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# Hydrocarbon levels in sediments and bivalve mollusks from Bahía Nueva (Patagonia, Argentina): An assessment of probable origin and bioaccumulation factors

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Effects of crude oil and its derived products on marine ecosystems are well known. Both aliphatic and aromatic fractions possess toxic properties that can affect marine organisms. Particularly, sixteen unsubstituted PAHs have been recognized as priority pollutants for the World Health Organization, the Economic European Community, and the USA Environmental Protection Agency (Hellow et al., 1994). Many PAHs have been found to be carcinogenic in mammals and, consequently, there is concern over the mobilization of PAHs and their metabolites into marine food chains via bioaccumulation and trophic transfer from benthic fauna (Ferguson and Chandler, 1998). Determination of PAHs in marine organism tissues is necessary because of their carcinogenic and mutagenic properties (Noreña-Barroso et al., 1999). Mussels have been considered as pollution sentinels by many authors (i.e. Hellow et al., 2002) because of their bioaccumulation capacity, and the National Status and Trends Program (NOAA, 1993) recommended them as a foreground matrix to environment monitoring. Sediments are also ideal matrices for chemical analysis, as they are the final fate for a variety of lipophilic pollutants (Hellow et al., 2002), and reflect long-term deposition. Coastal environments of Patagonia, Argentina, are threatened by petroleum residues resulting from port activities as well as crude oil transport. Studies of intertidal sediments along this coast showed anthropogenic hydrocarbon pollution in several areas (Commendatore et al., 2000; Esteves et al., 2006; Commendatore and Esteves, 2007). However, there is scarce information about hydrocarbon levels at many sites of the Patagonian coast due to its large extension and limited resources to conduct evaluations (~3000 Km). Bahía Nueva (BN) (42.75°S, 65.00°W Fig. 1) is a bay located in western Golfo Nuevo, at southern limit of Peninsula Valdés, UNESCO World Heritage Site. It has an area of 58 km<sup>2</sup> and a mean depth of 30 m. Water temperature varies from 10 °C in winter to 17.5 °C in summer. Puerto Madryn city (~80,000 inhabitants) located in this bay has tourism, fisheries and aluminum production as the most important economic activities. The city has two ports with an important maritime traffic. In addition, a high population growth rate and an increase in tourism during the last decade have augmented domestic sewage and groundwater drainage. Due to the lack of a complete sewage system, it is also very likely that polluted groundwater reaches the coast (Gil and Esteves, 2000). The main wastewater discharges into the Bay derive from fishery plant effluents; although the aluminum plant does not produce liquid effluents, pollutants likely to enter the sea through atmospheric deposition. These activities are potential sources of anthropogenic hydrocarbons which could affect economic resources and marine biodiversity. Water circulation inside the Bay flows northwards (Esteves et al., 1997) and is less than 2.5 cm s<sup>-1</sup>, depending mainly on the wind (Lanfredi, 1974; Krepper and Rivas, 1979; Rivas, 1983).

Twelve and eight stations to obtain sediments and organisms, respectively, were sampled in areas close to petroleum hydrocarbon sources (ports, stations 7 and 10), groundwater drainage areas (stations 3–5), fishery effluents (station 11), previous urban sew-

age outlet (station 9), sites not directly affected by human activities (stations 6 and 8), and the bay's northern and southern limits (stations 1, 2 and 12) (Fig. 1).

*Aulacomya atra atra* (mussel) and *Tellina petitiana* (clam) were obtained by scuba diving. They were selected because of their abundance in BN, sampling facilities, and the existence of previous information about their biology. *A. atra atra* is mainly a filter and suspension-feeder mussel, while, *T. petitiana* is mainly a suspension and detritus-feeder clam. Although they are not commercially exploited inside BN, *A. atra atra* is regularly consumed by the local population. To relate the relative hydrocarbon organism uptake from contaminated sediment particles through ingestion (dietary) and the hydrocarbon concentration found in sediments, organisms and sediments were sampled as close as was possible in the same area. Size range was 5–7 and 2–4 cm for mussels and clams, respectively. Organisms were washed, measured, and weighed; their tissues were removed, pooled, homogenized, and frozen at –20 °C. Each composite sample had 30 and 200 individuals for mussels and clams, respectively. Sub-samples were taken to determine water content, ashes, total lipids, and hydrocarbon concentration. A physiologic condition index (CI) (Wilde, 1975), that relates soft parts weight and valve length, was applied to evaluate mussel nutritional state. The value was compared with those obtained for the same species in BN by De Vido de Mattio (1983). Total lipid content (TL) was determined gravimetrically according to GERG, 2001. Water and ash contents were determined by drying tissue at 40 °C to constant weight and then calcining them at 550 °C (4 h).

Superficial sediments (0–3 cm) were sampled in the subtidal area using plexiglass tubes of 25 cm length and 4.5 cm internal diameter (7 tubes each station), and were homogenized in a single composite sample that was frozen at –20 °C. Sub-samples for determination of water content, ignition loss, grain size, and hydrocarbon analysis were taken. Redox potential (RP) was measured *in situ* with a platine electrode connected to a thermo pH meter. Altronix granulometry was determined by dry sieving in an automatic equipment using 2 mm and 63 µm mesh sieves (fine <63 µm, sand >63 µm and <2 mm, and gravel >2 mm). Dried sediments (105 °C) were calcined (450 °C, 4 h) to determine ignition loss, and it was assumed that ignition loss was related closely to sediment OM content. Hydrocarbon analysis was carried out according to UNESCO (1982) and Gold et al. (1987). Briefly, the wet matrix (sediment or organism tissue) was digested under reflux with methanol and potassium hydroxide. Non-saponifiable fraction was extracted with *n*-hexane, the organic phase was dried with anhydrous sodium sulphate, and evaporated to 0.2 ml (N<sub>2</sub>). Extract was seeded in alumina and alumina–silica gel columns for sediments and organisms, respectively, to carry out sample clean-up and hydrocarbon isolation. Fractions were obtained by elution with *n*-hexane (aliphatics, F1) and with *n*-hexane-dichloromethane (aromatics, F2). Both fractions were measured by High Resolution Gas Chromatography (HRGC). In F1, concentrations of Resolved Aliphatics (RALi), Unresolved Complex Mixture (UCM), Total Aliphatics (TALI, as the sum of RALi + UCM), and Pristane (Pr) and Phytane (Ph) isoprenoids, were measured. In F2, unsubstituted PAHs were determined, while substituted PAHs such as

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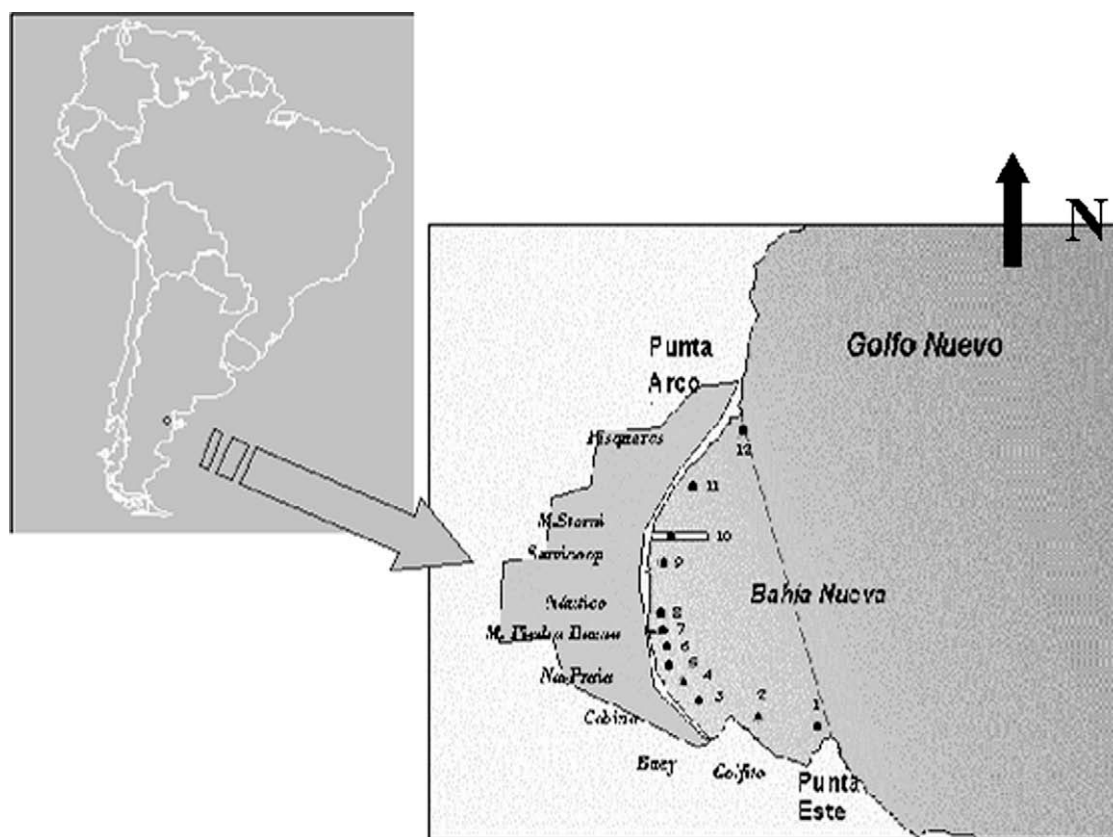
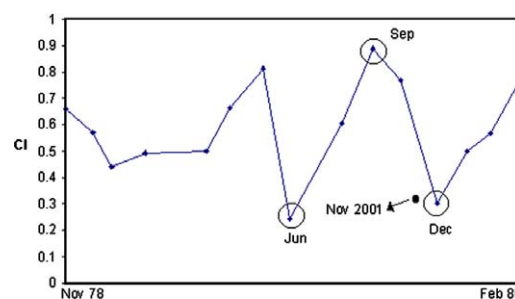


Fig. 1. Study area.

methyl phenanthrenes (MPs) were only identified considering the retention time (RT) obtained in previous chromatographic profiles under the same conditions. HRGC analysis was conducted as described in Commendatore et al. (2000). Hydrocarbon identification and quantification were made based on compound RT and response factors of an external standard mix 99.9% pure. Detection limit (LOD) in sediments was 0.014  $\mu\text{g/g}$  for TAli and 0.010  $\mu\text{g/g}$  for individual PAHs, while in organisms LOD was 0.152  $\mu\text{g/g}$  and 0.03  $\mu\text{g/g}$ , respectively ( $n = 7$ ). Data uptake was made with chromatographic Ezchrom Software and concentrations were expressed as  $\mu\text{g/g}$  of dry weight (dw). *n*-Alkane indices applied were: Major hydrocarbon (MH); Low/high molecular weight (LMW/HMW); *n*-C16, Carbon preference index (CPI); and Even/odd hydrocarbons ratio (E/O). In addition, pristane/phytane ratio (Pr/Ph), the sum of resolved aliphatic/unresolved complex mixture (RAli/UCM), and *n*-C17/Pr and *n*-C18/Ph relationships were calculated. Compositional parameters as *n*-alkanes homologous series and UCM presence were used to help in hydrocarbons origin assessment. Indices definition and values they can take according to hydrocarbons origin have been described by many authors (i.e. Clark and Finley, 1973; Broman et al., 1987; Colombo et al., 1989; Gearing et al., 1976; Boehm and Requejo, 1986; Volkman et al., 1992; Lecaros et al., 1991), and were applied in this study as explained in Commendatore et al. (2000). Bioaccumulation factors (BAFs) were calculated as the ratio between the concentration of a target compound in the organism tissue and its concentration in the sediment. Biota-Sediment Bioaccumulation Factors (BSBFs) were determined according to Baumard et al., 1999. OC was calculated from OM values according to Billen (1978).

From data on *A. atra atra* soft part weight and valve length reported by De Vido de Mattio (1983), corresponding CI values were calculated; these varied throughout the year as shown in Fig. 2. The

Fig. 2. Condition index for *A. atra atra*.

highest value (0.88) was found in September and lower values were found in June and December (0.24 and 0.30, respectively). In our study, the CI value found in November 2001 was  $0.32 \pm 0.04$  ( $n = 6$ ). TL content was close to 1% for mussels and less than or close to 0.65% for clams (Table 1).

Sediment granulometry was variable with sand as the predominant fraction (Table 2). A positive correlation between OM and fine material ( $r^2 = 0.72$ ,  $p < 0.05$ ,  $n = 12$ ) was observed. High amounts of fine material, high values of OM, and low values of RP were found at stations 3, 5, and 7.

TAli concentrations ranged between 0.03 and 9.13  $\mu\text{g/g}$  (Table 3). In F1 chromatographic profiles, a peak suit at *n*-C20 and *n*-C21 RT was visible in addition to resolved *n*-alkanes and Pr and Ph isoprenoids (Fig. 3). UCM was unimodal in shape and had an important contribution to TAli concentration (Table 3). At stations 3 and 5, relatively high TAli values (9.1 and 4.3  $\mu\text{g/g}$ ) could be associated to fine particles content and higher OM values. These stations are located in an area where groundwater drains to the sea

**Table 1**  
Organisms characteristic

Station	Size (mm)	Total W (g)	Soft parts (g)	Hu (%)	Ashes (%)	Lipids (%)
Mu1	63.38 (±4.85)	11.75 (±2.65)	3.70 (±0.83)	82.70	14.90	0.94 (±0.002)
Mu2	62.61 (±5.90)	15.32 (±4.48)	4.49 (±1.08)	82.30	16.23	1.01 (±0.002)
Cl4	27.11 (±3.03)	0.60 (±0.21)	0.29 (±0.18)	71.82	47.69	0.65 (±0.003)
Cl6	27.85 (±1.31)	0.70 (±0.14)	0.33 (±0.10)	75.69	35.85	0.66 (±0.003)
Mu7	59.17 (±5.16)	11.32 (±3.93)	3.63 (±1.12)	81.96	15.90	0.90 (±0.003)
Mu10	64.55 (±4.53)	14.49 (±3.13)	3.13 (±0.94)	80.44	14.65	1.11 (±0.002)
Mu11	58.12 (±5.61)	10.27 (±2.31)	3.38 (±0.74)	82.04	16.33	0.92 (±0.004)
Mu12	58.05 (±4.66)	10.64 (±3.06)	3.84 (±1.03)	81.00	15.00	1.02 (±0.002)

**Table 2**  
Sediments characteristic

Station	Depth (m)	Granulometry (%)			Hu (%)	OM (%)	OC (%)	Eh (mV)
		Gravel	Sand	Fine				
1 PE	8	29.43	70.19	0.38	18.77	1.06	0.40	138/114
2 G	5	21.27	77.28	1.46	17.67	0.76	0.27	129/–120
3 B	6.5	0	65.36	34.64	35.18	2.33	0.97	–113/–318
4 CS	4.5	0	92.53	7.47	23.42	1.07	0.41	
5 NP	10	0.25	67.14	32.60	31.88	1.95	0.80	–160/–396
6	MPBT	3.3	0.13	87.57	12.30	26.39	1.44	0.57
7 MPB	6	2.56	61.65	35.79	36.77	2.90	1.23	–97/–362
8 N	6	20.03	69.58	10.39	22.43	1.04	0.39	–30/–273
9 S	6	16.86	82.21	0.93	19.35	0.77	0.27	19/–28
10 MS	8	3.18	92.84	3.99	24.13	1.31	0.52	–6/–174
11 Pe	6.5	16.77	81.96	1.53	19.51	0.95	0.35	–227/–237
12 PA	11.5	27.74	70.56	1.70	22.38	1.88	0.77	54/32

**Table 3**  
Sediment hydrocarbon concentrations

Station	Hydrocarbon concentration (µg/g)			Total PAHs
	Resolved alip	UCM	Total alip	
1 PE	0.16	0.09	0.24	0.02
2 G	1.10	0.45	0.55	0.01
3 B	0.60	8.53	9.13	0.18
4 CS	0.02	0.01	0.03	0.05
5 NP	0.31	3.97	4.28	1.05
6 MPBT	0.35	0.94	1.29	0.31
7 MPB	0.20	1.23	1.43	2.50
8 N	0.10	0.54	0.64	0.15
9 S	0.11	0.64	0.75	0.11
10 MS	0.76	5.77	6.52	7.69
11 Pe	0.19	1.10	1.28	0.12
12 PA	0.32	1.64	1.96	0.03

(Gil, 2001). At Storni port (10), where OM was relatively low (1.3%) and sediment grain size corresponded mainly to sand (93%), Tali concentration (6.5 µg/g) can be associated to port activities. The higher PAH concentrations were detected in both ports: About 7.7 µg/g (Storni, 10) and 2.5 µg/g (Piedra Buena, 7) (Table 3). In most of the stations, between eight and fifteen of the sixteen PAHs EPA priority pollutants were identified and quantified. MPs were identified at stations 3–5, and at ports.

Tali hydrocarbons concentration in organisms ranged between 5.2 and 99.1 µg/g (Table 4). The higher values were found in mussels at both ports: Piedra Buena (Mu7, 99.1 µg/g) and Storni (Mu10,

93.0 µg/g). Except for station Mu2, the main contribution to Tali concentrations was due to UCM (between 76% and 89%) (Table 4). In mussel samples, a compound suit was resolved in the same RT than *n*-C21, while in clam samples the suit was less pronounced and of similar magnitude than in sediments (Fig. 3). As in sediments, it was difficult to identify *n*-C21. Higher PAH concentrations were 2.0 µg/g (Mu7, Piedra Buena port), and 1.8 µg/g (Mu11, fishery effluents). Values were also relatively high at Cl6 (near Piedra Buena port) and Mu10 (Storni port). The other stations presented values <1 µg/g (Table 4). MPs were observed only in clam samples.

In sediments of stations 3–5, 8 and 10–12 where the MH was odd (i.e. *n*-C17), the relation even/odd showed values lower than 1 (Table 5), indicating a biogenic hydrocarbon input from macroalgae and/or phytoplankton. LMW/HMW values higher than 1 for each of the stations indicate a dominance of LMW compounds (<*n*-C20). CPI and *n*-C16 values indicated anthropogenic inputs for all samples. A variable Pr/Ph relation showed the highest value (3.13) in Punta Arco (12) suggesting a biogenic contribution at this station. Relatively low values of *n*-C17/Pr and *n*-C18/Ph in both ports could be indicating biodegradation processes. RAli/UCM presented lower values in stations 3 and 5, where high UCM concentrations could be associated to OM content and fine particles present in these sediments. *n*-Alkanes homologous series and UCM, both detected in all stations, denote an anthropogenic hydrocarbon input.

In both mollusks, the chromatographic profiles of aliphatic fraction presented *n*-alkane homologous series, Pr and Ph isoprenoids, and UCM which contributed to Tali concentrations. Even/odd relationship was always greater than 1 (ranging from 1.21 in mussels collected at Storni port to 8.85 in clams collected at Piedra Buena port). LMW/HMW index and MH (*n*-C16, *n*-C26, and *n*-C30) indicated the presence of light and heavy compounds (Table 6). These indices, plus CPI and *n*-C16, could be evidence of anthropogenic hydrocarbon uptake by the organisms. Pr/Ph ratio had values close to 1 for bivalves in port areas (Cl4, Mu7, Mu10). Higher values were found in organisms further away from these areas, where pristane predominance was a sign of biogenic input. PAHs BAFs ranged between 0.16 (station 10, Storni port) and 106.21 (station 2, Golfo), while BSAFs for the same stations were between 0.01 and 5.

Relatively high values of Tali hydrocarbons in some stations close to the city's central sector can be associated to OM content and fine particles present in sediments. Many authors have found a relationship between hydrocarbon distribution in sediments and fine material (i.e. Phillips et al., 1987; Boehm and Requejo, 1986). In these stations, UCM greatly contributed to Tali concentrations. OM could be associated to the presence of microalgae and/or to a contribution of groundwater drainage that collects part of domestic effluents. Hellow et al. (2002) found that TOC distribution in sediments clearly indicated the importance of sewage inputs. In addition, negative values of RP (<–100 mV) were recorded in these stations. Fenchel (1969) considered that values between –110 and 400 mV corresponded to oxygenated sediments, and between –110 and –300 mV to anoxic sediments.

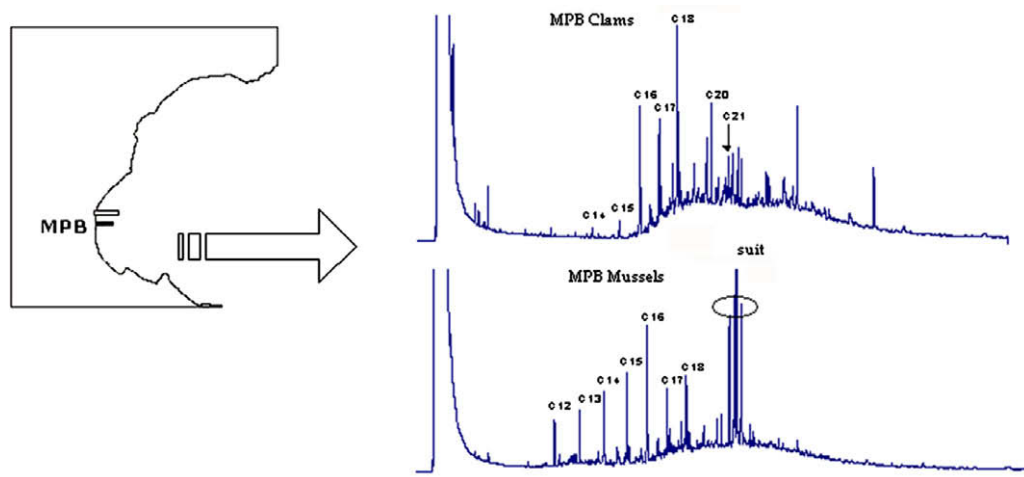


Fig. 3. Chromatography profiles of Piedra Buena pier's mussels and clams.

Table 4

Organism hydrocarbon concentrations

Station	Hydrocarbon concentration ( $\mu\text{g/g}$ )			Total PAHs
	Resolved alip	UCM	Total alip	
Mu1	8.14	25.25	33.39	0.78
Mu2	2.96	2.23	5.19	0.96
Cl4	6.39	33.88	40.27	0.86
Cl6	8.71	56.12	64.83	1.27
Mu7	10.57	88.49	99.06	2.01
Mu10	14.31	78.72	93.03	1.22
Mu11	5.18	35.54	40.72	1.82
Mu12	3.85	19.83	24.40	0.81

Anaerobiosis could affect hydrocarbon biodegradation processes. Higher petrogenic hydrocarbon concentrations could be associated with their particular persistence in anaerobiosis or in low oxygen concentrations (Muniz et al., 2002). At Storni port, hydrocarbon concentration was relatively high, although sediments were coarse and the OM value was low; this fact suggests hydrocarbon associ-

ation with source proximity and not with sediment granulometry. Values were lower at other stations, including Piedra Buena port, where OM and fine material were elevated. In this port, subtidal sediments sampled at higher depth than in the present study showed values between 2.98 and 30.06  $\mu\text{g/g}$  (Commendatore and Esteves, unpublished data). At chromatographic RT corresponding to *n*-C21, a peak suit presence was observed. Mille et al. (1992) reported a series of three compounds that elute just before *n*-C21, with RT and mass spectrums indicative of C25 branched alkenes and C21 monoenes. According to Wakeham (1996), most sediments contain significant but variable amounts of branched isoprenoids with a carbon number identical to C25 that could derive from diatoms. Previous studies showed that diatoms constitute the main component (over 80%) of the phytoplankton in the bay (Esteves et al., 1997).

PAHs showed the highest concentrations at ports and were higher than Tali. This fact could be the result of a greater PAHs accumulation due to port activities and/or differential aliphatic

Table 5

Sediment origin indices

Station	MH	Even/odd	LMW/HMW	PCI	<i>n</i> -C16	Pr/Ph	<i>n</i> -C17/Pr	<i>n</i> -C18/Ph	RA/UCM
1 PE	<i>n</i> -C16	1.97	4.16	1.25	5.12	0.63	5.30	4.41	1.79
2 G	<i>n</i> -C18	1.18	3.98	0.59	9.30	0.43	3.42	2.34	0.22
3 B	<i>n</i> -C17	0.87	3.41	1.28	8.81	1.20	1.95	1.45	0.07
4 CS	<i>n</i> -C17	0.49	1.92		7.81	0.89	3.33		2.52
5 NP	<i>n</i> -C17	0.75	2.34	2.42	10.20	0.76	3.80	2.14	0.08
6 MPBT	<i>n</i> -C16	1.12	4.00		7.06	0.92	2.42	2.02	0.37
7 MPB	<i>n</i> -C18/C26	1.47	1.11		17.48	1.39	0.70	1.76	0.16
8 N	<i>n</i> -C17/C19	0.88	3.39	0.78	10.76	1.42	1.66	1.44	0.19
9 S	<i>n</i> -C28	1.31	1.15	0.93	20.70	0.38	3.69	1.41	0.16
10 MS	<i>n</i> -C17	0.86	1.70	1.23	10.15	1.73	1.46	1.22	0.13
11 Pe	<i>n</i> -C11/C17	0.58	4.99	1.30	32.03	1.60	2.20	1.37	0.17
12 PA	<i>n</i> -C17	0.44	3.69	0.78	20.40	3.13	4.33	2.29	0.19

Table 6

Organism origin indices

Station	MH	Even/odd	LMW/HMW	PCI	<i>n</i> -C16	Pr/Ph	<i>n</i> -C17/Pr	<i>n</i> -C18/Ph	RA/UCM
Mu1	<i>n</i> -C16	1.86	4.24	0.57	6.18	1.29	3.33	6.16	0.32
Mu2	<i>n</i> -C16	2.38	4.51		5.61	1.72	2.12	3.18	1.33
Cl4	<i>n</i> -C16/C30	3.96	0.80		10.20	0.98	2.00	3.32	0.19
Cl6	<i>n</i> -C30	8.85	0.08	0.11	12.17	0.63	3.47	4.22	0.16
Mu7	<i>n</i> -C16	1.42	4.47	1.25	5.96	0.96	2.46	2.52	0.12
Mu10	<i>n</i> -C26/C30	1.21	0.46	0.28	10.61	0.18	1.73	3.32	0.18
Mu11	<i>n</i> -C26/C30	2.60	0.69		11.09	1.24	2.21	1.65	0.15
Mu12	<i>n</i> -C16	1.44	9.80		4.33	1.73	1.75	2.87	0.18

hydrocarbon degradation processes. Preferential degradation of *n*-alkanes in depth was demonstrated by Colombo et al. (1989) in samples taken at the Río de la Plata estuary through the assessment of *n*-alkanes/PAHs relationship from the superficial water column to the bottom sediments. PAHs concentrations were lower for the stations located away from ports.

Evaluation indices values and other indicators such as the detection of *n*-alkane homologous series, the UCM contribution, and phytane presence, can be associated with petroleum input signs in analyzed sediments. Relatively low values of *n*-C17/Pr and *n*-C18/Ph relationships at port stations could indicate some degree of hydrocarbon degradation, but further studies are needed to evaluate such processes. In some stations (such as 3–5, 8 and 10–12), presence of LMW odd *n*-alkanes suggests a marine biogenic input (macroalgae and/or phytoplankton). At Punta Arco station (12), greater density of macroalgae due to south–north water circulation inside the Bay (Esteves et al., 1997), could explain biogenic hydrocarbon occurrence. *Gracilaria* sp., *Ulva* spp. and *Undaria pinnatifida* were observed at different stations.

Despite of the predominant anthropogenic input on bay sediments, aliphatic hydrocarbon concentrations were lower than 10 µg/g, which is a value considered by UNEP (1992) as a reference to non polluted sediments. However, moderate PAH concentrations and identification of MPs at stations 3–5, and ports, indicate an anthropogenic input and, thus, measures should be taken to avoid further impacts to the bay and nearby environments. Comparing PAHs values in bay sediments with those found in other regions (Guinan et al., 2001; Botello et al., 1993; Baumard et al., 1999; Colombo et al., 1989; Pendoley, 1992; Wang et al., 2001, they can be considered as moderately polluted.

For the same station, aliphatic hydrocarbon levels were higher in bivalve mollusks than in sediments. Levels in bivalve mollusks were variable and predominant in both ports, showing values of a similar order of magnitude for *A. atra atra* and *T. petitiana*. Mussel pools, in chromatographic profiles had a biogenic compound suit (branched C25 isoprenoids) with a larger predominance than in sediments. These compounds are probably taken by mussels from micro algae (diatoms), through filtration or from suspended sediment particles. According to UNEP (1991), phytoplankton is capable to synthesize a compound suit that elutes around *n*-C21. Clams showed it to a lesser extent than mussels, but in a similar order of magnitude to the compound suit found in sediments. According to Zaixso (1997), subtidal clams are mainly detritus-feeders, while mussels are filter-feeders. This difference in feeding behavior between both bivalves could be related to the compound suit uptake (Fig. 3). Indices values, *n*-alkanes homologous series, and UCM could be indicating anthropogenic hydrocarbon uptake by bivalves, particularly UCM in mussels from both ports. According to Granby and Spliid (1995), *n*-alkanes in a petroleum hydrocarbon polluted area will be degraded through time while UCM compounds will be accumulated. Tavares et al. (1988) reported UCM values between 100 and 200 µg/g in mussels collected in bays and harbors from the US and Spain. UCM as the main contributor to TAl concentrations could indicate the organism capacity to uptake a great amount of different compounds. In addition, it is possible that they possess a slower metabolic degradation for UCM compounds than for resolved *n*-alkanes.

PAHs in clams and mussels showed moderate concentrations compared to those found in other studies (Baumard et al., 1998; Baumard et al., 1999; Michel and Zengel, 1998; Marrugo Gonzalez et al., 1999; Botello et al., 1993). The presence of MPs in clam samples only could be associated with higher clam-sediment than mussel-sediment contact, and therefore a more direct transfer of sediment-associated pollutants to *T. petitiana*. Hydrocarbon concentration in mussels may be related to a seasonal filter behavior (Baumard et al., 1998). This behavior and the organism reproduc-

tive cycle could explain seasonal variations in pollutant levels. The lipophilic character of these pollutants is well known, particularly of the PAHs that once inside the organism are fixed to fat tissues. The uptake of individual PAHs depends on both their degree of lipophilicity (Kow) and size (Camus et al., 2003), while remaining compounds depend on the lipid concentration in the organism and its metabolic capacity to biodegrade them.

According to Hellow et al. (1994), bivalves have been observed to display a yearly cycle in the uptake of contaminants due to changes associated with their reproductive cycle and lipid content. De Vido de Mattio (1983) reported minimum lipid values for mussels from BN between December and January (0.9%) and then an increase to reach 2%, denoting again a decrease during winter. This reduction is due to the use of energy reserves to cover metabolic requirements as a result of lowered food availability. Lipid values ( $0.9 \pm 0.17\%$ ,  $n = 6$ ) and CI (0.32) in bay mussels suggest a first partial spawning, probably as a result of a sudden temperature increase. This is in agreement with visual observation of mussel tissues that evidenced an early recovery period. When mussels were sampled in November, mean water temperature was  $15.6 \pm 1.1$  °C ( $n = 10$ ). According to Esteves and De Vido de Mattio (1980), the larger temperature increase (about 2.5 °C) occurs between October and November. The direct relationship between lipid content and hydrocarbon concentration in organisms (Granby and Spliid, 1995) could be indicating a pollutant increase in mussels which are in an advanced stage of recovery and previous to spawning. Clams mainly spawn between December and January. A similar comparison for clams was not possible due to the absence of previous data. Bioavailability of PAHs depends mainly on sediment granulometry, because PAHs are strongly adsorbed on fine grain sediments (Baumard et al., 1999). Bay sediments were predominantly coarse. Higher PAH concentrations in organisms were found in both ports and neighboring areas. PAH levels were independent of the grain size found in sediments, but were associated with source proximity. However, PAHs mean concentration value was  $0.85 \pm 0.08$  µg/g ( $n = 4$ ) at locations distant from ports (Fig. 4), suggesting a similar pollutant bioavailability for organisms.

BAFs and BSAFs values were variable. Both ports presented the lower bioaccumulation values although PAH concentrations were higher in port sediments. Baumard et al. (1999) found that large BSAF values in low polluted sediments were related to sediment characteristics. A better characterization of sediments in BN should be conducted to evaluate hydrocarbon bioavailability. In addition, calculations of bioaccumulation factors assume that mussels are in equilibrium with hydrocarbon levels found in sediment samples. According to Murray et al. (1991), it is possible that BSAF values reflect non-equilibrium conditions. As bioaccumulation depends on the organism recovery period, seasonal studies should be implemented to evaluate hydrocarbon content at different reproductive cycle stages to adequately assess these processes.

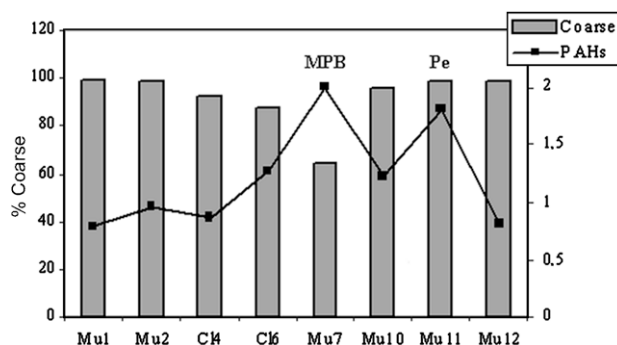


Fig. 4. Bioavailability of PAHs related with the granulometry.



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