



Baseline

Assessment of recent sediment influence in an urban polluted subantarctic coastal ecosystem. Beagle Channel (Southern Argentina)

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ARTICLE INFO

Keywords:

Eutrophication
Sediment and water quality
Sediment–water exchanges
Biochemical components
Beagle Channel

ABSTRACT

In this study, baseline information about the environmental status of Ushuaia (UB) and Golondrina (GB) bays is presented. Surface and bottom seawater and freshwater discharged from land were evaluated. Multivariate analysis identified different water quality zones within the bays, two of them located next to the north and northwest coastlines of UB, where the majority of human activities are developed. Porosity, total organic matter, biochemical components, ammonium, and phytopigments were determined in sediment samples from each quality zone. Benthic fluxes of nutrients and dissolved oxygen were assessed *in situ* using opaque chambers. In northwest zone of UB, carbon equivalents of proteins and carbohydrates in surficial sediments were the same order as in hypertrophic ecosystems, whereas ammonium and phosphate released from sediment greatly exceeded the allochthonous sources. Management of municipal wastewater is required to remediate this chronic pollution.

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Marine cultural eutrophication is the result of anthropogenic fertilization at the land–sea interface. It has been strictly defined as an increase in the supply rate of organic matter (Nixon, 1995) but includes numerous biogeochemical and ecological responses, either direct or indirect (Cloern, 2001). It changes water and sediment quality, stimulates plant growth, and disrupts the balance between the production and metabolism of organic matter in the coastal zone. In the coastal ecosystem, the sediments and the benthic communities are the most sensitive parts to eutrophication and hypoxia because much of the organic C, N, and P produced by the autotrophic organisms sink to the benthos where they are mineralized (Jørgensen, 1996). Sediments of shallow coastal environments play a key role in nutrient recycling (Niencheski and Jahнке, 2002). Net fluxes from the benthos to the overlying water may sometimes have the same order of magnitude or even greater than those coming from land (Billen, 1978; Fisher et al., 1982) and thus control the trophic level (Clavero et al., 2000; Sakamaki et al., 2006).

Some coastal environments of Patagonia (Argentina) are threatened by nutrient enrichment from urban effluents (Gil and Esteves, 2000; Torres et al., 2009). However, because of the large shoreline extension (~3000 km) and extreme weather conditions to conduct evaluations, there is little information about nutrient biogeochemical cycles. Beagle Channel is one of the southernmost environments of Argentina. Ushuaia city (54° 48'S, 68° 19'W) is the

only urban settlement located on its coasts, in front of Ushuaia (UB) and Golondrina (GB) bays (Fig. 1). It has nearly 60,000 inhabitants, 2 ports located in UB, and its main economic activities are tourism, fisheries, and electronic industries. Only a minor fraction of untreated urban wastewater is collected and sent to a sewage diffuser on the eastern coast of GB; the remainder reaches UB through natural streams, stormwater outfalls, and water exchange with Encerrada Bay (EB) (Torres et al., 2009). Climate is subpolar oceanic, with temperatures between −7 °C in July and 14 °C in January; rainfall (~600 mm/year) is distributed throughout the year, and snowfall are common between May and August (~23 mm/month). Irradiation ranges between 21 W/cm² in June and 344 W/cm² in December (Diaz et al., 2001).

There exists some information about the influence of land on this high-latitude marine ecosystem (Amin et al., *in press*), but the role of the sediments on nutrient coastal distribution has never been assessed. This study constitutes baseline data on physical, chemical, and biochemical parameters of coastal sediments from GB and UB and nutrient benthic fluxes in selected sites. Current environmental quality of marine water and continent water sources was analyzed in four seasonal samplings: August 2004 (winter), December 2004 (spring), March 2005 (summer), and June 2005 (fall). River and effluent water was collected immediately before their discharges. Temperature (*T*), dissolved oxygen (DO), pH, and conductivity were measured *in situ* (Horiba H-10), whereas total suspended solids (TSS), settleable solids (SS), DBO₅, ammonium (NH₄⁺), nitrate + nitrite (NO₃⁻), phosphate (PO₄³⁻), and silicate (SiO₃²⁻) were determined in the laboratory (APHA, 1980). Total

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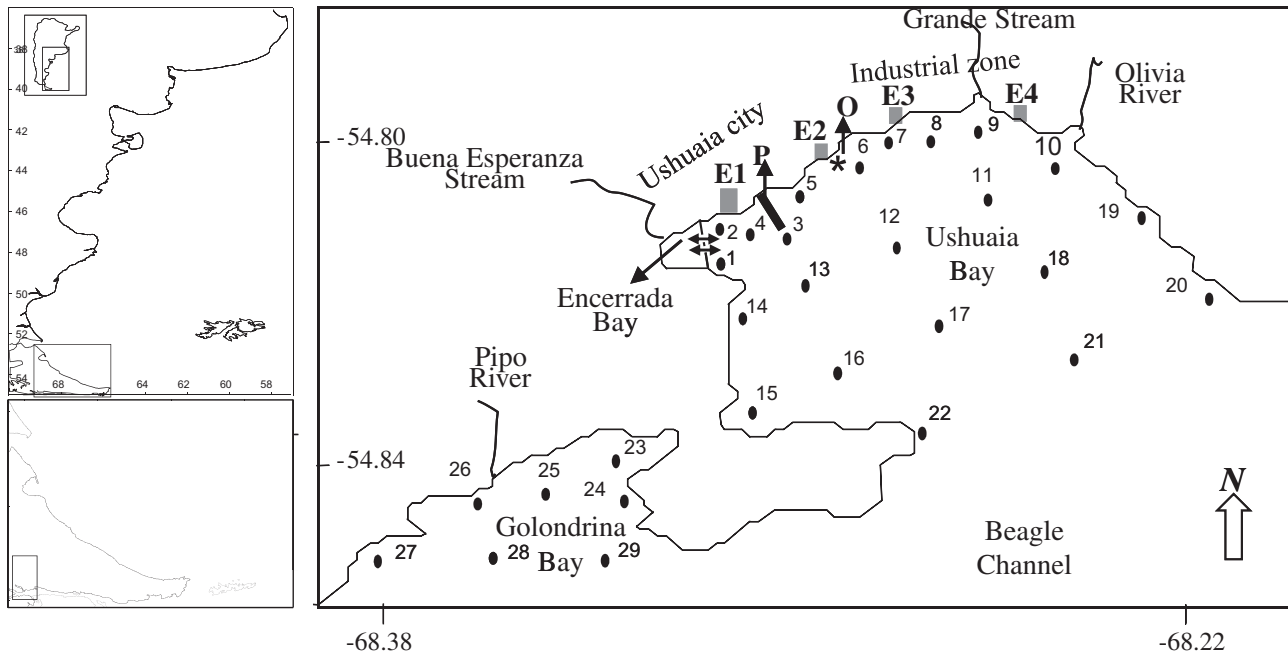


Fig. 1. Sampling stations in Ushuaia and Golondrina Bays. Mean surfaces and depths are $2 \text{ km}^2/50 \text{ m}$ and $4 \text{ km}^2/6 \text{ m}$ respectively. E1 to E4 are combined wastewater outfalls (storm/sewage or storm/sewage/industrial). P: commercial port, O: oil charge. The vents that communicate Encerrada and Ushuaia Bays are indicated for double sense arrows.

and fecal coliforms (Colilert[®] method; Yakub et al., 2002) were only determined in March. Loadings of nutrients, solids, and DBO_5 from each discharge also were estimated for this month, taking into account the corresponding flows. Fluxes from EB to UB were taken from Torres et al. (2009). Surface and bottom seawater was collected with a Van Dorn bottle in 22 stations of UB and 7 stations of GB (Fig. 1) to determine T, DO (Horiba H-10), salinity (S) (PORTASAL 8410 A salinometer), nutrients (Skalar autoanalyzer), chlorophyll-*a* (Chl-*a*), and pheophytin (Pheo) (Strickland and Parsons, 1972). Principal component analysis (PCA) was applied to assess the underlying pattern in the distribution of the nine parameters. The mean and standard deviation of the scores for each PC of each sampling station (4 campaigns, 2 sampling depths) were used as the input variables for cluster analysis (ward method) to form groups of stations with similar water quality.

Coastal sediment samples were collected with a Van-Veen dredge in March 2005. In the laboratory, they were dried at $100 \pm 5 \text{ }^\circ\text{C}$, and coarse particles ($>2 \text{ mm}$) were discarded by sieving. The fine ($<63 \text{ }\mu\text{m}$) and sandy fractions ($>63 \text{ }\mu\text{m}$ and $<2 \text{ mm}$), total organic matter content (TOM), and biochemical components were analyzed in the sieved samples. The content of TOM was obtained by weight loss after calcination ($450 \text{ }^\circ\text{C}$, 4 h) and expressed as total organic carbon (TOC) (Billen, 1978). Proteins (PRT), carbohydrates (CRB), and lipids (LIP) were analyzed according to Lowry et al. (1951), Dubois et al. (1956), and Bligh and Dyer (1959), respectively; they were expressed as carbon equivalents (C-PRT, C-CRB, and C-LIP), assuming the following conversion factors: 0.49, 0.40, and 0.70, respectively (Fabiano et al., 1995). Their sum is referred to as biopolymeric carbon (BPLC) (Fichez, 1991).

Benthic fluxes of nutrients and DO were determined in selected coastal stations (4, 8, 15, and 22) in March 2005 and 2006 using an opaque benthic chamber. *In situ* incubations and flux estimations were performed according to Torres et al. (2009). Three replicates for each station were performed, separated 3 m approximately from each other, to minimize intrastation heterogeneity. Fluxes from the sediment to the overlying water are expressed with positive values and the opposite with negative values. Simultaneously,

10 sediment cores were collected by scuba diving close to the area of the chamber experiment, using acrylic tubes with internal diameter of 4.5 cm and length of 30 cm. The overlying water in each tube was gently siphoned. After redox potential (Eh) measurement with a Pt-electrode (Altronix TPA-1), the first 3 cm strata of the 10 cores were joined to conform with composite samples that were divided to determine TOC, BPLC components, total NH_4^+ (after extraction with KCl 2 N), and phytopigments (chlorophyll-*a* and pheophytin) (Higgins and Thiel, 1988). The sum Chl-*a* + Pheo is referred to as chloroplastic pigment equivalents (CPEs), and the C-PRT/C-CRB ratio is used as a degradability index (Giordani et al., 2002). All sample manipulations were performed in glove box under inert atmosphere (N_2 gas) to avoid changes in redox conditions.

Characterization of water from land. In all discharges, the highest T was measured in March ($10.4\text{--}14.3 \text{ }^\circ\text{C}$) and the lowest in June ($0\text{--}4.9 \text{ }^\circ\text{C}$). In the rivers, conductivities were low and scarcely variable among samplings ($44\text{--}208 \text{ }\mu\text{S/cm}$). The contrary was observed in the effluents, with markedly higher conductivities in March ($1276\text{--}2722 \text{ }\mu\text{S/cm}$) than in December ($87\text{--}330 \text{ }\mu\text{S/cm}$), when the maximum mean rainfall occurred. Dissolved oxygen was higher than 87%. Settleable solids were always below 1 ml/l, and TSS ranged between undetectable and 534 mg/l (Olivia River). Concentrations of BOD_5 were maximum in E1 ($47\text{--}81 \text{ mg/l}$) and below 10 mg/l in the other discharges. Silicate was the prevailing nutrient in the rivers and NH_4^+ in the Grande Stream and effluents. The highest levels of NH_4^+ were measured in March in E1 ($3287 \text{ }\mu\text{M}$) and E3 ($2982 \text{ }\mu\text{M}$) effluents. Nitrate + nitrite concentrations were higher and more variable in effluents ($8.6\text{--}120 \text{ }\mu\text{M}$) than in rivers and Grande Stream ($0.6\text{--}5.5 \text{ }\mu\text{M}$). A similar pattern was observed for (PO_4^{3-}) (effluents and Grande Stream: $1.5\text{--}48.6 \text{ }\mu\text{M}$; rivers: undetectable- $1.1 \text{ }\mu\text{M}$) and (SiO_3^{2-}) (effluents: $28.0\text{--}278.1 \text{ }\mu\text{M}$; rivers and Grande Stream: $4.0\text{--}123.7 \text{ }\mu\text{M}$). The maximums of (NH_4^+), (PO_4^{3-}), BOD_5 , and TSS in E1 were the same order or higher than the levels expected in an untreated weak urban wastewater (Metcalf and Eddy, 1991). On the contrary, all of these parameters were minimal or undetectable in the rivers. Levels of total and fecal coliforms (March data) also were minimum in rivers and maximum in

Table 1

March sampling: Loadings of freshwater, nutrients, BOD₅ and TSS to Ushuaia and Golondrina Bays from Olivia to Pipo rivers, Grande Stream and E1 (the effluent with the highest flow). TSS: total suspended solids.

	Discharge	Flow (m ³ /d)	(NH ₄ ⁺) (mol/d)	(NO ₃ ⁻) (mol/d)	(PO ₄ ³⁻) (mol/d)	(SiO ₃ ²⁻) (mol/d)	BOD ₅ (mg/d)	TSS (mg/d)
Ushuaia Bay	Olivia river	587,520 ^a	1460	649	488	44,627	–	313,736
	Grande Stream	224,640 ^a	13,437	145	750	15,211	–	5841
	Effluent E1	4200 ^b	13,805	195	204	940	206	130
	Total	816,360	28,701	990	1442	60,779	206	319,707
Golondrina Bay	Pipo river	425,088 ^a	6650	496	387	40,495	–	37,408

^a Iturraspe and Schröder (1985).

^b Estimated.

E1. Except for the rivers and E4, both parameters were always higher than European directive requirements (Directive 91/27/EEC). Loadings of nutrients (mol/d) estimated for the March sampling (Table 1) were noticeably highest in UB. Effluent E1 and the Grande Stream were the principal sources of reduced nitrogen and the Olivia River of TSS. The latter would be mainly related to inorganic material, considering the low BOD₅ of this water flow. Torres et al. (2009) have estimated net loadings of (NH₄⁺) and (PO₄³⁻) from EB to UB of 2300 and 160 mol/d, respectively.

Characterization of seawater. Table 2 sums up the 2088 data obtained in seawater (9 parameters × 232 samples). Three components were extracted from PCA (PC1, PC2, and PC3). The loadings of the original variables and scores for each case are presented in Table 3 and Fig. 2, respectively. The highest loadings of T, DO, and Chl-*a* are observed on the positive axis of PC1 opposite (NO₃⁻) and (PO₄³⁻). Salinity (positive sign) is opposite (SiO₃²⁻) on PC2, and (NH₄⁺) and Pheo (both with positive signs) are on PC3. According to these patterns, PC1 was interpreted as the “phytoplanktonic biomass component,” PC2 as the “fresh-marine water component,” and PC3 as the “degraded organic matter component.” Score distributions show that August and June cases are

Table 2

Results for environmental parameters measured in seawater samples (*n* = 232) collected in Ushuaia and Golondrina Bays. SD: standard deviation, MAD: mean absolute deviation, ud: undetectable.

Parameter	Min	Max	Mean	SD	Median	MAD
T (°C)	2.0	14.6	8.2	2.4	7.8	1.8
DO (%)	66	118	93	12	97	7
S	5.000	34.270	29.740	3.620	30.440	0.850
(NO ₃ ⁻) (μM)	ud	15.77	6.98	5.53	6.65	5.46
(NH ₄ ⁺) (μM)	ud	31.44	2.08	4.79	0.90	0.43
(PO ₄ ³⁻) (μM)	0.04	2.92	0.84	0.45	0.90	0.38
(SiO ₃ ²⁻) (μM)	0.47	35.19	6.19	4.67	5.10	2.04
Chl- <i>a</i> (μg/l)	ud	21.00	3.28	4.74	1.12	0.89
Pheo (μg/l)	ud	9.45	0.30	1.13	0.21	0.16

Table 3

Principal components analysis carried out from data in the water of the bays: Factor loadings (after Varimax rotation) for the first three principal components.

	PC1	PC2	PC3
T	0.906200	-0.122953	0.001180
DO	0.634636	0.177781	-0.317650
S	-0.410789	0.856359	-0.019417
(NO ₃ ⁻)	-0.958686	0.058198	-0.015168
(NH ₄ ⁺)	-0.171277	-0.151499	0.813782
(PO ₄ ³⁻)	-0.900025	0.073382	0.295760
(SiO ₃ ²⁻)	-0.185562	-0.915635	0.088762
Chl- <i>a</i>	0.675591	0.268882	0.371058
Pheo	0.005190	-0.008631	0.857410
Expl. Var	3.642054	1.722558	1.731939
Prp. Total	0.404673	0.191395	0.192438

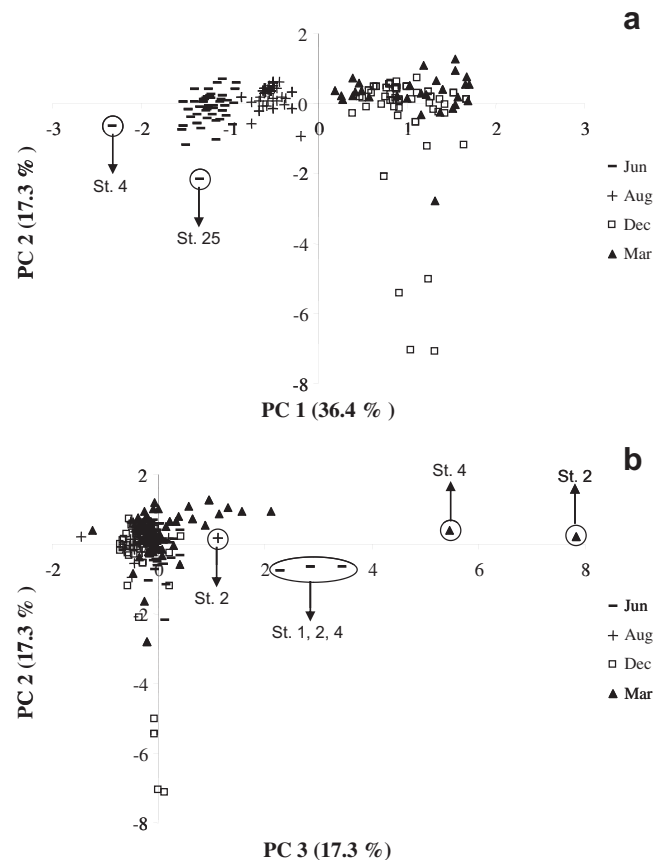


Fig. 2. Principal component analysis. Scores for each sample are plotted in (a) PC1 vs. PC2; and (b) PC2 vs. PC3. St.: station.

positioned toward the negative axis of PC1 (Fig. 2a), whereas positive signs are scored by samples collected in December and in March, when phytoplankton biomass, temperature, and irradiation were higher. Most June and August scores are clustered in their corresponding groups, indicative of spatial homogeneity of water quality. Only five June cases were relatively perturbed: station 4 on negative PC1; station 25 on negative PC2; and stations 1, 2, and 4 on positive PC3 (Fig. 2b). In August, station 2 is again outside the principal group, on positive PC3. Score dispersion was more important in December (mainly on negative PC2) and in March (mainly on positive PC3), suggesting higher spatial heterogeneity (Fig. 2b).

The cluster analysis of means and standard deviations of scores divided the 29 stations in three main groups and two subgroups (Fig. 3): Zone I – sites in the NW of UB (1, 2, 3, and 4), Zone II – sites in the northern coast of UB (5, 6, 7, and 8), and Zone III – the other sites. Two subgroups were included in the latter, distinguishing sites near river discharges (Zone III-R: stations 10 and 11 in front

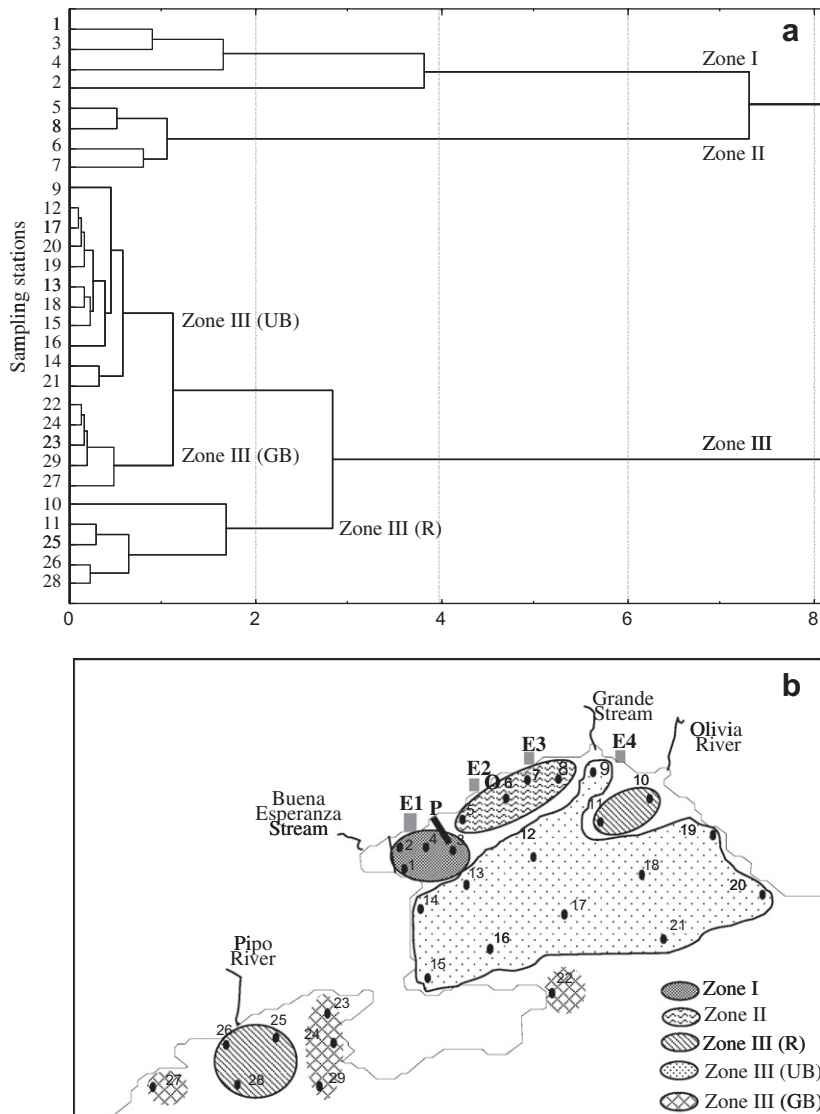


Fig. 3. Zones of different water quality in Ushuaia and Golondrina Bays: (a) Cluster analysis for the 29 cases (ward's method, Euclidean distances); and (b) Localization of the zones within the bays.

of the Olivia River and stations 25, 26, and 28 in front of the Pipo River), from the others. Within the others, those from UB (Zone III-UB) were separated from those from GB (Zone III-GB); station 9, located in front of the Grande Stream, was included in Zone III (UB). Interestingly, station 22 (located at extreme south of the UB) was included in Zone III (GB), and hence, it would be the less perturbed station within UB.

Characterization of coastal sediments. Texture and organic content was assessed in sediments collected with dredge in the five water-quality zones: station 4 (Zone I); station 8 (Zone II); stations 10, 25, and 26 (Zone III-R); stations 15, 19, and 20 (Zone III-UB); and stations 22, 23, 24, 27, and 29 (Zone III-GB). The percentage of discarded coarse particles varied from less than 1 (station 4) to 35 (stations 23 and 24). Ranges of fine fraction and TOC contents in the sieved samples were 7–86% and 0.38–4.4%, respectively, and a positive correlation was observed between both parameters ($r = 0.63$, $p < 0.05$). The BPLC varied from 1.5 to 15.7 mg/g; it was protein impoverished in all samples and lipid enriched near Pipo River discharge (stations 25–27) (Fig. 4). C-PRT/C-CRB ratios (index of degraded BPLC) were lower than one in all samples. Similar to TOC, fine particles distribution seems to control BPLC spatial pat-

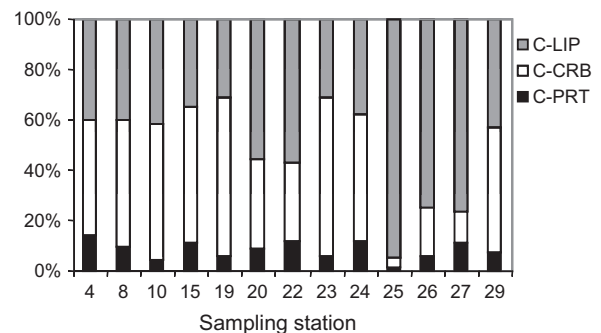


Fig. 4. Percentages of biochemical components in the biopolymeric carbon (BPLC).

terns (Fig. 5), except for sites 4, 8, and 15 (Zones I, II, and III UB, respectively), where concentrations were higher than expected.

Sediment–water exchanges. Benthic fluxes in stations 4, 8, 15, and 22 (the last selected as control) are shown in Fig. 6. In all cases, (NH_4^+) was released to the water, and DO was consumed by the sediment, with the highest values in station 4, followed by stations

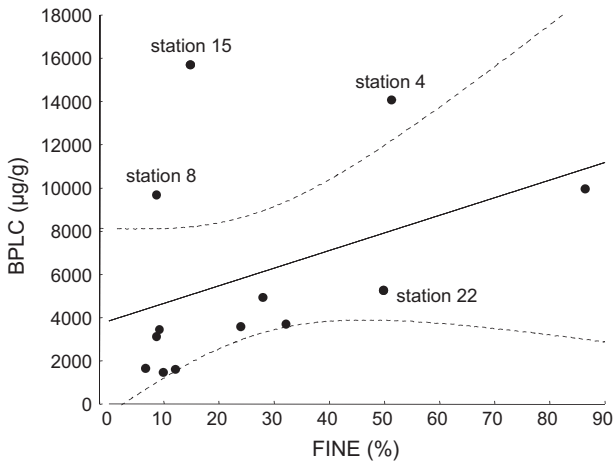


Fig. 5. Association between biopolymeric carbon (BPLC) and content of fine particles (FIN) in coastal sediments from Ushuaia and Golondrina Bays (Pearson coefficient $r = 0.40$, $p < 0.05$).

15, 8, and 22. Fluxes of (NO_3^-) were negative in station 4, undetectable in station 15 (2006) and positive in the other cases. Fluxes of (PO_4^{3-}) were only measurable in station 4, where it was released to the water column.

Redox potential in site 4 was below -300 mV, with only a very thin clear brownish surface layer, denoting high oxygen consumption in surface sediment. In station 15, the Eh ranged between oxidized (-95 mV in 2005) and reduced conditions (-200 mV in

2006), whereas in stations 8 (-20 mV; -10 mV) and 22 > 100 mV), results indicated the presence of oxidized species.

Concentrations of total ammonium, phytopigments, C-PRT, and C-CRB in most surficial sediments (0–3 cm) are shown in Table 4. The highest intrastation heterogeneity was observed in station 15, where variation coefficients (VCs) ($n = 3$ substations) for most parameters exceeded 40%. In the other stations, VCs were always below 25%. Stations 4 (both samplings) and 15 (second sampling) presented the highest values of chl *a* and Pheo, which were comparable to those reported in systems classified as highly productive (Dell'Anno et al., 2002). Most negative redox conditions also were observed in these cases. The maximum ratio of Pheo to Chl-*a* was registered in station 4, in agreement with the observations in the water column (Fig. 2b). On the opposite, the control site showed the lowest ratio (< 1). Higher Pheo than Chl-*a* is generally related to microbial degradation of dead phytoplankton, though factors affecting photosynthetic potential (such as toxic contaminants) also should be considered (Dell'Anno et al., 2002). This might be the case in Zones I and II, where the presence of aliphatic hydrocarbons and heavy metals related to ports and industries has already been reported (Amin et al., 1996; Esteves et al., 2006; Lozada et al., 2008).

The high correlation observed between CPE and BPLC concentrations ($r = 0.97$, $p < 0.05$) suggests that the autotrophic component would be the main source of C and N in the BPLC which, on the other hand, may be ranked in different trophic levels (Dell'Anno et al., 2002): eutrophic–hypertrophic (station 4); mesotrophic–eutrophic (station 15), mesooligotrophic (station 8), and oligotrophic (station 22). The different ratios C-PRT/C-CRB between

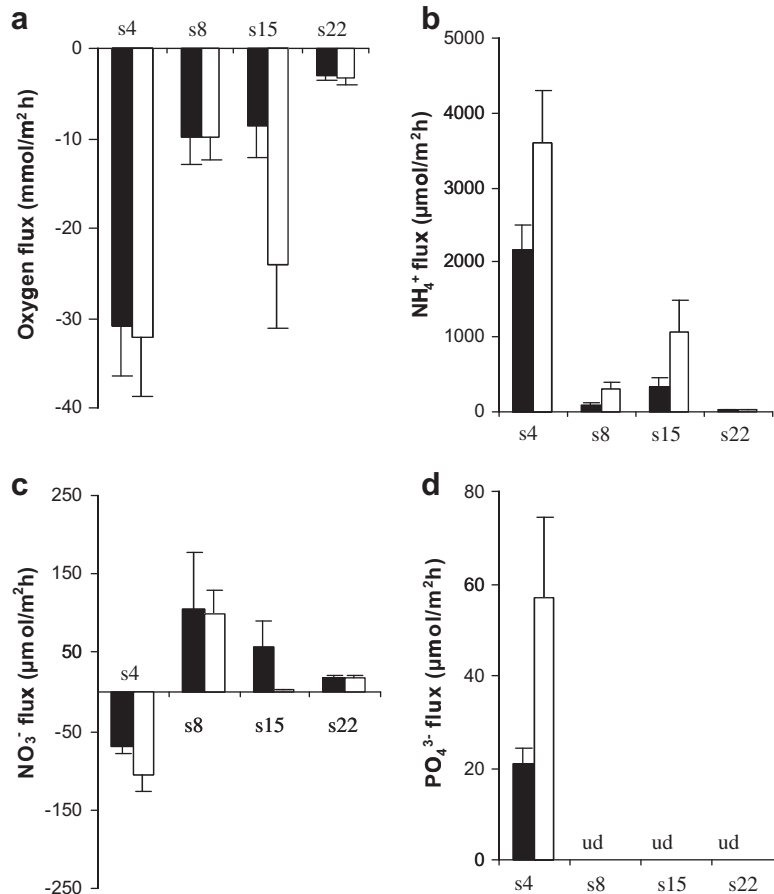


Fig. 6. Benthic fluxes of DO (a) (NH_4^+); (b) (NO_3^-); (c) (PO_4^{3-}); and (d) in stations 4 (s4), 8 (s8), 15 (s15), and 22 (s22). Filled bars: 2005 sampling; empty bars: 2006 sampling. Means from 3 experiences and 1 standard deviation. ud: undetectable.

Table 4
Mean concentrations ($n = 3$ substations) of C-PRT, C-CRB, phytopigments and total ammonium concentration in surficial sediments (0–3 cm). Degradation indexes (C-PRT/C-CRB) and ratios Pheo/Chl-*a* are also shown.

Station_year	Chl- <i>a</i> ($\mu\text{g/g}$)	Pheo ($\mu\text{g/g}$)	Pheo/Chl- <i>a</i>	C-PRT ($\mu\text{g/g}$)	C-CRB ($\mu\text{g/g}$)	C-PRT/C-CRB	Total (NH_4^+) (ng/g)
4_2005	66.4	143.9	2.2	10854	6186	1.8	1105
4_2006	38.1	64.2	1.7	2062	6663	0.3	3097
8_2005	7.7	10.3	1.3	1009	909	1.1	114
8_2006	4.4	5.7	1.3	150	320	0.5	161
15_2005	10.8	11.1	1.0	1198	775	1.5	177
15_2006	84.8	55.2	0.7	1659	5578	0.3	346
22_2005	10.0	5.5	0.6	45	39	1.2	78
22_2006	7.3	4.4	0.6	30	107	0.3	112

samples collected in 2006 (<1) and 2005 (>1) suggest higher biodegradation of BPLC in the former, probably because of higher water temperature (9.9 ± 0.4 and 5.6 ± 0.4 , respectively). In agreement, higher total (NH_4^+) concentrations were recorded in 2006 compared to 2005.

Some association was observed between sediment trophic state and spatial patterns of fluxes. Maximum (NH_4^+) release and DO demand were measured in sediments with the highest trophic level (station 4). Both of them were similar to the maximums measured in the highly eutrophic EB (Torres et al., 2009) and much greater than those measured in worldwide marine coastal environments (e.g., Santschi et al., 1990; Conley et al., 1997; Clavero et al., 2000; Eyre and Ferguson, 2002; Niencheski and Jahnke, 2002). The simultaneous consumption of (NO_3^-) and release of (PO_4^{3-}) that was observed in this area is in accordance with the anaerobic conditions, where (NO_3^-) is required as electron acceptor when DO is exhausted, and (PO_4^{3-}) is desorbed because of dissolution of iron hydroxide precipitates (Graca et al., 2006). In meso-oligotrophic to oligotrophic sediments, (NH_4^+) and DO fluxes were lower than those in station 4 and within the range of moderate to low polluted or unpolluted environments. Nitrate release in these cases was an index of nitrification within the sediment (Niencheski and Jahnke, 2002; Graca et al., 2006).

In summary, the results of this study show that Zone I (the NW area of UB) is the most impaired by organic matter, nutrient enrichment, and oxygen demand. The sector supports not only the pressure of urban water incoming from EB and E1 effluent, but also of the port activities. This effluent is the only one introducing a relatively important amount of BOD_5 to the whole Bay, and its loading of inorganic nitrogen and phosphorus is similar to that of Grande Stream, even when its flow is 2 orders of magnitude lower. Considering the area of Zone I ($\sim 1 \text{ km}^2$) and the estimated mean inputs of (NH_4^+) and (PO_4^{3-}) from EB (2300 and 160 mol/d, respectively), effluent (13805 and 204 mol/d, respectively), and the sediment (69024 and 960 mol/d, respectively), it is clear that loadings from the sediment exceeds the total loading from allochthonous sources (above 4 and 2.5 times, respectively). It is known that benthic nutrients fluxes to the water column may be reduced by the presence of microphytobenthos (MPB) (Hochard et al., 2010), which is not taken into account when using opaque chambers like in this study. However, although Zone I is a shallow environment, MPB primary production is not expected to be significant, considering light penetration (turbidity >90 NTU, Giarratano, per comm.) and prevailing mobile sediments resulting from wind action. As a consequence, related organic matter in these sediments would mainly derive from photosynthesis by phytoplankton and seaweeds, and recycled nutrients would be reintroduced in the water column. While (NH_4^+) release was the same order of magnitude as fluxes reported for hyper-eutrophic shrimp ponds (Sun et al., 2000; Burford and Longmore, 2001), the oxygen demand was 3–10 times higher than those commonly measured in such ponds. The principal sources that contribute to benthic oxygen consumption in this station are *in situ* carbon production (in water and benthos), exter-

nal loadings from EB and effluent E1 and bacterial metabolism. Similar OD fluxes were found in 2005 and 2006 despite a large decline in protein-carbon (C-PRT), but considering that sedimentary TOC level was the same order in both analyzed periods (4%), the presence of other kind of OM should not be discarded. In that sense, biodegradation of hydrocarbons by the indigenous bacterial populations could contribute to the sediment oxygen demand (Lozada et al., 2008). It is concluded that sediment–water interaction may be the main factor controlling metabolic processes during warm periods in this urban impacted high latitude system.

Acknowledgements

We wish to thank Mr. H. Ocariz, Dr. L. Comoglio, Mr. R. Samanigo, Dr. E. Giarratano and Lic. A. Nizovoy for their help during sampling. We are also grateful to Lic. E. Hasan and Lic. M. Faleschini for technical assistance in fieldwork and laboratory analyses and Msc M. Solís for laboratory support. We are also grateful to Lic. M. Comendatore for her comments on the manuscript. This research was supported by Agencia Nacional de Promoción Científica y Tecnológica (PICT-REDES 2002 N°090); FMAN/BIRF N° 28.385, B-CB-05 GEF Subproject; ARG 02/G31 UNDP-GEF Project from Fundación Patagonia Natural.

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