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Dynamics of nutrient cycling of the Valdes Bay-Punta Cero pond system (Peninsula Valdes, Patagonia) Argentine

Nutrient cycle
Land-sea interface
Peninsula Valdés
Patagonian
South Atlantic Ocean

Cycle des sels nutritifs
Interface eau-sédiment
Peninsula Valdés
Patagonie
Océan Sud-Atlantique

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ABSTRACT

Valdés Bay constitutes a very interesting land-sea interface (LSI) at Peninsula Valdes. A gravel bank separates the bay from the open sea. The general characteristics (physical, chemical and biological) of this ecosystem and the chemical composition of the seawater coming in and out were analyzed.
Nutrient cycling (nitrogen and phosphate) was very intense and involved a high primary productivity. These nutrients were principally produced at the gravel bank, where oxygen was consumed by heterotrophic activity and nitrification processes. The latter process consumed 1 to 7% of the oxygen. Extrapolating to the 35-km bank, a value of 6.8 metric tons of nitrogen would be produced daily.

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RÉSUMÉ

Dynamique du cycle des sels nutritifs dans le système côtier Valdes-Bassin punta cero (Peninsula Valdes, Patagonia), Argentine.

La calanque Valdés est une très intéressante interface eau-sédiment à Peninsula Valdés. Nous avons étudié les caractéristiques générales (physiques, chimiques et biologiques) et la composition chimique de l'eau entrant et sortant à travers le banc de graviers qui sépare cet écosystème de la mer. La production de micronutrients (azote et phosphore) est très intense et provoque une haute productivité primaire.Ces micronutrients ont été produits dans ce banc principalement, où l'oxygène a été consommé dans des processus hétérotrophes et de nitrification; dans ce dernier cas et dans des proportions de 1 à 7 °/₀, l'extrapolation à tout le banc (35 km), conduit à estimer la production d'azote à 6,8 t par jour.

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INTRODUCTION

The land-sea interface (LSI) constitutes both a region of high biological productivity and complexity and the portion of the ocean most heavily influenced by human activities. Major nutrients undergo rapid biogeochemical cycling in the LSI. This cycling is driven by organic and inorganic loading, primary production, respiration and tight coupling between the water column and sediments (Hollibaugh *et al.*, 1988).

One of the major ways in which these areas differ from the open sea is that a much larger fraction of the organic matter in shallow waters is remineralized on the bottom than through pelagic food webs (Rowe *et al.*, 1975; Billen, 1982; Pomroy *et al.*, 1983; Flint and Kamykowski, 1984; Blackburn, 1986; Pollehne, 1986). Valdes Bay, located on the eastern coast of Peninsula Valdes, is oriented in a north-south direction, and is separated from the open sea by a gravel bank parallel to the coastline. The whole system, comprising the bay itself, together with the islands and lagoons, is not under stress from human activities, because it is part of the "Peninsula Valdes" protected natural park. The nearest village is Puerto Pirámides (100 inhabitants), 80 km away. The system is visited only by tourists, mainly during the summer. The presence of marine mammals and birds is remarkable. These include southern elephant seals (*Mirounga leonina*), present throughout the year, right whales (*Eubalaena australis*) from August to November, and Magellanic penguins (*Spheniscus magellanicus*) during the summer period.

Peninsula Valdes is a desert where rain is scarce and freshwater sources (river, groundwater) do not exist.

The high dynamism of the entire coastal area produces a change in the location of the bay mouth and a variation of the amount of gravel deposited between the sea and the inner zones.

Bacteria which colonize the gravel bank receive a continuous food supply that permits their development and activity, due to the seawater flowing across the bank during each tidal wave.

In the present study, we analyze the general characteristics (physical, chemical and biological) and the chemical composition of the seawater coming in and out the bank, and extrapolate the results obtained in a restricted area to the whole length of the bay. The possible influence of the gravel bank on the primary productivity of the whole area is considered.

MATERIALS AND METHODS

Valdes Bay, 35 km in length, has a group of islands on its northern and coastal ponds on its southern sides (Fig. 1). Among these lagoons, Punta Cero pond (an old inlet of the bay) is the biggest (22 Ha.), and the one chosen for this study. The system is bounded by a gravel bank which separates it from the open sea. The width of the gravel bank varies between 50 and 200 m, and it is about 10 m high.

Within the bay and lagoons, the tidal exchange is produced through the bay mouth and through the gravel bank. At flood-tide, water flows from the open sea to the inner bay and to the pond; in this case, the inflow water comes from the open sea and the outflow water leaves the bank to the inner bay. Inversely, at ebb-tide, the flows change and the water withdraws from the system; in this case, the inflow water comes from the inner bay and the outflow water leaves the bank to the open sea. Tides are semidiurnal and their amplitude is 3.0 m in the open sea and 1.5 m in the inner bay. Figure 1 shows the area under study and the sampling sites. Two types of investigation were performed. The first was conducted during the years 1980-1983. Samples were taken at two-month intervals. In the second, water samples were obtained in the pond at irregular intervals but seasonally during 1986-1988. Samples were taken hourly on both sides of the bank during flood-tide and ebb-tide. Stations 1-4 were chosen in order to characterize the inner part of the bay; stations 5 and 6 to study the pond; stations 7, 8 and 9 to study open sea conditions; and stations 10-13 for the gravel bank analysis. Water samples at stations 1-7 were obtained at depths of 0 and 5 m; samples at 8 and 9 only were taken at the surface, and at 10-13 samples were taken manually at surface from the water flowing in or out the gravel bank at flood-tide and ebb-tide.

Analyses of salinity, chlorophyll *a*, dissolved oxygen and nutrients (nitrate, nitrite, ammonium and phos-

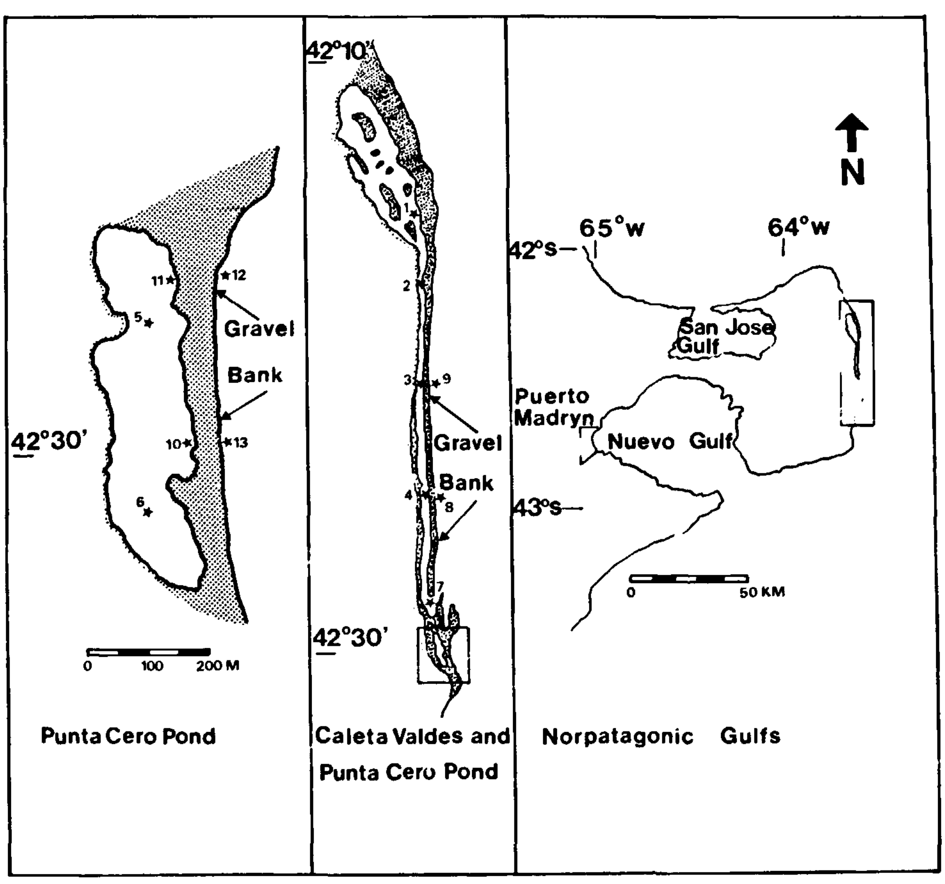

Figure 1
Sampling sites of Valdes Bay-Punta Cero pond system.
Stations de prélèvements dans le système côtier Valdes-Bassin Punta Cero.

phate) were performed on each sample, according to Strickland and Parsons (1972). Nitrate and nitrite were analysed by automatic methods (Autoanalyser Technicon). Temperature was also measured. State and height of the tide were recorded. Primary productivity was measured with the C^{14} uptake method in the pond and at inner bay at stations 5 and 2 respectively. Particulate organic carbon was analysed by wet oxidation with dichromate (Strickland and Parsons, 1972). In the second study, average values of five samples collected at each date were obtained for each tide and season. The differences between the internal and external values were subsequently calculated for each parameter considered.

RESULTS

Evolution of environmental parameters during the year

Figure 2 shows the evolution of the principal parameters studied. Temperature exhibited a typical cycle, with average winter values of 9°C and average summer values of 18°C. The largest difference between seasons was detected at the pond. The open sea stations presented less amplitude and more inertia to temperature changes, due to the influence of the adjacent ocean.

Salinity remained almost constant in the open sea, with values around 33.7 practical salinity units (psu), confirming the influence of the oceanic environment.

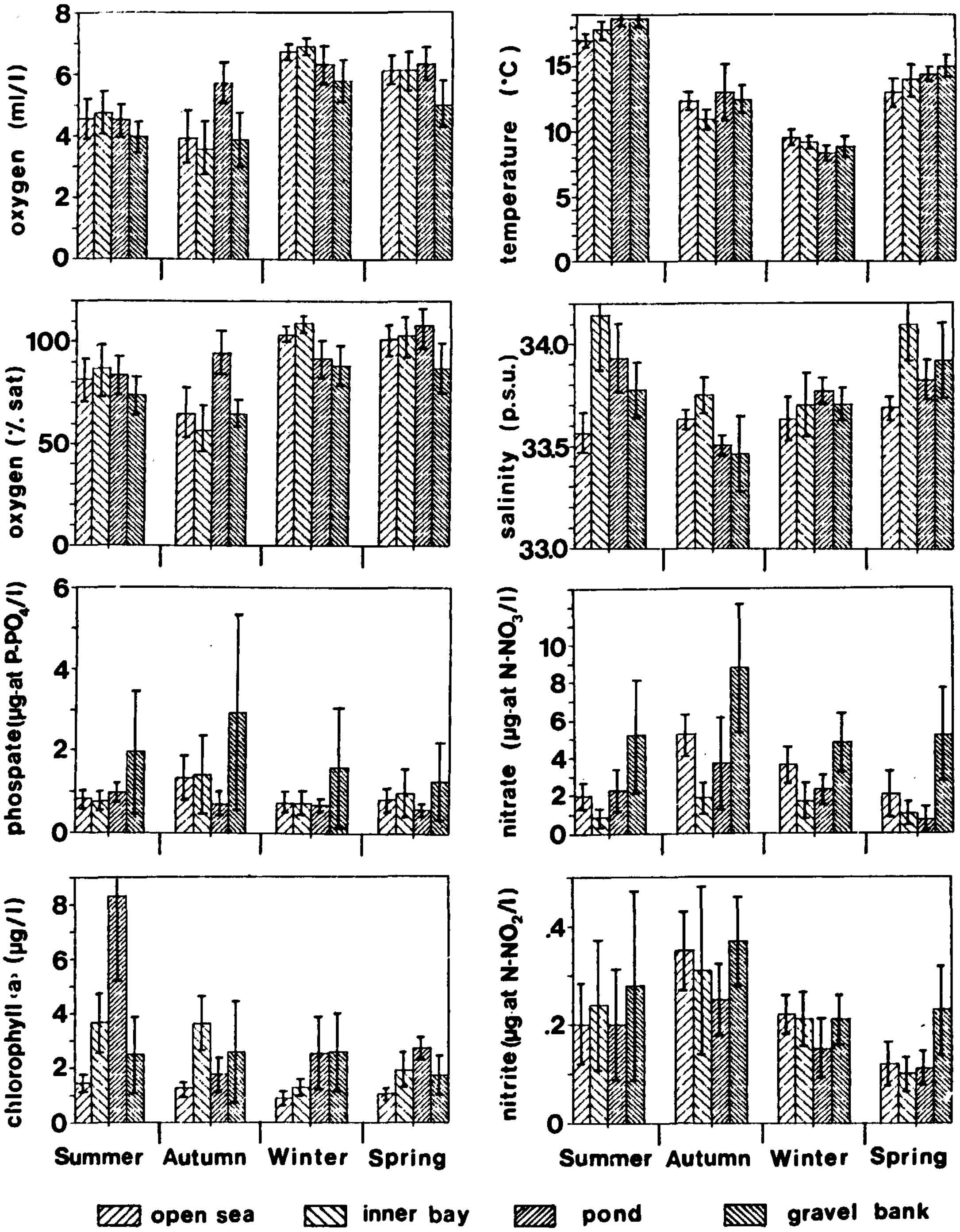

Figure 2

Seasonal evolution of physical, chemical and biological parameters for the four groups: open sea, bay, pond and bank.

Evolution saisonnière des paramètres physiques, chimiques et biologiques pour les quatre groupes: Océan, calanque, bassin et banc de graviers.

Larger variations were observed at the other sites. In general, values were higher than in the open sea. Highest salinities were measured during the summer in the pond and inner bay due to evaporation in the shallow closed water systems. Salinity was lower during the summer due to occasional rainfalls.

Nitrate concentrations were highest in the autumn and lowest in spring. In the open sea, nitrate concentrations range from 2 to 5 μg-at N-$NO_3.l^{-1}$. In the pond and inner bay, an intense utilization of this nutrient by phytoplankton was observed, the range being from 3.7 μg-at.l^{-1} to less than 1 μg-at.l^{-1} or lower. The gravel bank presented the highest concentrations of the entire system with mean values of 9 μg-at.l^{-1} during autumn and 5 μg-at.l^{-1} during periods of intense phytoplanktonic activity.

Variations in phosphate concentration were small among groups throughout the year. Mean concentrations were around 1 μg-at.l^{-1}. The gravel bank, however, presented very high values of 3 μg-at.l^{-1} during the autumn and 1.2 μg-at.l^{-1} during the spring.

Dissolved oxygen values were close to saturation level during winter and spring (6 ml.l^{-1}) but lower during summer and autumn. The gravel bank showed the lowest concentrations, ranging from 4 to 5.7 ml.l^{-1} (64 to 87% saturation level respectively), due to nutrient remineralization processes, whereas the concentrations at the inner bay and pond were the highest. In autumn, only the pond was at saturation level, whereas the other stations remained undersaturated.

The open sea stations showed the lowest concentration of chlorophyll *a*, with a minimum of 0.4 μg.l^{-1} in winter. At the inner bay and the pond, the mean values were around 4 and 8 μg.l^{-1} respectively during summer. At the gravel bank, a value of approximately 2 μg.l^{-1} through the year was observed.

Primary productivity and particulate organic carbon (POC) vary widely during the year (Tab. 1) at Punta Cero pond. The lowest values were observed in winter and coincided with the lowest chlorophyll *a* concentration. Summer and autumn showed the most important concentration of POC (more than 1,000 mg C.m^{-3}). Primary productivity reached 24 mg C.m^{-3}.h^{-1} in summer. Values for POC and primary productivity were the same order of magnitude in the inner bay.

Table 1

Seasonal variations of particulate organic carbon (POC) and primary productivity (PP) at Punta Cero pond. Values are means with standard deviations between parentheses. N.D.: No data.

Season	Number of determinations POC	PP	POC [mg C.m^{-3}]	Primary productivity [mg C.m^{-3}.h^{-1}]
summer	5	4	1 048 (343)	24.40 (17.9)
autumn	2	–	1 197 (642)	N.D.
winter	6	5	364 (127)	1.28 (0.90)
spring	6	5	475 (289)	7.15 (9.10)

Evolution of environmental parameters within the gravel bank

Table 2 shows the results obtained at different periods of the year. Oxygen was always consumed at the gravel

Table 2

Seasonal variations of values of each parameter in the inflow and outflow water at the gravel bank and their difference. Values are means with standard deviations between parentheses. Minus sign indicates that the compound is being consumed within the bank. n = number of trips. N.D.: No data.

Parameter	Autumn		Winter		Spring		Summer	
n	4		1		1		2	
Oxygen (ml.l^{-1})								
inflow	08.66	(02.88)	10.80	(01.60)	09.60	(00.98)	09.79	(01.60)
outflow	07.78	(00.51)	09.53	(00.57)	08.45	(01.24)	06.79	(01.26)
difference	−0.88	(00.54)	−1.27	(01.91)	−1.15	(1.23)	−3.01	(02.94)
Phosphate (μg-at P-$PO_4.l^{-1}$)								
inflow	01.63	(00.38)	N.D.		01.14	(00.09)	04.36	(03.28)
outflow	02.17	(00.57)	N.D.		01.51	(00.28)	04.64	(02.13)
difference	00.55	(0.42)	N.D.		00.37	(00.35)	00.28	(05.41)
Nitrate (μg-at N-$NO_3.l^{-1}$)								
inflow	08.90	(13.80)	07.37	(01.14)	01.76	(02.69)	08.67	(06.58)
outflow	19.18	(19.43)	00.56	(00.26)	17.68	(02.71)	16.96	(13.82)
difference	10.54	(10.23)	−6.81	(00.95)	15.92	(02.15)	08.29	(20.40)
Nitrite (μg-at N-$NO_2.l^{-1}$)								
' inflow	00.38	(00.27)	00.15	(00.11)	00.07	(00.2)	00.30	(00.03)
outflow	00.23	(00.12)	00.20	(00.17)	00.37	(00.27)	00.50	(00.37)
difference	−0.15	(00.35)	00.05	(00.06)	00.30	(00.28)	00.20	(00.34)
Ammonium (μg-at N-$NH_4.l^{-1}$)								
inflow	03.11	(01.58)	03.53	(00.19)	22.16	(03.91)	06.71	(00.82)
outflow	03.80	(01.66)	03.42	(00.39)	24.31	(05.32)	06.46	(00.07)
difference	00.69	(00.23)	−0.11	(00.26)	02.16	(01.99)	−0.25	(00.89)
Silicate (μg-at Si-$SiO_3.l^{-1}$)								
inflow	10.06	(07.83)	N.D.		09.03	(02.47)	11.81	(04.09)
outflow	13.31	(04.13)	N.D.		16.32	(03.92)	10.91	(05.23)
difference	03.25	(04.40)	N.D.		07.29	(06.48)	00.90	(00.48)
Chlorophyll *a* (μg.l^{-1})								
inflow	03.49	(03.63)	00.61	(00.47)	00.98	(00.31)	01.26	(00.07)
outflow	01.27	(00.66)	00.22	(00.07)	07.59	(06.48)	00.67	(00.55)
difference	−2.22	(04.29)	−0.39	(00.54)	06.61	(06.75)	−0.59	00.62)

bank, but more intensively during the summer. The oxygen concentration of the influx water was always at saturation level, whereas the outflow water was between 70-90% of the saturation level. Taking oxygen consumption into account, an aerobic microbiological process is to be expected inside the bank throughout the year. Phosphate was produced at a constant rate during the year. Nitrate was produced in autumn, spring and summer; the intensity was highest in spring. Ammonium was consumed in winter and summer, but produced in autumn and spring. During the latter, the concentration was abnormally high. The chlorophyll *a* concentration of the outflow water was higher than in the inflow in spring. We have no explanation for this result.

Occasionally, we found differences in the production and consumption of nutrients (principally in March and April), depending on the tidal flow direction. At flood-tide (Tab. 3), when the water flows from the open sea through the gravel bank to the pond, the nitrate concentration in the open sea side of the bank was 4.02 μg-at.l^{-1}. When the water leaves the bank to the pond, it was enriched with 26.7 μg-at.l^{-1}. Next day, during the ebb-tide, when the water flows from the pond through the bank to the open sea, the nitrate concentration in the pond was 13.3 μg-at.l^{-1}, being afterwards consumed inside the bank with a final concentration of 7.19 μg-at.l^{-1}. The same was found for nitrite and silicate. They were produced inside the bank during the flood-tide, when the water enters the inner bay. The day after, at ebb-tide, when the water leaves the system, nitrite and silicate were consumed in the gravel bank. A similar phenomenon occurred for silicate, in April 1988, when the silicate was consumed inside the bank at flood-tide and produced at the same place at ebb-tide. In all these cases, the nutrients were consumed when their concentration in the influx water was high. Despite these variations, the total seasonal balance was positive; the bank acts as a nutrient producer. Likewise, winter measurements obtained from one set of samples during ebb-tide showed that the influx of nitrate that reached the bank was high and nitrate was consumed in the bank.

The N/P (NO_3/PO_4) ratio (Tab.4) revealed a high nitrogen production throughout the year, with maximum values in spring and summer. This ratio can be observed in Figure 3, where nitrate values show greater variation than phosphate, which remains almost constant.

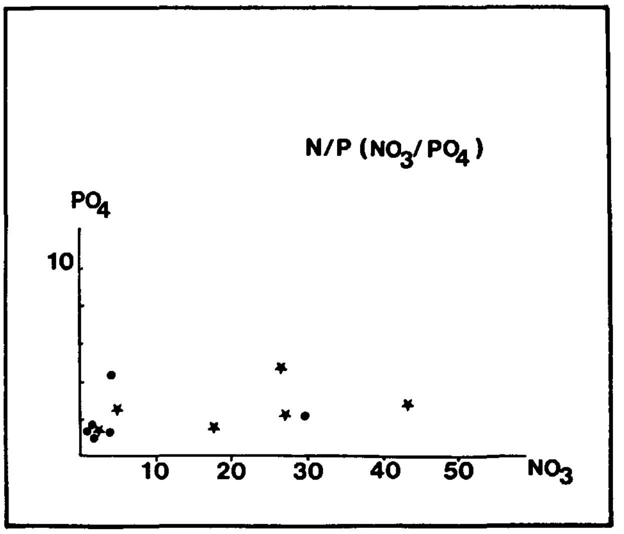

Figure 3
N/P ratio for seawater coming out of the gravel bank. (•) at flood-tide; (*) at ebb-tide.
Relation N/P pour l'eau de mer sortant du banc de gravier. (•) au marée montante; (*) au marée descendante.

The temperature and salinity of the water flowing across the bank did not show large variations.

DISCUSSION

There is very little historical environmental information available on the Valdes Bay system. Its geology has been studied by Beltramone (1981). The potential

Table 3
Values of each parameter considered, in inflow and outflow water and their differences during flood-tide and ebb-tide.

Parameter	Inflow to the bank	Outflow from the bank	Difference
12/3/87 flood-tide			
Nitrate (μg-at N-NO_3.l^{-1})	4.02 (1.07)	26.73 (9.23)	22.71 (9.37)
Nitrite (μg-at N-NO_2.l^{-1})	0.32 (0.07)	0.76 (0.49)	0.44 (0.52)
Silicate (μg-at Si-SiO_3.l^{-1})	8.91 (2.83)	14.61 (10.94)	5.70 (12.1)
13/3/87 ebb-tide			
Nitrate	13.33 (8.71)	7.19 (4.50)	−6.14 (4.95)
Nitrite	0.28 (0.02)	0.24 (0.08)	−0.04 (0.09)
Silicate	14.70 (2.97)	7.21 (6.14)	−7.49 (8.73)
20/4/88 flood-tide			
Silicate	15.60 (2.52)	10.39 (2.59)	−5.21 (0.95)
21/4/88 ebb-tide			
Silicate	4.52 (2.29)	16.23 (2.58)	11.71 (0.92)

Table 4
N/P ratio

Season	Inflow	Outflow	Increment (%)
autumn	4.36	7.94	182
spring	1.54	11.71	760
summer	0.92	5.75	625

growth of oysters (*Ostrea puelchana*) and mussels (*Mytilus edulis*) was analysed in a thesis study by Fernandez Castro (1986) and Fernandez Castro and De Vido (1987). These authors, working at Punta Cero pond, found high growth rates of *O. puelchana* reared south of its natural range in Argentina.

The pond and inner bay water is enriched with nutrients which are subsequently utilized by phytoplankton. Nutrients are consumed, therefore their concentrations remain low. Biomass, measured as chlorophyll *a*, is twice as great, in each season, as that the adjacent marine waters. Organic matter concentration is very high, and increases in summer and autumn, with values of 1,000 mg C . m^{-3}. Primary productivity reflects the richness of this ecosystem, with values of 16 mg C . m^{-3} . h^{-1} in summer at the pond. Such high productivity is similar to that found at Tamales Bay (Hollibaugh, 1988). This water was cited by Charpy and Charpy (1977) as the most productive within the northern Patagonian gulfs.

The land-sea system is influenced by a very dynamic gravel bank which produces important chemical alteration of the water that percolates through it. This gravel bank is, essentially, an aerobic oxidizing system for organic matter. Nitrate is the principal nutrient produced. The system acts as an oxidative reactor where water flows constantly and with a high remineralization rate. This gravel bank is responsible for the high biomass and primary productivity within the inner bay and the pond. Considering that the water flows in two direction, we can infer that water exiting is also enriched. This could be explained by Pedersen (1982) who showed that an increased flow through the biofilm enhances the production rate. On the other hand, development and activity of heterotrophic microorganisms are governed by the availability of organic substances (Rheinheimer G., 1977) which are abundant in coastal zones.

Ammonium was sometimes produced and, at other times, consumed. We believe that for the overall microbial metabolism in the bay, the ammonium ion is an intermediate between the organic matter oxidation and nitrification, a highly dynamic process despite its low variations. Phosphate was also produced inside the bank, but the mineralization mechanisms seemed to involve principally nitrogen.

The increase of nutrients is utilized by phytoplankton. Effectively, chlorophyll *a* concentration was high at the Laguna and Caleta sites, where the nutrients were consumed.

A simple model can be employed to explain the function of this ecosystem (Billen, personal communication). Valdes Bay acts as a chemostat that is fed with inorganic nitrogen produced at the gravel bank. The nitrogen is partly recycled *in situ* and partly exported to the ocean as organic or inorganic nitrogen after it percolates through the gravel bank (Fig. 4).

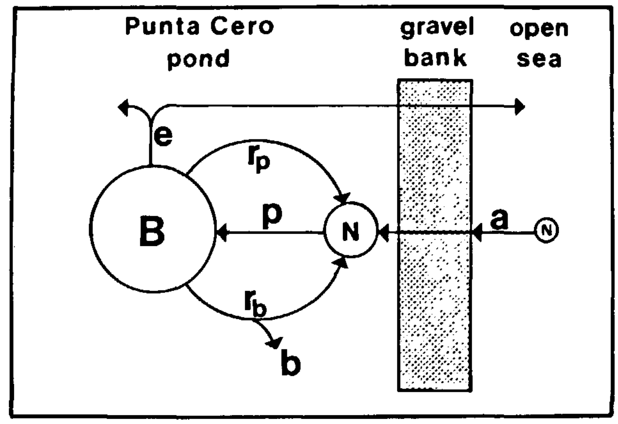

Figure 4
Punta Cero pond view as chemostat (see *text*).
Bassin Punta Cero vu comme un chemostat (*cf.* texte).

In the steady-state and when nitrogen concentrations remain constant and low because of phytoplankton uptake, the nitrogen balance and the biomass can be given by:

$$dN/dt = 0 = a - f(N) . B + (K_{rp} + K_{rb}) . B \quad (1)$$

$$dB/dt = 0 = f(N) . B - (K_{rp} + K_{rb} + K_e + K_b) . B \quad (2)$$

where:

a = rate of exogenous mineral nitrogen import [mass . $volume^{-1}$. $time^{-1}$].

B = biomass [mass . $volume^{-1}$].

$p = f(N) . B$ primary production of biomass. It is considered proportional to biomass and it is a complex function of mineral nitrogen concentration. [mass . $volume^{-1}$. $time^{-1}$].

$r_p = K_{rp} . B$ biomass recycling at the planktonic phase. It is considered as proportional to biomass [mass . $volume^{-1}$. $time^{-1}$].

$r_b = K_{rb} . B$ biomass recycling in the benthic phase. It is considered as proportional to biomass. [mass . $volume^{-1}$. $time^{-1}$].

$e = K_e . B$ biomass exportation to the open ocean. It is proportional to biomass [mass . $volume^{-1}$. $time^{-1}$].

$b = K_b . B$ final sedimentation of non-biodegradable organic nitrogen. It is considered proportional to biomass [mass . $volume^{-1}$. $time^{-1}$].

from (1) and (2), we obtain:

$$B = a/(K_e + K_b) \quad (3)$$

$$p = a\left[1 + \frac{K_{rp} + K_{rb}}{K_e + K_b}\right] \quad (4)$$

Relation (3) indicates that the biomass is proportional to the exogenous mineral nitrogen import, assuming that sedimentation is negligible. In (4) the primary production is coupled with the input of exogenous mineral nitrogen, with a feedback amplifier factor that depends on the endogenous nitrogen recycling in the planktonic and benthic phases, and on biomass export to the sea or to the sediment. In our case, the biomass export to the open ocean is determined by the circulation of water within the pond. The residence time can be evaluated approximately as 24 hours ($K_e = 0.041\,h^{-1}$) considering a volume of $1.2 \times 10^6\,m^3$ ($2.2 \times 10^5\,m^2$ surface and 5.5 m mean depth), and a water flux by tidal exchange of $5.05 \times 10^4\,m^3.h^{-1}$ (tidal amplitude within the pond: 1.5 m; tidal period: 6.5 hours). This is a very dynamic system where the water circulation is constant.

The rate constant of final sedimentation, k_b, can be put at $0.042 \times 10^{-3}\,h^{-1}$ according to Pettijohn (1963) for sedimentary rocks, and can be neglected when compared to K_e.

The experimental value for the aminoacid utilization rate using a flow-through system (Esteves *et al.*, 1986) at sediment-water interface of Punta Cero pond was $0.40\,\mu mol.cm^{-3}.h^{-1}$ (unpublished data). Considering the mean organic nitrogen concentration in this layer ($61\,\mu mol\,N.cm^{-3}$), the value of k_{rb} can be estimated as $0.007\,h^{-1}$.

From particulate organic carbon and assimilation rate (Tab. 1), we can estimate the K_{rp} value in summer as $0.023\,h^{-1}$.

Employing these values, seolution of equation (4) becomes:

$$p = 1.73\,a$$

This result means that the primary productivity, proportional to the imported nitrogen, is enhanced by a factor of 1.73.

There is an impermeable layer of sandy clay loam beneath the gravel bank, where microbiological redox reactions are not possible. This is why we think that infaunal respiration and microbial metabolism (principally heterotrophic activity with oxygen consumption and autotrophic metabolism with nitrification reactions), are the principal processes occurring at the bank.

We can estimate the oxygen demand for the nitrification process with a stoichiometric equation according to Delwiche (1970):

$$NH_4^+ + 2.0\,O_2 \rightarrow NO_3^- + 2\,H^+ + H_2O$$
$$\Delta G^0_{298} = -71.9\,kcal.$$

By this equation, $457\,\mu g\ O_2$ were necessary for the production of $7.14\,\mu g\text{-at}\ N\text{-}NO_3.l^{-1}$ ($100\,\mu g\,N.l^{-1}$). The oxygen demand for nitrification (Tab. 5) varied according to season, being maximum in spring and autumn (62 and 54% respectively), and minimum in summer (12%), when autotrophic and heterotrophic process were more active.

Table 5

Nitrate production and oxygen consumption in the bank, together with oxygen requirements for the nitrification process at different seasons. These processes take place while the water percolated through the gravel bank.

Season	NO_3 ($\mu g\,N.l^{-1}$)	O_2 (ppm)	O_2 for nitrification (ppm)	O_2 for nitrification (%)
autumn	148	1.26	0.68	54
summer	116	4.30	0.53	12
spring	223	1.64	1.02	62

The data of the table 5 was obtained for Punta Cero pond but the results may be extrapolated for all the bay. The volume of water flowing through the 35 km-bank at each tidal wave can be evaluated as $10.5 \times 10^9\,l$, if we consider at least 200 m width for the bay and 1.5 m for the tidal amplitude. This volume includes the water that flows through the mouth. An extrapolation of the nitrogen production in the entire system yields a value of 1.7 metric tons of nitrogen produced, according to Table 5, *i.e.* 6.8 metric tons per day for the total influx and outflux budget. This value must be corrected for the volume of water that actually percolates through the bank (not for the total volume), but we believe this value to be a good estimation of order of magnitude.

This study confirms the importance of land-sea interfaces (LSI) for enhancing coastal productivity. On the other hand, more detailed studies will be necessary to understand the mechanisms that take place in the whole system, the functioning of the gravel bank, the organisms responsible for this high activity and the total influence of Valdes Bay throughout the area.

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