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Winter and summer distribution of dissolved oxygen, pH and nutrients at the heads of fjords in Chilean Patagonia with possible phosphorus limitation

Distribución invernal y estival de oxígeno disuelto, pH y nutrientes en las cabeceras de fiordos de la Patagonia chilena con posible limitación por fósforo

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Resumen.- Información obtenida en agosto de 2006 y enero de 2007 en los fiordos Baker y Mitchell permite establecer que configuran un sistema permanentemente estratificado de dos capas, con más de 25% de agua dulce en la capa superior. Sus aguas presentan más oxígeno disuelto en verano, siendo la oxigenación impulsada por el flujo fluvial y la intensidad del viento. Estas primeras determinaciones de nutrientes obtenidas en verano en ambos fiordos de la Patagonia tienden a evidenciar que el suministro de nitrógeno inorgánico probablemente supera la demanda biológica y que la producción primaria puede estar allí limitada por fósforo.

Palabras clave: Estuario, phosphate, nitrate, silicate, Aysén, Patagonian Ice Field

Introduction

The Baker and Mitchell fjords, located south of the Peninsula of Taitao and north to the Magellan Strait are the far north-eastern part of an inlet region generated by the quaternary glacial erosion and tectonic sinking that took place south of Puerto Montt (Borgel 1970-1971) and whose submarine geomorphology are of dam terrace alternated with submarine moraines (Araya-Vergara 1999, 2006). This inlet system is one of the least studied marine areas of the whole Patagonia (Silva & Palma 2006). Oceanographic data focused on the fjords adjacent to the South Ice Camp are scarce and limited to physical characteristics of the water column (Chuecas & Ahumada 1980, Pinochet & Salinas 1996). Data for nutrients are almost non existent with the solely exception of an unpublished gross indication of the general profile up to 100 m of depth by the end of winter (middle August, Pizarro *et al*. 1995) and the more widespread information obtained in October 1996 (Silva & Calvete 2002). None of those studies reached the proper heads of fjords Baker and Mitchell, where they receive the large rivers Pascua and Bravo that provide a natural drain to the northern tip of the vast Southern Patagonian Ice Field.

The present study widens the scarce nutrient, pH and dissolved oxygen data gathered in this remote Chilean Patagonia inlet zone to the heads of both Baker and Mitchell fjords and also adds new information of nutrient concentration during summer, season during which the maximum freshwater discharge from the fusion of the Southern Patagonian Ice Field occurs.

Material and methods

The study zones are located southeast to the Peninsula of Taitao, at the east tip of the fjord called 'canal Baker' in the Chilean nautical cartography (47°55'S-48°S; 73°15'W-74°W) (Fig. 1). This is one of the longest Chilean fjords, with its main axis oriented northwest; having a total length of approximately 130 km measured from the river Pascua mouth to the connection with the Messier Channel. The fjord called 'estero Mitchell' in Chilean nautical maps joins a channel system connected to the Baker fjord. Its main axis is bended, oriented west in its first part and NNW in its second half, ending open to the north in its mouth. Its total length is approximately 22 km.

The sampling design of the water column was the required for the baseline study of the estuarine zone that currently receives the discharge of large rivers to be used by a hydroelectric megaproject (HydroAysen). It took into consideration the existing information about oceanographic and estuarine conditions as well as horizontal gradients in the fjord (Silva & Calvete 2002). The number of sampling stations to establish the existing gradients followed the recommendation of Grasshoff (1983), resulting in a total of five oceanographic stations at the head of the Baker fjord, located between the mouth of river Pascua, the mouth of the Steele inlet and Zoila Point, and four oceanographic stations at the head of the Mitchell fjord, located between the mouth of river Pascua and Puerto Yungay. Samplings were carried out in winter (August 2006) and summer (January 2007).

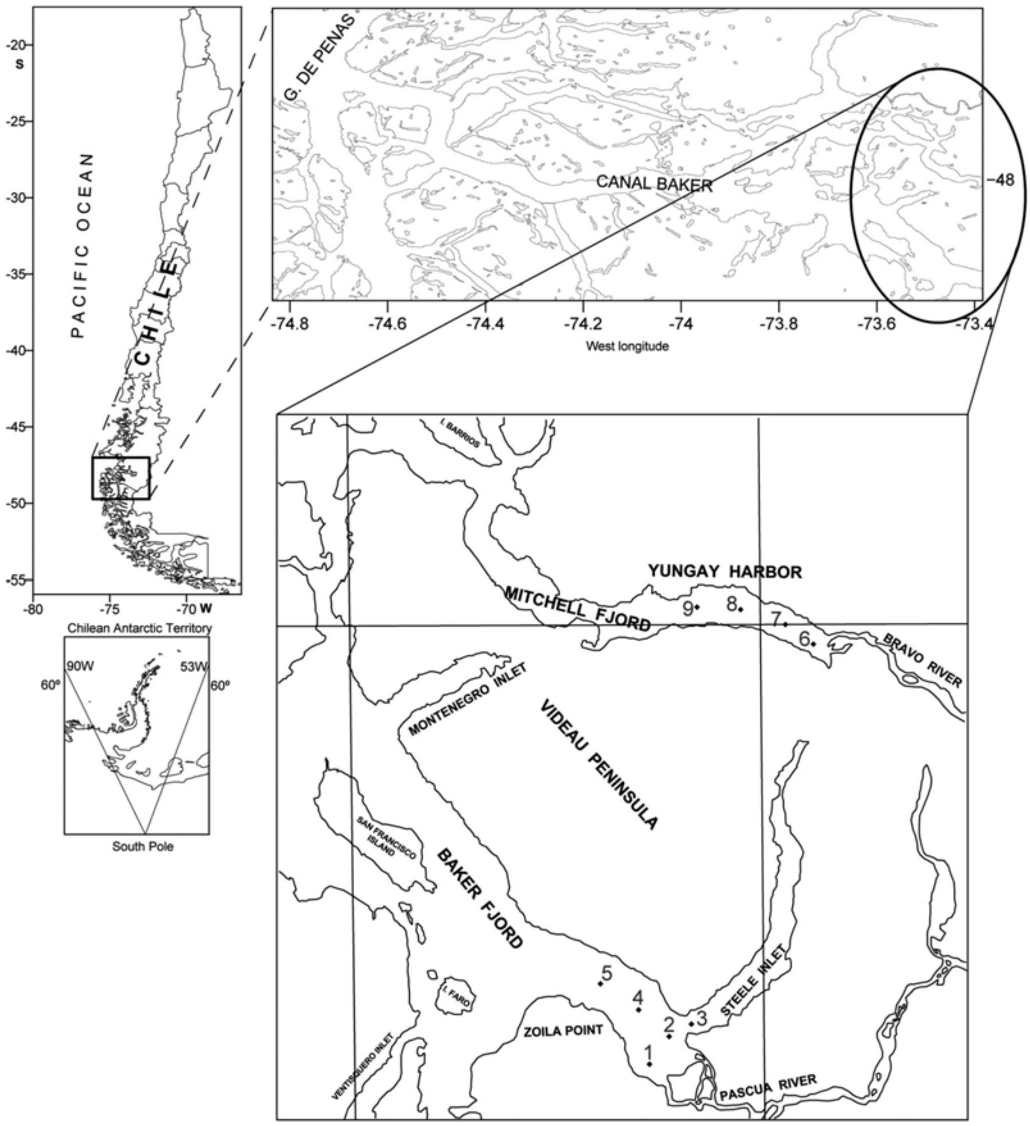

Figure 1

Study area of and location of the sampling stations at the fjords Baker (stations 1-5) and Mitchell (stations 6-9)

Área de estudio y ubicación de las estaciones de muestreo en los fiordos Baker (estaciones 1-5) y Mitchell (estaciones 6-9)

Dissolved oxygen was measured amperometrically by means of a RBR model XR-620 CTDO, automatically reading the concentration at 1 m depth intervals with a precision of ± 0.07 mL L^{-1}. Nutrients and pH were determined in samples obtained with polycarbonate TPN Hydrobios® water samplers at three depths: surface, 20 m and 200 m or a level situated between 10 and 20 m above sea floor in the case of the bottom having less than 200 m. The effective depth of this last sampling level depended on the regularity of the sea bed.

The pH was potentiometrically measured on board with a precision of ± 0.01 using NBS scale, by means of a digital pH-meter with glass electrode. NBS scale was preferred due to the extremely low salinity expected (and effectively measured) because of the intense flow of freshwater introduced by the Pascua and Bravo rivers.

Samples for nutrient determination were filtered through in line membrane filters when transferred from the sampling bottles to the preservation flasks. Those

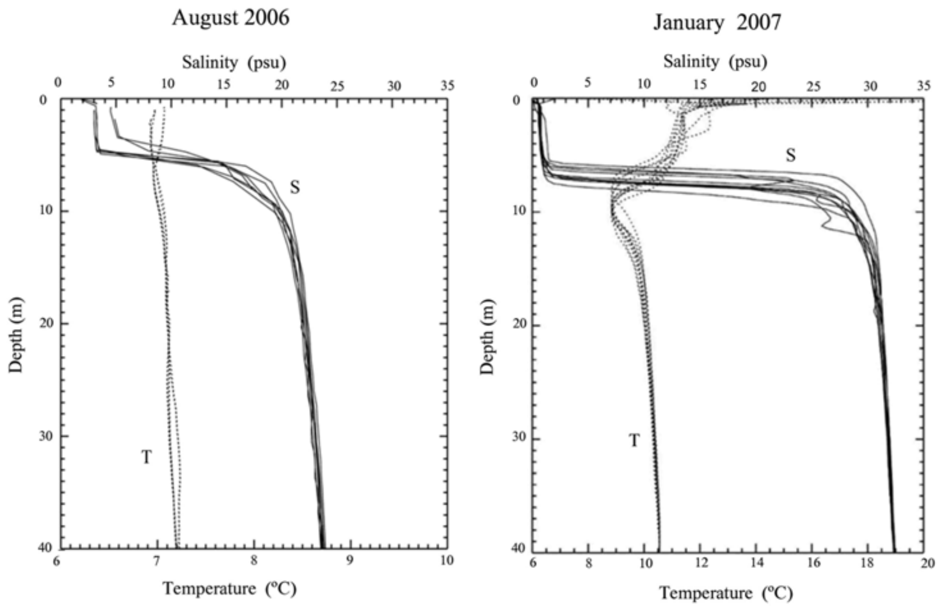

Figure 2

Vertical profiles of salinity (S) and temperature (T) during a tidal cycle at Mitchell Fjord in winter (August 2006) and summer (January 2007)

Perfiles verticales de salinidad (S) y temperatura (T) en el fiordo Mitchell durante un ciclo mareal de invierno (agosto 2006) y uno de verano (enero 2007)

samples for phosphate, nitrate and nitrite determination were first preserved refrigerated on board (2° to 4°C) during sampling and freezed to -18°C at the end of each sampling journey. Samples for silicate analysis were preserved acidified with HCl in plastic (PE) flasks without freezing and transported to Viña del Mar where they were analysed with the photometric method of Grasshoff *et al*. (1999).

Samples for phosphate, nitrate and nitrite analysis were transported frozen to the nearby city of Cochrane and determined photometrically with the methods indicated by Grasshoff *et al*. (1999) in a campaign laboratory temporarily installed there. Dissolved oxygen - pH correlations were calculated using Statistica for Windows 5.0. Vertical profiles were plotted using Grapher 2.0.

Results and discussion

Salinity, temperature and density

The salinity profiles obtained in the heads of both fjords (Baker and Mitchell) are characterised at surface by the intense effect of freshwater input coming from the great local rivers (Pascua and Bravo) that generates two layers separated by a halocline of 20 psu in 10 m depth (Fig. 2). In summer, the vertical distribution of salinity was characterised by a remarkable intensification of the halocline, having an increase of up to 1.5 psu m^{-1} in vertical gradient and an upper layer growing 3 to 5 m deeper compared with that of winter. Due to the considerable increase of river flow in summer the upper waters remained homohaline, with surface salinities close to zero in the whole studied area. In both seasons salinity increased gradually below halocline, reaching maximum values greater than 32 to 34 psu, depending on the maximum depth of the site.

Tidal salinity changes in winter as well as in summer were hardly noticeable indicating that the vertical structure of the waters in the fjords Baker and Mitchell configures a highly stable system that is permanently stratified. The resulting vertical distribution corresponds to a Pickard-Silva structure of type S1 (Pickard 1971, Silva *et al*. 1997), with a ratio greater than 25% of freshwater in the surface layer and homogeneous mixing by turbulence forced by wind, mixing that intensifies in summer.

In the case of temperature, vertical profiles were characterised in both fjords by a vertical homogeneity that remained unchanged between winter and summer in the lower layer. Differences between both seasons evidencing summer heating were observed in the thermal

Table 1

Data of pH, and nutrients (µmol L^{-1}) in waters of Baker and Mitchell fjords. Highest depth (m) (indicated as 'deep') are different for each station; they are given at the foot of each panel of the table. O_2 = dissolved oxygen; $Si(OH)_4$ = silicate; NO_3^- = nitrate; PO_4^{3-} = phosphate

Datos de pH y nutrientes (µmol L^{-1}) en aguas de los fiordos Baker y Mitchell. Las mayores profundidades (m) de cada estación (indicadas como 'deep') son diferentes y se indican al pie de cada panel de la tabla. O_{2} = oxígeno disuelto; $Si(OH)_4$ = silicato; NO_3^- = nitrato; PO_4^{3-} = fosfato

Site	Baker fjord at its head									
Season	Winter					Summer				
Station	1	2	3	4	5	1	2	3	4	5
pH										
0	8.16	8.13	8.15	8.14	8.18	7.67	7.57	7.66	7.55	7.26
20	7.87	8.07	8.06	8.04	8.07	8.17	8.17	8.18	8.05	8.17
deep	7.85	7.87	7.85	7.82	7.83	7.98	8.01	7.91	7.87	7.86
$Si(OH)_4$										
0	35.1	10.2	9.8	38.6	25.7	43.6	27.8	33.1	33.9	35.0
20	14.8	9.9	5.1	5.4	5.2	7.6	6.8	7.9	8.4	11.0
deep	13.2	12.8	11.5	-	23.1	11.0	13.0	14.7	12.2	11.7
NO_3^-										
0	6.8	6.8	8.2	2.6	5.4	6.8	3.9	3.6	6.8	2.9
20	7.1	9.5	18.8	8.8	9.6	11.5	11.0	9.4	8.5	13.4
deep	9.4	16.5	25.8	18.1	20.4	13.9	18.4	13.9	10.4	27.1
PO_4^{3-}										
0	0.48	0.90	0.83	0.61	0.47	0.14	-	0.15	0.16	0.19
20	1.01	0.98	1.09	0.82	0.91	0.71	0.99	0.80	1.02	1.17
deep	1.21	1.56	1.43	1.39	0.73	1.53	1.82	1.49	1.83	2.11
deep depths	125	123	180	179	155	130	65	198	200	200

Site	Mitchell fjord							
Season	Winter				Summer			
Station	6	7	8	9	6	7	8	9
pH								
0	-	7.46	7.57	7.61	8.06	8.05	8.06	8.10
20	8.07	8.11	8.18	8.13	8.03	8.06	8.04	8.07
deep	7.86	7.80	7.83	7.80	7.88	7.78	7.86	7.95
$Si(OH)_4$								
0	22.5	31.2	31.2	29.1	14.6	8.8	10.0	7.6
20	5.9	5.7	10.4	6.4	10.0	17.4	7.4	6.5
deep	26.5	14.6	15.7	19.0	19.5	22.5	9.3	10.9
NO_3^-								
0	5.1	1.5	3.5	2.0	11.9	8.6	-	14.5
20	12.8	6.9	6.9	10.6	10.1	12.3	11.2	14.7
deep	21.5	13.7	14.6	12.7	13.2	14.0	15.9	15.9
PO_4^{3-}								
0	0.17	0.08	0.07	0.06	0.74	0.59	0.98	0.79
20	1.08	0.76	0.79	0.83	1.15	0.99	1.09	1.31
deep	1.59	1.48	1.67	1.62	1.22	1.27	1.40	1.64
deep depths	120	159	109	150	99	200	198	199

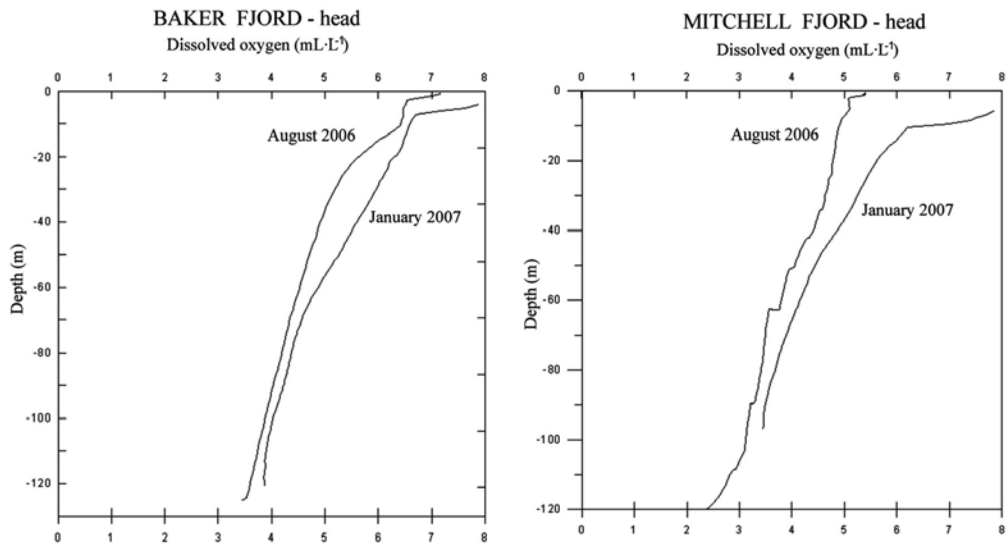

Figure 3

Vertical profiles of dissolved oxygen at the heads of Baker Fjord and Mitchell Fjord in winter (August 2006) and summer (January 2007)

Perfiles verticales de oxígeno disuelto en las cabezas de los fiordos Baker y Mitchell en invierno (agosto 2006) y verano (enero 2007)

structure of the upper layer (Fig. 2). Vertical distribution of density is mainly forced by salinity, generating a pycnocline whose vertical gradient is intensified in summer, surpassing 1 kg m^{-3} of variation per linear meter in the surface layer. The average lower limit of depth for the upper layer is 10 m, with an oscillation between a minimum of ca. 5 m in winter in the Mitchell Fjord and a maximum of ca. 12 m depth in summer in the head of Baker Fjord.

Dissolved oxygen, pH and nutrients

The results of this work are evidence for the river flow as the main determining forcing agent of the vertical structure of nutrients and dissolved oxygen content of fjords Baker and Mitchell. Both fjords have permanent high oxygen concentrations at surface, with summer values even greater than those of winter, the higher contents being found in the waters of Baker Fjord (Table 1). This unusual water oxygenation of both fjords in summer is attributed to the intensification of river flow in that season as shown by the remarkable decrease of salinity in the upper layer (Fig. 2). The increase of oxygen solubility due to salinity decrease in summer combined with a great intensity of wind in those areas during the same season (Cáceres, pers. com.)[1] counteracts the expected loss of oxygen solubility due to summer warming.

The vertical distribution of dissolved oxygen shows a two-layer structure, with a remarkable oxycline at the base of the upper layer that goes deeper and intensifies in summer (Fig. 3). This decrease of the dissolved oxygen concentration with depth is present in both fjords. It has a greater intensification of the vertical gradient at Mitchell Fjord, where an enhanced content of dissolved oxygen could be found at the same batimetric level in summer. In both fjords heads the deep dissolved oxygen in winter decreases to less than 3 mL L^{-1} (corresponding to ~40% saturations). These low oxygen contents were found at *ca*. 170 m depth in Baker Fjord and at a somewhat lower depth in Mitchell Fjord. In this last fjord, wintertime dissolved oxygen decreases with depth reaching concentrations not much greater than 2 mL L^{-1} at depths of more than 140 m, that corresponds to saturations between 30% to 40%.

The pH register obtained in January (Table 1) generates a distribution coincident with a structure of type pH6 of the classification proposed by Silva & Calvete (2002), that is characterised by a surface minimum followed by an increase of pH in the upper layer (first 10

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to 15 m) and a decrease in the deep layer. Those authors ascribe this pH structure to the presence of freshwater from the nearby rivers, characterised by its lower pH. In the dataset reported here surface pH reached values around the lower limit for seawater, with a maximum of 7.61 and a minimum slightly lower than 7.5 in the east end of the Mitchell Fjord that receives the discharge of Bravo River. At the same time, surface pH in the Baker Fjord ranged between 7.26 and 7.67. On the other hand the pH values obtained in winter in the heads of both fjords by the present work do not show a surface minimum but a maximum from where the pH decreases to the seabed. The number of data points gathered in this work were insufficient to enable the outline of a pH profile with the necessary detail to ascertain if it is one of type 1, 2 or 3 of the oxygen-pH classification proposed by Silva *et al*. (1997). Nevertheless, the data set does allow to establish the absence of the pH6 structure in the fjords Baker and Mitchell in winter. This absence coincides with lower freshwater input to these fjords in winter, since flow of the glacial rivers in the zone (like Pascua and Bravo) reach their minimum in August-September (Salas 2004). Since there is a highly significant direct correlation between pH and dissolved oxygen ($r = 0.866$, $P < 0.001$, $N = 45$) when the summer surface data altered by river discharge are excluded, the decrease of pH as the measurements go closer to the bottom can be interpreted as a consequence of CO_2 generation by the oxidation of sinking particulate organic matter.

Riverine influence in the heads of both fjords also determines the vertical structure and surface concentrations of nutrient compounds. This is the case for the permanent structure of two layers that exists for silicate as well as for phosphate and nitrate. The shape and extent of the silicate distribution shows the intensity of the discharge stemming from Pascua River and its substantial influence on the upper layer of Baker Fjord. This influence becomes evident in the presence of surface maximums in front of the river mouth. A similar condition, but with less intense gradients is found in the Mitchell Fjord. In both cases silicate concentrations in the upper layer are larger in summer (Table 1), season that coincides with the maximum fluvial flow. In summer (January) surface silicate concentrations of the latter fjord were 25% to 50% higher than in winter. These concentrations were larger than 15 µmol L^{-1} either in August or in January. This layer was separated from the lower one by a steep gradient of decrease that reached almost 20 m depth. At higher depths the direction of the gradient changed in both fjords to a gradual increase in silicate concentration up to the seabed.

The consequences of greater river flow derived from ice fusion in summer can also be distinguished in the surface concentrations of nitrate observed at Baker Fjord, determining a relatively small variation between winter and summer (Table 1). This riverine influence determines greater availability of nitrate near surface, so it is not used up after the usual spring bloom of phytoplankton and summer nitrate depletion is not noticed in the southeast part of the fjord head. The decrease of nitrate in summer compared to winter concentrations is not more than 50% in the rest of the studied area. This situation of the Baker Fjord contrasts with the more considerable decrease of nitrate during summer in the Mitchell Fjord (Table 1). That discrepancy should be related with differences in the sources of dissolved material and/or in flow between Pascua and Bravo rivers. Vertical distribution of nitrate in both fjords, either in August or in January was characterised by a steady increase of concentration with depth reaching more than 20 µmol L^{-1} at 160 m.

Except for a pair of values close to the limit of detection in the upper layer, in August nitrite was absent in the major part of the waters in both fjords. In summer no nitrite was found in the whole water column.

Phosphate concentrations at surface of both fjord heads were relatively high in August, ranging from less than 0.5 µmol L^{-1} to more than 0.9 µmol L^{-1} (Table 1). During summer, decrease of phosphate concentration in the upper layer is considerably higher than decrease of nitrate, dropping to almost a fifth of winter values in the head of Baker Fjord. This decline is even higher in Mitchell Fjord, where phosphate concentrations in January were an order of magnitude lower than those of August. The vertical distribution of phosphate in both fjords was characterised in August and January by an increase with depth in the whole extension of the studied area, having a steeper gradient in the upper layer. Maximum phosphate concentrations found near sea bottom fluctuated between practically 1.2 to 1.6 µmol L^{-1} according to the location’s depth. Summer concentrations were a slightly larger than those of winter at the same depth.

The existence of sufficient nitrate and high concentrations of silicate during summer make it possible that in these fjord systems, or at least in the first half of Baker Fjord planktonic primary production can be limited by phosphorus. The effectiveness of this hypothesis should be tested by means of productivity bioassays in that area. At least the possibility of primary production limitation by phosphorus in marine environments has been observed in the case of some temperate estuaries like Apalachicola in Florida and estuaries in the Dutch coast (Myers & Iverson 1981, Postma 1985, Brockmann *et al*. 1990). There are also records of major estuaries, as is the case of Chesapeake Bay, in which the limitation of primary productivity changes seasonally between nitrogen and phosphorus (Malone *et al.* 1996).

Finally, due to the considerable low transparency in the heads of both fjords, where Secchi disc transparencies measured in January were only 0.4 m at Baker Fjord and 0.9 m at Mitchell Fjord, light availability is another important factor besides phosphorus to be taken into account as potential control of the phytoplankton bloom size in the area of the present study. This lack of transparency is a condition derived of the presence of glacier flour carried by freshwater. The combination of moderate surface concentrations of nitrate (3 µmol L^{-1}) and low phosphate (< 0.5 µmol L^{-1}) with a permanent stratification and low transparency makes it feasible to expect a low potential for primary productivity, thus limiting the growth and abundance of phytoplankton at the head of both fjords.

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