PRESS

PERSPECTIVES ON INTEGRATED COASTAL ZONE MANAGEMENT IN SOUTH AMERICA

Eds.
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TITLE
Perspectives
on Integrated Coastal Zone Management
in South America

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ISBN
978-972-8469-74-0

LEGAL REGISTRATION
286710/08

DESIGN
Golpe de Estado – Produções Criativas, Lda.

PAGINATION
Paulo Tribolet Abreu

GRAPHIC ART PRODUCTION
Manuela Morais

PRINTED AND BOUND BY
Guide – Artes Gráficas

PUBLISHED AND DISTRIBUTED BY
IST Press

IST PRESS

DIRECTOR
Joaquim J. Moura Ramos

EDITORIAL COORDINATION
Eduardo Borges Pires

Instituto Superior Técnico
Av. Rovisco Pais
1049-001 Lisboa
Portugal
www.istpress.ist.utl.pt

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WATER CHEMISTRY AND NUTRIENTS OF THE BAHÍA BLANCA ESTUARY

R.H. FREIJE, C.V. SPETTER, J.E. MARCOVECCHIO, C.A. POPOVICH,
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1 INTRODUCTION

Different characteristics of the estuarine environments (i.e. geo-morphological, hydrographical, climatic or chemical ones) strongly condition the biodiversity within those systems (Harrison 2004). So, the range of values of the different parameters involved (temperature, salinity, pH, dissolved oxygen, inorganic nutrients, organic matter, etc) as well as their corresponding seasonality or anomalies would directly determine the scenario where the whole biological processes will occur also including populations movement along different spatial gradients due to physiological problems (Laprise and Dodson 1994). In addition, the distribution and availability of non-conservative constituents such as oxygen, nutrients or organic carbon determine the potential primary production of the system, and consequently the potential transfer of energy to higher trophic levels (Cantoni et al. 2003, Rydberg et al. 2006).

Bahía Blanca estuary has been the object of a large number of environmental studies over the last 30 years. From these studies, a large time-series database on physicochemical parameters has been assembled for the inner part of the estuary (Pto.Cuatreros and Pto.Ing.White; Figure 1). This database is a very useful tool to diagnose the environmental condition of the system considering that the inner part of the estuary includes not only the entry points of the main rivers from the region but also the largest human activities such as cities, industries and harbours, with their consequent impacts on the estuary. In addition, information has also been recorded through cruises along the Main Navigation Channel, as well as from many coastal studies on the tidal flats at Villa del Mar, Puerto Galván and Puerto Cuatreros (Fig. 1).

The main goal of the present chapter is to summarize the available information on the physicochemical condition of Bahía Blanca estuary, including the corresponding range of values of the considered parameters (temperature, salinity, turbidity, dissolved oxygen, inorganic nutrients (DIN, Dissolved Inorganic Nitrogen; DIP, Dissolved Inorganic Phosphorous and DSi, Dissolved Silicates), particulate organic matter and photosynthetic pigments (Chl-a and phaeopigments), and to identify seasonal variations, as well as the influence of external sources.

2 MAIN PHYSICAL-CHEMICAL CHARACTERISTICS WITHIN THE ESTUARY

2.1 Temperature

The analysis of the obtained data has shown a very stable behavior of this parameter along the Main Navigation Channel, from the head of the estuary and up to its mouth. In fact, non significant differences have been observed between the considered areas of the estuary (inner, middle and outer), which allows to sustain that both the ocean water temperature as

well as the air one are the main responsible for the variations of this parameter within the estuary. Water temperature measured in the inner zone has demonstrated to be strongly regulated by the air temperature of the region, and their corresponding curves of measured values have shown quite similar trend in their distribution of values (Figure 2).

Extreme values recorded for temperature along the 1996-2006 period within the estuary varied between 5.1 °C and 26.4 °C, which have been measured on July'02 (winter) and January'04 (summer) respectively. The distribution of temperature values has followed a sinusoidal curve, which indicates the occurrence of a thermic cycle characteristic of the estuarine conditions (Newton and Mudge 2003, Harrison and Whitfield 2006).

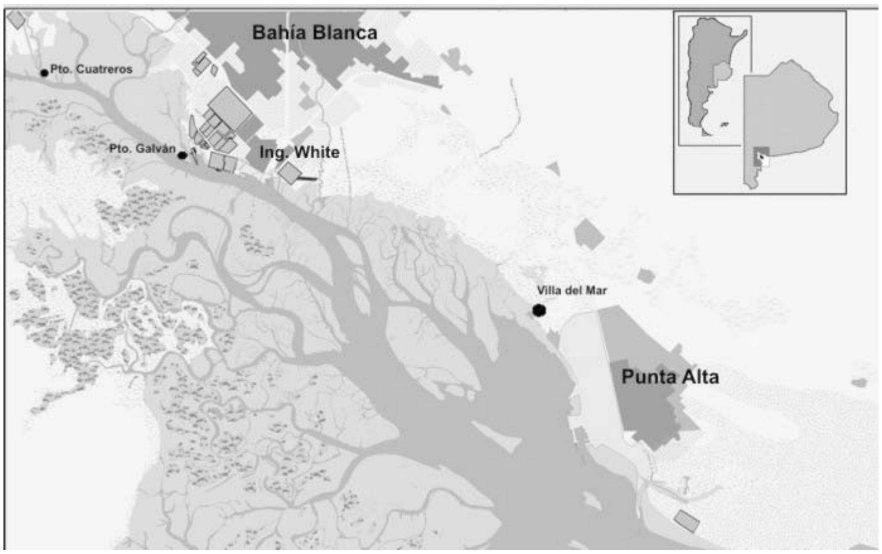

FIGURE 1: *Location of Bahía Blanca estuary and Villa del Mar, Puerto Galván and Puerto Cuatreros.*

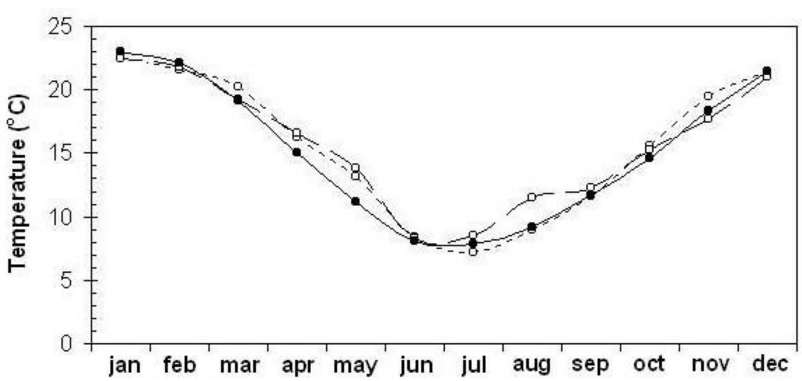

FIGURE 2: *Mean water temperature at Pto.Cuatreros (-○-) and Pto.Ing.White (- -○- -) (in 1974 - 2003) related to mean air temperature at Bahía Blanca (-●-) for the 1860-1990 period.*

2.2 Salinity

The distribution of salinity does not present a sharp gradient along the main channel of the estuary, as can be observed in many of these systems (Brockway et al. 2006, O'Callaghan et al. 2007). Even though a clear variation in salinity could be observed in the inner estuary, where a range from 17.9 psu to 41.3 psu has been recorded (Freije and Marcovecchio 2004). The very important fact that the estuary becomes "hypersaline" in almost every summer transforms it in a negative one during that period, allowing an inwards flux. The observed distribution of salinity values fully agrees with previous reports by other authors on different estuarine systems (Ahel et al. 1996, Ysebaert et al. 2003).

2.3 pH

The distribution of pH values along the estuary has presented low differences, usually linked to seasonal changes and related to biological processes. So, the highest pH values have been recorded just after the occurrence of large phytoplankton blooms (winter and summer), reaching up to levels of $\sim$9 (Popovich et al. 2008). This seasonal distribution pattern as well as the importance of this parameter has been highlighted by several authors for different estuarine systems (Jin et al. 2006, Melville and Pulkownik 2006).

2.4 Turbidity

Turbidity in the inner area of the estuary seems to decrease seawards, considering that near the head it ranges between 50 and 300 NTU, while seawards it decreases to less than 200 NTU in the middle area of the estuary, and at the open ocean observed values close to the mouth of the estuary are lower than 30 NTU. This fact can be related with both the occurring of the main sediment sources in the inner area (streams, rivers, sewage outfalls, harbours) as well as the increasing depth from the head to the mouth of the estuary which generates lower sediment resuspension (Cuadrado et al. 1994, Perillo et al. 2005). The analysis of Pto,Cuatreros and Pto.Ing White time series has shown a slightly lower mean values at IW than at PC, and in both cases the maximum values have been recorded during stormy winters. This distribution trend agreed with the reports from other authors for different estuaries at other latitudes, not only obtained from field work (Irigoien et al. 1999) but also from remote sensing ones (Chen et al. 2007).

2.5 Dissolved oxygen

The distribution of dissolved oxygen within Bahía Blanca estuary has shown adequate values to support a significant biological production, with average levels close to 7 mg l^{-1}, and reaching up to approximately 13 mg l^{-1} during the highest productive periods (winter and late summer) (Popovich and Marcovecchio 2008). The highest concentrations of dissolved oxygen were always recorded in the inner area of the estuary; the spatial distribution trend of this pa-

rameter has shown a very stable level along the whole estuary (Popovich and Marcovecchio 2008). This observation has also agreed with the corresponding distribution of the oxygen saturation percentage that also reached the highest values in the inner region of up to 130% during phytoplankton blooms (Popovich and Marcovecchio 2008).

2.6 Dissolved Nutrients

Bahía Blanca estuary has been recognized as a nutrient-enriched environment, maintaining significant levels of these inorganic compounds during most of the year (Freije and Marcovecchio 2004). A typical spatial pattern for nutrients has to decrease from the inner zone of the estuary to the mouth (Figure 3). Thus, the mean levels of NO_2^- + NO_3^- , PO_4^{3-} and Silicates have varied from 7.76 $\pm$ 6.13 μM, 1.85 $\pm$ 1.07 μM and 80.22 $\pm$ 27.53 μM, respectively, at the inner area; and 1.36 $\pm$ 1.61 μM, 1.30 $\pm$ 0.32 μM and 20.22 $\pm$ 9.62 μM respectively, at the mouth (Popovich and Marcovecchio 2008). On the other hand, a very high stock of ammonium is usually available within the system, mainly also in the inner area, with mean values of 32.32 $\pm$ 25.78 μM, and reaching up to a peak of 102.8 μM registered in Jun'02 (Figure 4) (Freije and Marcovecchio 2004, Popovich et al. 2008). This is a very important point, considering that this species has never been completely depleted, and so represents a permanent potential stock of nitrogen for the estuary.

2.6.1 Dissolved Nutrients on the Villa del Mar tidal flat

Villa del Mar is a small resort town located on the middle Bahía Blanca estuary, ~5 km from Punta Alta city ; it is a small dock where an intense sport fishery activity exist. This estuarine area shows predominant distribution of different fin-fish species, while the halophyte vegetation is dominated by *Spartina alterniflora* Loisel (Negrin et al. 2007).

Preliminary studies carried out in the tidal flat of Villa del Mar during 2006 and 2007, show that the concentration of DIN, DIP and DSi in surface estuarine water (SEW) (23.12 $\pm$ 10.46 μM, 2.91 $\pm$ 0.99 μM and 84.9 $\pm$ 7.3 μM, respectively) was lower than those determined in porewater of the usually flooded tidal flat (PW_I) (59.90 $\pm$ 49.22 μM, 16.96 $\pm$ 10.44 μM and 361.1 $\pm$ 66.1 μM, respectively) and in the occasionally flooded tidal flat (PW_{II}) (54.04 $\pm$ 8.97 μM, 20.40 $\pm$ 8.47 μM and 417.3 $\pm$ 37.20 μM, respectively) (Table 1). In these studies the occasionally flooded tidal flat was considered as the flat that only floods under certain climatic conditions, especially when strong winds came from the southern region. NH_4^+ was the dominant fraction of the DIN. In PW_I the concentration of NH_4^+ was significantly greater than in PW_{II}; meanwhile this one had the highest concentration of NO_3^-, especially during the springtime and the summer, which is being related to processes of nitrification.

The analysis of these results compared to the zones with vegetation showed a higher concentration of DIN (especially ammonium and nitrate) in flats without vegetation than in the vegetated ones. This fact has been related with the use by the vegetation (Negrín et al. 2008).

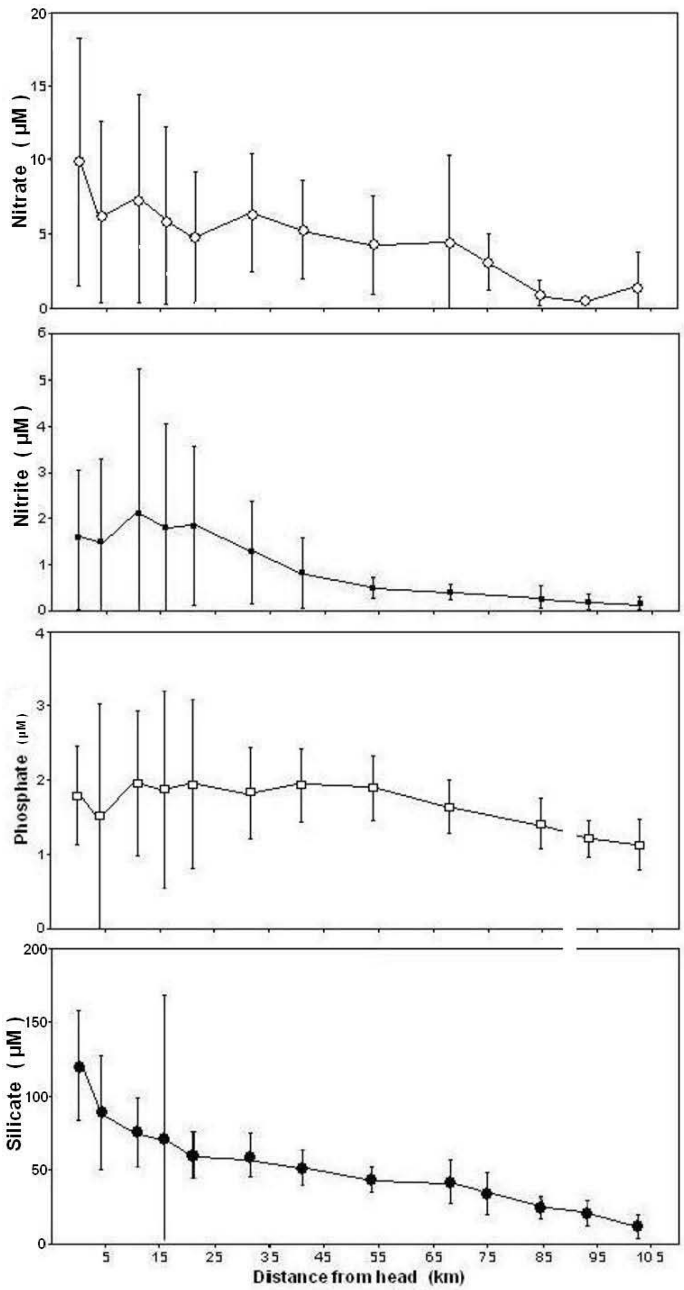

FIGURE 3: *Variation of nutrient concentrations (nitrate, nitrite, phosphate, silicate ; μM) along the Main Navigation Channel from Bahía Blanca estuary.*

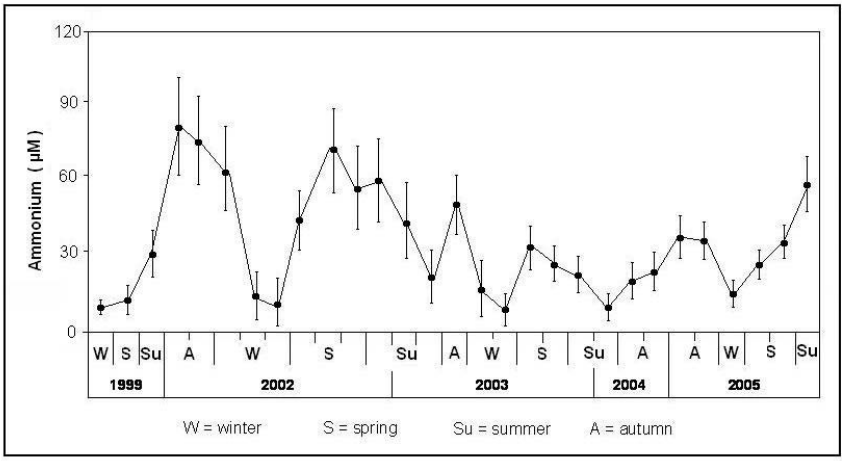

FIGURE 4: *Seasonal distribution of ammonium (mean value ± standard deviation ; μM) at the inner area of the estuary.*

2.6.2 Dissolved Nutrients in Puerto Galván tidal flat

Puerto Galván at the inner area of the estuary has a reduced surface due to the continuous increasing industries located within the area over the last decades. This site is surrounded by a large petrochemical nucleus, refineries and fertilizer plants, as well as deep water harbours. This means that periodical dredging, artisanal and commercial fisheries, and oil and cereal cargo vessel traffic usually affect this area, as well as the direct impact of both Bahía Blanca and Ing. White cities. The occurrence of both *Spartina alterniflora* and the benthic macroalgae *Enteromorpha* sp. characterize its higher intertidal area (Botté 2005).

TABLE 1: *Dissolved Inorganic Nitrogen, Dissolved Inorganic Phosphorus and Dissolved Silicates Concentrations (in μM) in Surface Estuarine Water (SEW), Porewater in usually flooded tidal flat (PW_I) and Porewater in occasionally flooded tidal flat (PW_{II}) in Villa del Mar.*

		winter	spring	summer	autumn
DIN	SEW	28.78	13.80	14.89	35.02
	PW_I	110.91	9.61	26.85	92.25
	PW_{II}		48.15	64.36	49.60
DIP	SEW	3.54	3.57	1.63	2.89
	PW_I	38.46	1.79	5.99	21.60
	PW_{II}	46.45	10.76	26.63	23.82
DSi	SEW	85.88	81.40	79.92	93.28
	PW_I	1025.84	437.20	328.71	317.47
	PW_{II}	470.59	459.15	404.63	388.03

According to the data compilation of dissolved inorganic nutrients in Surface estuarine water (SEW) and Pore water (PW) in the tidal flats of Puerto Galván from 2000 to 2002, obtained by Botté (2005), the concentrations of DIN, DIP and DSi were higher in PW than in SEW. In autumn 2001 (El Niño year), both in SEW and in PW were recorded the highest concentrations of DIN (150.57 $\pm$ 31.88 μM and 321.59 $\pm$ 29.80 μM, respectively) and DSi (113.1 $\pm$ 17.9 μM and 193.6 $\pm$ 54.5 μM, respectively); thus showing an important contribution from the terrestrial drainage due to the water-sediment interaction. Then, the concentration of DSi was stable around values of 90.5 $\pm$ 7.9 μM in SEW and 150.9 $\pm$ 13.7 μM in PW.

DIP did not show great variations in SEW (2.54 $\pm$ 1.18 μM), meanwhile in PW the highest concentrations were recorded in autumn (8.84 $\pm$ 2.80 μM) and winter (8.48 $\pm$ 3.20 μM). In winter the values of DIN were low (44.44 $\pm$ 0.24 μM in SEW) with minimum values in PW (74.20 $\pm$ 25.46 μM). In spring and summer the concentrations were 66.58 $\pm$ 8.82 μM and 44.91 $\pm$ 6.96 μM in SEW, and 133.90 $\pm$ 79.47 μM and 114.52 $\pm$ 50.03 μM.

Botté (2005) has made a comparison between concentrations of NH_4^+ in porewater of Puerto Cuatreros, Puerto Galván and Maldonado (a resort area placed between both harbours) where Puerto Galván highlighted with a total mean of $\sim$72 μM. In the above mentioned work it has been suggested that the tidal flat of Puerto Galván would act as a source of nutrients, without considering the important anthropogenic load that this place could be receivng.

2.6.3 Dissolved Nutrients in Puerto Cuatreros tidal flat

Puerto Cuatreros is a good representative example of the inner zone of the system, with scarce vegetation on the tidal flats, high nutrient concentrations, and high phytoplankton biomass (Gayoso 1998, Spetter 2006, Popovich et al. 2008). This area has an average depth of 7 m, with a vertically homogeneous and highly turbid water column (Píccolo and Perillo 1990). The Sauce Chico River, whose watershed comprises highly agriculture and cattle breeding lands, is the main freshwater source for the study area, with a mean annual runoff of 1.9 $m^3\ s^{-1}$, which can increase up to 10 to 106 $m^3\ s^{-1}$ with the autumn rainfall (Píccolo et al. 1990).

Puerto Cuatreros is the more evaluated site about nutrients dynamics in the inner zone of the Bahía Blanca estuary. Freije and Marcovecchio (2004) summarized the recorded information over more than 20 years of nutrient data compilation in surface estuarine water of this place. They concluded that the nutrient dynamics in Puerto Cuatreros has a typical behaviour in summer, when short duration pulses of growth of small phytoplankton species take place and they usually decrease the concentration of dissolved inorganic nutrients for some days; in autumn, when the maximum nutrient concentrations connected with the mode of rains of this place can be found; in the bloom period (a phase that recurs every year) when the concentration of nutrients abruptly falls, usually reaching its annual minima and therefore constituting a limitation to the bloom; and, at the end, a phase called ”recuperation” when the concentration of each nutrient increases and which occurs usually in springtime.

The distribution analysis of DIN, DIP and DSi in Puerto Cuatreros from 2001 to 2003 showed the previously depicted dynamics (Figure 5). However, Spetter (2006) observed during the years 2004 and 2005 some changes in the expected dynamics. The distribution of concentration of DIN in Puerto Cuatreros, in 2001 and 2002, presented a typical behaviour, with high values in autumn (92.04 $\pm$ 30.23 μM) and spring (57.91 $\pm$ 18.87 μM), coinciding with rainy periods (Spetter et al. 2008); and a large decrease in winter (28.72 μM, July 2001; 17.38 μM, July 2002), and summer (21.74 μM, Dec. 2001; 36.13 μM, Dec. 2002) (Figure 5). In contrast, lower concentrations than in previous years were observed from March 2003 to November 2005 (31.68 $\pm$ 13.43 μM) (Spetter et al. 2008).

The winter diatom bloom has been recognized as the most important event in the phytoplankton annual cycle in the Bahía Blanca estuary (Gayoso 1998, Popovich 2004). DIN -unlike P and Si- has been responsible for the highest primary production in this area (Popovich et al. 2008). Recent studies have demonstrated that the winter/early spring phytoplankton bloom (diatoms dominated by *Thalassiosira* spp. and *Chaetoceros* spp.) in the inner zone of the Bahía Blanca estuary starts in June consuming NO_3^- as first source of Nitrogen and depleting all dissolved inorganic nutrients until August (Popovich et al. 2008). The NH_4^+ seemed to be the main source of nitrogen (Spetter et al. 2008).

Small forms of phytoflagellates (10 - 20 μm) occurred year-round with maximal abundance in summer (Gayoso 1999); this suggests that they would be responsible for the strong DIN decrease (Spetter et al. 2008); however, in summer of years 2004 and 2005 other groups which could be responsible for the large decrease of nutrient concentrations were found (CA Popovich, personal communication). According to Perillo et al. (2004) the Sauce Chico River is the main freshwater input to the inner area of the Bahía Blanca estuary, in agreement with Lara and Pucci (1983) who have highlighted the influence of the above mentioned river in the studied area.

Seven years of historical data for DIN in Sauce Chico River give a mean concentration in the order of 60 μM. This high concentration of DIN compounds was related to the anthropogenic activities in the corresponding watershed, which cross trough an area intensively used for both agricultural and livestock farming activities. Spetter (2006), Spetter et al. (2008) have demonstrated that the Sauce Chico River is an important source of DIN in the inner zone of the estuary, especially during heavy rain periods.

Popovich et al. (2008) have considered Phosphorus as the main potential limiting nutrient for the winter diatom bloom such as it had been reported in many coastal and estuarine systems (Benitez Nelson 2000, Ehrenhauss 2004). Figure 5 shows that the distribution of DIP concentration from 2001 to 2005 followed the expected tendency, with high values in autumn (2.72 $\pm$ 0.54 μM) and spring (2.47 $\pm$ 1.49 μM), minima in winter (1.58 $\pm$ 0.72 μM) and values of 2.19 $\pm$ 0.78 μM in summer. It should be noted that the authors found, during this study, the minimum concentration of DIN and DIP (6.71 and 0.72 μM respectively) in January 2004, instead of in winter as it was previously depicted.

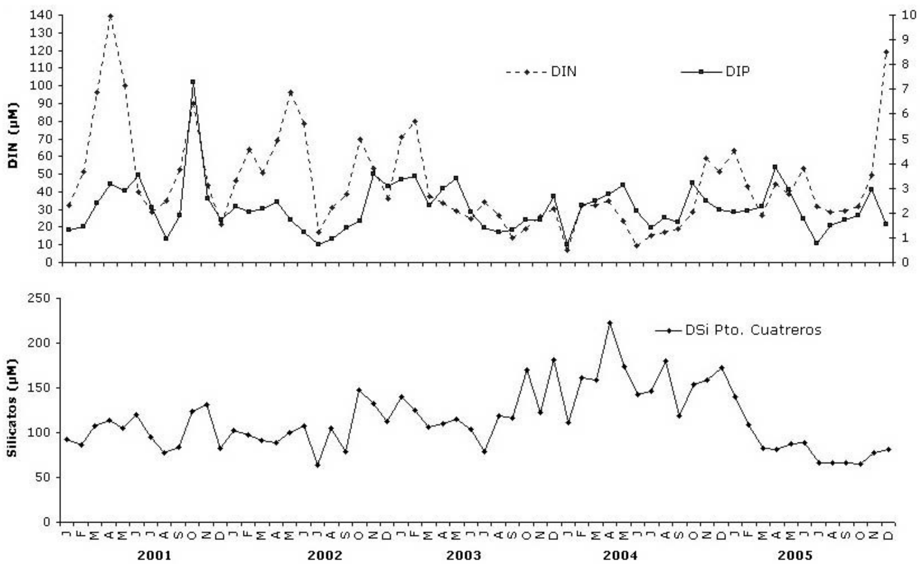

FIGURE 5: *Monthly distribution of DIN, DIP and DSi in surface estuarine water in Puerto Cuatreros. (Extracted from Spetter 2006, Spetter et al. 2008).*

The concentration of DSi showed minima in winter (104.1 $\pm$ 33.5 μM) and an increase in spring and summer (118.1 $\pm$ 33.0 μM) (Figure 5). In 2004, the highest concentrations of the whole studied period were observed (158.4 $\pm$ 28.9 μM) and they were related to the influence of the Sauce Chico River (956.0 $\pm$ 300.6 μM). During the year 2005 the concentrations of DSi were the lowest (84.4 $\pm$ 21.6 μM) of the whole analysed period. Those variations on the typical dynamics of the dissolved inorganic nutrients in surface estuarine water of Puerto Cuatreros are being connected with changes in the environmental factors such as lower precipitations and increase or decrease of temperature (Spetter et al. 2008). Studies carried out by Del Blanco (2007) show that the concentration of nutrients in the tidal flat of Puerto Cuatreros is not affected by the advance of tides.

During the years 2003 and 2004, the dynamics of dissolved inorganic nutrients in surface estuarine water (SEW) was analysed with respect to the observed dynamics in pore water (PW) (Figure 6) and the results showed that NO_2^- in SEW (1.30 $\pm$ 1.06 μM) was higher than in the PW (0.26 $\pm$ 0.19 μM); NO_3^- showed a similar trend (8.87 $\pm$ 6.46 μM and 0.99 $\pm$ 1.10 μM respectively). Unlike this, NH_4^+ presented an inverse trend, with higher levels in the PW (22.15 $\pm$ 13.50 μM) than in the SEW (14.37 $\pm$ 8.99 μM) (Spetter et al. 2007a). The nitrification, the biological process which transforms reduced forms of nitrogen to nitrate (Herbert 1999, Koops and Pommerening-Röser 2001), seemed to occur at the end of spring within sediments due to the presence of NO_3^- in PW. The ammonification, the release of NH_4^+ from the nitrogenous organic matter supplied to the sediments (Herbert 1999), would develop throughout the whole year, although nitrate reduction process would only be present in later summer (Spetter et al. 2008). Both processes take part in the stage of "recuperation" of nutrients described earlier.

In the case of DIP in surface estuarine water and porewater, it has not shown great differences (Figure 5 and 6) and its concentration in SEW was 1.99 $\pm$ 0.90 μM and in PW 1.57 $\pm$ 0.89 μM (Spetter 2006). With respect to the concentration of DSi, it was higher in porewater (207.9 $\pm$ 90.7 μM) than in SEW (144.9 $\pm$ 47.0 μM) (Figure 5 and 6). The comparison of the concentration of DSi in porewater extracted from the innermost fractions of sediment presented a marked tendency to increase with deeper sediments. It was suggested that this phenomenon is a consequence of the dissolution of biogenic silica in the sediments (Spetter 2006), according to Ehrenhauss et al. (2004).

2.7 Chlorophyll a

Simultaneously with the occurrence of these nutrient distribution processes within the estuary, the one for the corresponding photosynthetical pigments (i.e. chlorophyll a) have also been identified for this system (Figure 7). Thus, a clear decreasing trend of chlorophyll concentration from the inner area (mean value 10.77 $\pm$ 4.97 μg l^{-1} with values reaching up to 18 μg l^{-1} down to the outer one (mean value 3.19 $\pm$ 1.74 μg l^{-1}) has been observed (Figure 7). Nevertheless, it is important to highlight that the Chl-a levels within the estuary has never been null, which indicates that the system is a permanently productive estuary, and its lower values are similar to those usually recorded in coastal marine waters from the Argentine Sea (Marcovecchio 2000). In addition, during the last three decades Chl-a values of approximately 42 μg l^{-1} have been recorded in different years (Gayoso 1998, Popovich and Marcovecchio 2008). Simultaneously with this pigment distribution and concentrations, the values of net primary production (NPP) determined at the inner area of the estuary have reached up to $\sim$300 mg C m^{-3} h^{-1}, which could be mentioned as being among the highest records reviewed in the international literature (Marcovecchio and Freije 2004).

2.8 Particulate Organic Matter

The high primary production levels determine the occurrence of high concentrations of organic matter within the system (mean values $\sim$2000 mg C m^{-3} for both Pto.Cuatreros and Pto.Ing White), with the maximum levels coinciding with the peaks of chlorophyll a. The depletion of nitrate, nitrite and silicate together with the increase in dissolved oxygen levels, indicate that most of the determined POM originates from primary production. In addition, different organic matter sources occur within the system, including sewage outfalls, rivers and streams, etc., which could significantly modify the OM available stock for the system.

3 CONCLUDING COMMENTS

Bahía Blanca estuary is a very large system, whose functioning is clearly characterized by several processes that on the whole determine the extent of the biological production occurring there. The distribution of the structural parameters within the system is very stable, mainly in terms of temperature, pH and turbidity. Salinity presents a relative stability, though signifi-

cant variations occur at the inner area, where it could alternatively be increased or decreased according to the season. The estuary is usually nutrient enriched, and compounds of nitrogen (especially ammonium) are always available, even though the concentration of oxidized nitrogen compounds (NO_2^- and NO_3^-) and phosphorus used to be fully depleted during the periodical phytoplankton blooms. In addition, high levels of silicate are usually available in the estuary, mainly in the inner area, which is roughly adequate to support the biological demand within the system.

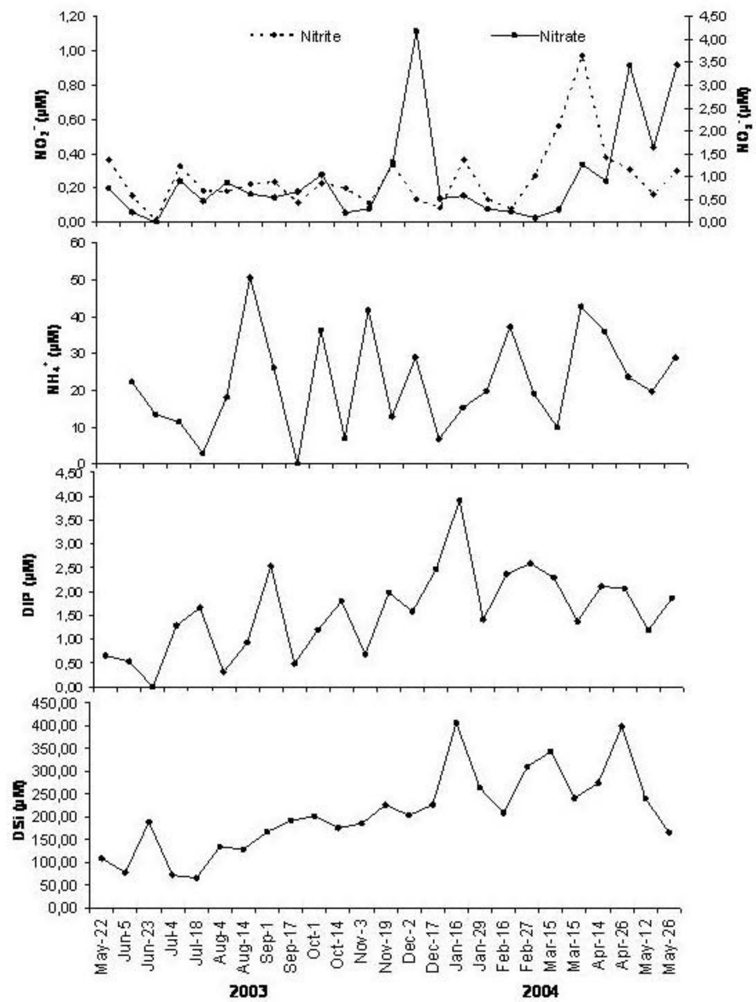

FIGURE 6: *Concentration of nitrite, nitrate, ammonium, DIP and DSi in porewater (PW) at Puerto Cuatreros during May 2003 - May 2004. All concentrations are in μM. (Extracted from Spetter 2006, Spetter et al. 2008).*

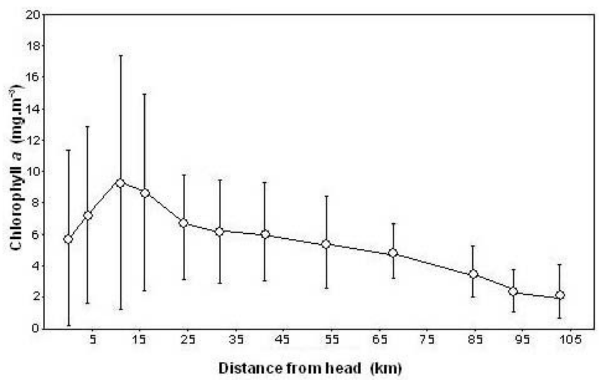

FIGURE 7: *Chl-a concentration along the Main Navigation Channel.*

Concerning primary production, the most important annual period is late winter - early spring, when the highest phytoplankton blooms have historically occurred. It is developed so, because during this time the nutrients (N, P and Si) are largely available, and both the temperature and light intensity are sufficiently low ($\sim$5 to 7 °C, and 400-700 μE m^{-2} s^{-1} respectively; after Popovich et al., this volume) as required by the dominant diatom species (*Thalassiosira curviseriata*) responsible for this bloom. Thus, very high levels of Chl-a were detected during this phenomenon (with values reaching up to 55 mg m^{-3}), representing densities of $\sim 13 x 10^6$ cells l^{-1} or net primary production of $\sim$300 mg C m^{-3} h^{-1}.

The very high amounts of organic matter generated by these biological processes ensure the regenerated nutrients production, through mineralization processes occurring within the estuary (Spetter 2006). The obtained results seemed to indicate that a predominant liberation of ammonium was observed from the estuarine sediments in the inner estuary, even significant amounts of oxidized nitrogen compounds (NO_2^- and NO_3^-) were eventually also produced (Spetter 2006). In addition, these are the first nitrogen nutrients to be consumed during the phytoplankton bloom, and just when both NO_2^- and NO_3^- were depleted the NH_4^+ started to be consumed (Popovich et al. 2008). This productive cycle, regulated through bio-geochemical joint processes has functioned well for a long time (at least during the past 30 years, when these studies first started). Consequently, this is a very good scenario to control the evolution and progress of the estuary chemical processes, as well as to monitor the potential occurrence of changes within the identified trends.

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