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Hydrocarbons in Coastal Sediments of Patagonia, Argentina: Levels and Probable Sources

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Intertidal superficial sediment from the Patagonian coastal zone were analysed to determine the concentration and probable source of aromatic and aliphatic hydrocarbons. Concentrations of aromatic and aliphatic hydrocarbons ranged from non-detected to 737.6 µg/g and non-detected to 1304.7 µg/g of dry sediment, respectively. High concentrations were observed in San Jorge Gulf, where the main economic activities are based on crude oil production. The highest aromatic and aliphatic hydrocarbon concentrations were present at Faro Aristizábal, 200 km away from oil charging areas. As suspected, hydrocarbon levels in harbour areas were generally more important than at nearby zones. Lower or non-detected hydrocarbon levels were recorded at locations with low or non-anthropogenic activity. Alkane distribution indices and hydrocarbon distribution patterns were used to identify natural and anthropogenic inputs. The results showed recent crude oil inputs and contribution from remaining weathered residues at various locations, whereas biogenic compounds or biogenic in combination with anthropogenic hydrocarbons predominated in others.

Keywords: superficial sediments; Patagonian coast; hydrocarbon levels; anthropogenic; biogenic; alkane indices.

Introduction

Oil production and transport are among the most important economic activities in Patagonia. However, these activities may result in large spills as a result of accidents and minor spills from transfer operations, bilge washing and elimination of ballast discharge. In addition, fishing vessels and cargo ships generate an important amount of hydrocarbon waste that may reach the coast affecting seabird and other marine organisms. Chronic pollution derived from these oil inputs affects the coastal and marine ecosystem and is necessary to study and quantify.

Oil activities on the Argentine coast include offshore exploitation platforms, loading buoys, and transport between ports in Patagonia (Cullén, Punta Loyola, Caleta Olivia, and Caleta Córdova) and those located in the northern Argentine coast (Bahía Blanca, La Plata, and Buenos Aires).

The goal of this study was to quantify the current levels of aliphatic and aromatic hydrocarbons along the Patagonian coastal zone, determine their possible sources using *n*-alkane distribution indices and compare these results with previous information obtained in Patagonia.

Study Area

The coasts of Patagonia extend throughout more than 2000 km between 40°S and 54°S. Samples were obtained at 15 locations (Fig. 1) located at river mouths, bays and gulfs. Punta Loyola, Caleta Olivia, Comodoro Rivadavia, and Caleta Córdova have charging petroleum ports. Punta Quilla, Puerto Rawson, Puerto Deseado, Bahía Camarones, Puerto Madryn, and San Antonio Oeste have important commercial fishing ports. Río Negro and Río Colorado are located at the mouth of important rivers.

Methods

Sediment sampling

Sediment samples were obtained between March and June 1995. At some locations, several stations were sampled. Superficial sediments were obtained at a depth of 0–3 and 3–6 cm in the intertidal area using plexiglass tubes of 25 cm length and 4.5 cm internal diameter, which were introduced vertically into the sediment. Gravel sediments were sampled using spatulas. In cases where sediment structure did not allow a stratified

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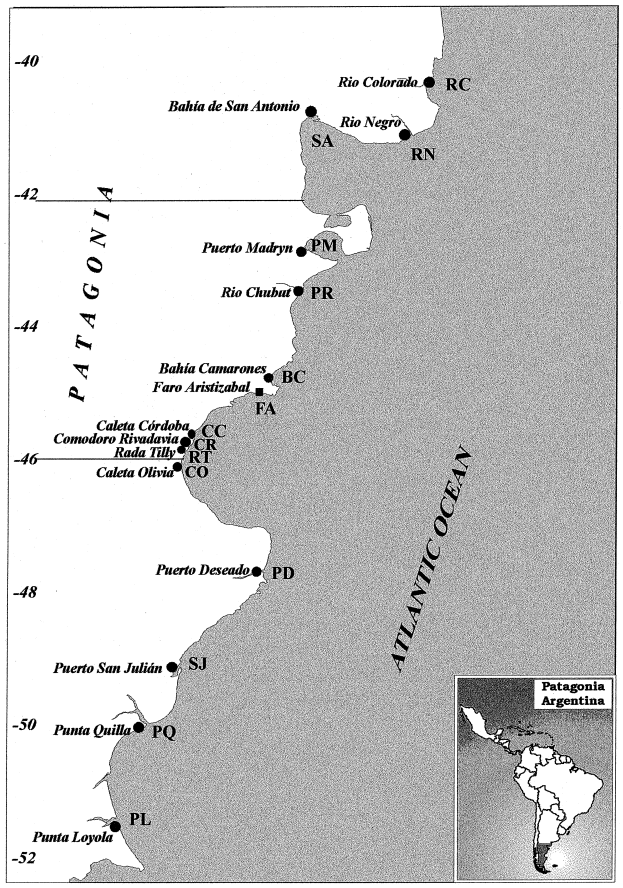

Fig. 1 Study area and sampling locations on Patagonian coastal zone. The circle symbols are locations: RC (Rio Colorado), RN (Rio Negro), SA (San Antonio), PM (Puerto Madryn), PR (Puerto Rawson), BC (Bahía Camarones), FA (Faro Aristizábal), CC (Caleta Córdova), CR (Comodoro Rivadavia), RT (Rada Tilly), CO (Caleta Olivia), PD (Puerto Deseado), SJ (San Julián), PQ (Punta Quilla) and PL (Punta Loyola).

sampling, only samples from 0 to 3 cm were obtained. Sediments were transferred to glass containers and frozen to −20°C until analysed.

Extraction and fractionation of hydrocarbons

We followed the methods and recommendations suggested in UNESCO Manuals and Guides (1982, 1984) and Gold *et al.* (1987). Frozen sediments were dried at 40°C to constant weight, and 50 g of the dry material was digested under reflux with 100 ml of methanol and 3 g of KOH. The non-saponificable fraction was obtained by extracting twice with 25 ml of hexane. The combined extracts were dried with anhydrous sodium sulphate, and the volume was reduced to 2 ml by rotary evaporation and to 0.2 ml under soft flowing N_2 gas at ambient temperature. The clean-up and isolation of hydrocarbon fractions were carried by column chromatography with totally activated alumina (activity grade I neutral). Elution with hexane gave a fraction consisting of aliphatic hydrocarbons while elution with hexane-dichlorometane yielded a fraction containing aromatic hydrocarbons. The aliphatic fraction was measured by high-resolution gas chromatography and the aromatic fraction by fluorescence.

Determination of aliphatic hydrocarbons through gas chromatography

High-resolution gas chromatography was conducted on a Konik 3000 gas chromatograph, equipped with a J & W DB1 fused silica column (30 m×0.25 mm i.d.), split/splitless capillary injection system, and a flame ionization detector (FID). The samples were analysed in the splitless mode using nitrogen as carrier gas, at a rate of 1 ml/min. The injector and detector temperatures were maintained at 250°C and 320°C, respectively. The column temperature was programmed from 60°C (2 min hold) to 135°C (2 min hold), at a rate of 15°C/min., then to 185°C (2 min hold), at a rate of 5°C/min, to a final temperature of 290°C at a rate of 5°C/min. The analogue signal was integrated with a Spectra Physics integrator. The identification of resolved aliphatic hydrocarbons was made by comparing retention times with corresponding standards (Chem Service). Resolved aliphatic hydrocarbons and unresolved complex mixtures (UCM) were calculated using the mean response factors of *n*-alkanes. Procedural blanks and standards were run in association with samples. Recovery assays were made by spiking a pristine sample. The results were 94.5 ± 11.6% ($n = 5$) for C20–C28 *n*-alkanes. Results were not corrected for recoveries. The reproducibility of the method for the synthetic standard mixture at the spiked level of 1 μg/g of dry weight sediment varied from 9.3% to 16.5%.

For each station, the individual *n*-alkane concentrations from *n*-C11 to *n*-C30, the isoprenoid pristane and phytane concentrations, the total resolved *n*-alkanes, the UCMs, and the total aliphatic fractions were calculated. The UCM involves cycloalkanes, branched alkanes, and other compounds unresolved by the capillary column which show as a 'hump' below the resolved compounds. The total aliphatic fraction was defined as the sum of the identifiable alkane peaks and the unidentifiable complex mixture, if present.

Evaluation indices

Since natural samples are extremely complex, different parameters in addition to absolute concentration have to be analysed in order to evaluate the probable origin of hydrocarbons (anthropogenic or biogenic). In addition, the combination of different indices applied to the same sample, reinforces this understanding. The anthropogenic source may be petroleum, but it can also be recycled organic matter of different origin, such as sewage, soil organic matter washed by rains and effluents from treatment plants. Biogenic sources may be, for example, algae, plankton, marine animals, terrestrial vascular plants and bacteria. The evaluation indices selected in this study were

(a) Major hydrocarbon (MH): denotes the highest *n*-alkane concentration. This index is often around C18

for oily samples (Clark and Finley, 1973). C15, C17, C19 and C21 have been described as important components in different types of algae (both macro and micro-algae), and C23, C25, C27, C29 and C31 for vascular land plants (Broman *et al.*, 1987; Colombo *et al.*, 1989).

(b) The low/high molecular weight hydrocarbons (LMW/HMW): it is the ratio of the sum of *n*-alkanes $\leqslant C20$ over the sum of *n*-alkanes $\geqslant 21$. Ratio values of 1.0 have been reported for algae, plankton and petroleum, while sedimentary bacteria, seawater, marine animals, higher plants and sediments show relatively lower values (Gearing *et al.*, 1976).

(c) *n*-C16 ratio: it is the sum of all *n*-alkanes/*n*-C16. This ratio tends to be small (< 15) for petroleum-contaminated samples, while it is larger (> 50) for biological samples (Clark and Finley, 1973).

(d) Carbon preference index (CPI): it is defined as $2(C27 + C29)/C26 + (2C28) + C30$ (Bohem and Requejo, 1986). Petrogenic hydrocarbons show values around 1, while vascular plants and uncontaminated sediments range from 3 to 6 (Colombo *et al.*, 1989).

(e) Even-to-odd ratio (even/odd): Petroleum usually shows a wide distribution range of *n*-alkanes and the even/odd ratio shows no predominance. In contrast, in most plant waxes, odd-chain alkanes are 8–10 times more abundant than even-chain *n*-alkanes (Volkman *et al.*, 1992).

(f) Pristane/Phytane ratio (Pri/Phy): Values close to 1.0 indicate petroleum-derived hydrocarbons (Broman *et al.*, 1987) and values from 1.4 to 6.7 indicate biogenic hydrocarbons (Lecaros *et al.*, 1991).

(g) *n*-C17/Pristane and *n*-C18/Phytane indices (*n*-C17/Pri, *n*-C18/Phy): These indices evaluate the presence of oil and the relative biodegradation of *n*-alkanes. Low values for these indices suggest the presence of degraded oil while higher indices suggest low degradation. When hydrocarbon concentrations are also high, higher indices indicate fresh oil inputs (Colombo *et al.*, 1989).

(h) Sum of the resolved aliphatic/unresolved complex mixture index (res/UCM): This index estimates the relative degradation degree; low values suggest a degradation process, while high values suggest fresh oil presence. The UCM magnitude is related to the degree of anthropogenic contribution.

Determination of aromatic hydrocarbons by fluorescence

The aromatic fraction was measured on a Farrand Optical fluorometer (excitation wavelength 310 nm, emission wavelength 360 nm). Standard response curves of fluorescence intensity versus concentration were done for appropriate oil standards (crude oil-CAPSA type) and for the standard aromatic hydrocarbon chrysene. CAPSA-type crude oil is similar to those generally found at these coastal zones. Response curves and blanks were run with each sample batch at identical instrument conditions. Recovery assays were made by spiking a pristine sample. The results were 80% ($n = 5$) for the crude oil standard used. Results were not corrected for recoveries.

Total organic matter

Total organic matter was determined by sediment calcination at 450°C for 5 h.

Granulometry

Granulometry was determined by dry sieving with 2 mm and 63 μm mesh sieves.

Results

The results of both aliphatic and aromatic hydrocarbons are presented based on the dry weight of sediments. Table 1 shows the granulometry and organic matter values for the sediment analysed. The granulometry analysis showed sediments with dominant fractions of sand and gravel (Fig. 2(a)).

Hydrocarbons

Aromatic hydrocarbons. The lowest values of aromatic hydrocarbons measured by fluorescence were recorded in coastal locations with human activity not directly related with the oil industry (Table 1). These were PQ, BC, PR and the mouth of the Negro and Colorado rivers. In some cases, such as PD, CO and SA, values varied within the same location. In these cases, the highest concentrations were found in areas near the ports.

The highest values were recorded in FA, CR and CC. The lowest values at the last two locations were in general higher than those found at the rest of the coastal locations. FA is a special case within the coast, and low (1.4 μg/g) and very high (737.7 μg/g) values were measured.

No significant differences were observed among the analysed depths. In general, the subsurface depths (3–6) cm showed similar or slightly lower concentrations than the upper depths (0–3) cm. An exception was found in CC, where the (3–6) cm depth had a concentration of 170 μg/g while the (0–3) cm depth had 108 μg/g. This could be associated to a spill event previous to the sedimentation of the upper layer.

Aliphatic hydrocarbons

Absolute concentrations. The concentrations of resolved aliphatic hydrocarbons, pristane, phytane, UCM and total aliphatic fraction are presented in Table 2. The *n*-alkanes in sediment samples ranged between *n*-C11 and *n*-C30.

For the three locations in Santa Cruz outside the San Jorge Gulf (PL, PQ, and SJ), the values for total aliphatic hydrocarbons were low, varying between 0.15 and 5.40 μg/g. The maximum value was obtained at SJ station while the lowest value was obtained at PQ2, where there was no contribution of UCM.

TABLE 1
Granulometry, total aromatic hydrocarbon concentrations and organic matter in Patagonian coastal sediments.[a]

Location	Station	Intertidal level	Depth (cm)	Granulometry (%)			Hydrocarbons (μg/g)[b]	Organic matter (%)
				Fine	Sand	Gravel		
Punta Loyola (PL)	PL1 (port)	U	0–3	15	63	21.8	7.1	0.8
	PL2 (port)	U	0–3	NA	NA	NA	6.3	0.8
Punta Quilla (PQ)	PQ1 (port)	U	0–3	0	27.6	72.4	ND	0.8
	PQ2 (port)	U	0–3	0	52.6	47.4	ND	1.0
San Julián (SJ)	SJ (pier)	U	0–3	58	42.3	0	4.6	3.4
Puerto Deseado (PD)	PD1 (Chaffers Island)	L	0–3	2.9	97.1	0	0.3	0.4
			3–6	3	98	0	1.0	0.5
	PD2 (port)	U	0–3	28	71.5	0.9	41.6	2.6
	PD3 (Port's Gulch)	U	0–3	7.4	75.4	17.2	1.4	1.3
		U	0–3	12	87.8	12	7.6	NA
		M	0–3	13	87.5	0	3.7	1.6
		M	0–3	8.1	72.1	19.8	0.4	0.7
			3–6	8.4	84.3	7.3	0.3	0.7
	PD4 (Quinta Island)	L	0–3	36	64.5	0	16.8	1.2
Caleta Olivia (CO)	CO1 (YPF pier)	U	0–3	2.7	97.3	0	8.9	2.0
			3–6	2.8	97.2	0	7.4	NA
	CO2 (Paula creek)	U	0–3	0	0	100	ND	NA
Rada Tilly (RT)	RT (beach)	U	0–3	0.3	99.7	0	1.3	1.5
			3–6	0.3	99.7	0	1.0	NA
Comodoro Rivadavia (CR)	CR1 (Port)	U	0–3	0.2	99.8	0	49.2	1.7
			3–6	0.2	99.8	0	36.9	1.8
	CR2 (Port)	U	0–3	0	0	100	75.7	0.9
	CR3 (Km.4/5)	U	0–3	0.1	27.4	72.5	20.2	0.8
	CR4 (Km.8)	U	0–3	NA	NA	NA	67.3	2.1
			3–6	NA	NA	NA	58.9	NA
Caleta Córdova (CC)	CC (Port)	U	0–3	0.1	50.3	49.6	107.8	1.6
			3–6	0.1	50.3	49.6	169.6	NA
Faro Aristizábal (FA)	FA1	U	0–3	0	0	100	737.6	2.4
	FA2	U	0–3	0.1	29.7	70.3	1.4	0.9
Bahía Camarones (BC)	BC (Elola beach)	U	0–3	0.1	69	30.9	0.7	NA
Rawson (PR)	PR (Port)	U	0–3	0	0.2	99.8	ND	NA
Puerto Madryn (PM)	PM1 (port)	U	0–3	NA	NA	NA	1.5	1.2
	PM2 (fish factories)	U	0–3	0.1	69.8	30.1	0.7	1.0
San Antonio Oeste (SA)	SA1 (Beach)	U	0–3	7.8	92.2	0	16.0	3.6
	SA2 (Coast Guard beach)	U	0–3	0.7	61	38.3	5.2	0.8
	SA3 (port)	U	0–3	0.8	82.2	17	25.3	0.8
Río Negro (RN)	RN (south coast)	U	0–3	0.1	99.9	0	0.6	0.5
			3–6	NA	NA	NA	0.8	NA
Río Colorado (RC)	RC (north coast)	U	0–3	1	99	0	0.9	0.8
			3–6	1.6	98.4	0	0.5	NA

[a] Intertidal level: U – upper; M – mid; L – lower; NA – not analysed; ND – not detected.
[b] Aromatic hydrocarbon concentrations in μg/g (dry weight) as crude oil equivalents.

At the stations located within San Jorge Gulf, from CO to CC, the concentrations of resolved aliphatic hydrocarbons were between 0.06 and 8.20 μg/g. In these same stations, the values of UCM varied between non-detected and 146.55 μg/g. The total aliphatic fraction varied between 0.06 and 150.01 μg/g. At CR1 and CO1 stations the (0–3) cm depths showed a higher value than the (3–6) cm depths, while the reverse was observed in CC and RT.

The larger variability was recorded at FA. While the station FA1 showed the highest value of the Patagonian coast, with a total of 109.70 μg/g for resolved aliphatic hydrocarbons, 1194.95 μg/g for UCM, and 1304.65 μg/g for the total aliphatic fraction, the station FA2 showed very low values of resolved hydrocarbons (0.22 μg/g), UCM (1.54 μg/g) and total aliphatic fraction (1.76 μg/g).

BC and PM showed low values ranging from 1.50 to 3.33 μg/g of total aliphatic fraction. In PR station, the values were non-detected.

At SA, the values obtained for the total aliphatic fraction were high, ranging between 33.38 μg/g in SA2 station and 138.85 μg/g in SA1. This last station is located close to the port, where the concentration reached 108.67 μg/g (SA3). The values for resolved aliphatic hydrocarbons ranged between 8.44 and 25.18 μg/g, and the values for UCM between 24.94 and 118.40 μg/g.

At the RN, values were 1.70 and 3.30 μg/g for the (0–3) and (3–6) cm depths, respectively, with contribution of UCM. In RC the total aliphatic fraction reached 0.50 and 0.57 μg/g for the (0–3) and (3–6) cm depths, respectively. In both cases, there was no contribution of UCM.

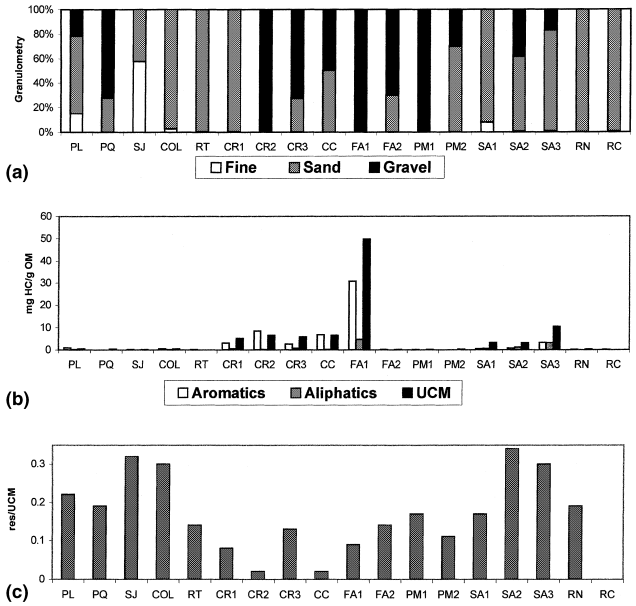

Fig. 2 Granulometry (2a), hydrocarbon concentrations (2b), and res/UCM (2c) ratios for Patagonic coastal sediments. The values correspond to the depth 0–3 cm. Hydrocarbon concentrations are normalized with respect to organic matter content [mg hydrocarbon (HC)/g organic matter (OM)].

When total aliphatic, UCM and aromatic hydrocarbon concentrations are normalized with respect to organic matter content (mg of hydrocarbons/g organic matter), higher values were observed at CR, CC, FA (FA1), and SA (Fig. 2(b)). In most cases, the concentration of total aliphatic hydrocarbons was higher than aromatic concentrations (Fig. 3).

Application of evaluation indices to sediment samples

Table 3 shows the values of evaluation indices for aliphatic hydrocarbons in sediment samples obtained in this study. Locations sampled along the Patagonian coast were grouped based on an association of these indices and the absolute hydrocarbon concentrations (Fig. 4):

1. Locations where hydrocarbons were mainly of anthropogenic origin and with low values of absolute concentrations: PL, PQ, RT, BC, PM, RN, and RC. The values of *n*-C17/Pri, *n*-C18/Phy, and res/UCM indices indicate relatively little degradation.

2. Locations where hydrocarbons were mainly of biogenic origin and with low values of absolute concentrations: SJ. The values of *n*-C17/Pri and Pri/Phy indices indicate a significant presence of pristane. The MH, LMW/HMW, *n*-C16, IPC and even/odd indices, confirm the natural origin for these hydrocarbons.

3. Locations where hydrocarbons were mainly of anthropogenic origin and with high values of absolute concentrations: CO, CR and CC. The low values of res/UCM index, particularly for CR1, CR2 and CC stations

TABLE 2

Concentration (in μg/g dry weight) of *n*-alkanes, pristane and phytane isoprenoids, UCM, and total aliphatics for sediment samples in coastal Patagonia.[a]

Location	Station	Depth (cm)	Res. Aliph.	UCM	Total Aliph.	*n*-C17	Pri	*n*-C18	Phy	*n*-C25
Punta Loyola (PL)	PL1 (port)	0–3	0.70	3.36	4.06	0.029	0.014	0.108	0.020	0.043
	PL2 (port)	0–3	0.89	4.09	4.98	0.047	0.026	0.148	0.040	0.039
Punta Quilla (PQ)	PQ1 (port)	0–3	0.35	1.80	2.14	0.038	0.011	0.056	0.020	0.007
	PQ2 (port)	0–3	0.15	ND	0.15	0.016	0.006	0.023	0.007	0.014
San Julián (SJ)	SJ (pier)	0–3	1.30	4.10	5.40	0.019	0.034	0.063	0.011	0.173
Caleta Olivia (CO)	CO1 (YPF pier)	0–3	2.45	8.27	10.72	0.226	0.137	0.280	0.082	0.109
		3–6	1.00	6.65	7.65	0.051	0.040	0.095	0.062	0.013
Rada Tilly (RT)	RT (beach)	0–3	0.06	ND	0.06	ND	ND	ND	ND	ND
		3–6	0.53	3.67	4.19	0.052	0.031	0.070	0.046	0.019
Cro.Rivadavia (CR)	CR1 (port)	0–3	8.20	101.75	109.95	0.638	0.437	0.832	0.485	0.201
		3–6	7.19	72.64	79.83	0.563	0.388	0.601	0.376	0.188
	CR2 (port)	0–3	1.40	57.48	58.88	0.079	0.05	0.083	0.029	0.038
	CR3 (Km 4/5)	0–3	5.80	45.71	51.51	0.514	0.305	0.556	0.215	0.233
Caleta Córdova (CC)	CC (port)	0–3	2.03	104.26	106.29	0.137	0.113	0.132	0.090	0.075
		3–6	3.46	146.55	150.01	0.155	0.148	0.184	0.106	0.148
Faro Aristizábal (FA)	FA1	0–3	109.70	1194.95	1304.65	0.407	0.271	1.287	0.203	16.262
	FA2	0–3	0.22	1.54	1.76	0.007	0.005	0.034	0.012	0.007
Bahía Camarones (BC)	BC (Elola beach)	0–3	0.21	1.29	1.50	0.020	0.007	0.031	0.022	0.015
Rawson (PR)	PR (port)	0–3	ND	ND						
Puerto Madryn (PM)	PM1 (port)	0–3	0.36	2.13	2.49	0.011	0.006	0.046	0.021	0.012
	PM2 (fish factories)	0–3	0.34	2.99	3.33	0.011	ND	0.044	0.017	0.007
San Antonio Oeste (SA)	SA1 (beach)	0–3	20.45	118.40	138.85	0.704	0.364	0.792	0.772	2.495
	SA2 (Coast Guard beach)	0–3	8.44	24.94	33.38	0.147	0.085	0.275	0.200	1.013
	SA3 (port)	0–3	25.18	83.38	108.67	0.647	0.596	0.976	1.112	2.916
Río Negro (RN)	RN (south coast)	0–3	0.27	1.43	1.70	0.029	0.012	0.040	0.012	0.006
		3–6	0.62	2.68	3.30	0.098	0.044	0.089	0.058	0.014
Río Colorado (RC)	RC (north coast)	0–3	0.50	ND	0.50	0.045	0.027	0.110	0.023	0.014
		3–6	0.57	ND	0.57	0.066	0.032	0.067	0.041	0.009

[a] ND – not detected; CO2, CR4, and PD stations were not analysed for aliphatic hydrocarbons.

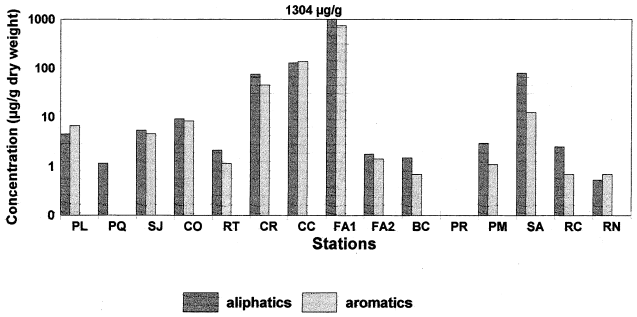

Fig. 3 Total aromatic and aliphatic hydrocarbon concentrations. Hydrocarbon concentrations are given as means for each location except for FA stations.

(Fig. 2(c)), reflect the biodegradation of *n*-alkanes. The distribution of UCM (Fig. 6(a)–(c)) suggests a mixed contribution of light crude oil and heavier fractions that could result from bacterial degradation or from other sources of organic matter. CO showed fresh oil with little degradation and a smaller contribution of UCM. In contrast, CC showed the most evident case of degradation, having mainly degraded residues and biogenic materials, and showing the lowest values of res/UCM, LMW/HMW and C17/Pris indices. In the CR1 station, the higher values of the LMW/HMW index suggest the presence of fresh oil. In all cases, C17/Pri and C18/Phy indices were greater than 1. These correspond to low degradation, and when the resolved hydrocarbon levels are also high, they indicate fresh crude oil contributions. In this case, the indices, in association with the concentration of resolved aliphatics and the presence of hydrocarbons of low molecular weight, indicate the contribution of fresh oil together with another degraded residual oil from previous inputs. The latter is supported by the important contribution of UCM. Fig. 5 shows the values of indices applied to sediment samples from stations within San Jorge Gulf and Fig. 6(a)–(c) the gas chromatograms of some stations.

4. Locations where hydrocarbons were mainly of anthropogenic origin and with high and low values of absolute concentrations: FA. At FA1, maximum values of *n*-alkanes were predominant between *n*-C20 and *n*-C26. This suggests the presence of a heavier oil type or a degraded crude oil with a preferential degradation of light compounds (LMW/HMW index = 0.2, significant value for UCM (1194.95 µg/g), and low res/UCM index = 0.09, suggest the latter hypothesis). The C17/Pri and C18/Phy indices greater than 1, associated with a high concentration of resolved *n*-alkanes (109.23 µg/g), the presence of low molecular weight compounds and an important contribution of UCM, indicate a contribution of recent oil together with a degraded residue. In addition, a contribution of biogenic material is also observed at this station, identified by the high values of *n*-alkanes with odd number of carbons (*n*-C23 and *n*-C25), and *n*-C16 index > 50. However, the values of the considered indices and the absolute concentrations strongly indicate that the hydrocarbons in these sediments have a

TABLE 3
Values of *n*-alkane evaluation indices applied to sediment samples in coastal Patagonia.[a]

Location	Station	Depth (cm)	MH	%*n*-alk.	LMW/HMW	*n*-C16 rel.	CPI	Res/UCM	*n*-C17/Pri	*n*-C18/Phy	Pri/Phy	Even/odd
Punta Loyola (PL)	PL1 (port)	0–3	*n*–C18	16.2	0.8	23.8	2.5	0.21	2.1	5.4	0.7	1.5
	PL2 (port)	0–3	*n*-C18	18.1	1.3	10.7	2.6	0.22	1.8	3.7	0.7	1.9
Punta Quilla (PQ)	PQ1 (port)	0–3	*n*-C18	17.8	1.4	21.0	0.1	0.19	3.5	2.8	0.6	1.6
	PQ2 (port)	0–3	*n*-C18	8.8	2.0	11.3	–	–	2.7	3.3	0.9	1.3
San Julián (SJ)	SJ (pier)	0–3	*n*-C29	17.6	0.2	125.9	4.7	0.32	0.6	5.7	3.1	0.6
Caleta Olivia (CO)	CO1 (YPF pier)	0–3	*n*-C16	13.2	1.4	7.6	1.2	0.30	1.7	3.4	1.7	1.2
		3–6	*n*-C21	12.0	1.3	9.2	0.5	0.15	1.3	1.5	0.7	1.3
Rada Tilly (RT)	RT (beach)	0–3										
Comodoro Rivadavia (CR)	CR1 (port)	0–3	*n*-C18/19	11.4	2.4	10.1	1.1	0.08	1.5	1.7	0.9	1.2
		3–6	*n*-C18	9.3	2.6	11.4	0.9	0.10	1.5	1.6	1.0	1.1
	CR2 (port)	0–3	*n*-C16/19	8.6	1.4	11.7	1.4	0.02	1.6	2.9	1.7	1.1
	CR3 (Km 4/5)	0–3	*n*-C18	10.5	1.8	9.7	1.0	0.13	1.7	2.6	1.4	1.0
Caleta Córdova (CC)	CC (port)	0–3	*n*-C19	8.0	1.0	12.9	1.4	0.02	1.2	1.5	1.3	1.0
		3–6	*n*-C27	10.3	0.8	18.1	1.5	0.02	1.1	1.7	1.4	1.1
Faro Aristizábal (FA)	FA1	0–3	*n*-C23	16.4	0.2	84.9	0.5	0.09	1.5	6.3	1.3	1.0
	FA2	0–3	*n*-C20	21.6	1.0	–	–	0.14	1.4	2.8	0.4	2.5
Bahía Camarones (BC)	BC (Elola beach)	0–3	*n*-C18/20	16.8	1.4	–	0.9	0.17	2.9	1.4	0.3	1.0
Puerto Madryn (PM)	PM1 (port)	0–3	*n*-C20	20.2	1.0	–	1.9	0.17	1.8	2.2	0.3	1.4
	PM2 (fish factories)	0–3	*n*-C20	19.9	0.8	–	–	0.11	–	2.6	–	2.9
San Antonio Oeste (SA)	SA1 (beach)	0–3	*n*-C23/25	12.9	0.3	76.3	1.0	0.17	1.9	1.0	0.5	0.9
	SA2 (Coast Guard beach)	0–3	*n*-C25	12.4	0.3	92.7	1.4	0.34	1.7	1.4	0.4	0.9
	SA3 (port)	0–3	*n*-C25	12.4	0.4	66.9	1.0	0.30	1.1	0.9	0.5	0.9
Río Negro (RN)	RN (south coast)	0–3	*n*-C18	16.1	1.1	19.2	1.2	0.19	2.4	3.3	1.0	1.5
		3–6	*n*-C16	21.0	4.9	4.7	–	0.23	2.2	1.5	0.8	1.2
Río Colorado (RC)	RC (north coast)	0–3	*n*-C16	27.1	7.2	3.7	–	–	1.7	4.8	1.2	3.3

[a] CO2, CR4, and PD stations were not analysed for aliphatic hydrocarbons.

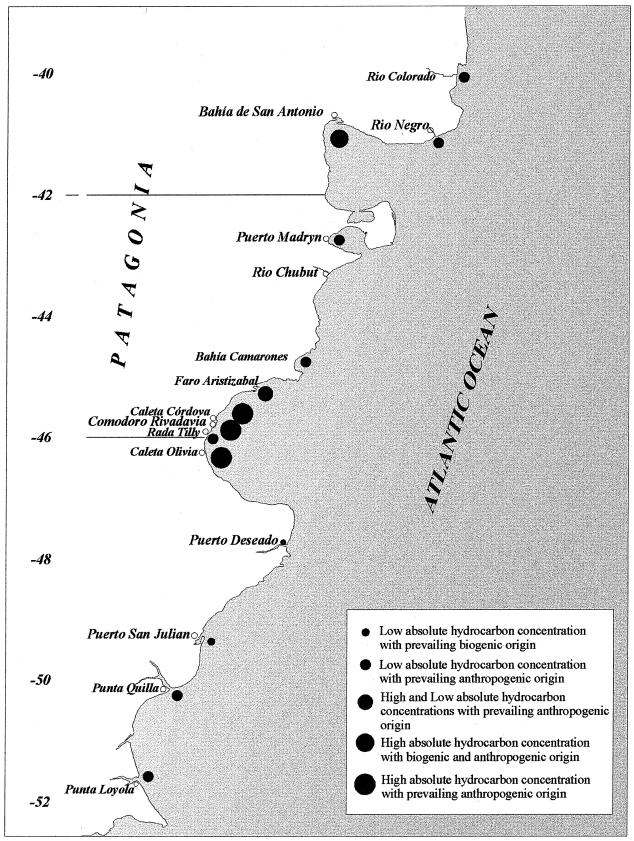

Fig. 4 Locations grouped by hydrocarbon concentrations and origin.

dominant petrogenic origin. The other station located in the same area, FA2, showed a very low value of total aliphatic hydrocarbons. The indices suggest the presence of hydrocarbons of anthropogenic origin.

5. Locations with hydrocarbons of biogenic and anthropogenic origin and with high values of absolute concentrations: SA. The analysis of some indices (HM, LMW/HMW, and rel. *n*-C16) suggests a contribution of hydrocarbons of biogenic origin. The values of CPI, Pri/Phy and even/odd indices, associated to the high concentration of resolved hydrocarbons, high concentrations of total hydrocarbons with an important contribution of UCM, and the presence of the continuous homologous series of normal alkanes from *n*-C12, suggest the contribution of hydrocarbons of anthropogenic origin. In addition, the values of the res/UCM relationship, the presence of low molecular weight compounds and the important UCM contribution, indicate an input of fresh oil in association with a degraded residue. The relative low values of C17/Pri and C18/Phy indices (1.1 and 0.9, respectively) at the port station suggest the existence of degradation processes.

A Principal Component Analysis run on the data set showed similar results (Fig. 7). The first three principal components explained 97% of the variance. The principal component 1 (51% of the variance), included locations with low absolute hydrocarbon concentrations and mainly anthropogenic origin (group A, Fig. 7). The principal component 2 (37% of the variance), included locations with high absolute hydrocarbon concentrations with mainly anthropogenic or anthropogenic-biogenic origin (group B, Fig. 7). The principal component 3 (9% of the variance), included a location with low absolute hydrocarbon concentration and biogenic origin and one station with relatively low absolute hydrocarbon concentration and anthropogenic-biogenic origin (group C, Fig. 7).

Discussion

The Patagonian coast has few human settlements and is considered relatively pristine. However, there are several sources of anthropogenic hydrocarbons that constitute a potential threat to the environment and to growing economic activities, such as ecotourism and fisheries. The present study shows evidence of pollution

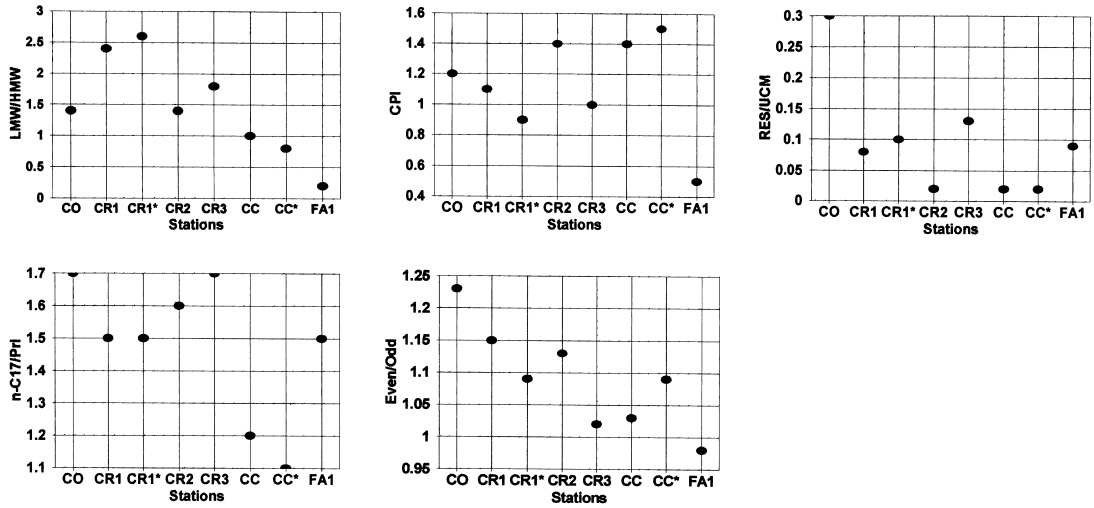

Fig. 5 Evaluation indices in San Jorge Gulf stations. * (3–6) cm depth.

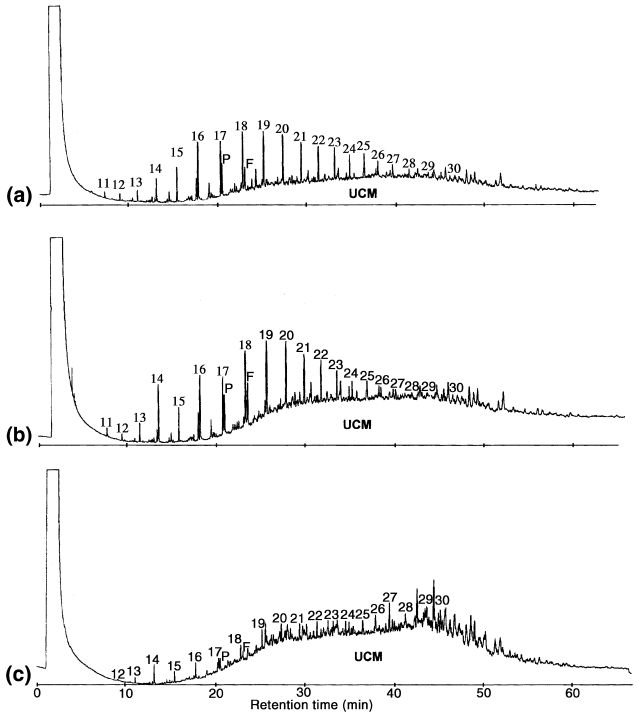

Fig. 6 Gas chromatogram of aliphatic fractions in sediments. Station CR3 (a), Station CR1 (b), and Station CC(c). Numbers 11–30 correspond to *n*-alkanes C11–C30, P and F are Pristane and Phytane isoprenoids. Chromatographic conditions are as described in the Methods Section.

from petroleum-derived hydrocarbons in variable levels on the coastal area. The highest hydrocarbon levels were found in San Jorge Gulf, where oil development activities take place, while in some locations such as Bahía Camarones and Rawson levels were low or non-detectable.

The sediments of San Jorge Gulf coastal zone are polluted with anthropogenic hydrocarbons. Fresh petroleum was detected at all sampled stations within this Gulf, associated with degraded petroleum or degraded organic material from multiple sources. Our data indicate an input from oil extraction operations and transport, resulting in chronic pollution. The highest hydrocarbon concentrations in this Gulf were associated with sandy sediments and gravel. In coastal sediments at other locations with similar granulometry, the hydrocarbon concentrations were low. According to the known higher affinity of hydrocarbons with fine than coarse sediment fractions (Boehm and Requejo, 1986; Colombo *et al*., 1989) these results suggest an important pollution in San Jorge Gulf. The three stations with the highest concentrations of both total fractions of aromatic and aliphatic hydrocarbons, showed a similar depth distribution of both types of hydrocarbons. CO and CR1 gave higher values at the surface level (0–3 cm), and CC at the sub-surface level (3–6 cm). This suggests a recent input of hydrocarbons in CO and CR1. CC with a granulometry dominated by coarse sediments (50% gravel and 50% sand), constitutes a higher energy area. The presence of high hydrocarbons concentration at 3–6 cm could be the result of deposition from an older spill.

The highest hydrocarbon concentrations were found at one of the two stations of Faro Aristizábal, far away from any human activities. The additional presence in this coastal sector of different types of solid waste, particularly derived from ship activities, suggests that pollutants tend to accumulate in this area due to marine current action. The different hydrocarbon levels observed in two adjacent stations showed the patchy distribution of these pollutants. This information suggests that sites adjacent to Faro Aristizábal may also show a high level of pollution and therefore further studies along the northern coast of San Jorge Gulf are needed.

The rest of the coast is mainly exposed to oil transport and shipping activities between southern and northern ports, and to port activity at a few coastal cities. Significant levels of hydrocarbons were recorded too in San Antonio Oeste and Puerto Deseado reflecting important activities in these ports. At San Antonio Oeste, such activities added to other potential urban sources explain the clear input of hydrocarbons of human origin. In

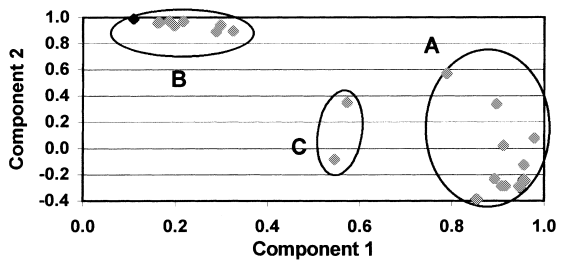

Fig. 7 Group A: PL, PQ, CO, RT, BC, PM, RN, RC locations and FA2 station. Group B: CR, CC locations and FA1, SA1 and SA3 stations. Group C: SJ location and SA2 station.

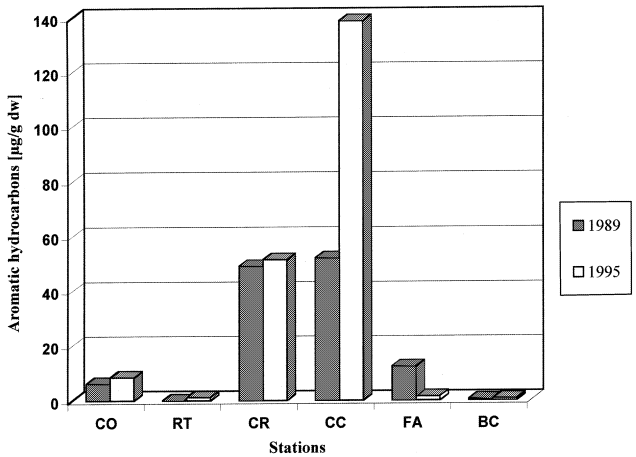

Fig. 8 Comparison between values of aromatic hydrocarbons obtained in 1989 (Esteves and Commendatore, 1993) and 1995 (this study). Hydrocarbon concentrations are given as means for each location. The value for aromatic hydrocarbon concentration at FA station (1995) corresponds to the lower concentration obtained.

TABLE 4

Comparison of hydrocarbon concentrations in coastal Patagonia with other coastal regions reported in the literature.[a]

Location		Sediment type	Resolved alkanes	Aliphatic	Aromatic	Total	Author
Río de La Plata Estuary, Argentina		Surface, subtidal (polluted and unpolluted)		0.06–240	0.05–17	–	Colombo *et al.* (1989)
Ile-aux-Grues, Canada	11 days after a spill	Surface, midlittoral (polluted)	1.46–34			24–185	Siron and Brochu (1991)
	2 years after a spill		3.55–7.30			14.5–219	
Australia							Volkman *et al.* (1992)
Davies Reef and Lizard Island		Surface, subtidal (unpolluted)				0.5–2	
Derwent River and D'Entrecasteaux Channel		Surface, subtidal (polluted)				> 500	
Eastern Harbour, Alexandria, Egypt	Within the harbour	Surface, subtidal (polluted)		61–1357			Tarek *et al.* (1995)
	Outside the harbour	Surface, subtidal (polluted)		102–454			
North-west Coast, Australia		Midlittoral (unpolluted)		0.015–0.050	0.002–0.005		Pendoley Kellie (1992)
Patagonian coastal zone		Surface, intertidal		ND – 1304	ND – 738		This study

[a] Values are given in μg/g dry weight.

addition, an important input of biogenic origin hydrocarbons might be also coming from terrestrial vascular plants such as *Salicornia* sp. and *Spartina alterniflora*. At other locations, such as Punta Quilla, Punta Loyola, Bahía Camarones, Puerto Rawson, and Puerto Madryn, there were no indications of significant hydrocarbon concentrations despite all such locations having some degree of shipping activity. The hydrocarbons detected at these sites were of anthropogenic origin.

Although San Julián presents some degree of human development, it was the only location where detected hydrocarbons were only of biogenic origin. The source of these hydrocarbons could be terrestrial vascular plants, as at this location *Salicornia* sp. and *S. alterniflora* are found throughout the coastal zone.

Grouping of stations and locations differed depending on the criteria used, as three groups were obtained using a Principal Component Analysis while five groups were obtained when non-statistical criteria were used. Differences found were because we classified both stations at Faro Aristizábal as a separate group, considering that this location had particular characteristics because of the presence of both very high and very low hydrocarbon concentrations. In addition, we classified the three stations at San Antonio Oeste as a separate group, given that this location showed most clearly a mixed input of hydrocarbons of both anthropogenic and biogenic origin. However, except for these stations which were classified differently, grouping of stations and locations was similar.

Little is known about hydrocarbon pollution in the Patagonian coastal zone. Previous information exists only from several stations in Chubut and the north of Santa Cruz, obtained during 1989 (Esteves and Commendatore, 1993) and from Cabo Vírgenes, Santa Cruz, in 1993 (Esteves *et al.*, 1993). The information from this study shows a similar pattern of hydrocarbon levels than the one observed in 1989 (Esteves and Commendatore, 1993) (Fig. 8). In both studies, the highest concentrations were observed in Caleta Córdova and Comodoro Rivadavia, followed by Caleta Olivia. The results from this study, however, show a higher concentration in Caleta Córdova than in 1989, probably as a result of recent spills.

The values for absolute hydrocarbon concentrations obtained in this study are within the range of those reported in the literature by other authors (Table 4). Values along the Patagonian coast ranged from non-detectable, similar to those found in unpolluted areas such as the north-west coast of Australia (Pendoley Kellie, 1992) to high values similar to the ones reported in polluted areas such as Eastern Harbour-EH-Alexandria, Egypt (Tarek *et al.*, 1995), reflecting the extension of the coast analysed and its variable exposure to human activities.

In summary, the Patagonian coast shows different levels of aliphatic and aromatic hydrocarbons. Polluted areas are in general associated with human uses related with oil development and port activities. These results suggest the need for improvements in loading and transport conditions, the reduction of ballast and bilge waste discharges, and minimizing fuel spills. In addition, the patchy distribution of hydrocarbon concentrations suggests the need for further evaluations at other specific locations of the extensive Patagonian coast.

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