



Sources and distribution of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina)

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ABSTRACT

The environmental quality of Ushuaia Bay, located at the southernmost tip of South America, is affected by the anthropogenic pressure of Ushuaia city. In this study, levels and sources of hydrocarbons in coastal sediments were assessed. Aliphatic hydrocarbon fractions ranged between 5.5 and 1185.3 $\mu\text{g/g}$ dry weight and PAHs from *not detected* to 360 ng/g . Aliphatic diagnostic indices, the nalkanes homologous series occurrence, Aliphatic Unresolved Complex Mixtures (AliUCMs), and pristane and phytane isoprenoids indicated a petrogenic input. Some sites showed biogenic features masked by the anthropogenic signature. Particularly in port areas biodegradation processes were evident. PAH ratios showed a mixture of petrogenic and pyrogenic sources. Aliphatic and aromatic UCMs were strongly correlated, reflecting chronic pollution. Three areas were distinguished inside the bay: (1) east, with low hydrocarbons impact; (2) central, where hydrocarbons accumulation was related to source proximity and sediment characteristics; (3) south-west, where sediment characteristics and current circulation favour hydrocarbons accumulation.

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1. Introduction

Increasing scientific attention has been devoted to obtaining information on natural and anthropic chemical markers. Hydrocarbons are naturally occurring compounds which are important components of the sedimentary organic matter from marine coastal areas. Their composition and distribution are significantly affected by human activities, particularly in recent decades. They are an assemblage of substances coming from biogenic, diagenetic, petrogenic, and/or pyrogenic sources (Yunker et al., 1993; Page et al., 1996; Hostettler et al., 1999; Wu et al., 2001; Gao and Chen, 2008), and have received much attention due to their ubiquitous distribution in marine sediments (Boehm and Requejo, 1986; Volkman et al., 1992). Aliphatic and polycyclic aromatic (PAHs) hydrocarbons are the major components of crude oil, which is one of the main pollutants in coastal marine ecosystems. Both large spills and chronic inputs of petroleum or its derived products contribute to degradation of the habitat of marine biota. PAHs have environmental significance due to their potential toxicity to organisms. They are often hydrophobic and easily accumulated in organisms through food chains, and present

a potential threat to aquatic ecosystems and even to human health (Colborn et al., 1993; Qiu et al., 2009). Hydrocarbon pollution is of great concern for natural resources conservation, which in many cases sustains regional economies. Ecosystem degradation causes environmental problems and could produce negative social and economic consequences also.

Sediments are recognized as excellent sinks for pollutants such as hydrocarbons (Mille et al., 2007) and constitute an appropriate matrix for chemical analysis (Hellou et al., 2002). Depending on the partitioning properties, a large fraction of hydrocarbons adsorbs onto suspended particles and accumulates in underlying sediments, which constitute long-term reservoirs and secondary sources of pollution (Latimer and Quinn, 1996; Colombo et al., 2005). Hydrocarbons may have multiple origins that can be discriminated through compositional parameters. A pool of aliphatic diagnostic indices and some particular signatures can be used to identify biogenic (terrestrial or marine) and/or anthropogenic sources. PAH distributions are also useful to differentiate the PAH main sources, particularly to distinguish petrogenic hydrocarbons from pyrogenic hydrocarbons (Asia et al., 2009).

In Patagonia, several coastal areas are suffering from anthropogenic impact, such as Ushuaia Bay, located in the Beagle Channel, Tierra del Fuego (Argentina). Ushuaia city is the only urban settlement on the southern coast of Tierra del Fuego island. The local economy mostly depends on tourism, trade, and industrial

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development, which involves intense maritime traffic around a commercial port. Fuel is supplied by maritime transport, discharged in a combustible port and accumulated in tanks near the coast. According to [Amin and Comoglio \(2002\)](#), the commercial port receives each year close to 900 vessels that are fuel-supplied in the combustible port. Ushuaia's population grew 24% in the last decade, reaching 57,000 in 2010 (National Census [INDEC, 2010](#)). Ushuaia Bay was identified as a suitable site for aquaculture development ([Luchini and Wicki, 2002](#)) and due to its relevant biodiversity was designated as a Special Protection Zone ([Prefectura Naval Argentina, 1998](#)). However, this area is exposed to urban and industrial wastes discharge ([Gil et al., 2010](#); [Torres et al., 2009](#)), and harbour operations. There is scarce information on hydrocarbons in the Ushuaia Bay sediments. A study carried out in 2001 about aliphatic hydrocarbons in intertidal sediments reported port areas inside the bay as the most polluted in Tierra del Fuego ([Esteves et al., 2006](#)). This work provides a more complete study of intertidal sediments and is the first to investigate the composition, origin, and distribution of aliphatic and aromatic hydrocarbons in subtidal sediments from this coastal region located on the southern tip of South America.

2. Materials and methods

2.1. Study area and collection sites

Ushuaia Bay (22 km²) has about 17 km of coast. Ushuaia city (54° 49 'S, 68° 19 'W) extends along the coasts of the Ushuaia, Encerrada and Golondrina bays ([Fig. 1](#)). The largest embayment, Ushuaia Bay, has a consolidated soft-bottom surface with stones and shells and a bathymetry ranging from 6 to 30 m in some western sections to up to 100–170 m in the east, close to the Beagle Channel ([Biancalana et al., 2007](#)). A permanent current moves west along the northern coast at 2 cm s⁻¹, and then southeast along the southern coast at 16.3 cm s⁻¹ ([Balestrini et al., 1998](#)).

Sediments collection was made during May 2006. Sampling stations ([Table 1](#)) were located close to sites with probable hydrocarbon inputs from anthropogenic activities (commercial port: E8, combustible port: E2 and E9, nautical pier: E4 and E7, area between ports: E3, industrial area and fishery processing plants: E10), in the mouth of the Pipo River (E1), and in other stations without direct exposure to human influence (i.e. the western Bay area; Aspirante

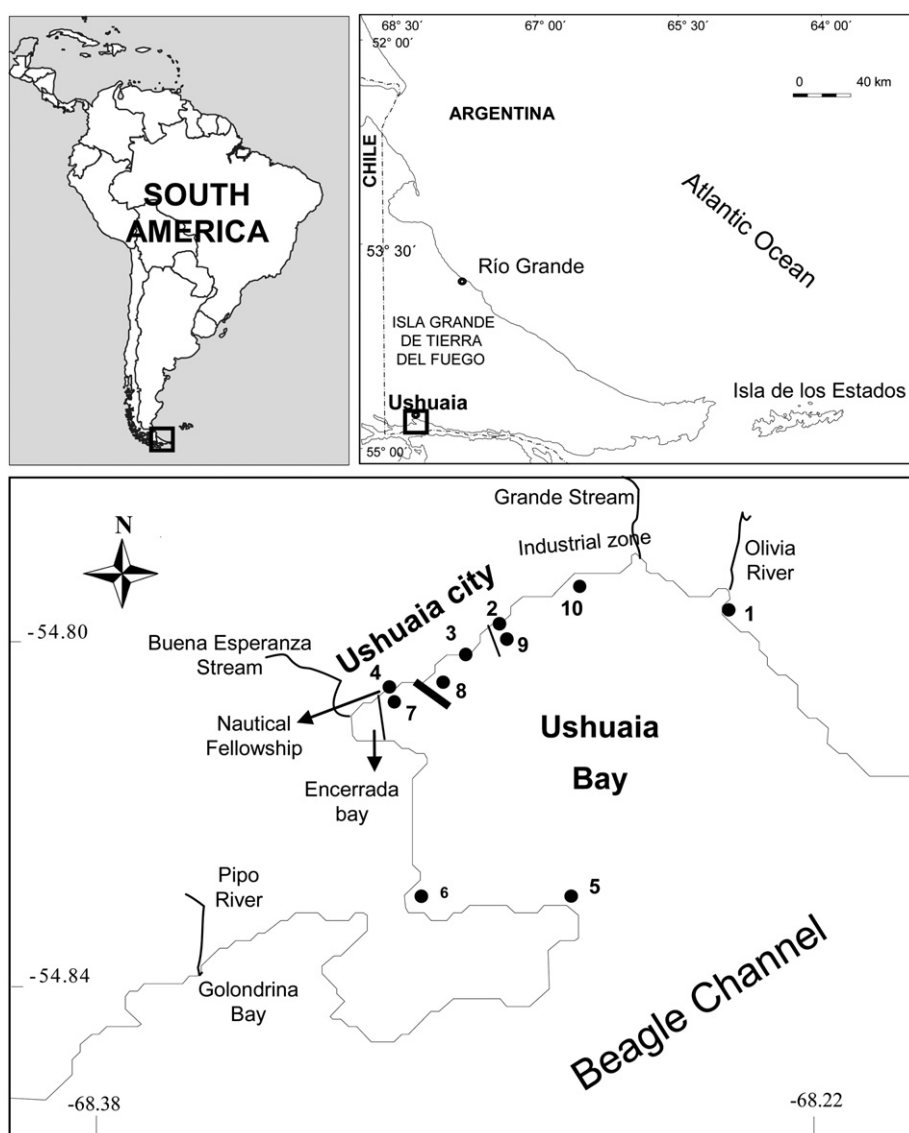


Fig. 1. Location of sampling sites in surficial sediments of Ushuaia Bay. Intertidal sediments: stations 1, 2, 3, and 4; submareal sediments: stations 5, 6, 7, 8, 9, and 10. See stations details in [Table 1](#).

Table 1
Location and characteristics of sampling sites.

Station	Name	Location	Lat (South)	Long (West)	Type of sediment	Depth (m)
E1	Pipo river	Intertidal	54° 48' 32"	68° 14' 50"	Sand	–
E2	Combustible port	Intertidal	54° 47' 56"	68° 16' 27"	Gravel	–
E3	Between ports	Intertidal	54° 48' 24"	68° 17' 24"	Sand	–
E4	Nautical pier	Intertidal	54° 48' 35"	68° 17' 30"	Sand	–
E5	Península	Subtidal	54° 50' 60"	68° 16' 00"	Sand/fine	6
E6	Aspirante creek	Subtidal	54° 49' 60"	68° 18' 12"	Sand	6
E7	Nautical pier	Subtidal	54° 48' 35"	68° 17' 30"	Sand/fine	4
E8	Commercial port	Subtidal	54° 49' 00"	68° 17' 23"	Sand/fine	4
E9	Combustible port	Subtidal	54° 47' 56"	68° 16' 27"	Sand/fine	8
E10	Industrial plants	Subtidal	54° 47' 53"	68° 15' 40"	Sand	5

creek: E5 and Península: E6). Surface sediments (0–3 cm) were obtained from the subtidal zone (4–8 m deep) in six stations (E5, E6, E7, E8, E9, and E10) using Van Veen grabs and from the intertidal zone in four stations (E1, E2, E3, and E4), as described in Commendatore et al. (2000). In each sampling site, sediments were taken in ten adjacent points selected randomly, homogenized in a single composite sample, placed in a cleaned solvent-rinsed glass flask, and frozen to -20°C until laboratory analysis.

2.2. Hydrocarbon analysis

Samples processing and hydrocarbon analysis was carried out as described in Commendatore et al. (2000) and Esteves et al. (2006). Hydrocarbons were determined by High Resolution Gas Chromatography (HRGC/FID – Konik 3000) by the external standard method under the following conditions: DB5 capillary column ($30 \times 0.25 \times 25$), flame ionization detector (FID) at 320°C , injector (splitless 1.2 min) at 250°C , N_2 as carrier gas (1 ml min^{-1}). For aliphatics, oven temperature was programmed from 60°C (2 min) to 290°C (20 min) at $8^{\circ}\text{C min}^{-1}$; while for aromatics, oven temperature was programmed from 60°C (0 min) to 150°C (0 min) at $15^{\circ}\text{C min}^{-1}$, then $3^{\circ}\text{C min}^{-1}$ to 220°C (0 min), and finally at $10^{\circ}\text{C min}^{-1}$ to 300°C (15 min). Identification and quantification of resolved nalkane and isoprenoids were accomplished by comparing with authentic external standard mix ($n\text{C}_9$ – $n\text{C}_{35}$ plus pristane and phytane isoprenoids). Aliphatic unresolved complex mixtures (AliUCM) and total resolved aliphatic (TRAli) were calculated using the mean response factors (RF) of nalkanes. Polycyclic aromatic hydrocarbons (PAHs) were identified and quantified by comparison with known standard mixture (16 EPA priority + 1-Methylnaphthalene). Methyl phenanthrenes (MPhe: 3MPhe, 2MPhe, 9MPhe, 1MPhe, and 2,7DMPhe) were identified by Gas Chromatography/Mass Spectrometry (GC/MS) in a Hewlett Packard HP5890 Serie II Plus gas chromatographer coupled to a HP5972 mass spectrometer (MS) with a HP5 column. Helium gas was used as carrier gas at 1 ml/min , with the same temperature program used for HRGC-FID. The MS was operated at 70 eV in total scan mode (TIC) with a 50 – 300 m/z scan range. Concentrations were estimated assuming equivalent RF between Phenanthrene and MPhe by HRGC-FID. Aromatic unresolved complex mixtures (AroUCMs) and total resolved aromatics (TRArO) were calculated using the mean RF of individual PAHs. Concentration of individual nalkanes (nalk), pristane (Pr) and phytane (Phy) isoprenoids, total nalkanes (Σnalk), resolved aliphatics (RALi: sum of nalkanes plus isoprenoids), aliphatic unresolved complex mix (AliUCM), total resolved aliphatics (TRAli), total aliphatic hydrocarbons ($\text{F1} = \text{TRAli} + \text{AliUCM}$), individual and total PAHs ($\Sigma 16$ EPA priorities no substituted + MPhe; see Table 4 for the

complete list of compounds and abbreviations), aromatic unresolved complex mix (AroUCM), total resolved aromatics (TRArO), and total aromatic hydrocarbons ($\text{F2} = \text{TRArO} + \text{AroUCM}$) were calculated on a dry weight basis. Blank samples were analyzed with each batch of five samples to confirm the absence of laboratory contamination. Duplicate analysis (two complete procedures) was made with three samples (E1, E2, and E3), and the percent of relative deviation (RDP%) value, considering both individual aliphatic and aromatic hydrocarbons, varied from 0.4% to 9.0%. For nalkanes $n\text{C}_{20}$ and $n\text{C}_{28}$ range, recovery assays of spiked pristine samples resulted in $95 \pm 12\%$; while PAHs recovery in certified marine sediment (NIST 1944) was $84 \pm 15\%$. Results were not corrected for recoveries. A control standard ($5 \mu\text{g/ml}$) was injected with each chromatographic sequence to check the chromatograph performance. The detection limits of the method (LOD) were 5 – 10 ng/g and close to 10 ng/g for individual aliphatic and aromatic hydrocarbons, respectively. LOD were determined as the lowest concentration that can be determined to be statistically different from a method blank ($n = 7$; 3 SD) at a 99% level of confidence.

2.2.1. Complementary analysis

Porosity, Organic Matter (OM) and granulometry were determined in sediment sub-samples as complementary analysis to the hydrocarbon content, according to the methodology describe in Commendatore et al. (2000). Total Organic Carbon (TOC) values were obtained indirectly from OM values according to Billen (1978).

2.3. Diagnostic indices

Aliphatic diagnostic indices (ADIs) were used to identify hydrocarbon sources (marine/terrestrial biogenic or petrogenic) and the relative degree of biodegradation between sites. In addition, the analysis of some particular signatures such as the presence/absence of nalkanes homologous series and AliUCM helped to elucidate hydrocarbons origin. The following indices were used: $\Sigma\text{Even}/\Sigma\text{Odd}$, $\Sigma\text{LMW}/\Sigma\text{HMW}$, CPI, $\Sigma\text{nalk}/n\text{C}_{16}$, MH, Pr/Ph, $n\text{C}_{17}/\text{Pr}$, $n\text{C}_{18}/\text{Ph}$, TRAli/UCM and %UCM (AliUCM/F1) (Commendatore et al., 2000; Commendatore and Esteves, 2004). ADIs and its reference values have been defined by several authors (e.g. Clark and Finley, 1973; Broman et al., 1987; Colombo et al., 1989; Gearing et al., 1976). The petrogenic/biogenic relationship (Pet/Biog) defined by Colombo et al. (2005) as $(\Sigma < n\text{C}_{22} + \text{isoprenoids})/(n\text{C}_{15} + n\text{C}_{17} + \Sigma > n\text{C}_{23})$ was used, considering only Pr and Ph isoprenoids. In addition, the “Natural nAlkane Ratio” (NAR), defined by Mille et al. (2007), was also used. This ratio is close to zero for petroleum hydrocarbons and crude oils and close to one for higher terrestrial or marine plants. Aromatic diagnostic criteria used in the interpretation of PAH sources were: abundance ratio of 2–3 ring hydrocarbons to 4–6 ring hydrocarbons

Table 2
Gravimetry, Organic Matter (OM), and Total Organic Carbon (TOC) of sampled sediments.

Station	Gravel %	Sand %	Fine %	OM % ^a	TOC % ^b
E1	12.0	87.9	0.0	0.7	0.2
E2	74.0	24.4	1.6	1.5	0.6
E3	14.5	84.6	0.9	0.8	0.3
E4	28.8	70.0	1.2	1.2	0.5
E5	8.7	51.2	40.1	7.6	3.3
E6	3.3	67.3	29.4	16.3	7.2
E7	2.8	47.4	49.8	10.5	4.7
E8	0.6	58.6	40.8	5.2	2.2
E9	3.3	51.0	45.7	9.5	4.2
E10	13.2	79.5	7.3	2.2	0.9

^a CV 1–4%.

^b TOC calculated according to Billen (1978).

Table 3Aliphatic hydrocarbon concentrations ($\mu\text{g/g dw}$) and diagnostic indices values.

Station	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
<i>Concentrations</i>										
Σnalk	0.28	11.72	1.93	0.85	1.74	1.92	1.42	1.82	3.11	0.98
Pr	0.017	1.542	0.108	0.051	0.028	0.092	0.191	0.179	0.346	0.036
Ph	0.019	1.347	0.122	0.056	0.043	0.076	0.192	0.229	0.429	0.043
Rali ($\Sigma\text{nalk} + \text{iso}$)	0.3	14.6	2.2	1.0	1.8	2.1	1.8	2.2	3.9	1.1
TRAli	1.5	147.2	36.3	20.9	50.3	51.8	40.7	47.1	67.4	27.5
AliUCM	4.0	1038.1	93.3	48.2	171.4	289.1	259.7	600.9	1054.1	79.3
F1 (TRAli + AliUCM)	5.5	1185.3	129.6	69.1	221.7	340.9	300.4	648.0	1121.5	106.8
<i>Indices</i>										
MH	$n\text{C17}-n\text{C18}$	$n\text{C20}-n\text{C18}$	$n\text{C20}-n\text{C18}$	$n\text{C17}-n\text{C18}$	$n\text{C29}-n\text{C18}$	$n\text{C25}-n\text{C21}$	$n\text{C25}-n\text{C17}$	Ph-Pr	$n\text{C21}-\text{Ph}$	$n\text{C16}-n\text{C17}$
$\Sigma\text{odd}/\Sigma\text{even}$	1.0	1.0	1.0	1.0	1.3	0.4	0.5	0.9	0.7	1.2
$\Sigma\text{LMW}/\Sigma\text{HMW}$	2.9	2.4	0.9	1.4	0.9	0.7	1.8	0.9	0.6	1.3
$n\text{C16}$	10.8	10.9	54.9	18.3	16.2	26.9	14.2	22.8	69.5	8.1
CPI	1.0	0.5	1.6	1.3	2.2	2.3	2.8	2.6	0.6	2.0
Pr/Ph	0.9	1.1	0.9	0.9	0.7	1.2	1.0	0.8	0.8	0.8
$n\text{C17}/\text{Pr}$	2.4	1.0	1.6	1.8	4.2	2.9	1.5	0.9	0.6	2.4
$n\text{C18}/\text{Ph}$	1.9	1.1	1.4	1.5	3.4	1.0	0.5	0.6	0.3	1.9
TRAli/UCM	0.375	0.142	0.389	0.434	0.293	0.179	0.157	0.078	0.064	0.347
%UCM	73	88	72	70	77	85	86	93	94	74
NAR	0.3	0.1	0.1	0.0	-0.1	0.6	0.4	-0.3	0.1	0.1
petr/biog	2.3	3.7	3.1	3.4	4.4	3.4	4.4	2.6	1.7	3.5

RPD% of F1calculated for stations E1, E2, and E3 varied from 0.4 to 9.0%.

(LMW/HMW), Phe/Ant, Flt/Pyr, Flt/(Flt + Pyr) and Phe/MPhe (Table 5). The %TRArO was also calculated.

2.4. Principal component analysis (PCA)

Aliphatic and aromatic hydrocarbons were analyzed separately in the PCA. For aliphatic hydrocarbons, a data matrix comprising 10 row (sampling sites, see Fig. 1) and 10 column variables were used. The aliphatic indexes (see Section 2.4) were used as variables, except the categorical MH and the TRAli/UCM, which is dependent on %UCM. For aromatic hydrocarbons, the data matrix was constructed with 9 sampling sites (E2–E10) and 19 column variables containing individual and lumped PAHs concentrations. The variables used were individual PAHs concentration (Phe, Ant, 1MPhe, 2MPhe, 3MPhe,

9Mphe, 2,7DMPhe, Flt, Pyr, B[a]A, Chr, B[b]F, B[k]F, B[a]P, B[ghi]P), ΣPAH , TRArO, AroUCM, and %TRArO. Only compounds detected over the LOD in at least one station were considered for the analysis. The site E1, in which all aromatic concentrations were non-detectable, was eliminated from the PCA (Scrimshaw and Lester, 2001). The data for both aliphatic and aromatic hydrocarbons were standardized to unit variance prior to PCA analysis. For aromatic hydrocarbon PCA, the PAHs concentration values detected below the LOD (10 ng g^{-1}) were assumed to be equal to half of the LOD (5 ng g^{-1}) in agreement with similar criteria used for trace element in geochemistry analysis, while non-detected compounds were assumed equal to zero (Farnham et al., 2002; Colombo et al., 2005). PCA analyses were performed using the Multi-Variate Statistical Package version 3.13b (MVSP[®], Kovach Computing Services, USA).

Table 4PAHs concentrations (ng/g dw) including unsubstituted parents, C1-methyl phenanthrenes, and 2,7-dimethyl phenanthrene.

Station	E1	E2	E3	E3	E4	E5	E6	E7	E8	E9	E10
Phe	nd	15	<LOD	<LOD	<LOD	<LOD	<LOD	19	46	24	<LOD
Ant	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	12	12	<LOD
3MP	nd	14	<LOD	<LOD	<LOD	<LOD	11	<LOD	<LOD	<LOD	<LOD
2MP	nd	17	<LOD	<LOD	<LOD	<LOD	43	19	14	22	<LOD
9MP	nd	19	<LOD	<LOD	<LOD	<LOD	<LOD	32	20	<LOD	<LOD
1MP	nd	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,7DMP	nd	36	<LOD	<LOD	<LOD	<LOD	<LOD	35	17	72	11
Flt	nd	11	<LOD	<LOD	<LOD	<LOD	15	33	62	48	<LOD
Pyr	nd	<LOD	<LOD	<LOD	15	<LOD	11	32	54	53	<LOD
B[a]A	nd	nd	nd	nd	nd	nd	nd	16	31	19	nd
Chr	nd	nd	nd	nd	nd	nd	nd	<LOD	35	26	nd
B[b]F	nd	nd	nd	nd	nd	nd	nd	nd	24	25	nd
B[k]F	nd	nd	nd	nd	nd	nd	nd	nd	22	16	nd
B[a]P	nd	nd	nd	nd	nd	nd	nd	<LOD	21	24	nd
IP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
DBA	nd	nd	nd	nd	nd	nd	nd	nd	nd	<LOD	nd
B[ghi]P	nd	nd	nd	nd	nd	nd	nd	nd	nd	15	nd
ΣPAHs	nd	123	<LOD	<LOD	15	<LOD	80	200	358	355	11
$\Sigma\text{parent PAHs}$	nd	26	<10		15	<10	26	100	307	261	<10
TRArO	nd	7200	2700	2410	1060	4930	10,050	8900	6030	9860	2430
UCMAro	nd	37,500	5130	2700	2000	5800	10,400	32,700	36,200	80,100	3000
F2	nd	44,700	7830	5110	3060	10,730	20,450	41,600	42,230	89,960	5430

Phe: phenanthrene, Ant: anthracene, 3MP: 3-methyl phenanthrene, 2MP: 2-methyl phenanthrene, 9MP: 9-methyl phenanthrene, 1MP: 1-methyl phenanthrene, 2,7DMP: 2,7-dimethyl phenanthrene, Flt: fluoranthene, Pyr: pyrene, B[a]A: benzo[a]anthracene, Chr: chrysene, B[b]F: benzo[b]fluoranthene, B[k]F: benzo[k]fluoranthene, B[a]P: benzo[a]pyrene, IP: indeneperylene, DBA: dibenzoanthracene, B[ghi]P: benzo[ghi]perylene.

RPD% of ΣPAHs calculated for stations E1, E2, E3, and E4 varied from 1 to 6.9%.

Table 5

Values of PAH ratios characteristic to different sources and those obtained in this study.

Ratio	LMW/HMW	Phe/Ant	Flt/Pyr	Flt/(Flt + Pyr)	P/MP
<i>Source</i>					
Pyrolytic	<1	<10	>1	>0.5	1–2
Petrogenic	>1	>15	<1	<0.5	0.17–0.5
References	Tam et al. (2001), Magi et al. (2002), Socio et al. (2000)	Baumard et al. (1998a,b)	Baumard et al. (1998a,b)	Budzinski et al. (1997), Gogou et al. (1998)	Pralh and Carpenter (1983)
<i>This work</i>					
E1	–	–	–	–	–
E2	1.4	–	–	–	0.2
E3	–	–	–	–	–
E4	–	–	–	–	–
E5	–	–	–	–	–
E6	–	–	1	0.5	<0.2
E7	0.3	–	1.5	0.6	0.2
E8	0.3	5	1.2	0.5	1
E9	0.1	2	1	0.5	0.2
E10	–	–	–	–	–

3. Results

3.1. Complementary analysis

Granulometry of intertidal sediments (E1–E4) showed a clear predominance of sand particles (from 70 to 88%), except for E2 (combustible port) where gravel fraction reached 74%, with low OM content ($1.05 \pm 0.35\%$) (Table 2). Subtidal sediments (E5–E10) showed fine material (from 7.3 in E10 to 49.8% in E7) and OM ($8.5 \pm 4.9\%$, $n = 6$) higher than those found in intertidal sediments (Table 2). OM and fine material were positively correlated ($r^2 = 0.5784$, $p < 0.05$, $n = 10$), and the correlation coefficient noticeably increased ($r^2 = 0.9268$, $p < 0.05$, $n = 9$) when E6 was excluded from the analysis.

3.2. Aliphatic hydrocarbons

3.2.1. Intertidal sediments

F1 levels were moderately associated with OM and fine particles ($r^2 = 0.608$ and $r^2 = 0.477$, respectively, $p < 0.05$, $n = 4$). $\Sigma nalk$ + isoprenoids ranged between 0.3 (E1) and 14.6 $\mu g/g$ (E2, combustible port) (Table 3 and Fig. 2a). AliUCM constituted a high percentage of F1, from 70% (E4) to 88% (E2). The homologous series of nalkanes (from nC_{12} to nC_{33} for E2, E3, and E4 and from nC_{12} to nC_{27} for E1), and Pr and Ph isoprenoids were detected in all the samples.

3.2.2. Subtidal sediments

F1 levels showed a weak relationship with fine materials ($r^2 = 0.274$, $p < 0.05$, $n = 6$) and no association with OM ($r^2 = 0.017$, $p < 0.05$, $n = 6$), but these correlations increased when both ports were excluded ($r^2 = 0.492$ and $r^2 = 0.937$, respectively; $p < 0.05$). $\Sigma nalk$ + isoprenoid values ranged from 1.1 to 3.9 $\mu g/g$; while the AliUCM reached the highest value at E9 (combustible port) (Table 3 and Fig. 2a). AliUCM contributed between 74% and 94% to F1 (Table 3). The highest F1 values were found in both ports (E8 and E9). Chromatographic profiles showed the homologous series of nalkanes ranging from nC_{12} to nC_{32} , nC_{33} or nC_{34} , and Pr and Ph isoprenoids.

3.2.3. PCA for aliphatic hydrocarbons

The analysis of the ADIs showed that the first three principal components (PC) explained 83.7% of the total variance (Fig. 3a and 3b). The positive axis of PC1 showed an association with %UCM, NAR and $\Sigma nalk/nC_{16}$, and the negative axis with the nalkane/isoprenoid and $\Sigma Even/\Sigma Odd$ indexes. Therefore, in sites with petrogenic content, the PC1 may be interpreted as the “fresh-weathering component,” from fresh hydrocarbon inputs (negative values) to

weathered hydrocarbons (positive values). For comparative purposes, two external petrogenic references were incorporated into the PCA plot: Fresh Bilge Waste (FBW), which had a composition similar to fuel oil#2, and Weathered Bilge Waste (WBW), which was a heavily biodegraded FBW (i.e. with more than 70% of weight loss) (Nievas et al., 2008). PC2 was positively associated with CPI and negatively associated with the Pet/Biog index, showing that the biogenic character of samples increases in the positive direction of PC2. Considering the absolute CPI values, which were all below 3, sites associated with the positive PC2 axis corresponded to a mixture of petrogenic and biogenic hydrocarbons. Thus, PC2 could be used to discriminate the contribution of petrogenic hydrocarbons (negative values, e.g. FBW and WBW) from mixtures of biogenic-petrogenic hydrocarbon content (positive values) (Fig. 3a).

3.3. Aromatic hydrocarbons

3.3.1. Intertidal sediments

$\Sigma PAHs$ (16 US EPA priority + MPhe) ranged from non-detected (nd) to 120 ng/g . The highest value was found in E2 (combustible port) where Phe, MePhe and Flt were detected over the LOD. In E3 and E4, $\Sigma PAHs$ were below the LOD, except for pyr (20 ng/g) quantified in E4 (nautical pier). TRARo ranged from nd to 7200 ng/g , AroUCM from nd to 37,500 ng/g , and F2 between nd and 44,700 ng/g (Table 4).

3.3.2. Subtidal sediments

A weak correlation between F2 and sediment fine particles ($r^2 = 0.312$, $p < 0.05$, $n = 6$) and no relationship between F2 and OM ($r^2 = 0.005$, $p < 0.05$, $n = 6$) were found. ΣPAH had levels between nd and 360 ng/g . Higher values corresponded to both ports (E8 and E9), which showed similar concentrations (Table 4). In ports Phe, Ant, MePhe, Flt, Pyr, B[a]A, Chr, B[b]F, B[k]F, and B[a]P were detected. B[ghi]P was identified and quantified only in E9 (Table 4, Fig. 4). Other sites presented lower PAH values than ports following the order $E7 > E6 > E10 > E5$. TRARo ranged from 2430 to 10,050 ng/g , AroUCM from 3000 to 80,100 ng/g , and F2 from 3060 to 89,960 ng/g (Table 4).

3.3.3. Subtidal and intertidal sediments

F1 and F2 levels were moderately associated as it was indicated by the correlation coefficient $r^2 = 0.487$ ($p < 0.05$, $n = 10$). This association strongly increased when F1 and F2 were normalized by TOC, both considering all stations ($r^2 = 0.859$, $p < 0.05$, $n = 10$) or excluding the extreme values of stations E8 and E2 ($r^2 = 0.842$, $p < 0.05$, $n = 8$) (Fig. 5). The correlation coefficients of F1 vs OM and F1 vs sediment fine material were higher when samples from both ports were

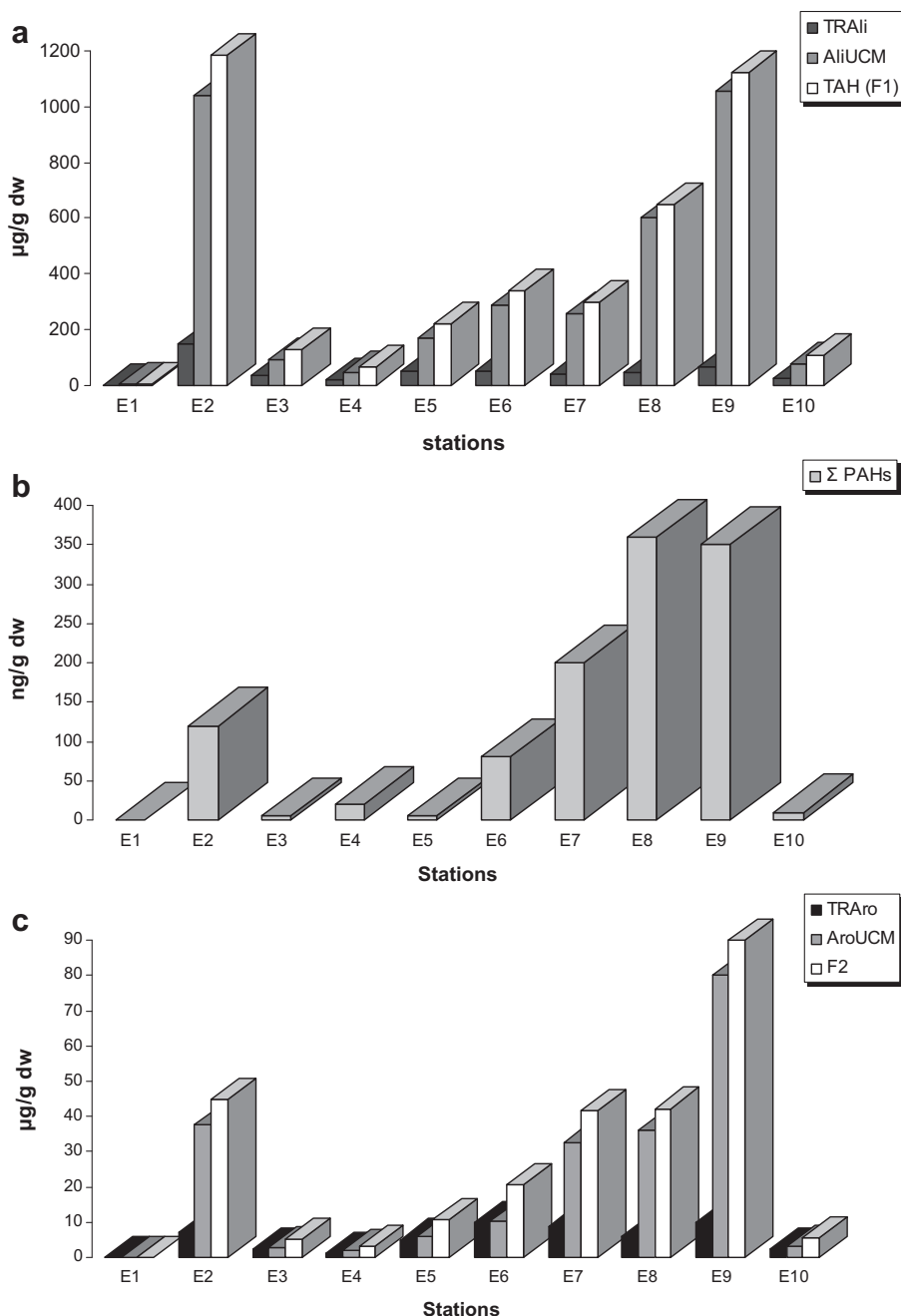


Fig. 2. Hydrocarbon concentration in surficial sediments of Ushuaia Bay. (a) Aliphatic hydrocarbons: TRAli, total resolved aliphatic; AliUCM, aliphatic unresolved complex mixture; total aliphatic hydrocarbons (F1). (b) Identified resolved aromatic hydrocarbons (ΣPAHs): 16 EPA priority PAHs plus methyl phenanthrenes and 2,7-dimethyl phenanthrene. (c) Aromatic hydrocarbons: TRARo: total resolved aromatic; AroUCM: aromatic unresolved complex mixture; F2: total aromatic hydrocarbons.

excluded (from 0.031, $n = 10$ to 0.885, $n = 7$ and from 0.091, $n = 10$ to 0.727, $n = 7$, $p < 0.05$, respectively). A similar trend was observed for F2 vs OM ($r^2 = 0.073$, $n = 10$ to 0.538, $n = 7$), and for F2 vs sediment fine material ($r^2 = 0.348$, $n = 10$ to 0.731, $n = 7$, $p < 0.05$).

3.3.4. Aromatic hydrocarbon PCA

The first three components in the PCA explained 89.9% of the total variance. The first PC (PC1), which explained 62.2% of the total data variance, showed positive loadings with parent PAHs, mainly with 4- and 5-ring compounds, Ant, ΣPAH and AroUCM (Fig. 3d). Therefore, the PC1 could be interpreted as a general indicator of the level of aromatic hydrocarbon pollution in the sampled sites, with lower values associated with the negative axis and both the higher

aromatic levels and PAHs of pyrogenic origin associated with the positive axis. The second PC (PC2) explained 17.3% of the data set variance with positive loadings of MPhe and TRARo concentrations, indicating that the positive PC2 axis is associated with increasing levels of aromatic hydrocarbons of petrogenic origin (Fig. 3d).

4. Discussion

4.1. Hydrocarbon levels

Ushuaia Bay sediments showed variable hydrocarbon levels, with a clear difference between concentrations in both ports and those found in the other stations (Fig. 2). In the combustible port, F1

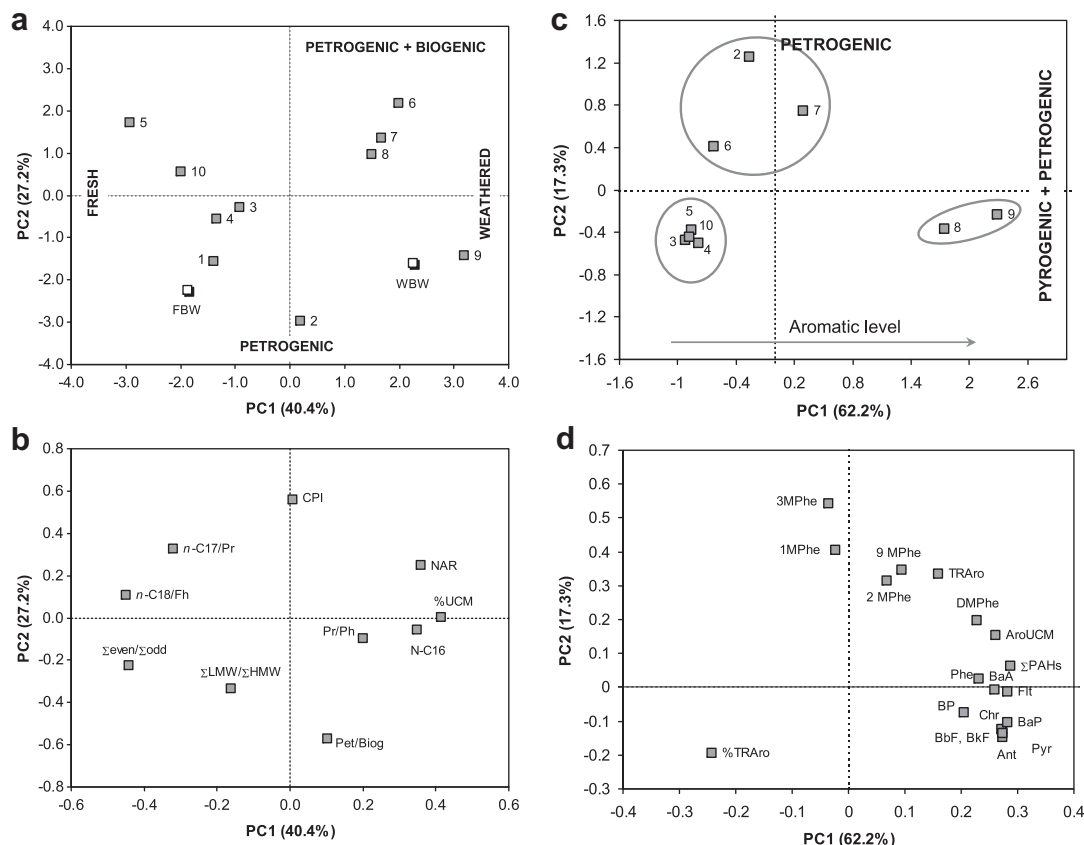


Fig. 3. Principal component analysis of hydrocarbon concentrations and compositional indexes. Aliphatic hydrocarbons: (a) Factor score of stations and (b) factor loadings of the aliphatic compositional indexes ($\Sigma\text{Even}/\Sigma\text{Odd}$, $\Sigma\text{LMW}/\Sigma\text{HMW}$, CPI, $\Sigma\text{nalk}/n\text{C16}$, Pr/Ph, $n\text{C17}/\text{Pr}$, $n\text{C18}/\text{Ph}$, Pet/Biog, NAR, and %UCM) as function of PC1 and PC2. Reference petrogenic data: Fresh Bilge Waste (FBW) and Weathered Bilge Waste (WBW). Aromatic hydrocarbons: (c) Factor score of stations and (d) factor loadings of the aromatic concentration and compositional ratios (Phe, Ant, 1MPhe, 2MPhe, 3MPhe, 9MPhe, 2,7DMPhe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, BP, ΣPAHs , TRArO, AroUCM, %TRArO). See [Material and methods](#) for indexes and composition abbreviations.

values for intertidal and subtidal sediments (E2 and E9, respectively) were close to 1100 $\mu\text{g/g}$. F2 and PAH levels in E9 were higher than those found in E2, probably as result of the adsorption of aromatic hydrocarbons in the former due to the sediment characteristics. At commercial port (E8), subtidal sediments showed relatively elevated F1 and F2, with the highest PAHs concentration found (360 ng/g). Individuals compounds ranged, according to GC retention times, from Phe to B[a]P. Thus, F1 levels of both ports were typical of those of polluted sediments from areas related to

port and industrial activities ($\sim 650\text{--}1200 \mu\text{g/g}$, [UNEP/IOC/IAEA, 1992](#)). The hydrocarbon content in ports was mainly associated with the source proximity than to the sediment characteristics, as is suggested by the F1 and F2 vs the OM and fine material

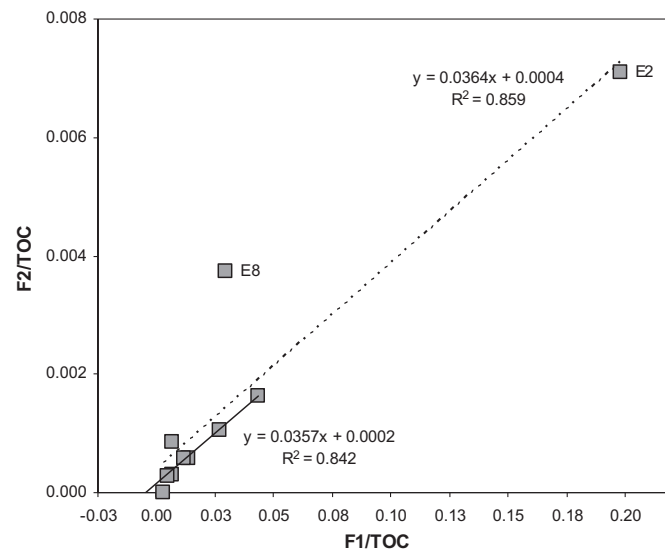


Fig. 5. Correlation between total aromatic (F2) vs total aliphatic hydrocarbons (F1) concentrations normalized by TOC in the Ushuaia Bay sediment samples: all station (n = 10, dashed line) and excluding the extreme values from station E2 and E8 (n = 8, solid line).

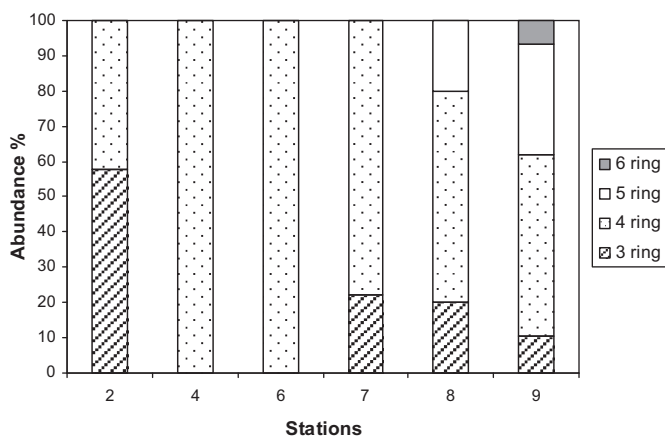


Fig. 4. Relative abundance of parent PAHs of LMW PAH (3-ring PAH) and HMW (4–6 ring PAH) in the Ushuaia Bay sediment samples.

correlations. Moreover, when aliphatic hydrocarbons were normalized by TOC, F1/TOC from samples near ports (E2, E8, E9 and the inter-port E3) were from 3 to 25 times larger than the mean for the rest of the samples (0.0077 ± 0.0043 , $n = 6$). The same was observed for F2/TOC, with values from 2.4 to 16 times larger than the mean for the rest of the samples (0.00045 ± 0.00031 , $n = 6$).

Several urban sewage systems located in the nautical pier area (E4 and E7) discharge effluents in the marine coastal zone (Torres et al., 2009; Gil et al., 2010). Levels for F1 were relatively low to moderate and more than four times larger in subtidal (E7, 300 $\mu\text{g/g}$) than in intertidal sediments (E4, 69 $\mu\text{g/g}$). The same trend was observed for F2 (42 and 3 $\mu\text{g/g}$) and PAHs (200 and 20 ng/g). These facts suggest that the bottom sediments could be acting as a hydrocarbon trap, in agreement with its fine material ($\sim 50\%$) and OM (11%) content.

Although farther away from hydrocarbon sources, stations located on the south-west of the bay (E5 and E6), showed relatively high hydrocarbon levels and AliUCM and AroUCM presence. PAHs were only detected in E6, where OM% was the highest in the bay sediments, suggesting an accumulation of OM and hydrocarbons in this area. This fact was reinforced by the association between OM and fine particles, which noticeably increased when E6 was excluded from the regression analysis. In the bay's eastern section (E1), intertidal sediment had F1 level close to 5 $\mu\text{g/g}$, and F2 was *nd*. The unpolluted status in this sector, according to the criteria for surface marine sediments, may be determined by no evident influence of hydrocarbon sources and sediment characteristics (UNEP, 1992; Zegouagh et al., 1998). In station 10, located close to an industrial zone northeast from the ports, hydrocarbon levels were relatively low and sediments had low OM and fine particles.

Hydrocarbon levels in sediments of Ushuaia Bay were within the range reported for other studies worldwide (Table 6). Although Ushuaia is a relatively small city, hydrocarbon concentrations in some sections of the embayment, mainly ports, are similar to those recorded in large urban areas such as Buenos Aires city or even higher than those found in industrial areas such as the gulf of Fos (Table 6). Relative to other studies carried out in the Patagonian coastal zone (Table 6), aliphatic hydrocarbon levels reported in this work could be classified as non-polluted (E1 < 10 $\mu\text{g/g}$), low-polluted (E4; 10–100 $\mu\text{g/g}$), moderately polluted (E3, E5, E6, E7, E8 and E10; 100–500 $\mu\text{g/g}$), and highly polluted (E2 and E9; >500 $\mu\text{g/g}$). PAH concentrations showed in general lower ranges than others reported in Table 6. According to Baumard et al. (1998a) the parent PAH levels (the sum of the 18 compounds, including the 12 parent PAHs from Table 4) can be considered as low, moderate, high, and very high when are in the range 0–100, 100–1100, 1000–5000, and >5000 ng g^{-1} , respectively. Accordingly, taking into account the sum of parent PAHs analyzed in the bay's sediment, they can be considered to be at least moderately polluted in both ports (E8, E9), low-polluted in the intertidal combustible port (E2), in the nautical pier (E7 and E4), E5, E3, E6 and E10, and non-polluted in E1.

Esteves et al. (2006), who studied aliphatic hydrocarbons in intertidal sediments of Tierra del Fuego, reported the highest levels of this area in Ushuaia port's zone. They stated that in the Ushuaia Bay, an enclosed area, hydrocarbons could be easily accumulated. In the current study, F1 levels recorded in port's stations (from 648 to $\sim 1185 \mu\text{g/g}$) were one order of magnitude higher than those found in 2001. Several studies have demonstrated that sediment contamination by aliphatic hydrocarbons and PAHs is a growing problem faced by many urban ports (Wu et al., 2001; Maskaoui et al., 2002; Zhou and Maskaoui, 2003). Ushuaia Bay appears to be another case showing

Table 6
Values of aliphatic and aromatic hydrocarbons in sediments from other sites of the world.

Location	AR $\mu\text{g g}^{-1}$	UCM $\mu\text{g g}^{-1}$	$\Sigma\text{PAHs ng g}^{-1}$	References
Gironde Estuary, France ($n = 31$)			18.5–4888	Budzinski et al. (1997)
Xiamen Harbour, China ($n = 9$)			247–480	Zhou et al. (2000)
Yenisey Bay, Arctic ($n = 4$)			443–657 (18)	Dahle et al. (2003)
Deep Bay, China ($n = 12$)			237–726 (16)	Zhang et al. (2004)
Hugli Estuary, India ($n = 10$)			25–1081	Guzzella et al. (2005)
Río de la Plata Estuary, Argentina ($n = 39$)	0.11–14 ^b	0.1–800		Colombo et al. (2005)
Masan Bay, Korea ($n = 20$)			207–2670 (24)	Yim et al. (2005)
Pearl River Estuary, China ($n = 9$)			189.1–636.7	Luo et al. (2006)
Río de la Plata Estuary, Argentina ($n = 39$)			3–2100	Colombo et al. (2006)
Jiaozhou Bay, Qingdao, China ($n = 25$)	0.5–8.2 ^e		20–2200 (16)	Wang et al. (2006)
Meiliang Bay, Taihu Lake, China ($n = 25$)			1207–4754 (16)	Qiao et al. (2006)
Gemlik Bay (Marmara Sea, Turkey) ($n = 61$)			50.8–13,482 (14)	Ünlü and Alpar (2006)
Bohai Sea ($n = 66$)			25–2079 (10)	Liu et al. (2007)
Eastern Aegean Sea, Izmir Bay ($n = 16$)	0.087–4.48 ^a		2.5–113 (16)	Darilmaz and Kucuksezgin (2007)
Gulf of Fos, France ($n = 11$)	0.55–6.85 ^c		34–13,780 (13)	Mille et al. (2007)
Mar Piccolo, Taranto (Ionian Sea, Italy) ($n = 9$)			380–12,750 (16)	Cardellicchio et al. (2007)
Daliao River Estuary, China ($n = 40$)			276.26–1606.89 (16)	Men et al. (2009)
Daya Bay, South China ($n = 14$)			42.5–158.2 (16)	Yan et al. (2009)
Abu Qir Bay, Egypt ($n = 20$)			<MDL–2660 (16)	Khairy et al. (2009)
Gulf of Aden, Yemen ($n = 17$)			22–604 (46)	Mostafa et al. (2009)
Deep Bay, South China ($n = 7$)			353.8 \pm 128.1 (15)	Qiu et al. (2009)
Cienfuegos bay, Cuba ($n = 17$)	2.25–7.25 ^d	45–590	450–10,500 (40)	Tolosa et al. (2009)
Marseille Bay (France) ($n = 16$)			34–1825 (13)	Asia et al. (2009)
Bahía Blanca Estuary ($n = 24$)			15–10,260 (17)	Arias et al. (2010)
Tierra del Fuego, Patagonia ($n = 44$)	0.01–36.7 ^b	nd–56.6		Esteves et al. (2006)
Patagonia Coast ($n = 31$)	nd–109.7 ^b	nd–1195		Commendatore et al. (2000)
Patagonia Coast ($n = 86$)	nd–460 ^b	nd–1195	10–7690	Commendatore and Esteves (2007)
Bahía Nueva, Patagonia ($n = 12$)	0.02–1.10 ^b	0.01–8.53	10–7690	Massara Paletto et al. (2008)
Bahía Ushuaia, Patagonia ($n = 10$)	0.3–14.6 ^b	4–1054	nd–360 (16)	This study

^a $\Sigma 5$ aliphatic hydrocarbons.

^b nalk + isoprenoids.

^c nalk 14–32.

^d nalk 14–34.

^e nalk.

this trend. Regarding aromatic hydrocarbons, there is little information on PAH in sediments from the southern Patagonian zone. [Lozada et al. \(2008\)](#) reported levels for 16 EPA PAHs in intertidal sediments of Ushuaia Bay (from 30 to 1800 ng/g), in four sites in 2004–2006, in the frame of a study of genes coding enzymes of PAH-biodegradation pathways. PAH concentrations measured in bivalves collected in Ushuaia Bay in 2003 were up to five times higher than those found in 1999 ([Amin et al., 2010](#)).

4.2. Hydrocarbon composition and probable origin

4.2.1. Aliphatic hydrocarbons

A common petrogenic hydrocarbon source was strongly suggested in all sites by the correlation found between the normalized by TOC F1 and F2 levels, ADIs and signatures such as high F1 and AliUCM levels, and *n*-alkanes homologous series occurrence ([Table 3](#); [Simoneit, 1984, 1985](#)). The presence of Pr and Ph in all samples and Pr/Ph ratios close to 1 in most stations reinforced this origin ([UNEP/IOC/IAEA, 1992](#)).

Intertidal samples (E1, E2, E3, and E4) had a fresher hydrocarbons character relative to the most polluted subtidal stations (E6, E7, E8, and E9), which showed advanced weathering processes. This was evidenced in the PC1 vs PC2 space plot, where intertidal samples were positioned to the left (closer to the FBW reference) relative to the most polluted subtidal stations E6, E7, E8, and E9 (closer to the WBW reference) ([Fig. 3a](#)). PC1 represents the hydrocarbon weathering degree with highest factor scores for % AliUCM, NAR, and Σ nalkanes/*n*C16 (values for biogenic hydrocarbons >50 or petrogenic input <15, [Clark and Finley, 1973](#)). However, Σ nalkanes/*n*C16 is expected to increase for petrogenic biodegradation processes, as lighter nalkanes (including *n*C16) are faster degraded than the heavier ones (i.e. the index value increased from 8.1 for FBW to 29.4 for WBW, data from [Nievas et al., 2008](#)). The negative axis of PC1 represents the contribution of fresh petrogenic hydrocarbons, associated with *n*C17/Pr, *n*C18/Ph ratios, and Σ even/ Σ odd nalkanes. The *n*C17/Pr and *n*C18/Ph are useful to assess the occurrence of crude oil and the early effect of microbial biodegradation of nalkanes ([Pichard and Costa, 1991](#); [Wang and Fingas, 2003](#); [Diez et al., 2007](#)); while the Σ even/ Σ odd nalkanes index takes values close to and below 1 for petrogenic and biogenic inputs, respectively. In subtidal sediments, hydrocarbons settled in the bottom would have suffered previous physical weathering and microbial biodegradation, which mainly reduce the quantity of resolved aliphatics ([Wang and Fingas, 2003](#)). In agreement, *n*C17/Pr, *n*C18/Ph, and TRAli/UCM relationships were lower in subtidal than in intertidal sediments, a trend clearly observed in sites with closer intertidal-subtidal samples (E2–E9, E3–E8, and E4–E7). According to [Simoneit and Mazurek \(1982\)](#), values higher than 0.3 for the ratio TRAli/UCM indicate a recent petroleum contamination while for severe degraded petroleum residues this ratio is generally very low (<0.05). All samples located in the negative PC1 axis had TRAli/UCM values near or above 0.3. Sites E1, E4 and E3 (lower left quadrant in [Fig. 3a](#)), evidenced a petrogenic character indicated by the Pet/Biog index value, MH between *n*C16 and *n*C20, and a shorter distance to the FBW reference. Although for these stations hydrocarbons levels were low, they showed clear petrogenic fresh signs.

In the combustible port, intertidal and subtidal sediments had a strong petrogenic character indicated by the Pet/Biog values (within the same range than the petrogenic references: FBW 3.0 and WBW 3.7, respectively, [Table 3](#)). These sites were located at the lower right quadrant in the PC1–PC2 plot in agreement with the moderate (E2) to high (E9) petrogenic hydrocarbon degradation extent. Among the intertidal samples, E2 was the most petrogenic polluted site but also the most degraded according the ADIs nalkanes/isoprenoids, TRAli/UCM, %AliUCM, and Σ LMW/ Σ HMW. Similarly, E9 showed the highest

F1 level, the highest weathering degree among the subtidal samples, and Pr and Ph as MH ([Simoneit, 1984, 1985](#)). These facts reflect that E2 and E9, have a larger biodegradation activity in comparison to less contaminated zones of the bay, as it has been reported for sediments with a history in hydrocarbon pollution ([Atlas, 1995](#)).

Subtidal samples associated with the positive axis in the PC1 ([Fig. 3a](#)) had biogenic hydrocarbon contribution, though with a general petrogenic signature. Biogenic signs are mainly influenced by the CPI and NAR indexes ([Fig. 3a](#)) and could be ordered as E6 > E7 > E8 > E9 according to the site's position along the "petrogenic–biogenic character component" PC2. [Asia et al. \(2009\)](#) reported a NAR value of 0.6 where terrestrial inputs were strongly significant. At E6, E7 and E8 the biogenic contribution was mainly from terrestrial vascular plants (NAR index values 0.6, 0.4 and 0.3, and CPI 2.3, 2.8 and 2.6 respectively, [Table 3](#)) evidenced by odd nalkanes presence between *n*C19 and *n*C31. In addition, E6 had *n*C25 and *n*C21 as the MH. Inputs of marine biogenic hydrocarbons from phytoplankton or algae are also suggested in E7 and E9, as *n*C17 and *n*C21 appears as MH, respectively.

Sites E5 and E10, with relatively low to moderate levels of aliphatic hydrocarbons (80–200 µg/g), were highly associated with *n*C17/Pr and *n*C18/Ph ratios, indicative of fresh petrogenic inputs. However, CPI values of around 2 also indicated a biogenic hydrocarbon contribution. At site E5, in the south-western limit of the study area, the terrestrial biogenic input was also evidenced by the MH *n*C29.

4.2.2. Aromatic hydrocarbons

Compositional patterns of unsubstituted PAHs in subtidal sediments were dominated by 3- (Phe, Ant), 4- (Flt, Pyr, B[a]A and Chr), and 5-ring (B[b]F, B[k]F, B[a]P) compounds, while intertidal sediments showed only 3- (Phe) and 4-ring (Flt and Pyr) compounds. B[ghi]P, a 6-ring PAH, was only detected in subtidal sediments from the combustible port (E9), representing 3% of the total PAH content. HMW compounds constitute the major proportion of the whole sediment PAH load, particularly the 4-ring compounds (3-, 4-, and 5-ring PAHs to total PAHs were 16, 60 and 21%, respectively).

Molecular indices have been widely used to identify potential PAH sources in sediment samples, based on the difference in thermodynamic stability observed in these compounds ([Readman et al., 1987](#)). Hydrocarbons of both petrogenic and pyrogenic origin were found in the sediments of Ushuaia Bay in agreement with the aromatic diagnostic criteria used ([Table 5](#)). The PCA of aromatic hydrocarbons pooled sites into three groups, ordered according to their increasing concentration from left to right of the PC1. Higher hydrocarbon levels were associated with the CP1 positive axis, as it is shown by the variable loadings found for Σ PAHs, AroUCM and 3-, 4-, 5- and 6-ring PAH parents abundance. The first group was composed by subtidal sediments from both ports (E8 and E9). These sites exhibited a mixture of petrogenic (3-ring PAH and AroUCM) and pyrogenic PAHs (HMW PAHs with 4-ring predominance), associated with the positive axis of PC1. In addition, LMH/HMW, Phe/Ant, P/MP, and Flt/Pyr ratios indicated pyrogenic inputs, except for the P/MP relationship which showed petrogenic inputs at E9. Pyrogenic PAHs are introduced to the marine environment mainly through atmospheric transport and deposition. Sites other than E8 and E9 did not show a high abundance of HMW PAHs. Therefore, maritime activity related to harbours appears to be the likely source of pyrogenic PAHs deposited in sediments. In addition, the characteristics of the subtidal sediments favoured the accumulation of HMW, since larger compounds are generally more likely to be transported to the sediment bed due to their increased particle sorption affinity and resistance to degradation ([Darilmaz and Kucuksezgin, 2007](#); [Kanally and Harayama, 2000](#); [Prah and Carpenter, 1983](#); [Readman et al., 1984](#)).

A second group of more dispersed sites (E7, E2 and E6) had intermediate aromatic levels with a higher petrogenic contribution

than the subtidal port stations, evidenced by the association with the PC2 positive axis. This group showed an alkylated-phenanthrene concentration of over 50% (53–79%) of the Σ PAHs, while in port stations the ratio Σ MP/ Σ PAHs was less than 24%. In addition, values less than 0.2 for the P/M index in the three stations and an LMW/HMH ratio larger than 1 for E2 are indicative of petrogenic contribution. Molecular index values for the subtidal E7 in the proximity of an urban effluent also suggest PAHs input from pyrolytic sources. Ushuaia Bay is not a crude oil exploitation zone. Therefore, petrogenic PAHs found likely come from spills associated with the transport and discharge of refined fuel at the combustible port which supplies the industrial activities of the Island, as well as from the charge of diesel oil to commercial, tourism, and fishery vessels that use the commercial port.

A third group of sites (E3, E4, E5 and E10) was associated with low aromatic levels. This group was also associated with %TRAr, with values of $56 \pm 6\%$, compared to E8–E9 with 11–14%, which suggests a relatively recent hydrocarbon input into the environment, although these compounds were only found at trace levels in the sediments.

4.3. Hydrocarbon distribution in Ushuaia Bay

Three different areas were identified along the coastal zone of Ushuaia Bay, according to the sediment characteristics and hydrocarbon levels found: northeast (E10 and E1), central (E2, E3, E4, E7, E8, and E9), and south-west (E5 and E6). The central area, where subtidal sediments of ports (E8 and E9) and the nautical pier (E7) were polluted with anthropic hydrocarbons, is probably the place where most of the hydrocarbon load is introduced into the environment. The main sources of such chronic pollution by petrogenic and pyrogenic hydrocarbons are very likely the port activities. However, Ushuaia Bay also receives several fresh water inputs (small streams and natural runoff) and effluent discharges (Gil et al., 2010; Torres et al., 2009). E7 is close to the most polluted drainage from an urban discharge, equivalent to untreated weak urban wastewater, and is also exposed to water exchange with Encerrada Bay which contributes to most of the OM and nutrient content into this area from external sources (Gil et al., 2010; Torres et al., 2009). Intertidal sediments (E3 and E4) were less impacted by anthropic hydrocarbons than subtidal ones, reflecting petrogenic inputs with fresher signatures which may be caused by hydrocarbon slicks that reached the shore. This situation was more critical at the combustible port (E2). Sediments in the subtidal central area were organic-matter-rich (OM from 5 to 10%; Tissot and Welte, 1984) and its granulometry (40–50% fine material) also supports favourable conditions for hydrocarbon accumulation. Gil et al. (2010) have reported anoxic conditions at a site near E7 in 2006, in agreement with its eutrophic status. Although anaerobic hydrocarbon biodegradation occurs in marine sediments, the degradation rate is negligible in comparison with that of well aerated environments (Atlas, 1995). Thus, hydrocarbon input in the central area, anaerobic sediments, and low temperatures seem to favour hydrocarbons' accumulation, such as it is suggested by the increasing in aliphatic levels over the last five years (Esteves et al., 2006). Aromatic compounds due to their lipophilic character also have a strong affinity for fine particles in the sediment (Baumard et al., 1999). PAH levels in bottom sediments were three times higher than those found in the intertidal zone, probably due to an accumulation process. A different situation exists in the south-western and eastern areas of the Bay. Stations located in the south-western (E5 and E6) are not exposed to direct hydrocarbon sources, and no wastewater discharge occurs in this area. However, sediments presented relatively moderate hydrocarbon levels ($F1 + F2 \sim 230\text{--}360 \mu\text{g/g dw}$), probably due to sediment characteristics (OM up to 16%) and the hydrocarbons transport associated

with fine material from the central area of the bay, favoured by the counterclockwise water circulation that flows close to shore (Balestrini et al., 1998). In addition, E5 and E6 showed the strongest biogenic contribution from terrestrial plants, probably from biogenic material transported by fresh water streams and effluents. In contrast, the bay's eastern area (E10 and E1) exhibited lower hydrocarbon levels as well as little OM and fine material in sediments.

4.4. PAHs toxicity assessment

The toxicity of PAHs was assessed by comparing PAH concentrations in sediments with threshold effect concentrations to place current levels into ecological perspective (Long et al., 1995). None of the concentrations found for individual PAHs in Ushuaia Bay exceeded the ISQG range recommended by the Canadian Sediment Guidelines for the Protection of Aquatic Life (2002). However, total hydrocarbon amounts, except for stations E1 and E4, exceeded the $100 \mu\text{g/g}$ chronic effect threshold for oil hydrocarbons reported for benthic communities (Howarth, 1989; Colombo et al., 2005). In addition, AroUCMs are constituted by thousands of individual branched alkyl-substituted aromatic compounds. Although each individual compound occurs at low concentration, their overall presence results in a high AroUCM concentration in environmental samples. Due to their overall structural similarities to the major resolved hydrocarbons, toxic effects of the AroUCM compounds have been reported, such as nonspecific narcotic toxic effects in the mussel *Mytilus edulis* when concentrations of up to $125 \mu\text{g/g}$ of dry tissue were found (Booth et al., 2007). In the current study, AroUCMs in sediments were up to $80 \mu\text{g/g}$, similar to values reported by Colombo et al. (2006) from coastal sediments of the Río de la Plata Estuary ($0.01\text{--}78 \mu\text{g/g}$). There are still no reported values of ISQG for this important group of aromatic compounds.

5. Conclusions

Coastal sediments of Ushuaia Bay showed inputs of petrogenic aliphatic hydrocarbons and some biogenic compounds, particularly from vascular plant waxes (terrestrial detritus), while sedimentary PAHs come from pyrogenic and petrogenic sources. This bay has suffered anthropogenic pressures in recent years, resulting in coastal sediment degradation due to a chronic increase of hydrocarbon pollution, as has been reported by many urban harbours. In this study, three areas with different degrees of impact were identified within the bay: (1) the eastern area, with a small hydrocarbon impact probably associated with sediment characteristics and the direction of the current circulation within the bay, (2) the central area, where hydrocarbons have accumulated due to the sources' proximity (ports) and favoured by sediment characteristics, and (3) the south-western area, where sediment characteristics and direction of the current circulation may have favoured hydrocarbon accumulation. Occurrence of both AliUCM and AroUCM were clear signs of anthropogenic inputs and chronic hydrocarbon pollution. None of the concentrations found for individual PAHs exceeded the ISQG range recommended for the protection of aquatic life. However, AroUCM, which represents an important group of toxic and overlooked environmental pollutants, were present in the bay's sediment up to $80 \mu\text{g/g}$. The bay, located at the southern tip of Argentina, constitutes a Special Protection Zone. The implementation of monitoring plans is needed to improve management guidelines aimed at minimizing hydrocarbon pollution, so as to conserve this coastal area where relevant natural resources may be affected.

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References

- Amin, O., Comoglio, L., 2002. Toxicity of diesel-oil in the first larval stage of the southern king crab (*Lithodes santolla*) and false southern king crab (*Paralomis granulosa*). *Revista de Biología Marina y Oceanografía* 37, 139–144.
- Amin, O.A., Comoglio, L.I., Sericano, J.L., 2010. Polynuclear aromatic and chlorinated hydrocarbons in mussels from the coastal zone of Ushuaia, Tierra del Fuego, Argentina. *Environmental Toxicology and Chemistry* 30, 521–529.
- Arias, A., Vazquez-Botello, A., Tombesi, N., Ponce-Vélez, G., Freije, H., Marcovecchio, J., 2010. Presence, distribution, and origins of polycyclic aromatic hydrocarbons (PAHs) in sediments from Bahía Blanca estuary, Argentina. *Environmental Monitoring and Assessment* 160, 301–314.
- Asia, L., Mazouz, S., Guiliano, M., Doumenq, P., Mille, G., 2009. Occurrence and distribution of hydrocarbons in surface sediment from Marseille Bay (France). *Baseline/Marine Pollution Bulletin* 58, 424–455.
- Atlas, R.M., 1995. Petroleum biodegradation and oil spill bioremediation. *Marine Pollution Bulletin* 31, 178–182.
- Balestrini, C., Manzella, G., Lovrich, G.A., 1998. Simulación de corrientes en el Canal Beagle y Bahía Ushuaia, mediante un modelo bidimensional. Servicio de Hidrografía Naval, Departamento de Oceanografía. Informe técnico 98, 1–58.
- Baumard, P., Budzinski, H., Garrigues, P., 1998a. Polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of the western Mediterranean Sea. *Environmental Toxicology and Chemistry* 17, 765–776.
- Baumard, P., Budzinski, H., Michon, Q., Garrigues, P., Burgeot, T., Bellocq, J., 1998b. Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal and Shelf Science* 47, 77–90.
- Baumard, P., Budzinski, H., Garrigues, P., Dizer, H., Hansen, P.D., 1999. Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: occurrence, bioavailability and seasonal variations. *Marine Environmental Research* 47, 17–47.
- Biancalana, F., Barria de Cao, M.S., Hoffmeyer, M.S., 2007. Micro and mesozooplankton composition during winter in Ushuaia and Golondrina Bays (Beagle Channel, Argentina). *Brazilian Journal of Oceanography* 55, 83–95.
- Billen, G., 1978. A budget of nitrogen recycling in North Sea sediments of the Belgian Coast. *Estuarine and Coastal Marine Science* 7, 127–146.
- Boehm, P., Requejo, A.G., 1986. Overview of the recent sediment hydrocarbon geochemistry of Atlantic and Gulf coast outer continental shelf environments. *Estuarine, Coastal and Shelf Science* 23, 29–58.
- Booth, A., Sutton, P., Lewis, C., Scarlett, A., Chau, W., Widdows, J., Rowland, S., 2007. Unresolved complex mixtures of aromatic hydrocarbons: thousands of overlooked persistent, bioaccumulative, and toxic contaminants in Mussels. *Environmental Science & Technology* 41, 457–464.
- Broman, D., Colmsjo, A., Ganning, B., Naf, C., Zebuhr, Y., Ostman, C., 1987. Fingerprinting petroleum hydrocarbons in bottom sediments, plankton, and sediment trap collected seston. *Marine Pollution Bulletin* 18, 380–388.
- Budzinski, H., Jones, I., Bellocq, J., Pitchard, C., Garrigues, P., 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry* 58, 85–97.
- Canadian Council of Ministers of the Environment, 2002. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Summary Tables. Updated in 2002. Canadian Environmental Quality Guidelines, 1999, Winnipeg, Canada, 1–7 pp.
- Cardellicchio, N., Buccolieri, A., Giandomenico, S., Lopez, L., Pizzulli, F., Spada, L., 2007. Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). *Marine Pollution Bulletin* 55, 451–458.
- Clark, R.C.J., Finley, J.S., 1973. Techniques for analysis of paraffin hydrocarbons and for interpretation of data to assess oil spill effects in aquatic organisms. In: *Proceedings of Joint Conference on Prevention and Control of Oil Spills*, pp. 161–172.
- Colborn, T., vom Saal, F.S., Soto, A.M., 1993. Developmental effects of endocrine-disrupting chemicals in wildlife and humans. *Environmental Health Perspectives* 101, 378–384.
- Colombo, J.C., Pelletier, X., Brochu, Ch., Khalil, M., Catoggio, J.A., 1989. Determination of hydrocarbon sources using n-alkane and polyaromatic hydrocarbon distribution index. Case study: Rio de la Plata Estuary, Argentina. *Environmental Science & Technology* 23, 888–894.
- Colombo, J.C., Barreda, A., Bilosa, C., Cappelletti, N., Demichelis, S., Lombardi, P., Migoya, M.C., Skorupka, C., Suárez, G., 2005. Oil spill in the Rio de la Plata estuary, Argentina: 1. Biogeochemical assessment of waters, sediments, soils and biota. *Environmental Pollution* 134, 277–289.
- Colombo, J.C., Cappelletti, N., Lasci, J., Migoya, M., Speranza, E., Skorupka, C., 2006. Sources, vertical fluxes, and equivalent toxicity of aromatic hydrocarbons in coastal sediments of the Rio de la Plata Estuary, Argentina. *Environmental Science & Technology* 40, 734–740.
- Commendatore, M.G., Esteves, J.L., Colombo, J.C., 2000. Hydrocarbons in coastal sediments of Patagonia, Argentina: levels and probable source. *Marine Pollution Bulletin* 40, 989–998.
- Commendatore, M.G., Esteves, J.L., 2004. Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). *Marine Pollution Bulletin* 48, 910–918.
- Commendatore, M.G., Esteves, J.L., 2007. An assessment of oil pollution in the coastal zone of Patagonia, Argentina. *Environmental Management* 40, 814–821.
- Dahle, S., Savinov, V., Matishov, G., Evensen, A., Næs, K., 2003. Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara Sea shelf, Gulf of Ob and Yenisei Bay. *The Science of the Total Environment* 306, 57–71.
- Darilmaz, E., Kucuksezgin, F., 2007. Distribution and origin of hydrocarbons in surficial sediments from the eastern Aegean Sea (Izmir Bay). *Baseline/Marine Pollution Bulletin* 54, 1813–1838.
- Diez, S., Jover, E., Bayona, J.M., Albaiges, J., 2007. Prestige oil spill III. Fate of a heavy oil in the marine environment. *Environmental Science & Technology* 41, 3075–3082.
- Esteves, J.L., Commendatore, M.G., Nievas, M.L., Massara Paletto, V., Amin, O., 2006. Hydrocarbon pollution in coastal sediments of Tierra del Fuego islands, Patagonia Argentina. *Marine Pollution Bulletin* 52, 582–590.
- Farnham, I.M., Singh, A.K., Stetzenbach, K.J., Johannesson, K.H., 2002. Treatment of nondetects in multivariate analysis of groundwater geochemistry data. *Chemometrics and Intelligent Laboratory Systems* 60, 265–281.
- Gao, X., Chen, S., 2008. Petroleum pollution in surface sediments of Daya Bay, South China, revealed by chemical fingerprinting of aliphatic and alicyclic hydrocarbons. *Estuarine, Coastal and Shelf Science* 80, 95–102.
- Gearing, P., Gearing, J., Lytle, T.F., Lytle, J., 1976. Hydrocarbons in 60 northeast Gulf of Mexico shelf sediments: a preliminary survey. *Geochimica et Cosmochimica Acta* 40, 1005–1017.
- Gil, M.N., Torres, A.I., Amin, O., Esteves, J.L., 2010. Assessment of recent sediment influence in an urban polluted subarctic coastal ecosystem. Beagle Channel (Southern Argentina). *Marine Pollution Bulletin* 62, 201–207.
- Gogou, A., Bouloubassi, I., Stephanou, E.G., 1998. Determination of organic molecular markers in marine aerosols and sediments: one-step flash chromatography compound class fractionation and capillary gas chromatographic analysis. *Journal of Chromatography A* 799, 215–231.
- Guzzella, L., Roscioli, C., Viganò, L., Saha, M., Sarkar, S.K., Bhattacharya, A., 2005. Evaluation of the concentration of HCH, DDT, HCB, PCB and PAH in the sediments along the lower stretch of Hugli estuary, West Bengal, northeast India. *Environment International* 31, 523–534.
- Hellou, J., Steller, S., Zitko, V., Leonard, J., King, T., Milligan, T.G., Yeats, R., 2002. Distribution of PACs in surficial sediments and bioavailability to mussels, *Mytilus edulis* of Halifax Harbour. *Marine Environmental Research* 53, 357–379.
- Hostettler, F.D., Pereira, W.E., Kvenvolden, K.A., van Geen, A., Luoma, S.N., Fuller, C.C., Anima, R., 1999. A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment cores. *Marine Chemistry* 64, 115–127.
- Howarth, R.W., 1989. Chapter 4: determining the ecological effects of oil pollution in marine ecosystems. In: Levin, S.A., Harwell, M.A., Kelly, J.R., Kimball, K.D. (Eds.), *Ecotoxicology: Problems and Approaches*. Springer-Verlag, New York, pp. 69–97.
- Instituto Nacional de Estadística y Censo (INDEC), 2010. Retrieved from: http://www.censo2010.indec.gov.ar/preliminares/cuadro_tierra.asp.
- Kanally, R.A., Harayama, S., 2000. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. *Journal of Bacteriology* 182, 2059–2067.
- Khairy, M., Kolba, M., Mostafa, A., EL-Fiky, A., Bahadira, M., 2009. Risk assessment of polycyclic aromatic hydrocarbons in a Mediterranean semi-enclosed basin affected by human activities (Abu Qir Bay, Egypt). *Journal of Hazardous Materials* 170, 389–397.
- Latimer, J., Quinn, J.G., 1996. Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: the sedimentary record. *Environmental Science & Technology* 30, 623–633.
- Liu, X., Chen, J., Lin, X., Tao, S., 2007. Spatial distribution and species composition of PAHs in surface sediments from the Bohai Sea. *Baseline/Marine Pollution Bulletin* 54, 97–116.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19, 81–97.
- Lozada, M., Riva Mercadal, J.P., Guerrero, L.D., Di Marzio, W.D., Ferrero, M.A., Dionisi, H.M., 2008. Novel aromatic ring-hydroxylating dioxygenase genes from coastal marine sediments of Patagonia. *BMC Microbiology*. doi:10.1186/1471-2180-8-50.
- Luchini, L., Wicki, G.A., 2002. Evaluación del potencial para acuicultura en la Provincia de Tierra del Fuego. Información Básica. Secretaría de Agricultura, Ganadería, Pesca y Alimentos (SAGPyA), 29 pp.
- Luo, X., Chen, S., Mai, B., Yang, Q., Sheng, G., Fu, J., 2006. Polycyclic aromatic hydrocarbons in suspended particulate matter and sediments from the Pearl River Estuary and adjacent coastal areas, China. *Environmental Pollution* 139, 9–20.
- Magi, E., Bianco, R., Ianni, C., Di Carlo, M., 2002. Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environmental Pollution* 119, 91–98.
- Maskaoui, K., Zhou, J.L., Hong, H.S., Zhang, Z.L., 2002. Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China. *Environmental Pollution* 118, 109–122.
- Massara Paletto, V., Commendatore, M.G., Esteves, J.L., 2008. Hydrocarbon levels in sediments and bivalve mollusks from Bahía Nueva (Patagonia, Argentina): an

- assessment of probable origin and bioaccumulation factors. *Baseline/Marine Pollution Bulletin* 56, 2082–2105.
- Men, B., He, M., Tan, L., Lin, C., Quan, X., 2009. Distribution of polycyclic aromatic hydrocarbons in the Daliao River Estuary of Liaodong Bay, Bohai Sea (China). *Marine Pollution Bulletin* 58, 818–826.
- Mille, G., Asia, L., Guiliano, M., Malleret, L., Doumenq, P., 2007. Hydrocarbons in coastal sediments from the Mediterranean Sea (Gulf of Fos area, France). *Marine Pollution Bulletin* 54, 566–575.
- Mostafa, A., Wade, T., Sweet, S., Al-Alimi, A., Barakat, A., 2009. Distribution and characteristics of polycyclic aromatic hydrocarbons (PAHs) in sediments of Hadhramout coastal area, Gulf of Aden, Yemen. *Journal of Marine Systems* 78, 1–8.
- Nievas, M.L., Commendatore, M.G., Esteves, J.L., Bucalá, V., 2008. Biodegradation pattern of hydrocarbons from a fuel oil-type complex residue by an emulsifier-producing microbial consortium. *Journal of Hazardous Materials* 154, 96–104.
- Page, D.S., Boehm, P.D., Douglas, G.S., Bence, A.E., Burns, W.A., Mankiewicz, P.J., 1996. The natural petroleum hydrocarbon background in subtidal sediments of Prince William Sound, Alaska, USA. *Environmental Toxicology and Chemistry* 15, 1266–1281.
- Pichard, P.H., Costa, C.F., 1991. EPA's Alaska oil spill bioremediation project. *Environmental Science & Technology* 25, 372–379.
- Prefectura Naval Argentina, 1998. Designación de zonas de protección especial en el litoral Argentino. Ordenanza N° 12/98 (DPMA), Tomo 6: Régimen para la Protección del Medio Ambiente. Prefectura Naval Argentina, Buenos Aires, 30 pp.
- Prahl, F., Carpenter, R., 1983. Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediment. *Geochimica et Cosmochimica Acta* 47, 1013–1023.
- Qiao, M., Wang, C., Huang, S., Wang, D., Wang, Z., 2006. Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. *Environment International* 32, 28–33.
- Qiu, Y., Zhang, G., Liu, G., Guo, L., Li, X., Wai, O., 2009. Polycyclic aromatic hydrocarbons (PAHs) in the water column and sediment core of Deep Bay, South China. *Estuarine, Coastal and Shelf Science* 83, 60–66.
- Readman, J.W., Mantoura, R.F.C., Rhead, M.M., 1984. The physico-chemical speciation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. *Fresenius Zeitschrift Analytische Chemie* 319, 126–131.
- Readman, J.W., Mantoura, R.F.C., Rhead, M.M., 1987. A record of polycyclic hydrocarbon (PAH) pollution obtained from accreting sediments of the Tamar Estuary, U.K.: evidence for non-equilibrium behaviour of PAH. *The Science of the Total Environment* 66, 73–94.
- Simoneit, B.R.T., 1984. Organic matter of troposphere-III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmospheric Environment* 18, 51–67.
- Simoneit, B.R.T., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliation. *International Journal of Environmental Analytical Chemistry* 22, 203–233.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere-II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. *Atmospheric Environment* 16, 2139–2159.
- Scrimshaw, M.D., Lester, J.N., 2001. Multivariate analysis of U.K. salt marsh sediment contaminant data with reference to the significance of PCB contamination. *Environmental Science & Technology* 35, 2676–2681.
- Soclo, H.H., Garrigues, P.H., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin* 40, 387–396.
- Tam, N.F.Y., Ke, L., Wang, X.H., Wong, Y.S., 2001. Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps. *Environmental Pollution* 114, 255–263.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*, second ed. Springer, Berlin, 699 pp.
- Tolosa, I., Mesa-Albernas, M., Alonso-Hernandez, C., 2009. Inputs and sources of hydrocarbons in sediments from Cienfuegos bay, Cuba. *Marine Pollution Bulletin* 58, 1624–1634.
- Torres, I., Gil, M.N., Amin, O.A., Esteves, J.L., 2009. Environmental characterization of a eutrophicated semi-enclosed system: nutrient budget (Encerrada Bay, Tierra del Fuego Island, Patagonia, Argentina). *Water Air and Soil Pollution* 204, 259–270.
- UNEP/IOC/IAEA, 1992. Determination of petroleum hydrocarbons in sediments. In: *Reference Methods for Marine Pollution Studies* N° 20, p. 75.
- Ünlü, S., Alpar, B., 2006. Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay (Marmara Sea, Turkey). *Chemosphere* 64, 764–777.
- Volkman, J., Holdsworth, D., Neill, G., Bavor, H., 1992. Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. *The Science of the Total Environment* 112, 203–219.
- Wang, Z., Fingas, M.F., 2003. Development of oil hydrocarbon fingerprinting and identification techniques. *Marine Pollution Bulletin* 47, 423–452.
- Wang, X., Sun, S., Ma, H., Liu, Y., 2006. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Marine Pollution Bulletin* 52, 129–138.
- Wu, Y., Zhang, J., Mi, T., Li, B., 2001. Occurrence of n-alkanes and polycyclic aromatic hydrocarbons in the core sediments of the Yellow Sea. *Marine Chemistry* 76, 1–15.
- Yan, W., Chi, J., Wang, Z., Huang, W., Zhang, G., 2009. Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. *Environmental Pollution* 157, 1823–1830.
- Yim, U., Hong, S., Shim, W., Oh, J., Chang, M., 2005. Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea. *Marine Pollution Bulletin* 50, 319–326.
- Yunker, M.B., Macdonald, R.W., Cretney, W.J., Fowler, B.R., McLaughlin, F.A., 1993. Alkane, terpene and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie shelf: riverine contributions to Beaufort Sea coastal sediment. *Geochimica et Cosmochimica Acta* 57, 3041–3061.
- Zegouagh, Y., Derenne, S., Largeau, C., Bardoux, G., Mariotti, A., 1998. Organic matter sources and early diagenetic alterations in Arctic surface sediments (Lena River delta and Laptev Sea, Eastern Siberia), II.: molecular and isotopic studies of hydrocarbons. *Organic Geochemistry* 28, 571–583.
- Zhang, J., Cai, L., Yuan, D., Chen, M., 2004. Distribution and sources of polynuclear aromatic hydrocarbons in Mangrove surficial sediments of Deep Bay, China. *Marine Pollution Bulletin* 49, 479–486.
- Zhou, J.L., Hong, H., Zhang, Z., Maskaoui, K., Chen, W., 2000. Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. *Water Research* 34, 2132–2150.
- Zhou, J.L., Maskaoui, K., 2003. Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. *Environmental Pollution* 121, 269–281.