

Assessment of land influence on a high-latitude marine coastal system: Tierra del Fuego, southernmost Argentina

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Abstract The study deals with the determination of physico-chemical parameters, inorganic nutrients, particulate organic matter, and photosynthetic pigments on a monthly basis during an annual cycle from nine sampling sites of the coastal zone of a high-latitude ecosystem (Tierra del Fuego, Argentina). Nitrites and phosphates concentrations were similar to other systems of the south Atlantic coast (median, 0.30 and 1.02 μM , respectively), while nitrates were higher in all sampling periods (median, 45.37 μM), and silicates were significantly smaller (median, 7.76

μM). Chlorophyll *a* and phaeopigments have shown median values of 0.38 and 0.85 mg m^{-3} , respectively, while saturated values of dissolved oxygen were recorded throughout the study. The analysis reflected that nutrient enrichment seems to be linked to an anthropogenic source, the presence of peatlands areas, and a sink of *Nothofagus pumilio* woods. The area could be characterized in three zones related to (1) high urban influence, (2) natural inputs of freshwater, and (3) mixed inputs coming from moderate urban impacts.

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Introduction

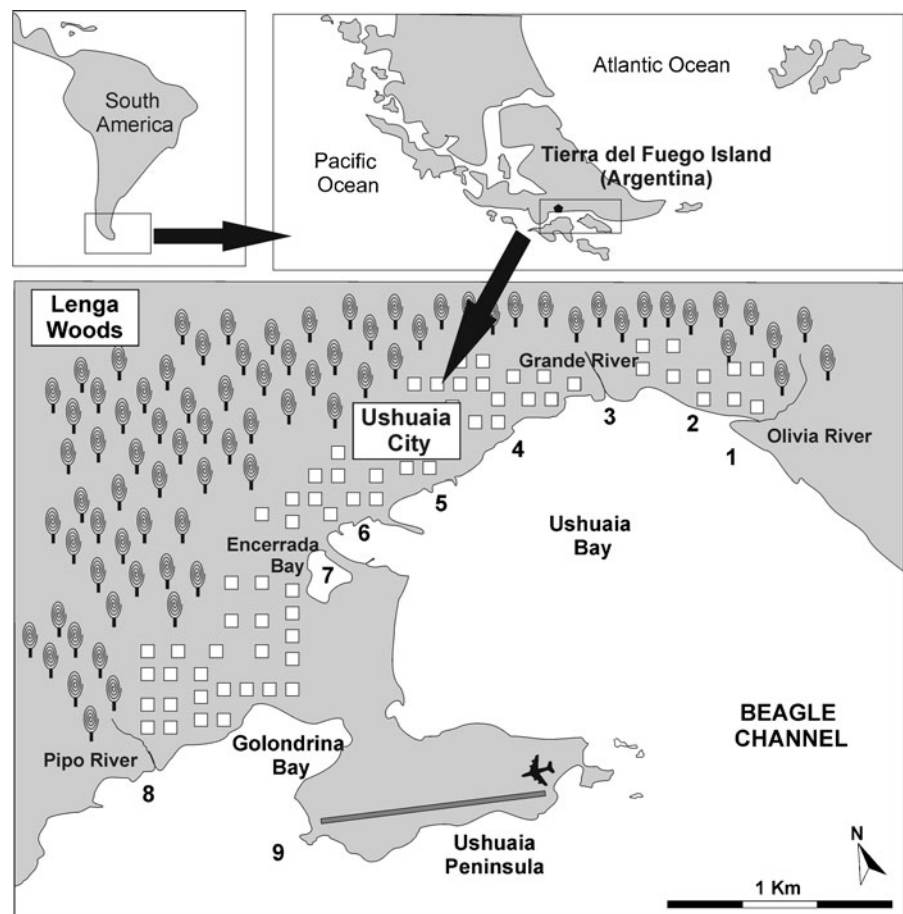
The principal problems affecting coastal waters quality are related to human activities, such as urbanization, industries, harbor location, oil and derivatives transport and storage, and solid waste and liquid effluents final disposal (Marcovecchio 2000). In addition, numerous substances from different sources flow toward the coastal zone through rivers or inland water bodies outlets (Dagg et al. 2004). The effect of these compounds in seawater can disturb the natural system or even interfere with the normal development of

the corresponding biological systems (Strain and Macdonald 2002).

In the particular case of inorganic nutrients, their concentrations regulate the corresponding effects they produce on biological systems, generating not only biological dysfunctions by defect but also deleterious processes in excess (Tett et al. 2003). Thus, the knowledge on the processes controlling the distribution and transformation of both autochthonous and allochthonous nutrients within natural systems is of outmost importance, considering that significant imbalance can modify their natural biogeochemical cycle within the involved environment (Bellotto and Carmouze 1995).

Tierra del Fuego, in the southernmost South America subcontinent, is a region with a large biodiversity and characterized by very extreme and sudden changes in its environmental conditions,

Fig. 1 Location of sampling stations at the studied area



including rigorous winters with strong snowstorms. Ushuaia city, ~60,000 inhabitants, is located on the Beagle channel that discharges its effluents (including sewage) into the Ushuaia and Golondrina bays (Fig. 1). Systematic information on inorganic nutrients distribution, temporal distribution, or associated hydrographic parameters are not available for this region, and only eventual measurements within the area have been developed so far (Amin et al. 2000).

The present study is focused on the assessment of inorganic nutrients (NO_2^- , NO_3^- , PO_4^{3-} , and SiO_3^{3-}), photosynthetic pigments (chlorophyll *a* and phaeopigments), organic matter and hydrographic parameters [temperature, salinity, pH, and dissolved oxygen (DO)], concentrations, and distributions in a very high-latitude coastal ecosystem: Ushuaia bay and Golondrina bay, both close to Ushuaia city, in Tierra del Fuego; it is also aimed at understanding their variation along an annual cycle and its relation with point sources along the coast.

Methods

Study area

Nine sampling stations were located along both the Ushuaia and Golondrina bays, at 54°47' to 54°55' S and 68°05' to 68°35' W, on the Beagle channel, Tierra del Fuego, Argentina (Fig. 1). Ushuaia bay has received the discharge of both

municipal and industrial effluents for a long time, and the fact that the population has increased three times since 1980s should be highlighted. In addition, several natural tributaries to the system (rivers and streams) have added a large amount of land uses and urbanization with its consequent anthropogenic impact. Sampling stations have been located taking into account the particularities of each one described below (Table 1).

Sampling and analytical treatment

Surface coastal seawater samples were taken monthly by hand in the intertidal zone from February to December 2000. Water samples were placed in approximately 2-l polyethylene stoppered bottles previously rinsed with hydrochloric acid (5%), stored in ice-cooled boxes, transported to the laboratory, and kept under refrigeration (4°C) until analysis within the following few hours. Seawater physical–chemical parameters (temperature, salinity, pH, and dissolved oxygen) were measured in situ using a WTW® multiline P4 multisensor probe. Seawater samples directed to determine inorganic nutrients (SiO_3^{3-} , NO_3^- , NO_2^- , and PO_4^{3-}), particulate organic matter (POM), and photosynthetic pigments (chlorophyll *a* and phaeopigments) concentrations were obtained as follows:

Water samples for the study of dissolved inorganic nutrients were filtered through Whatman GF/C filters and frozen (−20°C) in plastic bottles until analyses in the laboratory. Silicate (SiO_3^{3-}),

Table 1 Description of sampling stations at the studied area

Station	Identification name	Description
1	Olivia river east estuary	Major tributary (east): natural input. Low anthropogenic impact
2	Olivia river west estuary	Major tributary (west): natural input. Low anthropogenic impact
3	Grande river	Major tributary: Next to industrial zone and influenced by urban settlements along its course
4	Power plant	Next to electric power plant
5	Shipping area	Diffuse urban inputs (storm water runoff) near shipping area
6	Yacht club	Locate urban inputs (storm water runoff with probably domestic effluents)
7	Encerrada bay	Locate urban inputs. Connection of Encerrada bay with Ushuaia bay. The first one receives different minority tributaries with natural and untreated urban discharges. This station is close to station 6
8	Pipeline	Next to marine pipeline on Golondrina bay
9	Pipo river	Major tributary with low land-use urbanization

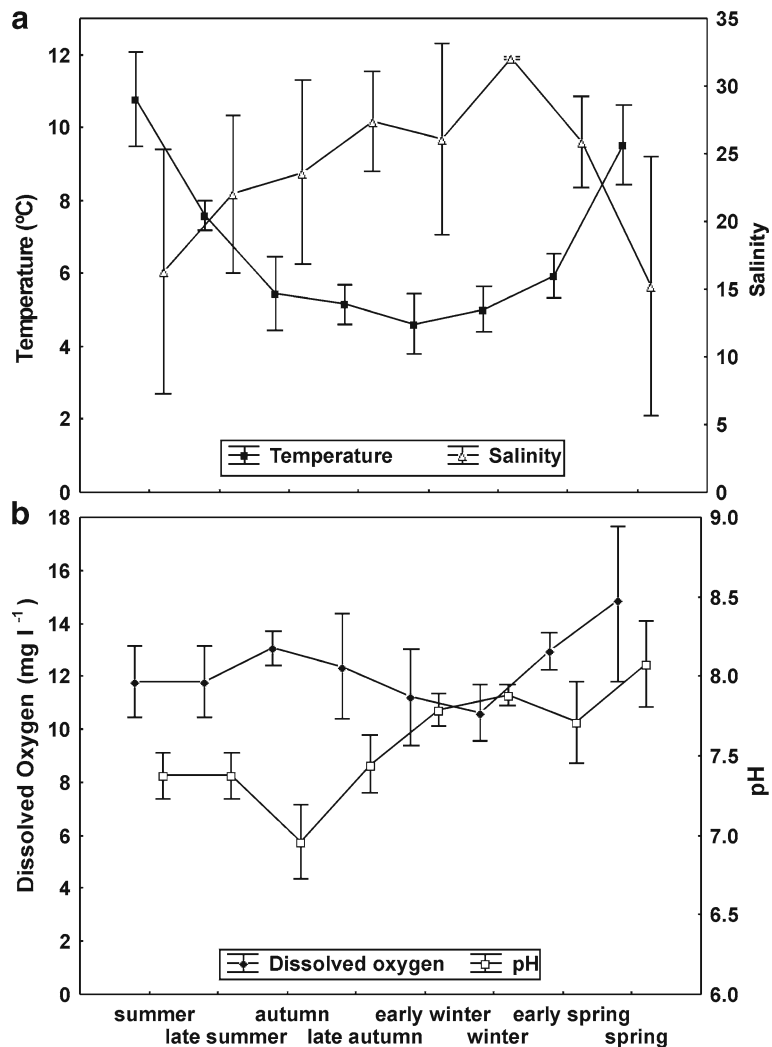
nitrate (NO_3^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) were determined following the methods previously described (Technicon® 1973; Treguer and Le Corre 1975; Grasshoff et al. 1983; Eberlein and Kattner 1987, respectively). A four-channel automatic analyzer Technicon® AA-II Autoanalyzer was used to perform the corresponding nutrient analyses.

On the other hand, seawater samples were filtered (300 ml for each parameter) through Whatman GF/C membranes, which were stored at -20°C for posterior photosynthetic pigment

and POM analysis. Chlorophyll *a* (Chl *a*) and phaeopigments concentrations were spectrophotometrically determined at 750 and 665 nm, respectively (APHA-AWWA-WEF 1998); and POM, at 440 nm (Strickland and Parsons 1968). An UV-VIS Beckman DU-2 spectrophotometer was used to carry out the corresponding measurements.

Analytical grade reagents were used for all the treatments, blanks, and standards applied to build up the corresponding calibration curves. In all the cases, triplicate analyses were performed.

Fig. 2 Temporal distribution of seawater physical–chemical mean values from the studied area. **a** Temperature ($^\circ\text{C}$) and salinity. **b** pH and dissolved oxygen (mg l^{-1})



Statistical analysis

The relationship between physico-chemical parameters and sampled sites was examined by factorial analysis using a data matrix of 11 descriptors (four physico-chemical parameters, four inorganic nutrients, particulate organic matter, and two photosynthetic pigments) and 9 sampling sites along 8 months. Due to scale differences between variables, the analysis was based on correlation matrix and treated by Varimax rotation in order to maximize the load of each variable on one factor. Factors were extracted by principal components and factor scores (mean values); the actual values of individual cases (observations) for the factors were plotted in the coordinates of factors 1 and 2 for each station. All the statistical tests were performed using the Statistica software package (version 7.1). Significance was set at $p < 0.05$.

Results

Water temperature was similar at the nine sampling stations and showed a common temporal variation throughout the year (Fig. 2a).

Only during winter, salinity of the studied area presented values characteristic of coastal marine environments (32.01), decreasing in all the other months down to levels of 15.21 in springtime (Fig. 2a).

The pH values have demonstrated to be stable and homogeneous along the study area and during the considered period, with values ranging between 6.96 and 7.88 (Fig. 2b). In addition, non-significant seasonal differences on pH values have been recorded. On the other hand, the analysis of DO values within the study area has shown that the whole system is continuously well oxygenated, and the corresponding DO values have ranged

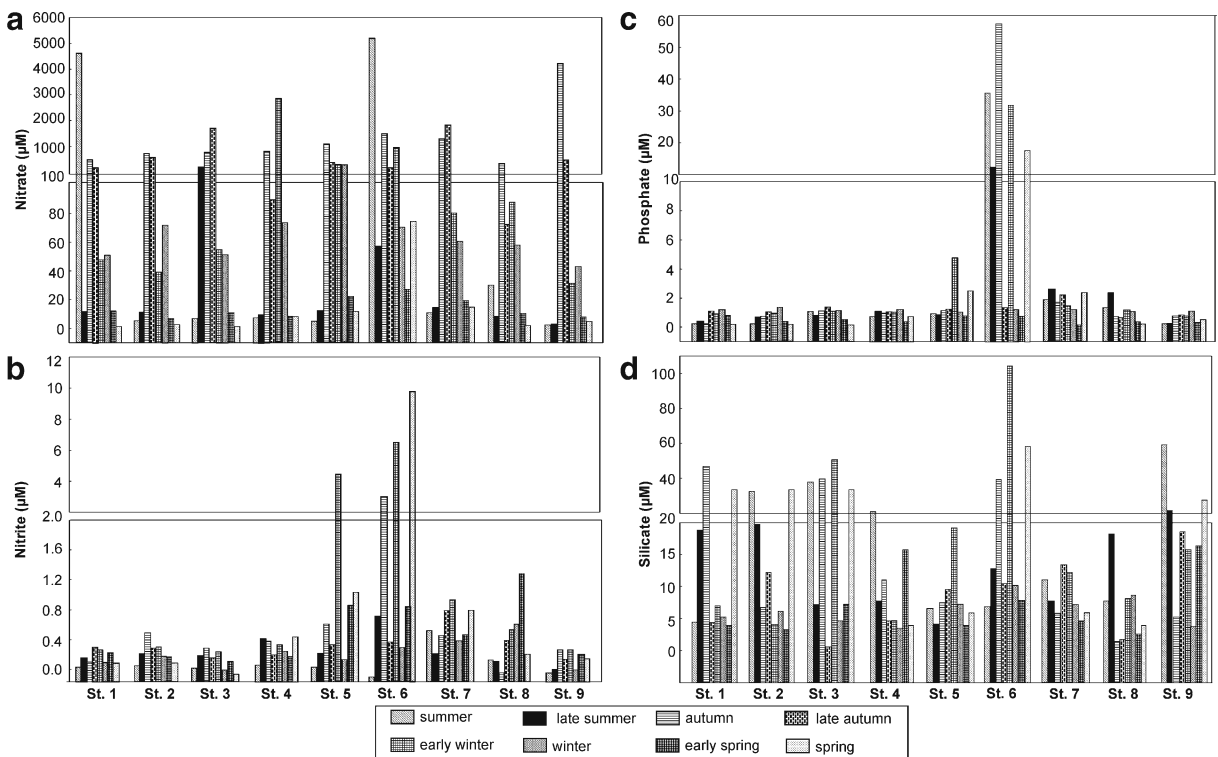


Fig. 3 Seasonal distribution of inorganic nutrient concentrations (μM) within seawater from the studied area. **a** nitrate, **b** nitrite, **c** phosphate, and **d** silicate

between 10.61 and 14.87 mg l⁻¹ (Fig. 2b). These DO values represent percentages of oxygen saturation within seawater of 102.66% and 140.01%, which clearly mean that the seawater was always overoxygenated.

The data of inorganic nutrients is shown in Fig. 3. Levels of NO₃⁻ have varied between 1.43 and 1860.29 μM (median value, 45.37 μM), presenting outlying values at stations 1, 4, 6, and 9 that reached values up to 5,179 μM (Fig. 3a). NO₃⁻ distribution was different during summer, when a significant decrease was recorded for most of the analyzed sampling stations (ranging from 2.35 to 30.05 μM), even describing two peaks of nitrate within the studied period (4,592.76 and 5,179.80 μM at stations 1 and 6, respectively).

Unlike this, the levels of nitrite recorded during the studied period were of the same magnitude for most of the coastal environments, varying between 0.04 and 6.43 μM (median, 0.30 μM) and presenting only one outlying trend within station 6 (values up to 9 μM NO₂⁻; Fig. 3b). This distribution trend was exactly the same observed for phosphate, with varying values between 0.14 and 35.71 μM PO₄³⁻ (median value, 1.02 μM), being the maximum value of 57.47 μM recorded at station 6 (Fig. 3c).

On the other hand, silicate occurrence along the studied period shows a heterogeneous distribution during the whole year, with values ranging between 0.58 and 59.4 μM (median value, 7.76 μM; Fig. 3d), corresponding the higher value to station 6 (104.27 μM).

The seasonal distribution of photosynthetic pigments has showed a trend that included a homogeneous distribution of chlorophyll *a* values within most of the studied period (with values ranging between 0.01 and 4.1 mg Chl *a* m⁻³; median value, 0.38 mg Chl *a* m⁻³), with higher values on early spring at station 4 (~7 mg Chl *a* m⁻³) and on autumn at stations 3 (6.77 mg Chl *a* m⁻³) and 6 (18.45 mg Chl *a* m⁻³; Fig. 4a). The corresponding distribution of phaeopigments along the same period has shown a similar outcome (median value, 0.85 mg m⁻³) but presented a very high level only at station 6 in autumn (~88 mg m⁻³; Fig. 4b). In addition, the distribution of POM has fully agreed with that one described for pigments, presenting values varying

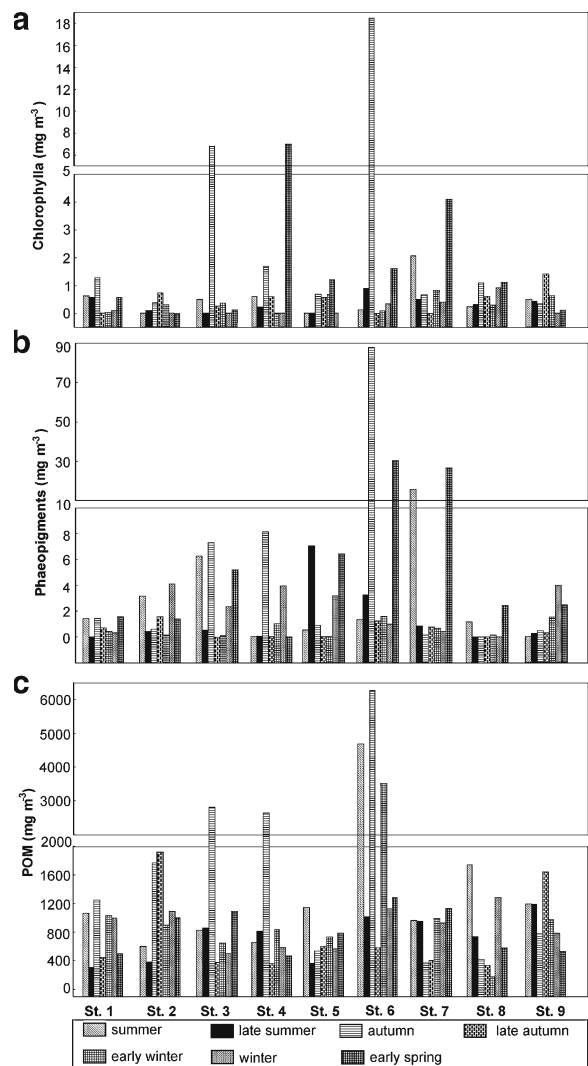


Fig. 4 Seasonal distribution of photosynthetic pigments (mg m⁻³) and organic matter (mg C m⁻³) within suspended particulate matter from the studied area. **a** Chlorophyll *a*, **b** phaeopigments, and **c** POM

from 180 to 1,829 mg C m⁻³ (median value of 802.77 mg C m⁻³). Once again, unusual high values of POM of up to 6,274 mg C m⁻³ have been recorded in autumn at station 6 (Fig. 4c).

The factorial analysis of the physico-chemical parameters recorded showed that 74.86% of the total variance could be explained by four factors (Table 2). The first factor accounts for 33.58% of the variance including PO₄³⁻, photosynthetic pigments, and POM, associated with urbanization

Table 2 Rotated varimax factor loadings for ambient variables, eigenvalues, and explained variance for each factor extracted

Variables	Factor 1	Factor 2	Factor 3	Factor 4
Temperature	0.03	0.02	0.89	0.02
Salinity	0.03	-0.53	-0.66	0.17
Dissolved oxygen	0.16	-0.45	0.49	0.38
pH	-0.21	-0.03	0.27	0.65
Chlorophyll <i>a</i>	0.90	0.05	-0.07	-0.02
Phaeopigments	0.92	0.01	-0.04	0.01
POM	0.79	0.22	0.18	-0.32
Nitrites	0.27	0.70	-0.03	0.13
Nitrates	0.11	-0.10	0.24	-0.86
Phosphates	0.77	0.37	0.10	-0.28
Silicates	0.14	0.91	0.14	-0.02
Eingenvalue	3.69	1.79	1.46	1.30
% of total variance	33.58	16.32	13.26	11.81
Cumulative variance	33.58	49.90	63.16	74.96

Extraction: principal components. Marked loadings are $p > 0.6$

inputs. This factor explains more than a quarter of the total variation, meaning that it is a dominant factor. Factor 2 is correlated with NO_2^- and SiO_3^{3-} , explaining 16.32% of the variance, representing areas with input of freshwater. The third factor (13.26% of total variance) presented positive correlation with temperature and negative correlation with salinity, related to defrost event. The fourth factor (11.80%) is represented by pH and negatively by nitrates, which could be related mainly to natural biogenic input.

Figure 5 showed the mean score for factors 1 and 2 of the nine stations. This graph presents three groups, one represented by stations 1, 2, 3, and 9; the second group including stations 4, 5,

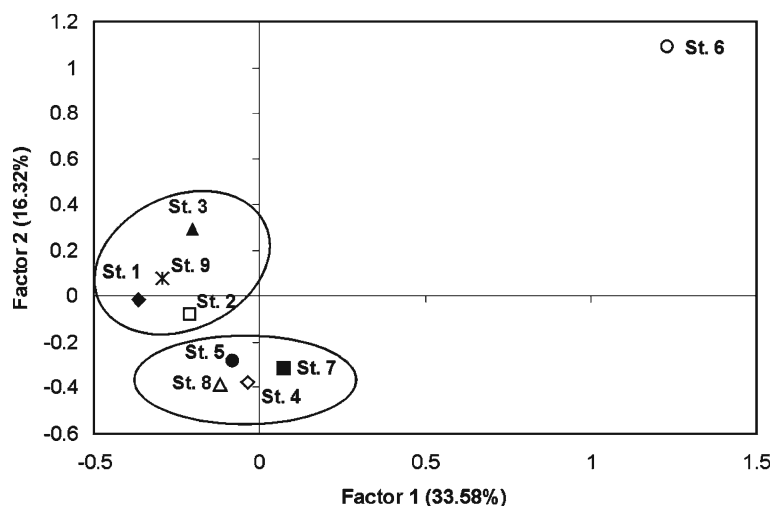
7, and 8; and station 6 standing alone in the third group with the highest average scores.

Discussion

Time trend of temperature and pH values are in agreement with previous reports by other authors (Newton and Mudge 2003) for other coastal zones where seasonal temperature changes were significant. Moreover, in the study area, temperature is higher in water than in air during winter (Iturraspe et al. 1989).

The study system is characterized by the surrounding high mountains (Olivia and Le Martial

Fig. 5 Plots of scores (mean values for each station) from factor analysis (factors 1 and 2, principal component extraction)



averaging 1,400 and 1,200 m, respectively), which are completely covered with snow and ice along the whole winter; in this sense, it is possible to assign the decreasing trend in salinity within the system to the large volume of freshwater incoming to the bays from the ice and snow melting processes along spring and summer. Comparable processes have been described for the Southwestern area of the Ross Sea in Antarctica (Arrigo and van Dijken 2004) and for the Southern Ocean surrounding Antarctica (Barnes et al. 2006).

On the other hand, nitrate concentrations were significantly higher than those recognized as typical for marine waters, even coastal ones (Aranda-Cirerol et al. 2006; Sakamaki et al. 2006). Moreover, considering high-latitude seawater as nitrate-enriched (Granskog et al. 2005; Semeneh et al. 1998; Serebrennikova and Fanning 2004), the values found here are on the top of the previously reported for similar environments. These NO_3^- levels can be extremely high due to the great amount of freshwater that is incorporated to the coastal system after running across dense woods and very large peatlands, which characterize the Archipelago of Tierra del Fuego (Roig 2004). Thus, this water leaches through top soils usually covered by tree leaves and vegetation remains, with very high humidity content that encourages organic matter degradation and, consequently, inorganic nutrients release. The peatlands originated in the last 10,000 years (Rabassa et al. 2000) from vegetation rests with a high occurrence of mosses and Cyperaceae (i.e., *Sphagnum* sp. and *Carex* sp., respectively), producing large loads of organic matter. It must be underlined that peatlands have been recognized as potential sources of N to associated aquatic environments (Kløve et al. 2010; Laiho 2006; Lepistö et al. 2006). The discharges of this freshwater into both Ushuaia and Golondrina bays bring in an unusual amount of nutrients. Presumably, this is not the exclusive source of N to the Bay, and in this sense, it must also be considered the income of waters from Circumpolar Antarctic Current (highly enriched in nutrients; Marcovecchio et al. 2010), which mix with that from the Bay, increasing the N level. Our results have showed that the environmental conditions within seawater favor the dominant occurrence of nitrate against other inorganic forms

of nitrogen. According to that, relative low values of nitrite were obtained, and they were similar to those reported by other authors for different high-latitude environments, such as in the Ross Sea in Antarctica (Sweeney et al. 2000) or in the Gulf of Finland in the Baltic Sea (Granskog et al. 2005).

The concentration of the nitrogen forms are probably a consequence of the usual oxygen supersaturation condition generating a clearly oxidizing system. This phenomenon might be directly related with the wind frequency and intensity within the studied area. Predominant wind within the area blows from SW, with average speed of 5.2 km h^{-1} and a maximum of 57 km h^{-1} (data provided by the Meteorological Station from CADIC), producing a strong mixture within seawater column and incorporating high levels of oxygen. A similar process has been previously described for the northwestern North Pacific (Honda et al. 2002) or at the Antarctic Polar Front (Dickson and Orchardo 2001).

The phosphate and silicate concentrations are in a similar order of magnitude compared to other environments. In the case of phosphate (with the exception of the detected outliers), the values obtained were similar to those reported for the Ross Sea at Antarctica (Sweeney et al. 2000) and for the Circumpolar Current at Antarctica (Morrison et al. 2001). Likewise, levels of silicate are quite usual on coastal systems (Dandonneau et al. 2006; Taguchi and Smith 1997) and similar to previous reports for high-latitude environments, like those on the GLOBEC region at the Southern Ocean (Serebrennikova and Fanning 2004).

Chlorophyll *a* values were lower than those that characterize coastal environments (Carreto et al. 1995) including those from high latitudes (Landry et al. 2002; Moore and Abbott 2002) and are in agreement with those reported for Beagle Channel (Hernando 2006). This study reported values ranging from less than 0.5 to $11.5 \text{ mg Chl } a \text{ m}^{-3}$, with peaks that always occur during springtime months (October and November).

From a global perspective, these results obtained on inorganic nutrients have allowed to support that the study area is a nutrient-enriched coastal system, with an unusual level of nitrate along the whole year and an occurrence of inorganic nutritive compounds of phosphate and

silicate in adequate levels to allow the biological development.

This combination of low photosynthetic pigments concentrations with high particulate organic matter could be indicating the occurrence of external sources of POM within the area, such as the leaching of all surrounding woods and related soils, or even anthropogenic ones such as sewage discharges, garbage, and waste disposal. In this way, it is possible to consider that this environment functions as a high-nutrient low-chlorophyll one, as it has been defined by other authors for the southwest Pacific sector of the Southern Ocean (Fennel et al. 2003). This situation can be explained in terms of other environmental parameters, which could limit the biological production. Consequently and considering the latitude of the studied system, the low light intensity that characterizes Tierra del Fuego region (Booth 1992–2003) would presumably be the main limiting factor conditioning phytoplankton production, even though all these processes occurred on a highly-enriched nutrient environment. Thus, only a small percentage of the mentioned nutrient stock would be used within the studied environment through biological consumption of the associated phytoplankton assemblage, and complementary studies will be necessary to determine if this surplus of nutrients is exported to the main channel in a first stage and to the South Atlantic Ocean in a final one.

As regards the factorial analysis, Fig. 5 shows that the stations form three groups, each in agreement with the profile described in Table 1. Station 6 showed singular data presumably related to a high urban influence of stormwater and untreated sewage in this point of the coast. Stations 1, 2, 3, and 9 represent natural inputs of freshwater from streams and rivers with low anthropogenic impact. The rest of the stations, which belong to the last group, reflect areas influenced by mixed inputs coming from moderate urban impacts.

Nothofagus pumilio (“lenga”) woods seem to be a nutrient-rich forest acting as a nutrient sink (Frangi et al. 2005). Taking this into account, we could find out an explanation that supports several data that could fall out the expected ones, especially in stations close to the main natural effluents. In this lenga forest, other authors have

reported values of total N and P up to 11 and 1 mg g⁻¹ and up to 81.5 and 32 ppm, respectively, in the corresponding soil samples (Carranza 2008; Romanyá et al. 2005).

Conclusions

The studied system receives different inputs from the surrounding area that is characterized by the presence of high mountains covered with snow, rivers, streams, dense woods, and peatlands. All of them contribute to coastal waters with significant amounts of freshwater that temporally change its physico-chemical characteristics and influence the nutrients distribution as well as on its primary production. The most important evidence is the dominant occurrence of nitrate against other inorganic forms of nitrogen. Nutrient enrichment in the coastal zone appears to be linked with anthropogenic sources (based on the organic matter value observed), presence of peatlands, and lenga woods in the area that seem to be a nutrient-rich forest acting as a nutrient sink.

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