Gulf. HS = highly stratified. NS = Not stratified.

higher concentrations in the deep layer (Figure 5). The NO_3^- and PO_4^{3-} concentrations were especially sensitive to stratification, showing well-defined ranges during spring and summer. Furthermore, when stratification is low or nonexistent, the surface concentration of these nutrients increases, and the bottom concentration decreases because of mixing.

The behavior of $Si(OH)_4$ was somewhat more variable. Although NO_3^- and PO_4^{3-} are necessary for all the primary producers, $Si(OH)_4$ is more important to diatoms and silico-flagellates. Because there are no rivers that discharge into the SJG, there must be other sources of $Si(OH)_4$. Desiage et al. (2018, in this issue) observed that 50% of the sediments in the SJG come from oceanic inputs. The Malvinas Current, which flows northward along the Atlantic coast of Patagonia, may bring with it $Si(OH)_4$ and inject it into the Argentine continental shelf at different latitudes through submarine canyons.

Fishing Activity as Nutrient Source in the San Jorge Gulf

The results from our DO analysis (Figure 2) partially agree with previous studies conducted by Fernández et al. (2007), who recorded high DO at the bottom but hypoxic values along the southern gulf coast. This condition would be associated with a rich organic matter layer located below 40 m depth. Our data also show that DO correlated positively with nutrient concentrations, indicating that in large part of the SJG, organic matter is decomposing at depth, consuming DO and releasing nutrients.

We suggest that another important nutrient source could be the decomposition of fish feces. There are large spawning and hatchery areas for Argentine hake and Patagonian grenadier in the SJG. Bycatch that is discarded dead from the fishing vessels may be among the major causes of increased nutrient concentrations at depth; among the most abundant species discarded are invertebrates, bony fishes, cartilaginous fishes (Bovcon et al., 2013), lobster (Varisco et al., 2015), and Argentine hake (Góngora, 2011). Between 1998 and 2004, the biomass discarded south of 41°S ranged from 6,000 tons to 22,000 tons in the hake fishery, and from 17,000 tons to 46,000 tons in the grenadier fishery; the maximum value (105,000 tons) was recorded in 1997 (Cordo, 2006; Góngora, 2011). Because bycatch in the SJG is discarded in a different area from where it is collected, we do not have enough information available to calculate the mass balance between the amount of discharged organic matter and the decrease of DO. Furthermore, as the organic matter reaches the deepest waters, it consumes DO while decomposing and supplies nutrients that remain below the pycnocline. This process occurs in a large section of the SJG that exhibits stratification in the water column during the warm seasons.

Additional Nutrient Sources for San Jorge Gulf

Other significant sources of nutrients into the gulf might be aeolian dust, submarine groundwater discharge (SGD), and benthic fluxes. Because of its large silica content (Paparazzo et al., 2018, in this issue), aeolian dust could be considered an external nutrient source for the SJG. For example, based on the high amounts of smectite (a clay mineral) found in seafloor surface sediment samples, Desiage et al. (2018, in this issue) suggest that aeolian transport contributes up to 10% of SJG sediments. Furthermore, Paparazzo et al. (2018, in this issue) propose that the aeolian material can supply nutrients, such as nitrate, to the water column and modify the stoichiometry of its upper layer. In addition, Patagonia's atmospheric dust contributes insignificant amounts of phosphorus to the seawater, though it is not a limiting

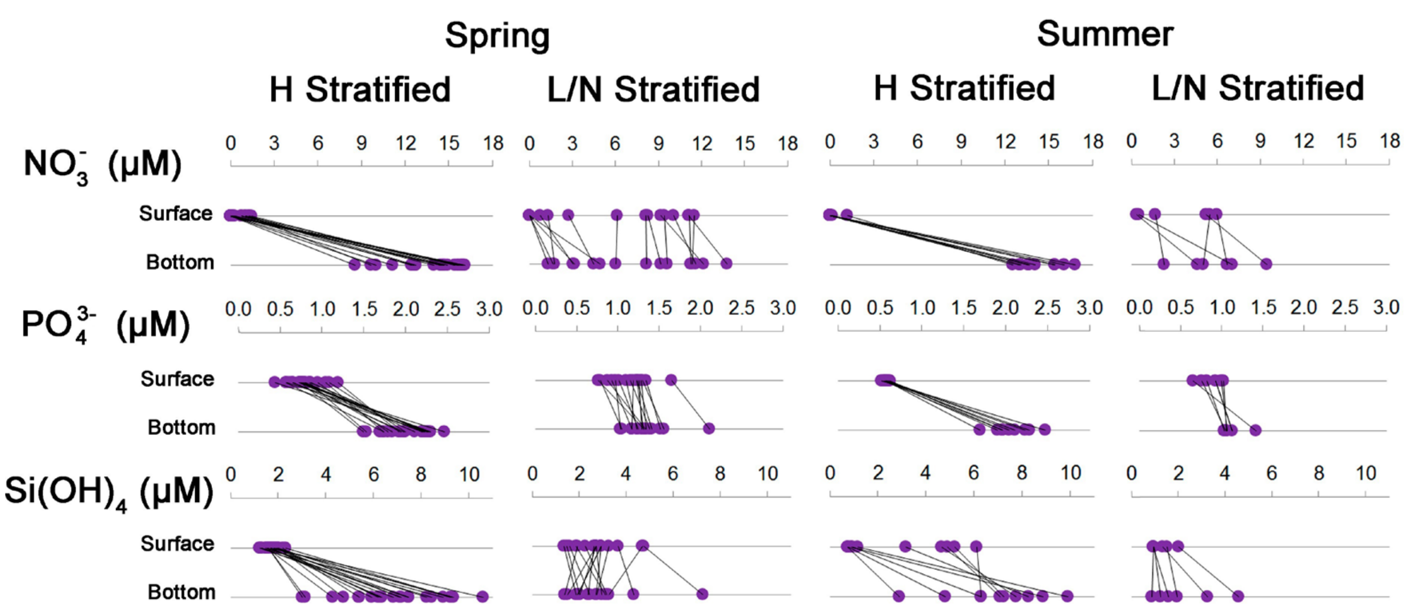

FIGURE 5. Macronutrient concentration in waters exhibiting high (H) and low or no stratification (L/N) at surface and bottom during spring and summer in San Jorge Gulf.

nutrient in the Argentine Sea. However, high-intensity windstorms, typical during spring and summer, and catastrophic events such as volcanic eruptions, may also sporadically fertilize the Argentine Sea (Simonella et al., 2015).

SGD is another source of nutrients to the SJG. Through this complex hydrological process, freshwater from the land enters both in the coastal zone and/or several tens of kilometers offshore, depending on local hydrogeological characteristics (Kroeger and Charette, 2008). From a chemical point of view, SGD is a potential transport vector for dissolved inorganic nutrients, carbon, trace elements, and gases, and their concentration appears to be three to four times greater than that found in a river's surface freshwater (Moore, 2006, 2010; Swarzenski et al., 2006). Therefore, such nutrient contributions from the continent may affect the biogeochemical cycles of coastal environments (e.g., Garcia-Solsona et al., 2010; Godoy et al., 2013). In addition, measurements of ^{222}Rn activity, an SGD tracer, were made in the SJG's coastal zone. Although the flux of SGD was not determined, its presence in the coastal marine zone from the Chubut and Santa Cruz provinces was observed by Torres et al. (2018). In addition, Desiage et al. (2018, in this issue) determined that 40% of the surface sediment in the SJG originates from the inner gulf shores and is associated with runoff and erosion.

Another pathway for nutrients into the aquatic system is through benthic fluxes at the sediment-water interface. The magnitude of these fluxes is characteristic of each environment because the fluxes are strongly influenced by physical processes such as sediment resuspension, hydrodynamic conditions, sediment granulometry, and seawater temperature (Niencheski and Janhke, 2002; Sakamaki et al., 2006; Grenz et al., 2010). In addition, bioturbation and bio-irrigation (Fanjul et al., 2007), pore water chemistry, and organic matter content contribute significantly to nutrient concentrations (Torres et al., 2009, 2016; Gil et al., 2011, 2014). Torres et al. (2016) made the only measurements of benthic fluxes in the northern zone of the SJG and found that sediment consumed DO and nitrate, and released phosphate, silicic acid, and ammonium into the water column.

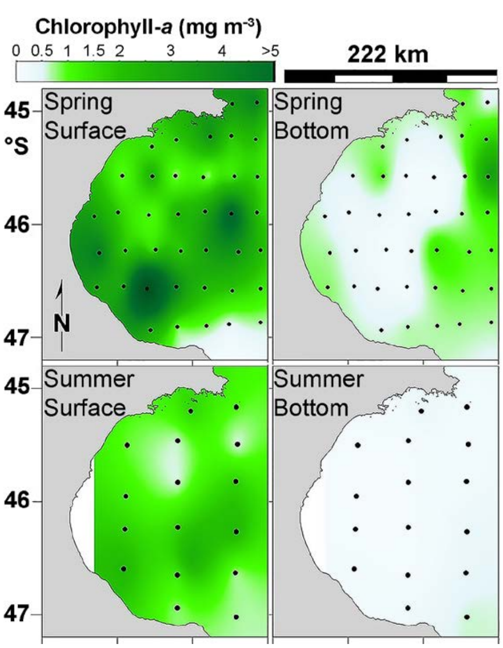

FIGURE 6. Chlorophyll-*a* concentration at surface and bottom during spring and summer in San Jorge Gulf. Black dots indicate the sampling stations conducted during two cruises in spring 2016 and summer 2014.

Organic Matter Remineralization

Currently, there are no studies on mineralization rates of organic matter in the gulf. However, Farías (1994) reported values of 110–190 g m^{-2} yr^{-1} and 14–30 g m^{-2} yr^{-1} for carbon and nitrogen, respectively, for Concepción Bay in central Chile. The trawling net mainly used in the grenadier fishery in the SJG increases resuspension of sediment and organic matter previously deposited below the pycnocline. Furthermore, trawling fosters resuspension of large amounts of aggregates—65% of which are of inorganic origin—that consume DO as they decompose, and that were observed in situ through FlowCam equipment (Gustavo Ferreyra, CADIC, *pers. comm.*, February 2, 2018). In addition, Fernández et al. (2005) measured total organic carbon (TOC) in SJG surface sediments ranging between 0.32% and 3.98%, and organic matter content ranging from 0.6% to 14.2%. These values are high compared to those measured in environments without anthropogenic impact. In addition, maximum values of TOC were found in the central SJG in summer and winter (Fernández et al., 2005). Although sedimentation rate was not measured in this austral marine environment, there is enough evidence to conclude that it is intense (Valérie Massé-Beaulne, Université du Québec à Rimouski, *pers. comm*., 2018).

Chlorophyll Spatial Distribution

In situ spatial Chl-*a* surface distribution showed high relative concentrations in spring (~4.0 mg m^{-3}) over almost the entire area of the gulf (Figure 6). In summer, higher relative concentrations were observed along the south coast and in the central zone near the mouth (~3.0–4.0 mg m^{-3}). The high photosynthesis activity found in the upper layer requires CO_2 consumption and favors high pH values. These results agree with previous work where strong spatial and temporal variability in Chl-*a* concentration was observed throughout the year (Akselman, 1996; Cucchi Colleoni and Carreto, 2001; Romero et al., 2006; Carreto et al., 2007; Glembocki et al., 2015). In this sense, the annual cycle of Chl-*a* estimated by remote sensing in the central and western region of the SJG (Glembocki et al., 2015) is typical of temperate regions whose waters are seasonally stratified and where annual maxima were observed in autumn and spring. The annual cycle in the southern and northern areas of the SJG mouth is not typical of temperate waters. It is modified by the presence of a non-stratified water column that maintains high nutrient levels. This cycle is characterized by high nutrient concentrations throughout spring and summer associated with the development of a well-defined tidal front (Rivas et al., 2006; Romero et al., 2006; Rivas and Pisoni, 2010; Glembocki et al., 2015). In addition, the tidal front allows nutrient-rich waters to be pumped into the euphotic zone, promoting high productivity during spring and summer. Carbajal et al. (2018, in this issue) specifically describe the physical mechanism that supplies nutrients in the stratified area of the SJG.

The Chl-*a* at depths greater than 60 m in spring and 45 m in summer showed concentrations of 0.2 mg m^{-3} and 0.5 mg m^{-3}, respectively (Figure 6). These concentrations are significantly lower than those observed at the surface, indirectly indicating the low biomass of phytoplankton that is typical of those depths where, although there are available nutrients (Figure 1), sunlight and grazing pressure limit the growth of these microorganisms. The depth of the euphotic zone in summer was estimated between 20 m and 40 m and coincided with the location of the pycnocline (Latorre et al., 2018, in this issue). Additionally, according to the Lee et al. (2007) algorithm, and monthly euphotic zone data from https://giovanni.gsfc.nasa.gov/giovanni/, the average euphotic zone depth (2003–2017) of the SJG area was 28 m in November and 29 m in February. Furthermore, in the Argentine Sea, Lutz et al. (2009) reported that the depth of the euphotic zone in spring was 13 m (1% Io ~13 m), so light is likely a limiting factor below that depth.

SUMMARY AND CONCLUSIONS

This study provides information about the chemical, physical, and biological factors that rule macronutrient distribution in the SJG during spring and summer. An intense increase in nutrient concentrations and a decrease in DO levels with depth were observed during these seasons. In addition, in a large section of the gulf we found a strongly stratified zone separating the nutrient-poor, high-DO upper layer from the nutrient-rich, low-DO deeper layer. On the surface, nitrate concentration limited primary production over a large area. The marked decrease in DO levels toward the bottom could be associated with the strongly stratified water column and oxygen intake by organisms for respiration, and enhanced by the mineralization of bycatch from the intense fishing activity in the region. A low N/P ratio was observed in the surface layer with a marked decrease in the sectors where nitrate was limiting. Three non-stratified areas where nutrients are injected into gulf waters were recognized in the SJG: a tidal front close to the southern limit, an upwelling region along the southwestern coast, and a possible tidal mixture in the northern end of the gulf. We did not find large differences in the distribution of nutrients between spring and summer, although a strengthening of the stratification and a lower concentration of Chl-*a* were evident. Future studies in this region should focus on sediment-water and atmosphere-sea interactions, ammonium concentration in the water column, and SGD. Finally, we believer that benthic fluxes of nutrients and DO, as well as aeolian dust and SGD, play a significant role in the biogeochemistry of the SJG water column.

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