Journal of Marine Systems 172 (2017) 43–50

Contents lists available at ScienceDirect

Journal of Marine Systems

journal homepage: www.elsevier.com/locate/jmarsys

Linking phytoplankton nitrogen uptake, macronutrients and chlorophyll-*a* in SW Atlantic waters: The case of the Gulf of San Jorge, Argentina

Flavio E. Paparazzo [a,*], Gabriela N. Williams [a], Juan P. Pisoni [a], Miriam Solís [a], José L. Esteves [a], Diana E. Varela [b]

[a] *Centro para el Estudio de los Sistemas Marinos, CONICET, 2915 Brown Boulevard, U9120ACD Puerto Madryn, Argentina*
[b] *Department of Biology and School of Earth and Ocean Sciences, University of Victoria, P.O. Box 1700, Stn CSC, Victoria, BC V8W 2Y2, Canada*

ARTICLE INFO

Article history:
Received 17 August 2016
Accepted 22 February 2017
Available online 24 February 2017

Keywords:
Uptake
Nutrients (mineral)
Chlorophylls
Biological production
Southwest Atlantic
Gulf of San Jorge

ABSTRACT

We compared biological and chemical parameters in surface waters of the Gulf of San Jorge to better understand carbon export and the factors that control phytoplankton production in an area of the Argentinian Continental Shelf, a vastly under sampled region of the SW Atlantic Ocean. In April of 2012, we estimated new and regenerated primary production in the Gulf by measuring nitrate and ammonium uptake, respectively. We also measured macronutrient, and *in situ* chlorophyll-*a* concentrations, which were compared to chlorophyll-*a* estimates from remote sensing. Although the Gulf of San Jorge presents high levels of chlorophyll-*a* and primary production, the relationship between these parameters is not straightforward. Previous studies showed that surface chlorophyll-*a* explains only part of the variance in euphotic-zone integrated primary production, and that satellite-derived chlorophyll-*a* underestimates *in situ* primary production. Our results showed large spatial variability in the Gulf, with transitional physico-chemical conditions, such as fronts, that could favor an increase in biological production. *In situ* chlorophyll-*a* concentrations were highest at the mid-shelf station (6.0 mg m^{-3}) and lowest at the northernmost location by an order of magnitude. Remote sensing measurements of chlorophyll-*a* underestimated our *in situ* chlorophyll-*a* concentrations. Total nitrogen (nitrate + ammonium) uptake showed relatively similar rates throughout the study area (≈130 nM-N d^{-1}), except in the northernmost station where it was much lower (53 nM-N d^{-1}). This north region had a distinct water mass and maximal levels of macronutrients (nitrate ≈ 6 μM, ammonium ≈ 1.2 μM, phosphate ≈ 1.2 μM and silicic acid ≈ 4 μM). For the entire sampling region, chlorophyll-*a* concentrations strongly correlated with total nitrogen uptake ($r = 0.76$, $n = 8$, $p < 0.05$) and new primary production ($r = 0.78$, $n = 8$, $p < 0.05$). Values of the f-ratio were 0.9 in mid-shelf, and ranged between 0.35 and 0.45 in inner and coastal stations. Our results indicate that highest carbon export may occur in the outer part of the Gulf, closer to the mid-shelf region. Further studies will be necessary to better understand the functioning of this ecosystem, including the impact of fisheries and horizontal transport by currents in the overall CO_2 balance.

1. Introduction

The Argentinian Continental Shelf is an area with high primary production and biodiversity (*e.g.* Moreno et al., 2012; Song et al., 2016) and with some of the highest marine chlorophyll-*a* values of the world ocean (Gregg et al. 2005, Rivas et al. 2006; Romero et al., 2006). In this region, frontal zones enhance surface chlorophyll-*a* concentrations during the summer (Rivas, 2006, Schloss et al. 2007). Although chlorophyll-*a* has traditionally been used as a proxy of phytoplankton biomass (Margalef, 1967), it may not be the proper indicator for primary production in this region. Evidence for this is that surface chlorophyll-*a* explains only part of the variance in integrated primary production (Schloss et al., 2007; Garcia et al., 2008; Segura et al., 2013), and that satellite-derived chlorophyll-*a* data underestimate measured primary production rates (Dogliotti et al., 2009; Lutz et al., 2010; Dogliotti et al., 2014).

In the Southwest Atlantic Ocean, nitrate is usually the limiting macronutrient for phytoplankton and is negatively correlated to chlorophyll-*a* concentrations (Garcia et al., 2008; Paparazzo et al. 2010). Despite the importance of understanding nitrogen-phytoplankton dynamics because of its implications on recycling *versus* export of organic matter, only Paparazzo et al. (2013) reported rates of nitrate uptake for this region. The present study extends on this previous work by measuring both new and regenerated primary production. New production is the fraction of primary production driven by

* Corresponding author.
E-mail address: paparazzo@cenpat-conicet.gob.ar (F.E. Paparazzo).

http://dx.doi.org/10.1016/j.jmarsys.2017.02.007
0924-7963/

allochthonous nutrients (mostly nitrate) introduced to the euphotic zone from outside the system, while regenerated production is fuelled by recycled nitrogen (*e.g.* ammonium) produced *in situ* by heterotrophic processes (Dugdale and Goering, 1967). Assuming an upper ocean steady-state nutrient budget and the absence of nitrate regeneration in the euphotic zone, new production can be assumed to be equivalent to export production. The f-ratio (defined as the proportion of new to total primary production based on N uptake, Eppley and Peterson, 1979) is widely used to indicate the efficiency of the biological pump for carbon export to the deep ocean (Longhurst and Harrison, 1989) and can also represents the capacity of the system to produce higher levels of biological production.

The goal of this study is to link measurements of new and regenerated primary production (as nitrate and ammonium uptake rates) with those of macronutrients, and chlorophyll-*a* obtained by *in situ* measurements and by remote sensing in the Gulf of San Jorge. This is the first time that both new and regenerated primary production were measured simultaneously in the Argentinian Sea. The study region was the San Jorge Gulf (SJG), a half-open basin located between 45°S and 47°S, which has been identified as a priority strategic area of research within the framework of the Political Science and Technology of Argentina Pampa Azul Program for marine conservation and commercial fishing.

2. Methods

The present study was conducted as part of the "Expedition Patagonia Austral 2012" (EPA-12) on board of the R/V "Puerto Deseado". Six stations were sampled in SJG (Fig. 1) from April 9th to 11th of 2012.

In situ temperature and salinity profiles were recorded by a Sea-bird 911 Plus® CTD probe. Data were calibrated with a final precision of 0.02 °C in temperature and 0.05 in salinity. To observe the vertical structure of the water column in the SJG region, sections of temperature, salinity and density were performed between stations (3-6-1, 4-5-1 and 3-5-2, dotted lines in Fig. 1). Seawater samples were collected using Niskin bottles placed on a General Oceanic® rosette system at 0 and 10 m depth (within the euphotic zone) from stations 1 to 4 (Fig. 1) for the measurement of macronutrient (nitrate, nitrite, ammonium, phosphate and silicic acid), chlorophyll-*a* concentrations and nitrogen uptake experiments. Bottles for the collection of nutrient samples were previously washed with detergent, distilled water and 5% HCl, and

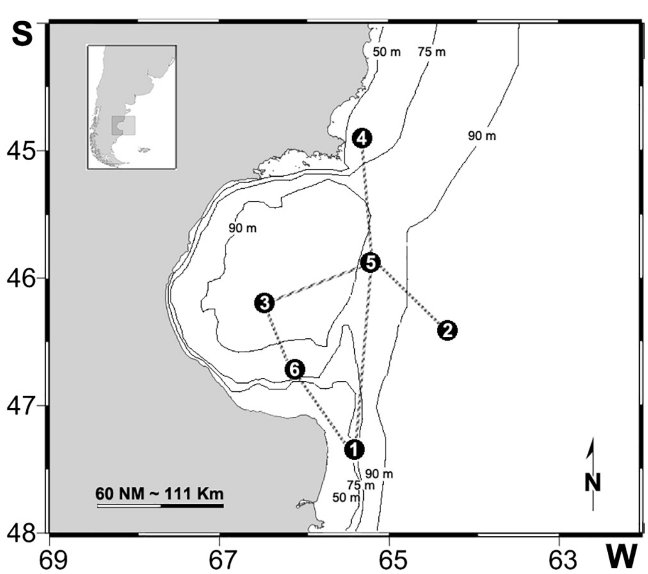

Fig. 1. Location of the stations in the San Jorge Gulf (SJG) sampled during EPA-12 from April 9–11, 2012. Physical parameters were measured along the water column at all stations. Chemical and biological parameters were measured at 0 and 10 m depth at stations 1 to 4. Dotted lines show the sections 3-6-1, 4-5-1 and 3-5-2 between stations.

rinsed with distilled water. Samples for chlorophyll-*a* determination were collected onto pre-combusted Whatman® GF/F filters (0.7 µm nominal porosity) and the resulting filtrates were used for nutrient determinations. Seawater samples and filters were preserved at −20 °C until analysis ashore.

Nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3+}), and silicic acid ($Si(OH)_4$) concentrations were determined using a Skalar San Plus autoanalyzer (Skalar Analytical® V.B. 2005a,b,c). Given the low concentrations of NO_2^-, $NO_2^- + NO_3^-$ concentrations were expressed as NO_3^-. Ammonium (NH_4^+) concentrations were measured manually following the Solórzano's phenol-hypochlorite method (Strickland & Parsons 1972).

Chlorophyll-*a* was extracted in 90% acetone and measured by fluorometry in a Turner Designs® fluorometer Model 111 (Strickland & Parsons 1972).

Rates of new (NPP) and regenerated (RPP) primary production, measured as NO_3^- and NH_4^+ uptake, respectively, were determined by means of incubations of 600 ml of seawater from the same stations (1 to 4) and depth levels (0 and 10 m) sampled for nutrients and chlorophyll-*a*. Seawater samples were spiked with 0.1 µM of $Na^{15}NO_3$ (98% ^{15}N; Sigma-Aldrich®) or $^{15}NH_4Cl$ (98% ^{15}N; Sigma-Aldrich®) immediately after water collection. The concentration of the added tracer varied from 1.6% to 10% of ambient NO_3^- and from 8.4% to 16% of ambient NH_4^+. Bottles for the 10 m samples were covered with Cole-Parmer filter bags that allow the transmittance of 50.5% of surface irradiance. All samples were incubated for 24 h using a rack system at the same temperature as surface seawater, located on the ship's upper deck. At the end of the incubation, seawater samples were filtered onto pre-combusted Whatman GF/F filters for the measurement of ^{15}N abundance and total N content in particulates, using an elemental analyzer coupled to an isotope-ratio mass spectrometer (Integra CN, Sercon®). Rates of NH_4^+ and NO_3^- uptake were calculated according to Dugdale & Goering (1967). Total nitrogen uptake rates were estimated as the sum of NO_3^- and NH_4^+ uptake, and were expressed as nM-N d^{-1}. In this paper, total nitrogen uptake rates are used as an index of total primary production (TPP) expressed in terms of N. To enable a comparison with satellite chlorophyll-*a* data, *in situ* chlorophyll-*a* measured at 0 and 10 m were averaged. The nitrogen uptake rates presented here also represent the averages for 0 and 10 m.

Uptake rates of NO_3^- and NH_4^+ were compared using two different indices. The relative uptake of NO_3^- (f-ratio = NO_3^- uptake / NO_3^- + NH_4^+ uptake) was computed according to Eppley and Peterson (1979). The Relative Preference Index (RPI) for each N source was also calculated (McCarthy et al. 1977) to assess the degree to which a particular N form is preferred over the other. For each N form, the percent uptake is divided by its percent availability (*e.g.* for NO_3^-: NO_3^- uptake / NO_3^- + NH_4^+ uptake) / (ambient NO_3^- / ambient NO_3^- + NH_4^+). Values > 1.0 reflect preference for a particular N form, values < 1.0 lack of preference for that N form, and values equal to 1.0 indicates that uptake was equitable with their availability.

The turnover rate of each N form in the surface layer (0–10 m) was calculated by dividing the ambient nutrient concentration by its removal (or uptake) rate, which indicates the time of N removal under the observed conditions.

For the dates and location of the EPA-12 cruise, MODIS-Aqua spatially extracted Level-2 files were acquired from the NASA ocean color web page (http://oceancolor.gsfc.nasa.gov) with concurrent *in situ* Sea Surface Temperature (SST) and chlorophyll-*a* data using SeaDAS v7.3 software. We obtained the standard chlorophyll-*a* product derived from the OC3 algorithm (OC3 updated version after the 2014 reprocessing) and the daytime SST 11 µM product (that uses the 11 and 12 µM bands). Temporal coincidence between satellite and *in situ* measurements was 24 h to match-up to *in situ* data. Values of satellite SST and chlorophyll-*a* used in the match-up were the averages of all unmasked pixels within a 3 × 3 pixel box centered on the *in-situ* target. Flags of SST and chlorophyll-*a* products were used for assessing the comparison of *in* *situ vs*. satellite chlorophyll-*a* data. Moreover, we acquired an 8-day composite MODIS-Aqua spatially extracted Level-3 files (4 km) coincident with the days of the EPA-12 cruise to show the general SST and chlorophyll-*a* spatial distribution for the region.

A Pearson correlation coefficient was used to assess the relationship between variables. Sample size calculation was verified to obtain a 95% significance and an 80% statistical power. Where necessary, data were log transformed.

3. Results

Vertical profiles and sections of temperature, salinity and density showed two extreme conditions (Fig. 2a and b): well-mixed waters near the south, north and center of the SJG mouth (stations 1, 4 and 5), and vertically stratified waters outside (station 2) and inside of the Gulf (stations 3 and 6). At station 5, located in the center of the mouth, a less intense pycnocline near the bottom was observed, which was the result of incoming colder bottom water.

Bottom temperature at station 3, inside of the Gulf, was near 1 °C lower than at offshore station 2, and surface temperature at station 3 was >1 °C higher than at station 2. A subsurface minimum of salinity was present at station 2 at 48 m, but it was more evident at stations 3 and 6, inside of the Gulf.

Average nitrogen concentrations for 0 and 10 m were low at stations 1 to 3, with average NO_3^- values of around 1 μM and NH_4^+ values between 0.6 and 0.9 μM (Fig. 3). Station 4 was the exception, showing concentrations higher than 6 μM NO_3^- and 1.2 μM NH_4^+. Average PO_4^{3+} and $Si(OH)_4$ showed values from 0.6 to 1.2 μM and from 1.0 to 4.0 μM respectively, with higher concentrations in northern station 4 and southern station 1.

Nutrient variability between 0 and 10 m can also be observed in Fig. 3. NO_3^- concentration was not different between 0 and 10 m, with the exception of St. 1 in which the surface concentration was twice that

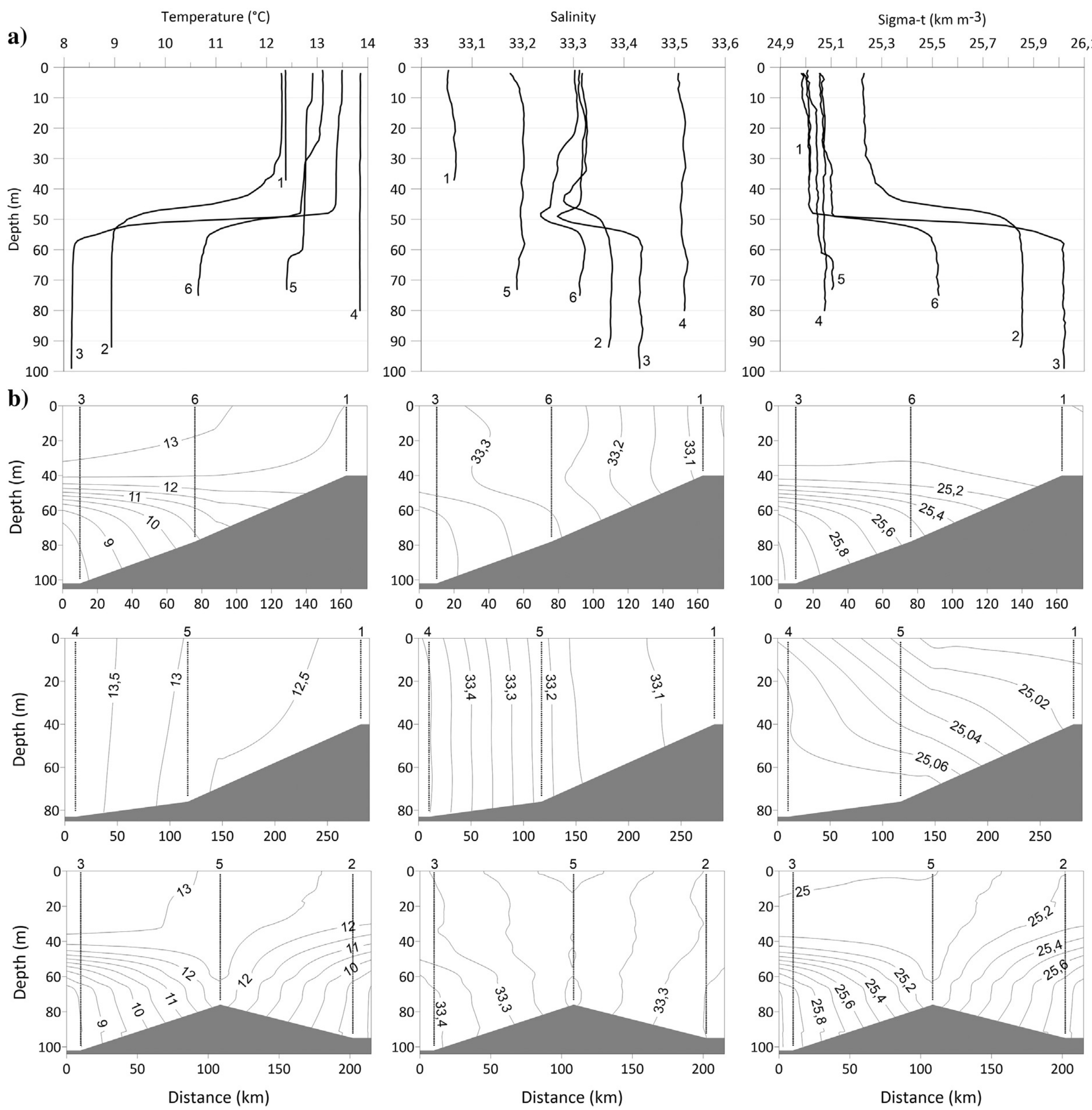

Fig. 2. Vertical profiles (a) and sections (b) of temperature, salinity and density. See Fig. 1 for the location of the sections 3-6-1, 4-5-1 and 3-5-2.

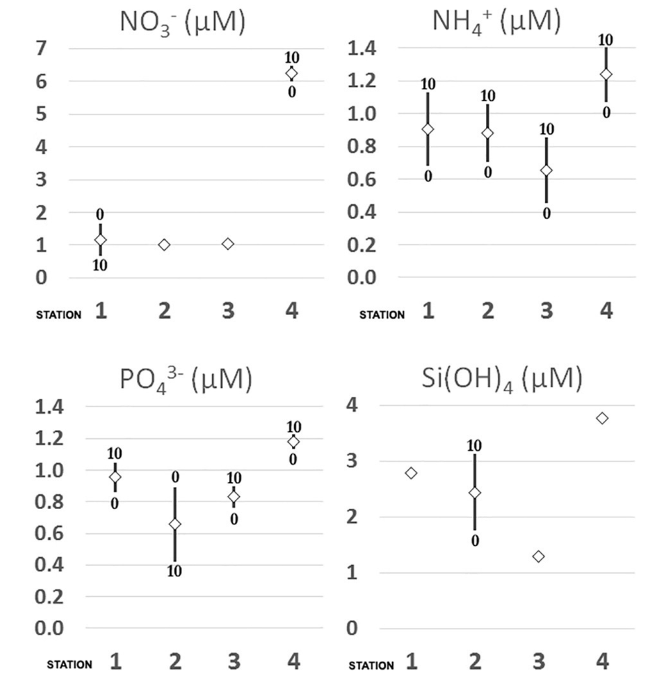

Fig. 3. Nutrient concentrations at 0–10 m depth in SJG stations 1 to 4 during EPA-12. Diamonds represent the average values for measurements taken at 0 and 10 m. The line that extends from the average concentration represent the range of values between 0 and 10 m. The line is not shown when the range is smaller than the symbol.

observed at 10 m depth. At the 4 stations, NH_4^+ was between 20% and 40% higher at 10 m than at 0 m. PO_4^{3+} was 10% higher at 10 m, with the exception of the St. 2, where the surface concentration was twice that observed at 10 m. $Si(OH)_4$ showed the same values at 0 and 10 m, except at St. 2 where the concentration at 10 m was twice that observed at 0 m.

Total primary production ($NO_3^- + NH_4^+$ uptake) was 130 nM-N d^{-1} in stations 2 and 3, slightly lower in station 1 (118 nM-N d^{-1}), and

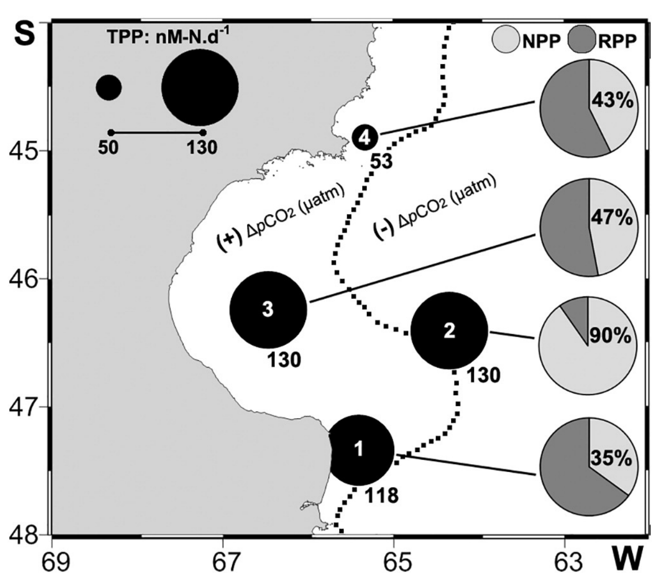

Fig. 4. Average total nitrogen uptake (black circles and values below the circles) expressed as nM-N d^{-1} and the average proportions of new and regenerated primary production (grey circles on the right hand side) for the 0–10 m depth range in SJG stations 1 to 4 during EPA-12. Percent values inside the grey circles correspond to the proportion of NPP to TPP. The dotted line represents the limit between positive and negative values of ΔpCO_2 (µatm) (taken from Bianchi et al., 2005). Numbers inside the black circles refer to station numbers.

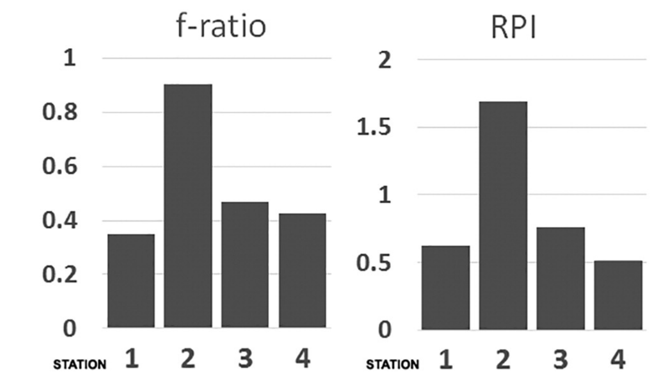

Fig. 5. Average f-ratio and Relative Preference Index (RPI) for nitrate 1 to 4 during EPA-12.

much lower in station 4 (53 nM-N d^{-1}) (Fig. 4). The proportions of NPP (NO_3^- uptake) and RPP (NH_4^+ uptake) showed clear variability between stations (Fig. 4). At stations 1 and 4, NPP was 35% and 43% of total N uptake, respectively, at station 3, RPP and NPP showed similar proportions (53 and 47% respectively), while at station 2, NPP was substantially higher than RPP, with a value of 90% of total N uptake.

The highest f-ratio was observed at the station 2 (0.9) and the lowest at station 1 (0.35) (Fig. 5). For stations 3 and 4, the f-ratio was similar ($\approx$0.45). The RPI indicates that these nitrogen forms were not used in equitable proportions with their availability. RPI on station 2 was 1.69 (Fig. 5), while the remaining stations showed RPI values between 0.51 and 0.76. This means that there was a high offshore phytoplankton preference for NO_3^- over NH_4^+, and that the preference for NH_4^+ increased near the coast. No significant correlation between the RPI values and nutrient availability was found.

Average turnover rate for the 0–10 m layer is shown in Fig. 6. Values lower than 20 days represent higher removal rate and therefore lower replenishment of the N form. Stations 1, 3 and 4 showed higher availability of NO_3^-, and the NH_4^+ availability at Station 2 was even higher. It should be noted that the NO_3^- concentration in station 4 far exceeded the rate of removal and therefore turnover rate is much higher than in the other stations.

Satellite images that match the EPA-12 timing and regions showed considerable cloud cover except for April 10, 2012 (Fig. 7a). On this day, the surface layer presented temperatures of 14 °C inside and in the north area of the Gulf, while offshore and southern temperatures within the Gulf were one degree lower, suggesting a northward flow of cold water. Chlorophyll-*a* showed concentrations of 1.0–1.5 mg m^{-3} in the center of the Gulf, while concentrations of 2.0–5.0 mg m^{-3} were detected along the coast. A patch of high chlorophyll-*a* (5.0 mg m^{-3}) was observed in the offshore area (65°W, 46°S) (Fig. 7b). To cover the entire EPA-12 period, 8-day composite images of temperature and chlorophyll-*a* (April 6–13, 2012) are presented in Fig. 7c and d.

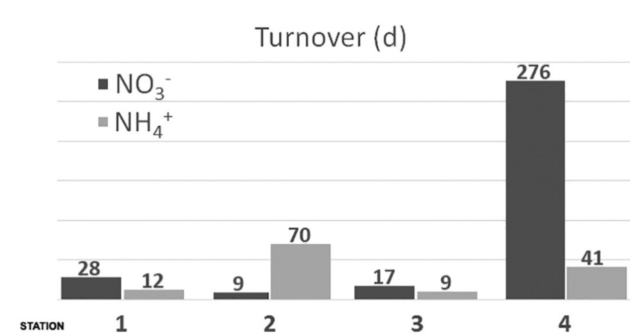

Fig. 6. Average NO_3^- and NH_4^+ turnover rate (in days) for 0–10 m for stations 1 to 4 during EPA-12.

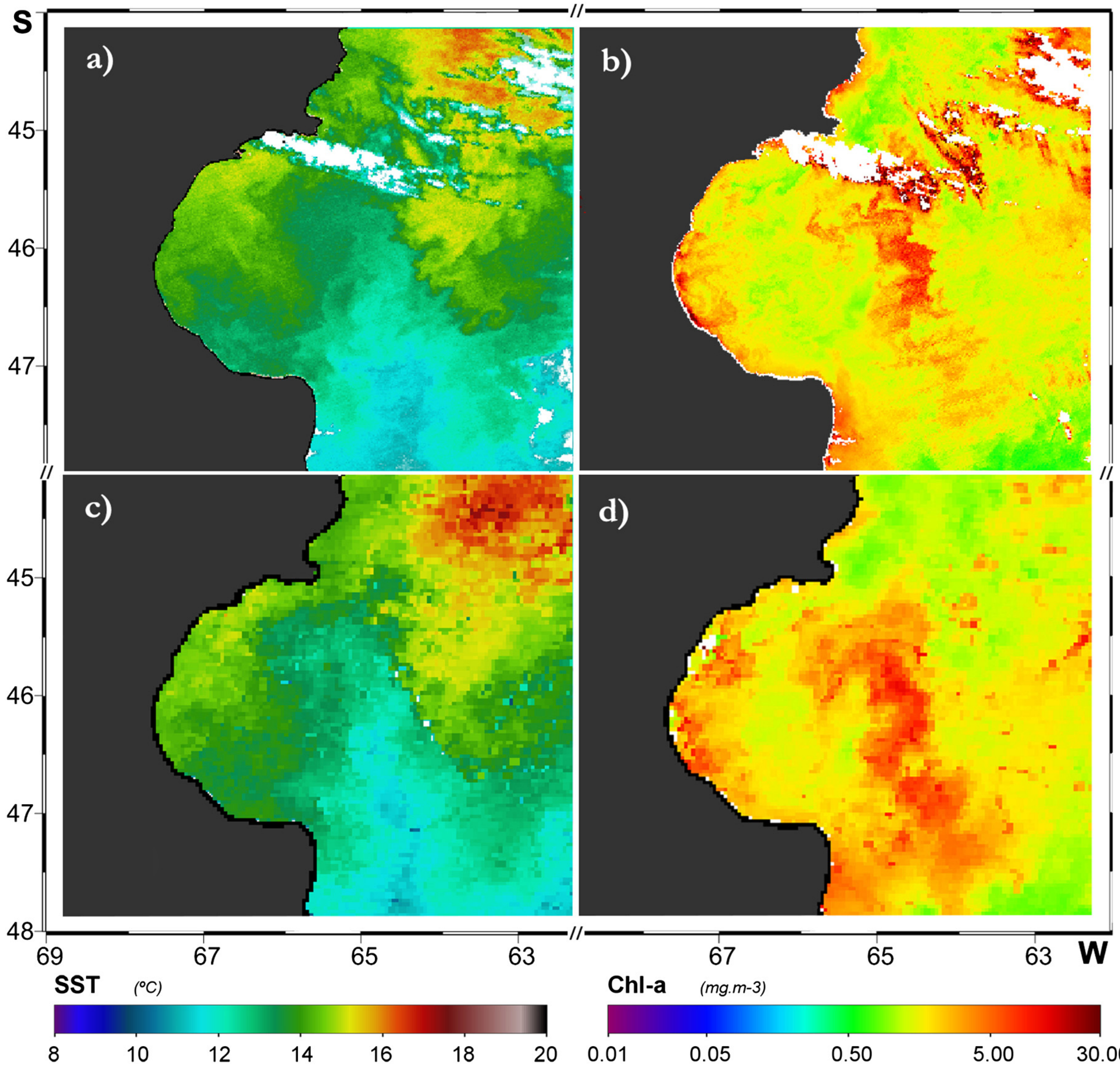

Fig. 7. MODIS surface temperature (SST) (a, c) and chlorophyll-*a* (b, d) for April 10 (a, b) and 8-day composite images for April 6-13, 2012 (c, d) as obtained from NASA Goddard Space Flight Center, Ocean Ecology Laboratory, Ocean Biology Processing Group. Moderate-resolution Imaging Spectroradiometer (MODIS) Aqua Ocean Color Data; 2014 Reprocessing. NASA OB.DAAC, Greenbelt, MD, USA.
Source: doi: 10.5067/AQUA/MODIS_OC.2014.0.doi: 10.5067/AQUA/MODIS/L3B/CHL/2014. Accessed on 05/24/2016.

Measured chlorophyll-*a* concentrations were highest in offshore station 2 (6.0 mg·m^{-3}) (Fig. 8), and lowest in northern station 4 (0.6 mg·m^{-3}). Stations 1 and 3 showed values of 3.2 and

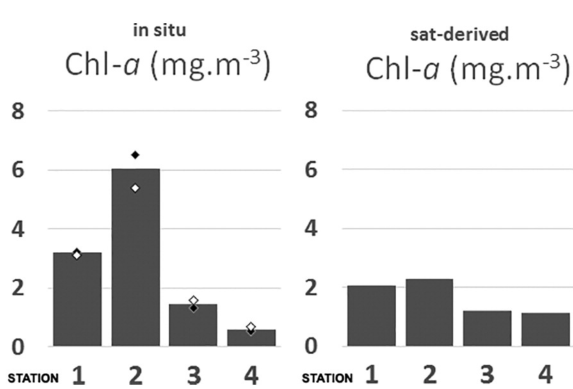

Fig. 8. Measured (*in situ*) and satellite-derived chlorophyll-*a* (Chl-*a*) concentrations for SJG stations 1 to 4 during EPA-12. Black diamonds show 10 m values and white diamonds show 0 m values.

1.5 mg·m^{-3}, respectively. Remote sensing chlorophyll-*a* showed a similar trend, but with lower values (Fig.8).

The log-transformed satellite-derived MODIS and measured chlorophyll-*a* data were tightly correlated ($n = 8$, $r = 0.93$, $p < 0.05$), as shown in Fig. 9. However, remote sensing chlorophyll-*a* underestimated high measured values, especially for Station 2 (Fig. 9, insert). A negative correlation between *in situ* SST and *in situ* chlorophyll-*a* was observed ($n = 8$, $r = -0.87$, $p < 0.05$). A similar relationship was observed between SST and chlorophyll-*a* values from remote sensing ($r = -0.74$). Measured chlorophyll-*a* was also correlated with NPP ($n = 8$, $r = 0.78$, $p < 0.05$) and TPP ($r = 0.76$, $n = 8$, $p < 0.05$), but such correlation was not observed when comparing chlorophyll-*a* data from remote sensing with NPP and TPP.

4. Discussion

4.1. Linking parameters

Our measured (*in situ*) chlorophyll-*a* concentrations were very similar at 0 and 10 m at all stations, except at station 2 where there was a small variation between surface and 10 m. Therefore, our *in situ* average

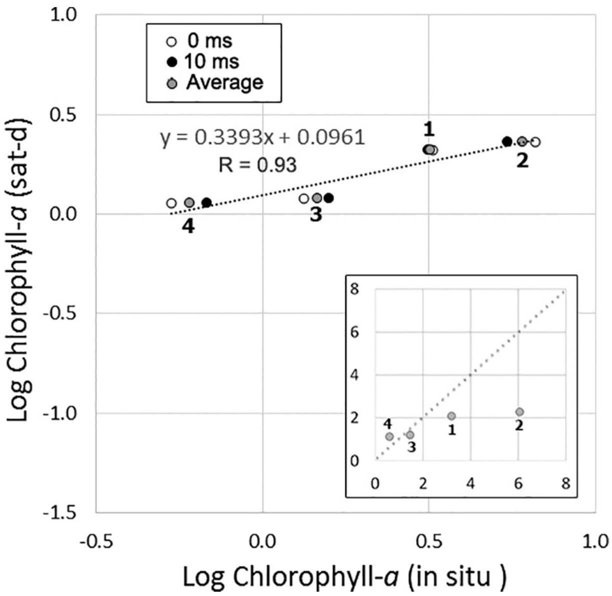

Fig. 9. Log-transformed satellite-derived *vs*. log-transformed measured (*in situ*) chlorophyll-*a* concentrations. Dotted line shows the linear correlation ($n = 8$, $r = 0.93$, $p < 0.05$). The insert shows satellite-derived *vs*. average measured chlorophyll-*a* values (not log transformed) with the dotted line representing the 1:1 relationship.

values for 0–10 m are considered to be representative of the top 10 m of the ocean in this region. Since only one-fifth of the euphotic zone can be measured by remote sensing using ocean color (upper ~10 m) (Gordon and Clark, 1980; Smith, 1981), we believe that it is fair to compare our *in situ* with the satellite-derived data of chlorophyll-*a* for this study period.

In general there was strong agreement between our *in situ* chlorophyll-*a* data and that estimated by remote sensing, but high *in situ* chlorophyll-*a* concentrations were underestimated by remote sensing, as it was also observed in previous studies in the Patagonian Continental Shelf (Dogliotti et al., 2009, 2014; Lutz et al., 2010; Segura et al., 2013). Satellite-derived chlorophyll-*a* data is useful because it provides estimates of ocean productivity in broad temporal and spatial scales (*e.g.* Marrari et al., 2016). However, the lack of agreement between *in situ* chlorophyll-*a* and remote sensing data, when *in situ* chlorophyll-*a* is high, suggests that ocean color algorithms can be improved to better match up with observations and/or that there is not a complete correspondence between the time when the image was taken and seawater sampling. In addition, due to the presence of clouds, the time window match-up (*in situ vs.* satellite data) was between a few hours and 24 h. For remote sensing data, there were higher chlorophyll-*a* values very close to the site of sampling pixels in certain locations (Fig. 7). This may suggest that between the time when the image was taken and the *in situ* sampling, there could have been a spatial shift in the area (*e.g.* a patch with high concentration of chlorophyll-*a* could have moved into the area and been sampled), resulting in the underestimation of chlorophyll-*a* values observed in the satellite image. If satellite data do not adequately represent the concentration of *in situ* chlorophyll-*a*, this error automatically translates to erroneous estimates of primary production based on that information (see Segura et al., 2013).

The comparison between NO_3^- with NH_4^+ uptake rates by phytoplankton provides insights into the potential fate of primary production and can be used to estimate the amount that is exported to deeper waters or available to higher trophic levels *versus* the amount that is remineralized within the euphotic zone. Our *in situ* chlorophyll-*a* data correlates with total nitrogen uptake (TPP) ($r = 0.76$, $n = 8$, $p < 0.05$). This result is important because it contrasts with previous studies in the region that showed differences between chlorophyll-*a* and primary production based on O_2 (Schloss et al., 2007), ^{13}C (Lutz et al., 2010; Segura et al., 2013) and remote sensing (Dogliotti et al., 2014). Variability in chlorophyll-*a* concentration can be the result of shifts in intracellular pigments in response to changing growth conditions due to light, nutrients and temperature (Behrenfeld and Boss 2006), or changes in community structure (Bricaud et al., 2004; Lutz et al., 2010; Segura et al., 2013; Dogliotti et al., 2014). It is quite possible that one or several of these variables could be interfering with the reciprocity of these parameters.

An expectable result was the positive correlation observed in this study between chlorophyll-*a* and NPP ($r = 0.78$, $n = 8$, $p < 0.05$). It has been reported that phytoplankton biomass tends to increase when new production is high and regenerated production is low (Kristiansen et al., 1994; Garneau et al., 2007). This could be associated with the fate of biological production, which is discussed in the next section.

Phytoplankton abundance and taxonomy for EPA-12 were published by Krock et al. (2015), who showed that diatoms were dominant at stations 1 and 4, where the water column was not stratified. However dinoflagellates were dominant at stations 2 and 3, with highly stratified water columns. Krock et al. (2015) also noted that the total number of phytoplankton cells was negatively correlated with *in situ* temperature ($r = -0.96$) but positively correlated with *in situ* chlorophyll-*a* ($r = 0.88$). Combining the results of Krock et al. (2015) with ours, we determined that the abundance of dinoflagellates was related to RPI ($r = 0.99$), chlorophyll-*a* ($r = 0.75$) and NPP ($r = 0.94$). This is an interesting result, since high levels of chlorophyll-*a* and NPP are normally associated with a greater presence of diatoms (*e.g.* Schloss et al., 2007; Paparazzo et al., 2010). High f-ratio values are also normally correlated with large algal (mainly diatom) blooms (Kristiansen et al., 1994; Maguer et al., 1998; Bode et al., 2002; Kudo et al., 2015), but in our study, the highest f-ratio in station 2 coincided with a dinoflagellate bloom (Krock et al. 2015).

4.2. The case of the Gulf of San Jorge

Our results show large spatial variability in the SJG, reflecting the highly dynamic nature of the physical oceanography of the region. For example, there was an increase in surface temperature in a SE-NW direction, an increase in salinity in a S-N direction, thermal stratification in the central region and well-mixed waters in the northern and southern locations. The well-mixed conditions observed at stations 1 and 4 could be due to high tidal dissipation on the southern and northern areas of the Gulf (Palma et al. 2004). In addition, the differences in surface and bottom temperatures at similar depths between stations 2 and 3 could indicate that water from the Gulf was partially isolated from shelf water. Therefore, this physical variability in the region produces transitional regions (or frontal zones) that could enhance (or decrease) biological production.

Total nitrogen uptake showed relatively similar values throughout the study area, except for the northern part of the Gulf, where it was considerably lower. Coincidentally, the macronutrients were maximal (especially NO_3^-) at that location, which resulted in a very high turnover rate. Bianchi et al. (2005) mentioned that the isohaline of 33.4 separates low salinity coastal waters from shelf waters. The station located in the north of SJG was the only location where salinities were >33.4. Therefore, since this station was situated within a different water mass, this can explain the differences in the measurements at this location in comparison to the other stations sampled during this study.

Nitrogen availability and uptake rates were not correlated during this study, which may indicate that primary productivity was not limited by the concentration of nitrogen sources. However, in coastal stations RPI were <1, which means that there was a preference for NH_4^+ over NO_3^- as a nitrogen source. This preference for NH_4^+ positively correlates with a higher concentration of NO_3^- ($n = 6$, $r = 0.8715$, $p < 0.05$). The differences between inner and offshore waters were also reflected in the homogeneity of PO_4^{3+} and $Si(OH)_4$ in the 0–10 m layer. These nutrients have a predominant coastal origin, and lower concentration would be observed offshore. With respect to NO_3^-, although the concentration was low in most stations, it never reached limiting values for primary production (Millero 2013). In addition, micronutrient (*e.g.* iron) availability may also play an important role in controlling phytoplankton growth. Although there has been evidence of enhanced supply of trace metals by atmospheric dust input along the Patagonian coast (Erickson et al., 2003; Gaiero et al., 2003; Gassó and Stein, 2007), bio-availability of iron has not yet been determined in this region.

Chlorophyll-*a* showed high concentrations in the southern region, especially in the offshore shelf. The Blanco Cape Tidal Front (Paparazzo et al., 2010) and the abrupt reduction in depth in the mouth of the Gulf could be directly associated with the observed increase in phytoplankton biomass due to enhanced upwelling of nutrients (Bianchi et al., 2005, 2009; Schloss et al., 2007; Glembocki et al., 2015).

Another important observation is that RPP was predominant throughout the inner and coastal areas, while NPP was higher in the offshore location. This has major implications from the point of view of C export. During summer and fall, east of the tidal fronts of the mid-shelf region, there is a strong CO_2 sink (Bianchi et al., 2005; Schloss et al., 2007). Under the assumption of steady state, NPP is directly related to C export and our results reflect the association between these two parameters. Fig. 4 shows the boundary between positive and negative values of ΔpCO_2 taken from Bianchi et al., 2005 and the NPP and RPP ratio to TPP from this study. Further studies should consider the fate of this new production. Offshore primary production could sink to deep waters, but also a portion of this production could be exported horizontally (as mentioned by Jacques, 1991), and/or can enter the food chain and feed higher trophic levels. Intense fishing activity in this area can then remove a portion of this production from the oceanic system. Fisheries of hake (*Merluccius hubbsi*; Marini, 1933) and shrimp (*Pleoticus muelleri*; Bate, 1888) extract large amounts of organic matter from the Gulf of San Jorge (Góngora et al., 2012). Large fishing efforts near areas of high NPP would therefore be expected.

5. Conclusions

This study presents the first simultaneous measurements of NO_3^- and NH_4^+ uptake by phytoplankton, carried out with incubations using ^{15}N, off the coast of Argentina. *In situ* chlorophyll-*a* positively correlates with total nitrogen uptake ($r = 0.76$, $n = 8$, $p < 0.05$) and new primary production ($r = 0.78$, $n = 8$, $p < 0.05$). We observed spatial difference in the preference of nitrogenous species by phytoplankton in the SJG. In the inner and coastal stations, uptake of NH_4^+ and NO_3^- were similar. While at the mid-shelf station, we calculated a strong preference for NO_3^- uptake together with differences in other parameters, such as nutrients and chlorophyll-*a* concentrations. Longer time-series are required to determine the frequency of upwelling events both offshore and inshore, and therefore the annual contribution of this new nitrogen to total primary production. In addition, the fate of primary production should be carefully considered, including the impact of fisheries and horizontal transport by currents in the overall CO_2 balance.

Chlorophyll-*a* estimated by remote sensing appears to be a weak indicator of phytoplankton biomass in this region during the sampling period. Estimates of chlorophyll-*a* made by remote sensors showed good correlation with *in situ* data, but remote sensing underestimated high *in situ* chlorophyll-*a* values. An increase in chlorophyll-*a* concentrations have been observed by remote sensing in the Patagonian shelf in greater magnitude than in other ocean regions, which has been attributed to climate change effects (Gregg and Conkright, 2002; Dandonneau et al., 2004; Gregg et al., 2005). Assuming that these changes are not associated with differences in ocean color sensors or in the calculation of algorithms, this result motivates further studies to understand the reasons behind increases in chlorophyll-*a* over time and the linkages between *in situ* and satellite-derived data. We recommend that detailed seasonal studies should be performed for each of the sectors of interest to better understand the processes that govern the biological production of this area of economic and ecological importance.

Acknowledgements

We are grateful to CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) for financial support, in the form of a postdoctoral fellowship awarded to FEP. We thank the NASA Goddard Space Flight Center, Ocean Ecology Laboratory, Ocean Biology Processing Group. NASA OB.DAAC, Greenbelt, MD, USA for the production and distribution of MODIS data, respectively and the project PICT 2013 0687 (ANPCyT, Argentina) for obtaining MODIS data. We would like to thank to Gustavo A. Lovrich (CADIC), the chief scientist of EPA-12 aboard the R/V Puerto Deseado (CONICET-MINDEF, Argentina), Ana Baldoni (INIDEP) for providing CTD data, and crew members of the R/V Puerto Deseado for their technical assistance.

References

Behrenfeld, M.J., Boss, E., 2006. Beam attenuation and chlorophyll concentration as alternative optical indices of phytoplankton biomass. J. Mar. Res. 64 (3), 431–451.
Bianchi, A.A., Bianucci, L., Piola, A.R., Pino, D.R., Schloss, I., Poisson, A., Balestrini, C.F., 2005. Vertical stratification and air-sea CO_2 fluxes in the Patagonian shelf. J. Geophys. Res. Oceans 110 (C7).
Bianchi, A.A., Pino, D.R., Perlender, H.G.I., Osiroff, A.P., Segura, V., Lutz, V., ... Piola, A.R., 2009. Annual balance and seasonal variability of sea-air CO_2 fluxes in the Patagonia Sea: their relationship with fronts and chlorophyll distribution. J. Geophys. Res. Oceans 114 (C3).
Bode, A., Castro, C.G., Doval, M.D., Varela, M., 2002. New and regenerated production and ammonium regeneration in the western Bransfield Strait region (Antarctica) during phytoplankton bloom conditions in summer. Deep-Sea Res. II Top. Stud. Oceanogr. 49 (4), 787–804.
Bricaud, A., Claustre, H., Ras, J., Oubelkheir, K., 2004. Natural variability of phytoplanktonic absorption in oceanic waters: influence of the size structure of algal populations. J. Geophys. Res. Oceans 109 (C11).
Dandonneau, Y., Deschamps, P.Y., Nicolas, J.M., Loisel, H., Blanchot, J., Montel, Y., ... Bécu, G., 2004. Seasonal and interannual variability of ocean color and composition of phytoplankton communities in the North Atlantic, equatorial Pacific and South Pacific. Deep-Sea Res. II Top. Stud. Oceanogr. 51 (1), 303–318.
Dogliotti, A.I., Schloss, I.R., Almandoz, G.O., Gagliardini, D.A., 2009. Evaluation of SeaWiFS and MODIS chlorophyll-a products in the Argentinean Patagonian continental shelf (38 S–55 S). Int. J. Remote Sens. 30 (1), 251–273.
Dogliotti, A.I., Lutz, V.A., Segura, V., 2014. Estimation of primary production in the southern Argentine continental shelf and shelf-break regions using field and remote sensing data. Remote Sens. Environ. 140, 497–508.
Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol. Oceanogr. 12 (2), 196–206.
Eppley, R.W., Peterson, B.J., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. Nature 282, 677–680.
Erickson, D.J., Hernandez, J.L., Ginoux, P., Gregg, W.W., McClain, C., Christian, J., 2003. Atmospheric iron delivery and surface ocean biological activity in the Southern Ocean and Patagonian region. Geophys. Res. Lett. 30 (12).
Gaiero, D.M., Probst, J.L., Depetris, P.J., Bidart, S.M., 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 (19), 3603–3623.
Garcia, V.M., Garcia, C.A., Mata, M.M., Pollery, R.C., Piola, A.R., Signorini, S.R., ... Iglesias-Rodriguez, M.D., 2008. Environmental factors controlling the phytoplankton blooms at the Patagonia shelf-break in spring. Deep-Sea Res. I Oceanogr. Res. Pap. 55 (9), 1150–1166.
Garneau, M.È., Gosselin, M., Klein, B., Tremblay, J.É., Fouilland, E., 2007. New and regenerated production during a late summer bloom in an Arctic polynya. Mar. Ecol. Prog. Ser. 345, 13–26.
Gassó, S., Stein, A.F., 2007. Does dust from Patagonia reach the sub-Antarctic Atlantic Ocean? Geophys. Res. Lett. 34 (1).
Glembocki, N.G., Williams, G.N., Góngora, M.E., Gagliardini, D.A., Orensanz, J.M.L., 2015. Synoptic oceanography of San Jorge Gulf (Argentina): a template for Patagonian red shrimp (*Pleoticus muelleri*) spatial dynamics. J. Sea Res. 95, 22–35.
Góngora, M.E., Gonzalez-Zevallos, D., Pettovello, A., Mendia, L., 2012. Characterization of the main fisheries in San Jorge Gulf, Patagonia, Argentina/Caracterización de las principales pesquerías del golfo San Jorge Patagonia, Argentina. American Journal of Aquatic Research]–>Lat. Am. J. Aquat. Res. 40 (1), 1–12.
Gordon, H.R., Clark, D.K., 1980. Remote sensing optical properties of a stratified ocean: an improved interpretation. Appl. Opt. 19 (20), 3428–3430.
Gregg, W.W., Conkright, M.E., 2002. Decadal changes in global ocean chlorophyll. Geophys. Res. Lett. 29 (15).
Gregg, W.W., Casey, N.W., McClain, C.R., 2005. Recent trends in global ocean chlorophyll. Geophys. Res. Lett. 32 (3).

Jacques, G., 1991. Is the concept of new production—regenerated production valid for the Southern Ocean? Mar. Chem. 35 (1–4), 273–286.
Kristiansen, S., Farbrot, T., Wheeler, P.A., 1994. Nitrogen cycling in the Barents Sea–seasonal dynamics of new and regenerated production in the marginal ice zone. Limnol. Oceanogr. 39 (7), 1630–1642.
Krock, B., Borel, C.M., Barrera, F., Tillmann, U., Fabro, E., Almandoz, G.O., ... Lara, R., 2015. Analysis of the hydrographic conditions and cyst beds in the San Jorge Gulf, Argentina, that favor dinoflagellate population development including toxigenic species and their toxins. J. Mar. Syst. 148, 86–100.
Kudo, I., Hisatoku, T., Yoshimura, T., Maita, Y., 2015. Primary productivity and nitrogen assimilation with identifying the contribution of urea in Funka Bay, Japan. Estuar. Coast. Shelf Sci. 158, 12–19.
Longhurst, A.R., Harrison, W.G., 1989. The biological pump: profiles of plankton production and consumption in the upper ocean. Prog. Oceanogr. 22 (1), 47–123.
Lutz, V.A., Segura, V., Dogliotti, A.I., Gagliardini, D.A., Bianchi, A.A., Balestrini, C.F., 2010. Primary production in the Argentine Sea during spring estimated by field and satellite models. J. Plankton Res. 117.
Maguer, J.F., L'Helguen, S., Madec, C., Le Corre, P., 1998. Uptake and regeneration of nitrogen in the well-mixed waters of the English Channel: new and regenerated productions. Oceanol. Acta 6 (21), 861–870.
Margalef, R., 1967. Some concepts relative to the organization of plankton. Oceanogr. Mar. Biol. Annu. Rev. 5, 257–289.
Marrari, M., Piola, A.R., Valla, D., Wilding, J.G., 2016. Trends and variability in extended ocean color time series in the main reproductive area of the Argentine hake, *Merluccius hubbsi* (Southwestern Atlantic Ocean). Remote Sens. Environ. 177, 1–12.
McCarthy, J.J., Taylor, W.R., Taft, J.L., 1977. Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. Limnol. Oceanogr. 22 (6), 996–1011.
Millero, F.J., 2013. Chemical Oceanography. CRC Press.
Moreno, D.V., Marrero, J.P., Morales, J., García, C.L., Úbeda, M.V., Rueda, M.J., Llinás, O., 2012. Phytoplankton functional community structure in Argentinian continental shelf determined by HPLC pigment signatures. Estuar. Coast. Shelf Sci. 100, 72–81.
Palma, E.D., Matano, R.P., Piola, A.R., 2004. A numerical study of the Southwestern Atlantic Shelf circulation: Barotropic response to tidal and wind forcing. J. Geophys. Res. Oceans 109 (C8).
Paparazzo, F.E., Bianucci, L., Schloss, I.R., Almandoz, G.O., Solís, M., Esteves, J.L., 2010. Cross-frontal distribution of inorganic nutrients and chlorophyll-a on the Patagonian Continental Shelf of Argentina during summer and fall. Rev. Biol. Mar. Oceanogr. 45 (1), 107–119.
Paparazzo, F.E., Farias, L., Santinelli, N., Alder, V.A., Esteves, J.L., 2013. Incorporación de nitrato por fitoplancton en dos ambientes marinos diferentes de la provincia de Chubut (42–46 S, Argentina). Rev. Biol. Mar. Oceanogr. 48 (3), 591–600.
Rivas, A.L., 2006. Quantitative estimation of the influence of surface thermal fronts over chlorophyll concentration at the Patagonian shelf. J. Mar. Syst. 63 (3), 183–190.
Rivas, A.L., Dogliotti, A.I., Gagliardini, D.A., 2006. Seasonal variability in satellite-measured surface chlorophyll in the Patagonian Shelf. Cont. Shelf Res. 26 (6), 703–720.
Romero, S.I., Piola, A.R., Charo, M., Garcia, C.A.E., 2006. Chlorophyll-a variability off Patagonia based on SeaWiFS data. J. Geophys. Res. Oceans 111 (C5).
Schloss, I.R., Ferreyra, G.A., Ferrario, M.E., Almandoz, G.O., Codina, R., Bianchi, A.A., Balestrini, C.F., Ochoa, H.A., Ruiz Pino, D., Poisson, A., 2007. Role of plankton communities in sea–air variations in pCO_2 in the SW Atlantic Ocean. Mar. Ecol. Prog. Ser. 332, 93–106.
Segura, V., Lutz, V.A., Dogliotti, A., Silva, R.I., Negri, R.M., Akselman, R., Benavides, H., 2013. Phytoplankton types and primary production in the Argentine Sea. Mar. Ecol. Prog. Ser. 491, 15–31.
Smith, R.C., 1981. Remote sensing and the depth distribution of ocean chlorophyll. Mar. Ecol. Prog. Ser. 5, 359–361.
Song, H., Marshall, J., Follows, M.J., Dutkiewicz, S., Forget, G., 2016. Source waters for the highly productive Patagonian shelf in the southwestern Atlantic. J. Mar. Syst. 158, 120–128.
Skalar Analytical® V.B, 2005a. Skalar Methods - Analysis: Nitrate + Nitrite - Catnr. 461-031 + DIAMOND Issue 081505/MH/99235956. Breda (The Netherlands).
Skalar Analytical® V.B, 2005b. Skalar Methods - Analysis: Phosphate - Catnr. 503-010w/r + DIAMOND Issue 081505/MH/99235956. Breda (The Netherlands).
Skalar Analytical® V.B, 2005c. Skalar Methods - Analysis: Silicate -Catnr. 563-051 + DIAMOND Issue 081505/MH/99235956. Breda (The Netherlands).
Strickland, J.D., Parsons, T.R., 1972. A practical handbook of seawater analysis. Fishery Research Board of Canada, second ed.Bulletin 167 (310 pp).