

Oil spill in the Río de la Plata estuary, Argentina: 1. Biogeochemical assessment of waters, sediments, soils and biota

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The Oil spill impact in the Río de la Plata was evaluated by HRGC and multivariate techniques applied to waters, sediments and biota.

Abstract

Aliphatic (ALI) and aromatic (ARO) hydrocarbon concentrations, composition and sources were evaluated in waters, sediments, soils and biota to assess the impact of ~1000 tons of oil spilled in Río de la Plata coastal waters. Total ALI levels ranged from 0.4–262 µg/l in waters, 0.01–87 µg/g in sediments, 5–39 µg/g in bivalves, 12–323 µg/g in macrophytes to 948–5187 µg/g in soils. ARO varied from non-detected 10 µg/l, 0.01–1.3 µg/g, 1.0–16 µg/g, 0.5–6.9 µg/g to 22–67 µg/g, respectively. Offshore (1, 5, 15 km) waters and sediments were little affected and contained low background hydrocarbon levels reflecting an effective wind-driven transport of the slick to the coast. Six months after the spill, coastal waters, sediments, soils and biota still presented very high levels exceeding baseline concentrations by 1–3 orders of magnitude. UCM/resolved aliphatic ratio showed a clear trend of increasing decay: coastal waters (3.3) < macrophytes (6.7) < soils (9.4) < offshore sediments (13) < coastal sediments (17) < clams (52). All environmental compartments consistently indicated that the most impacted area was the central sector close to Magdalena city, specially low-energy stream embouchures and bays which acted as efficient oil traps. The evaluation of hydrocarbon composition by principal component analysis indicated the predominance of biogenic (algae, vascular plant cuticular waxes), background anthropic, pyrogenic and diagenetic hydrocarbons, offshore and in non-impacted coastal sites. In contrast, polluted stations presented petrogenic signatures characterized by the abundance of isoprenoids, low molecular weight *n*-alkanes and methylated aromatics in different stages of alteration. The petrogenic/biogenic ratio ($<n\text{-C}_{22} + \text{isoprenoids}/n\text{-C}_{15} + n\text{-C}_{17} + >n\text{-C}_{23}$) and petrogenic/pyrogenic relationship (methylated/unsubstituted PAH) discriminated the samples according to the different degree of impact. The following paper present the results of the study of the progress of hydrocarbon disappearance in sediments and soils 13 and 42 months after the spill.

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1. Introduction

Petroleum hydrocarbons are ubiquitous contaminants in the aquatic environment, specially in

major rivers and estuaries which support a strong urban-industrial development. Chronic spillages from land-based facilities, ports and vessels, crude effluent discharges and accidental spills, continuously introduce large amounts of hydrocarbons to these ecosystems. According to local environmental characteristics and the distinct physico-chemical properties of the

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numerous petroleum components, hydrocarbons undergo a differential fractionation in the environment. After the initial steps of slick spreading, evaporation, dissolution of smaller molecules, emulsification, photochemical oxidation of susceptible aromatics and biodegradation of labile components, a large percentage (>30–50%) of spilled hydrocarbons enriched in heavier more recalcitrant compounds are deposited in bottom sediments, beaches and soils which then act as long-term reservoirs and secondary sources (Albaigés, 1980; Gearing et al., 1980; Lee, 1980; Olsen et al., 1982).

The Río de la Plata estuary is a funnel-shaped, turbid, coastal-plain estuary 300 km long, 30–220 km wide and 0.5–25 m deep with a total surface area of 35,000 km² (Fig. 1). In spite of the large dimensions and dilution capacity of the estuary, the vast urban-industrial zone developed in the first 100 km of the Argentinean coast produced a significant impact on the coastal area (review in Colombo 2000). Polluted waters and toxic materials are discharged daily to the estuary via untreated effluents close to Buenos Aires city. The hydrocarbon composition of bottom sediments (Colombo et al., 1989) show the dominance of petrogenic sources in tributaries and nearby coastal areas affected by petrochemical effluents, tanker ballast washings and furtive spillages. Offshore sediments denote the contribution of vascular-plant waxes and pyrogenic polycyclic aromatic hydrocarbons (PAHs) transported from major fossil fuel combustion sources. The hydrocarbon load to the estuary is also evident in biota such as a specialized detritivorous fish which

present clear petrogenic aliphatic signatures in the muscle (Colombo et al., 2000).

In addition to these chronic hydrocarbon inputs, on January 15th 1999, the collision of the cargo ship Sea Parana and the tanker Estrella Pampeana in the Intermediate Channel, 20 km away from the Argentinean coast, produced a spill of ~1000 tons of oil. In the next 2 days, strong southeast winds pushed the uncontrolled slick against the shoreline of Magdalena, located 120 km SE from Buenos Aires in the less impacted intermediate freshwater sector of the estuary (Fig. 1). This is a temperate (mean 18 °C), dynamic coastal environment modeled by the strong freshwater discharge, small tides and winds. The coast physiognomy is dominated by sandy beaches colonized by water grasses and macrophytes, particularly developed in low areas like stream embouchures and bays, and young soils covered by grass and a patchy forest of small autochthonous species. The massive oiling of the beach, soils and even trees was favored by the flood driven by intense SE winds. The cleaning activities were limited to a partial mechanical removal of major oil patches on the beach and most affected vegetation.

In order to evaluate the impact produced, a monitoring project was coordinated by the Buenos Aires Environmental Policy Agency (SPA) and the Natural Sciences Faculty from the National University of La Plata. This paper presents the results of the biogeochemical assessment of hydrocarbons in waters, sediments, soils and biota. Specific objectives were: (a) to quantify hydrocarbon levels in the different environmental compartments; (b) to compare results with previous baseline levels; (c) to identify critical areas; (d) to characterize hydrocarbon composition and sources. The following paper presents the results of the study of the progress of hydrocarbon attenuation in sediments and soils 13 and 42 months after the spill. Both papers are intended to illustrate the fate of oil residues and the natural recuperation capacity of this southern temperate estuary.

2. Methods

Sampling was performed 6 months after the spill in July 1999 in offshore waters over four 15-km transects, and along the coast covering the most impacted area (Fig. 1). A total of 26 stations were visited, 12 offshore and 14 over 45 km of shoreline (Table 1), for the collection of surface waters (1–4 l in amber glass bottles), sediments and soils (Hydro-Bios stainless steel grab sampler and spatula in 300 ml glass jars), macrophytes (*Schenoplectum californicus*) and Asiatic clams (*Corbicula fluminea*). All glass material was pre-cleaned for trace organic analysis (detergent, distilled water, 10% nitric acid, acetone). Samples were maintained in portable

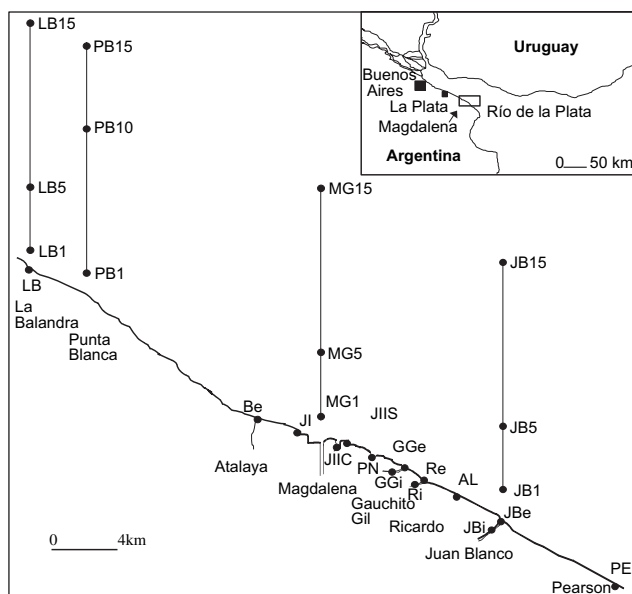


Fig. 1. Study area and station location along offshore transects and the shoreline of the Río de la Plata estuary. Station abbreviations are given in Table 1.

Table 1
Description and abbreviation of sampling stations

Station	Description	Abbreviation
La Balandra offshore	Transect at 1, 5 and 15 km from the shoreline	LB1,5,15
Palo Blanco offshore	Transect at 5, 10 and 15 km from the shoreline	PB5,10,15
Magdalena offshore	Transect at 1, 5 and 15 km from the shoreline	MG1,5,15
Juan Blanco offshore	Transect at 1, 5 and 15 km from the shoreline	JB1,5,15
La Balandra	Open beach with macrophytes, recreation	LB
Buñirigo stream	Open beach, stream embouchure	Be
Juncal I	Macrophyte colonized embayment, recreation	JI
Juncal II Center	Forested embayment, recreation, low human impact	JIIC
Juncal II South	Open beach with macrophytes, recreation	JIIIS
Playa Nueva	Open beach, recreation	PN
Gauchito Gil stream	Small stream, 50 m inside, low human impact	GGi
Gauchito Gil stream	Stream embouchure, low human impact	GGe
Ricardo	Small channel with macrophytes, 15 m inside	Ri
Ricardo	Open beach with macrophytes, low human impact	Re
Alborada	Open beach with macrophytes, low human impact	AL
Juan Blanco stream	Long stream with macrophytes, 15 m inside	JBi
Juan Blanco stream	Open beach, stream embouchure with macrophytes	JBe
Pearson	Open beach with macrophytes, low human impact	PE

coolers until arrival at the laboratory and then were acidified (waters, pH=2), refrigerated (sediments, soils ~5 °C) or frozen (biota, –20 °C).

Chemical analyses were performed by previously standardized techniques (Colombo et al., 1989, 1996a, 2000; Commendatore et al., 2000) which included petroleum ether/dichloromethane (1:1) extraction by liquid-liquid partitioning (2 times for 1.6 l total water), ultrasonic treatment (4 times for ~40 g of partially dried sediments), or Soxhlet extraction (40 cycles of homogenized and partially dried tissues) and silica gel fractionation of aliphatic (F1: ALI, petroleum ether) and aromatic hydrocarbons (F2: ARO, petroleum ether/dichloromethane 1:3). Quantification of individual hydrocarbons was performed by high resolution gas chromatography/flame ionization detection using two Konik gas chromatographs HRGC 3000 and HRGC 4000A equipped with split-splitless injectors maintained at 260 °C, flame ionization detectors operating at 320 °C and 30 m capillary columns (DB-5, HP-5). Column temperature was programmed from 65 °C (2 min) to 130 °C (1 min) at 10 °C/min and from 130 to 300 °C (10 min) at 5 °C/min. Data acquisition and integration was carried out with Konikrom 6.7 chromatography software. Compound quantification was performed with individual response factors calculated with authentic standards (Supelco, Accustandard Inc.) for the aliphatic fraction (ALI) including C₁₂–C₃₀ *n*-alkanes, isoprenoids (farnesane, norpristane, pristane, phytane), and aromatic hydrocarbons (ARO) including methylated aromatics (methyl naphthalenes, methyl phenanthrenes, methylchrysene, methylpyrenes) and unsubstituted aromatic hydrocarbons with 2–5 rings. The aliphatic and aromatic unresolved complex mixtures (ALI and AROUCM, respectively) were quantified based on total area calculation and the response of

overlying resolved peaks. Procedural blanks were run with each batch of processed samples. The method quantification limits for individual hydrocarbons ranged from 0.02 µg/l in waters, 0.01 µg/g in biota to 0.001 µg/g in sediments. The method accuracy ranged from 60 to 101% according to PAH analysis of certified reference sediments (NIST 1941a and NRCC HS6). Fig. 2 shows representative chromatograms of the aliphatic fraction in different environmental compartments.

3. Results and discussion

3.1. Total hydrocarbon concentrations

Tables 2 and 3 and Fig. 3 present total hydrocarbon data, including resolved and unresolved components for offshore and coastal waters and sediments, soils and biota.

Due to their hydrophobic nature, the environmental distribution of hydrocarbons reflects the increasing affinity sequence: waters << sediments < biota < soils. Total resolved aliphatic hydrocarbon concentrations range from 0.4–262 µg/l in waters, 0.01–87 µg/g in sediments, 5–39 µg/g in bivalves, 12–322 µg/g in macrophytes, to 948–5187 µg/g in soils. Aromatic hydrocarbons varied from non-detected 10 µg/l, 0.01–1.3 µg/g, 1.0–16 µg/g, 0.5–6.9 µg/g, to 22–67 µg/g, respectively. These high hydrocarbon levels denote the strong impact of the spill on the coast as has been frequently observed in this type of incidents. For example, after the 320 tons Czanatoria oil spill in the St. Lawrence estuary, most contaminated intertidal sediments contained up to 34 µg/g *n*-alkanes and ~1 µg/g aromatics (Siron et al., 1991). The spill of 600,000 l of petroleum during the Bahia Paraiso grounding in Antarctica, resulted in high

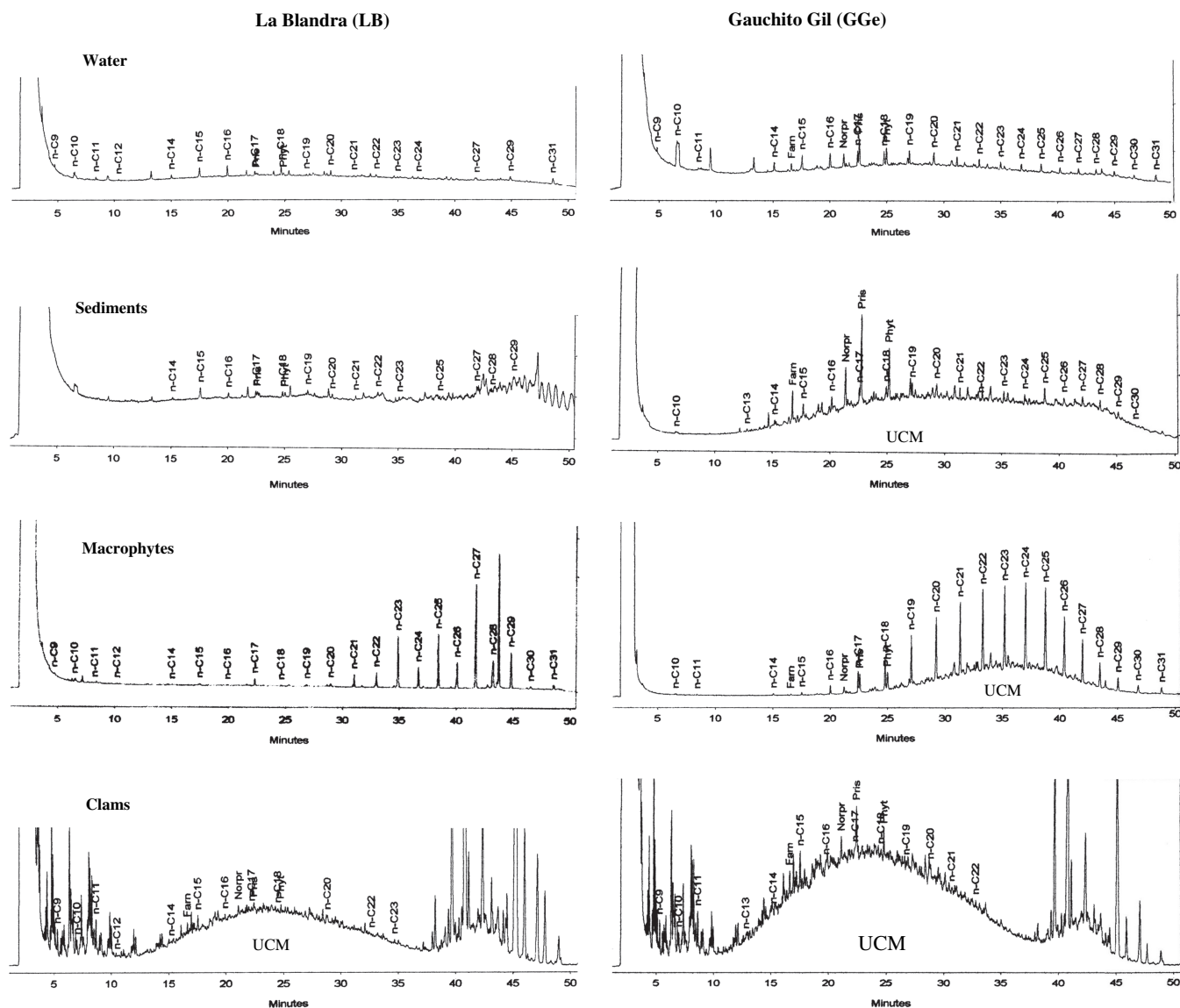


Fig. 2. Aliphatic chromatograms of waters, sediments, macrophytes and clams from stations with contrasted impact of the spill (LB: low vs. GG: high).

hydrocarbon levels in water oil slicks (50–100 $\mu\text{g/l}$ PAHs), sediments (0.1–1.7 $\mu\text{g/g}$ aliphatics; and 0.2–1.6 $\mu\text{g/g}$ PAHs) and clams (1.2–17.5 $\mu\text{g/g}$ PAHs; Kennicutt et al., 1991). According to Boehm et al. (1998), Bay of Isles and Drier Bay sediments affected by the Exxon Valdez oil spill, contained from 0.08–0.4 $\mu\text{g/g}$ background to 1.5 $\mu\text{g/g}$ PAHs. Jewett et al. (1999), reported higher PAH values for Bay of Isles sediments (15 $\mu\text{g/g}$).

Fig. 3 shows that the mean hydrocarbon concentrations in Río de la Plata waters and sediments are consistently lower in offshore stations (transects) relative to the littoral fringe. The difference averages 12 times for waters and 3–28 times for sediments. This pattern has some residual contribution of background anthropic and natural organic inputs which are higher on the coast due to increased primary productivity and terrestrial

inputs. This probably explains the decreasing trend with distance to the coast observed in sediments along the transects, e.g. 1.1–2.5 to 0.1–0.4 $\mu\text{g/g}$ resolved aliphatics at LB and PB (Table 2). However, the marked difference between offshore stations and the coast reflects the rapid and efficient transport of the oil to the coast by strong SE winds, i.e. no significant deposition of oil residues occurred in offshore waters (see composition). The petrogenic UCM evidenced as an envelop of unresolved components below resolved aliphatics and aromatics, confirms the shift from low background levels in offshore waters (non-detected) and sediments (1.1 ± 0.9 – 11 ± 16 $\mu\text{g/g}$ AROUCM and ALIUCM) to 20–40 times higher loads on the coast (171 ± 238 $\mu\text{g/l}$ and 42 ± 68 – 265 ± 423 $\mu\text{g/g}$, respectively, Table 2). This ALIUCM coastal average is 125 times higher than

Table 2

Total concentrations of aliphatic and aromatic hydrocarbons in offshore and coastal waters and sediments

Transects	Waters						Sediments					
	ALI (µg/l)	Petro/ biog	ALI UCM (µg/l)	ARO (µg/l)	Petro/ pirog	ARO UCM (µg/l)	ALI (µg/g)	Petro/ biog	ALI UCM (µg/g)	ARO (µg/g)	Petro/ pirog	ARO UCM (µg/g)
LB1	4.8	0.7	–	–	–	–	1.1	0.2	13.2	0.3	0.07	1.1
LB5	3.2	1.8	–	–	–	–	0.6	0.2	8.4	0.1	–	0.6
LB15	2.5	0.9	–	–	–	–	0.4	0.1	1.3	0.1	0.07	1.5
PB5	2.2	0.9	–	–	–	–	2.5	0.1	56.3	0.5	0.08	3.0
PB10	1.4	0.8	–	–	–	–	1.1	0.1	8.9	0.2	0.05	0.8
PB15	2.5	1.1	–	–	–	–	0.1	0.02	0.9	0.04	–	–
MG1	1.7	1.0	–	–	–	–	0.1	0.6	1.0	0.01	–	–
MG5	2.9	0.4	–	–	–	–	0.4	0.1	10.9	0.1	0.06	0.6
MG15	2.3	0.7	–	–	–	–	0.01	–	–	0.02	–	–
JB1	3.5	1.1	–	–	–	–	na	na	na	na	na	na
JB5	0.4	–	–	–	–	–	0.3	0.5	5.4	0.1	–	0.2
JB15	0.6	0.1	–	–	–	–	0.1	1.1	0.1	0.01	–	–
Mean	2.3	0.9	–	–	–	–	0.6	0.3	10.6	0.1	0.07	1.1
SD	1.2	0.4	–	–	–	–	0.7	0.3	15.9	0.1	0.01	0.9
Coast												
LB	2.9	0.2	–	1.1	1.2	–	0.1	0.3	1.2	–	–	–
Be	1.7	0.4	–	0.6	1.7	–	1.0	0.6	19.7	0.4	0.3	8.9
J1	3.5	0.6	–	1.5	2.2	–	0.3	0.6	8.7	0.01	1.0	0.6
J1IC	262.3	1.7	592	10.0	2.6	–	na	na	na	na	na	na
J1IS	8.6	0.3	16	1.3	1.7	–	13.1	1.8	220.0	0.2	0.6	36.6
PN	0.5	0.1	–	0.8	1.0	–	1.8	0.6	23.9	0.02	0.2	2.0
GGi	17.9	1.6	56	3.4	2.2	–	86.6	1.8	1445.0	1.3	0.4	205.7
Gge	2.0	2.3	–	0.9	0.4	–	58.9	1.5	311.0	0.6	1.1	20.7
Ri	10.3	2.0	78	2.2	1.8	–	16.4	1.6	689.2	1.2	0.2	139.1
Re	1.1	1.5	–	0.6	0.6	–	1.0	1.6	27.2	0.04	0.5	4.2
AL	0.6	2.6	–	0.8	0.9	–	5.1	1.5	57.5	0.1	0.7	7.3
Jbi	62.3	1.6	112	3.2	39.2	–	34.2	1.6	310.0	0.8	0.5	30.6
Jbe	3.4	0.9	–	0.7	5.1	–	6.6	1.9	67.6	0.1	1.1	0.9
PE	1.0	0.4	–	0.3	1.1	–	0.02	–	–	–	–	–
Mean	27.0	1.1	171	1.9	4.4	–	17	1.3	265	0.4	0.6	41.5
SD	69.6	0.8	238	2.5	10.1	–	27	0.6	423	0.5	0.3	67.5

ALI, total resolved aliphatic hydrocarbons; Petro/biog, petrogenic/biogenic=isoprenoids + <C22/C15+C17+>C23; ALIUCM, aliphatic unresolved complex mixture; na, not available; ARO, total resolved aromatic hydrocarbons; Petro/pirog: petrogenic/pirogenic=methylated/unsubstituted ARO; AROUCM, aromatic unresolved complex mixture; –, below quantification limit.

background values (2.1 ± 1.0 µg/g). Since the UCM is composed of degraded petrogenic residues (e.g. Killops and Al-Juboori, 1990), the higher UCM loads along the coast also indicate the progress of hydrocarbon decay 6 months after the spill. The UCM/resolved aliphatic ratio shows a clear trend of increasing degradation from waters to clams: coastal waters (3.3) < macrophytes (6.7) < soils (9.4) < offshore sediments (13) < coastal sediments (17) < clams (52). The high values in the clams probably reflects the accumulation of recycled and partially degraded residues, whereas in offshore sediments relatively high ratios may represent the background petrogenic signal of the estuary.

The impact of the spill is also reflected by the higher variability observed in the coast due to the presence of heavily polluted sites relative to more homogeneous offshore values. The contrast is more important

for waters (128–258 vs. 50% RSD; coastal vs. offshore ALI and ARO) relative to sediments (111–156 vs. 106–115%) which integrate anthropic and natural signals over time.

3.2. Spatial variability

General averages discussed previously give the general pattern of hydrocarbon distribution and accumulation in biotic and abiotic compartments. However as indicated previously, coastal means include large variability relating to the different impact of the spill along the shore. Fig. 4 presents total aliphatic and aromatic hydrocarbon concentrations in waters, sediments, soils and biota at the different coastal stations compared with baseline levels determined at

Table 3
Total concentrations of aliphatic and aromatic hydrocarbons in soils, plants and bivalves

	Soils						Macrophytes						Bivalves					
	ALI (µg/l)	Petro/biog	ALI UCM (µg/l)	ARO (µg/l)	Petro/pirog	ARO UCM (µg/l)	ALI (µg/l)	Petro/biog	ALI UCM (µg/l)	ARO (µg/l)	Petro/pirog	ARO UCM (µg/l)	ALI (µg/l)	Petro/biog	ALI UCM (µg/l)	ARO (µg/l)	Petro/pirog	ARO UCM (µg/l)
LB							16	0.1	–	0.5		–	7.3	2.6	447	1.8	0.2	46
Be							12	0.3	–	0.5	0.3	–	7.3	2.6	418	1.0	0.4	80
J1							33	0.3	61	0.5	0.4	5	5.2	4.8	472	2.1	0.2	161
J1IC	948	1.9	15725	21.9	0.2	966	34	0.6	530	1.6	0.7	44	na		na	na		na
J1IS							25	0.2	273	1.4	0.2	39	32.3	6.3	944	15.8	0.2	281
PN							48	0.2	93	2.1	0.2	31	19.8	13.6	839	3.2	0.2	172
GGi							128	0.8	429	3.2	0.3	23	na	na	na	na	na	na
GGe	5187	1.1	20218	24.5	0.6	4130	176	0.6	777	2.9	0.5	76	21.6	3.3	1291	7.9	0.2	328
Ri	4900	1.6	37178	68.8	0.6	5751	242	0.6	2203	6.9	0.6	457	na	na	na	na	na	na
Re							73	0.7	744	–	0.3	43	20.1	4.6	892	14.4	0.2	515
AL							323	0.7	2262	5.8	0.4	277	38.7	5.6	1943	7.3	0.2	198
JB1							na	na	na	na	na	na	na	na	na	na	na	na
JBe							256	0.6	1656	2.9	0.6	118	27.4	6.0	941	8.4	0.2	259
PE							12	0.1	35	0.9	0.3	11	na	na	na	na	na	na
Mean	3678	1.5	24374	38.4	0.5	3616	106	0.4	824	2.4	0.4	102	19.9	5.5	910	6.9	0.2	227
SD	2369	0.4	11314	26.4	0.2	2434	108	0.3	834	2.1	0.2	141	11.7	3.3	483	5.4	0.1	141

ALI, total resolved aliphatic hydrocarbons; Petro/biog, petrogenic/biogenic=isoprenoids + <C22/C15+C17+>C23; ALIUCM, aliphatic unresolved complex mixture; na, not available; ARO, total resolved aromatic hydrocarbons; Petro/pirog: petrogenic/pirogenic=methylated/unsubstituted ARO; AROUCM, aromatic unresolved complex mixture; –, below quantification limit.

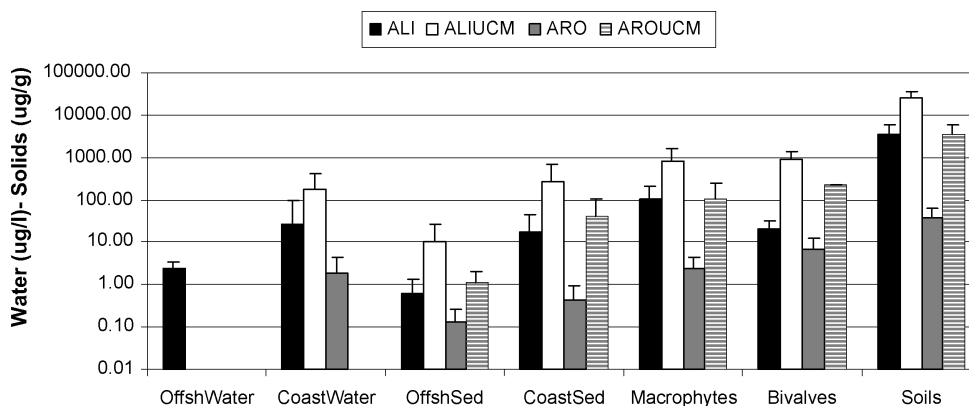


Fig. 3. General average hydrocarbon concentrations in offshore and coastal waters, sediments, macrophytes, bivalves and soil.

three sites previous to the spill in 1998 (Colombo, unpublished).

Hydrocarbon data for all environmental compartments give a consistent picture of the most impacted area which covers basically the central sector of Magdalena, from JI, JIIC, JIIS, GG, R to the stream Juan Blanco (JB). Hydrocarbon levels in this area are very high, specially in low-energy sites such as small streams and bays which acted as oil traps (e.g. JIIC, JIIS, GGi, Ri, and JBi). The general mean of aliphatic concentrations in coastal waters (27 ± 70 $\mu\text{g/l}$) is >20 times higher than baseline levels (1.2 $\mu\text{g/l}$) with most contaminated sites up to 200 times higher. In contrast, average aliphatic concentration in offshore waters (2.3 ± 1.2 $\mu\text{g/l}$) and in the distant, non-impacted coastal stations LB and PE (1.0 – 2.9 $\mu\text{g/l}$) are in the order of baseline levels. Aromatic hydrocarbons are detected all along the coast at relatively high levels (1.9 ± 2.5 $\mu\text{g/l}$) as opposed to offshore stations or to previous baseline studies which showed undetectable levels.

The spatial patterns of sediments are less variable and more reliable than those of waters but agree in highlighting the central sector of Magdalena as the most impacted area (Fig. 4). The aliphatic coastal sediment average (17 ± 27 $\mu\text{g/g}$) is >75 times higher than previous baseline levels (0.23 $\mu\text{g/g}$) with extreme values as high as 150–380 times in rivulets such as GG and JB. Again, offshore sediments and the distant, non-impacted coastal sites LB and PE show lower background values (0.6 ± 0.7 and 0.02 – 0.1 $\mu\text{g/g}$, respectively). PAHs display essentially the same pattern, coastal concentrations are on average 87 times higher than baseline levels (0.005 $\mu\text{g/g}$) and up to 270 times in most contaminated sites, which are nevertheless below the reported sediment toxicity threshold (1.2 – 1.3 vs. 4 $\mu\text{g/g}$; Boehm et al., 1998). However, compared to Canadian individual PAH sediment guidelines for protection of aquatic life (0.032 – 0.057 $\mu\text{g/g}$ for benzo[*a*]anthracene, pyrene, and chrysene), these sediments are 5–8 times higher. Also, the total amount of resolved and

unresolved aliphatic and aromatic hydrocarbons in most contaminated sites JIIS, GG, Ri, JBi (270 – 1739 $\mu\text{g/g}$), largely exceeds the 100 $\mu\text{g/g}$ chronic effect threshold of oil hydrocarbons for benthic communities (Howarth, 1989). Offshore stations and non-impacted coastal sites show lower background PAH levels (not detected– 0.1 $\mu\text{g/g}$).

Hydrocarbon concentrations in coastal soils are very high and relatively uniform in the central most affected area (38 ± 26 and 3678 ± 2369 $\mu\text{g/g}$ for ARO and ALI, respectively). This reflects the formation of an asphaltic-like pavement after the oil was deposited by the wind-induced flood. Soil general averages are 90–200 times higher than in coastal sediments (Fig. 3).

The evaluation of spatial patterns in biota is complicated by the presence of natural hydrocarbons and the variability of lipid pools according to the physiological status of organisms. Nevertheless, the distribution of aliphatic and aromatic hydrocarbons in macrophytes and clams is consistent with that observed for waters and sediments indicating higher levels in the central sector from JI to JB (Fig. 4). Comparison with previous baseline levels in biota is complicated by the already mentioned natural variability of lipids. Aliphatic hydrocarbons in 1998-affected macrophytes ranged from 10 to 50 $\mu\text{g/g}$ with an average of 18 $\mu\text{g/g}$ dry weight. The general aliphatic mean in this campaign (106 ± 108 $\mu\text{g/g}$ dry weight) is about 6 times higher, with extremes almost 20 times higher. Macrophytes collected at LB and PE show lower background values (12 – 16 $\mu\text{g/g}$ dry weight). A similar pattern is observed for aromatic hydrocarbons in the plants; the general average (2.4 ± 2.1 $\mu\text{g/g}$) is 5 times higher than baseline levels (0.5 $\mu\text{g/g}$) but LB and PE are in the same order (0.5 – 0.9 $\mu\text{g/g}$). Lipid normalized concentrations display more homogeneous values: average aliphatic and aromatic concentrations are three times higher than baseline levels (14700 ± 8780 vs. 5140 $\mu\text{g/g}$ ALI and 387 ± 155 vs. 143 $\mu\text{g/g}$ ARO). Asiatic clams show comparable differences with baseline hydrocarbon concentrations (2 – 3

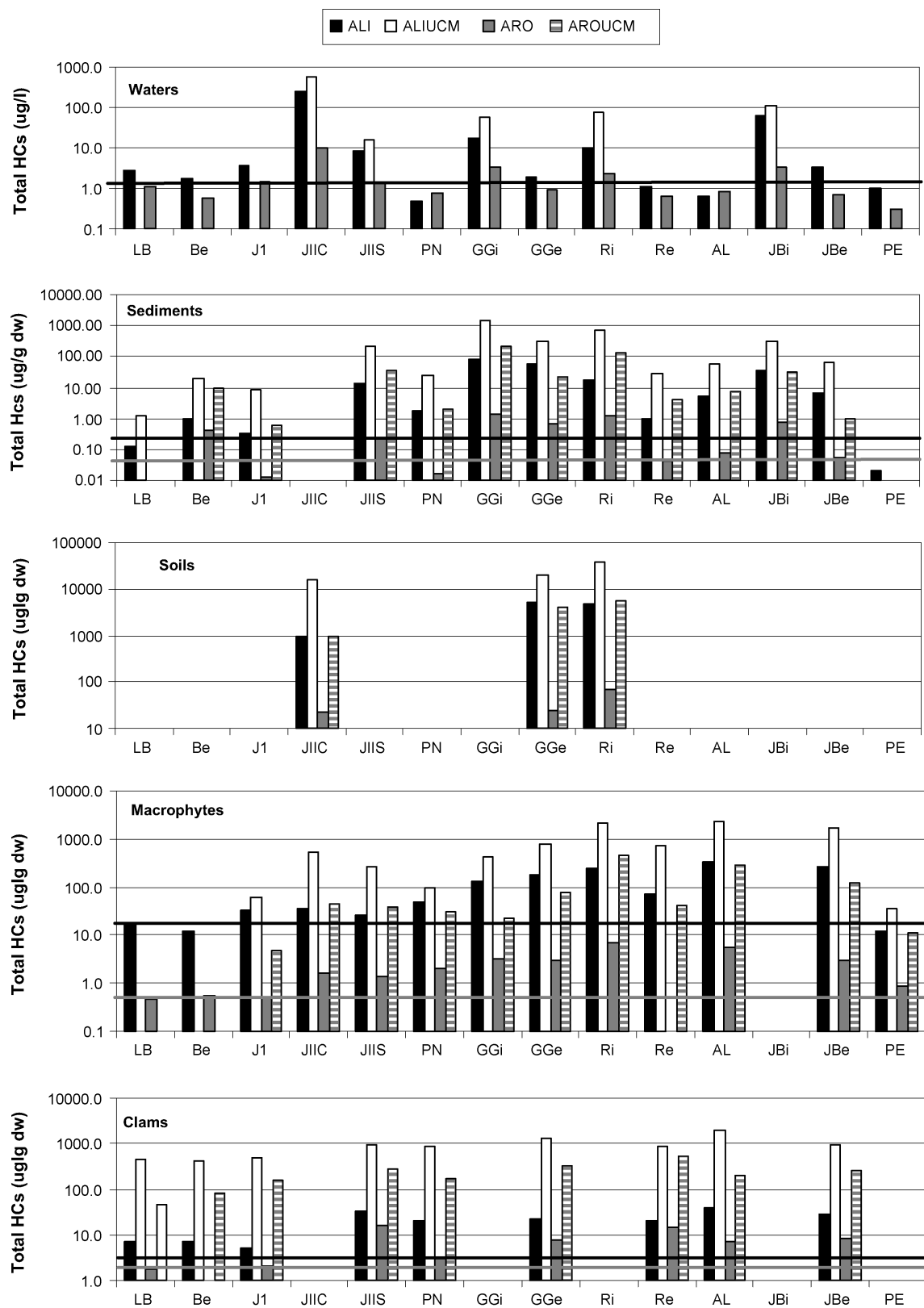


Fig. 4. Spatial distribution of total resolved and unresolved aliphatic and aromatic hydrocarbons along the studied area compared with previous baseline levels for aliphatic (black) and aromatic hydrocarbons (gray). Station abbreviations as in Table 1.

µg/g for ARO and ALI, respectively): average levels are 3–7 times higher with extremes of 13 times, and more comparable concentrations at the limits of the distribution, i.e. LB. Lipid normalized concentrations indicate a 4–9 times hydrocarbon enrichment in the clams relative to baseline levels (205 ± 94 vs. 22 µg/g ALI and 69 ± 49 vs. 16 µg/g ARO).

3.3. Hydrocarbon composition in abiotic compartments

The composition of aliphatic and aromatic hydrocarbons in the environmental compartments showed contrasted patterns 6 months after the spill (Fig. 2). These were evaluated by principal component analysis (PCA) performed by the covariance technique with the relative abundance of the individual components in each sample (XLSTAT 4.0). Fig. 5 presents the results for waters and sediments. Except in the most polluted sites (e.g. JIIC, GGi), hydrocarbon detection in waters was irregular with frequent undetected compounds. In these cases, half the quantification limit (0.01 µg/l) was employed for the PCA in order to preserve the most complete data base. This may introduce some uncertainty, but the results are rather consistent and reproducible.

The first two components of the aliphatic PCA for waters explains 66% of the total variability, 52% the first and 14% the second. The first component is basically determined by the abundance of petrogenic isoprenoids (farnesane, norpristane, pristane and phytane), and some low molecular weight *n*-alkanes (*n*-C13,14,15) possibly reflecting background and biogenic signals (e.g. Colombo et al., 1996b; Wang et al., 1999). The second component includes a major contribution of high molecular weight odd-carbon *n*-alkanes (*n*-C27, 29, 31) characteristic of vascular plant cuticular waxes. Samples from the most contaminated area with the highest hydrocarbon levels (JI to JB) are clearly discriminated by the abundance of isoprenoids close to a local crude included in the PCA for comparison. All offshore samples present the dominance of some low molecular weight *n*-alkanes, possibly from background petrogenic sources and algae inputs (*n*-C15). Non-affected coastal stations (LB and PE) and some intermediate sites show a prevailing contribution from vascular plant waxes (terrestrial detritus). The pollution pattern is clearly reflected by the petrogenic/biogenic ratio defined as $<n\text{-C}22 + \text{isoprenoids}/n\text{-C}15 + n\text{-C}17 + >n\text{-C}23$ (Table 2). Values are highest in most polluted sites, e.g. JIIC, GG, R, JB (1.7–2.6) and decrease in offshore waters (0.9 ± 0.4) and less impacted coastal stations such as LB, Be, and PE ($0.2\text{--}0.4$).

The first two components of the aromatic PCA explain 67% of the total variability and cluster most polluted sites close to the crude based on their

contribution of dimethyl phenanthrenes, trimethyl naphthalenes, methylpyrenes, benzo[*a*]fluorene, benzo[*a*]anthracene and chrysene. Less polluted coastal samples show a prevailing contribution of 4,5-methylene phenanthrene and pyrene possibly from pyrogenic sources (Colombo et al., 1989). The load of phenanthrene to the same component is more difficult to interpret (e.g. other recent inputs), since this compound is abundant in fresh fuels and is generally lost in the first stages of decay.

Soils and sediments have been included together in a single PCA. The first two components of the aliphatic PCA explain 80% of the total variability. This PCA is basically determined by the opposition between petrogenic inputs (isoprenoids < *n*-C22 alkanes) and biogenic sources composed of vegetal detritus (*n*-C25, 27, 29, 31 alkanes) on the negative and positive side, respectively of component 1 (67% total variability). This PCA shows that almost all coastal samples show a prevailing petrogenic signature as opposed to offshore sediments which present dominant biogenic inputs. As isoprenoids contribute to PC1 to the extreme negative side, this PCA also indicates a higher degree of alteration of most polluted coastal samples relative to the fresh crude. This isoprenoid predominance reflects the selective decay of *n*-alkanes as indicated by the *n*-C17/pristane and *n*-C18/phytane ratios which are low in contaminated soils and sediments (0.32 ± 0.29 and 0.57 ± 0.27) compared to the fresh crude (1.6 and 3.1, respectively). The petrogenic/biogenic ratios (Table 2) show consistently lower values in offshore vs. coastal sediments (0.3 ± 0.3 vs. 1.3 ± 0.6), compared with a fresh crude (1.7) and previous coastal baseline values (0.3 ± 0.2).

The first two components of the aromatic PCA of soils and sediments explain 63% of the total variability and show a consistent pattern with other water and sediment results. The principal contributors to component 1 (48% variability) are perylene (+PC1), a natural pentacyclic PAH formed diagenetically from terrestrial precursors or transported as preformed detrital hydrocarbon, and benzo[*a*]fluorene and methylated species of chrysene, phenanthrene and pyrene (–PC1, –PC2), characteristic of fossil fuels (e.g. Colombo et al., 1989; Boehm et al., 1998). Contaminated coastal soils and sediments are again clustered together with the crude based on the methylated PAH abundance, whereas most offshore samples are discriminated by their higher proportion of perylene. The methylated/unsubstituted PAH ratio illustrates the relative magnitude of petrogenic vs. pyrogenic inputs (Colombo et al., 1989). This ratio clearly reflects the impact of oil residues on the coast (0.6 ± 0.3 compared to 1 in crude oil) relative to offshore stations (0.07 ± 0.01 ; Table 2). Pyrogenic background PAH inputs in offshore sediments appear to be basically

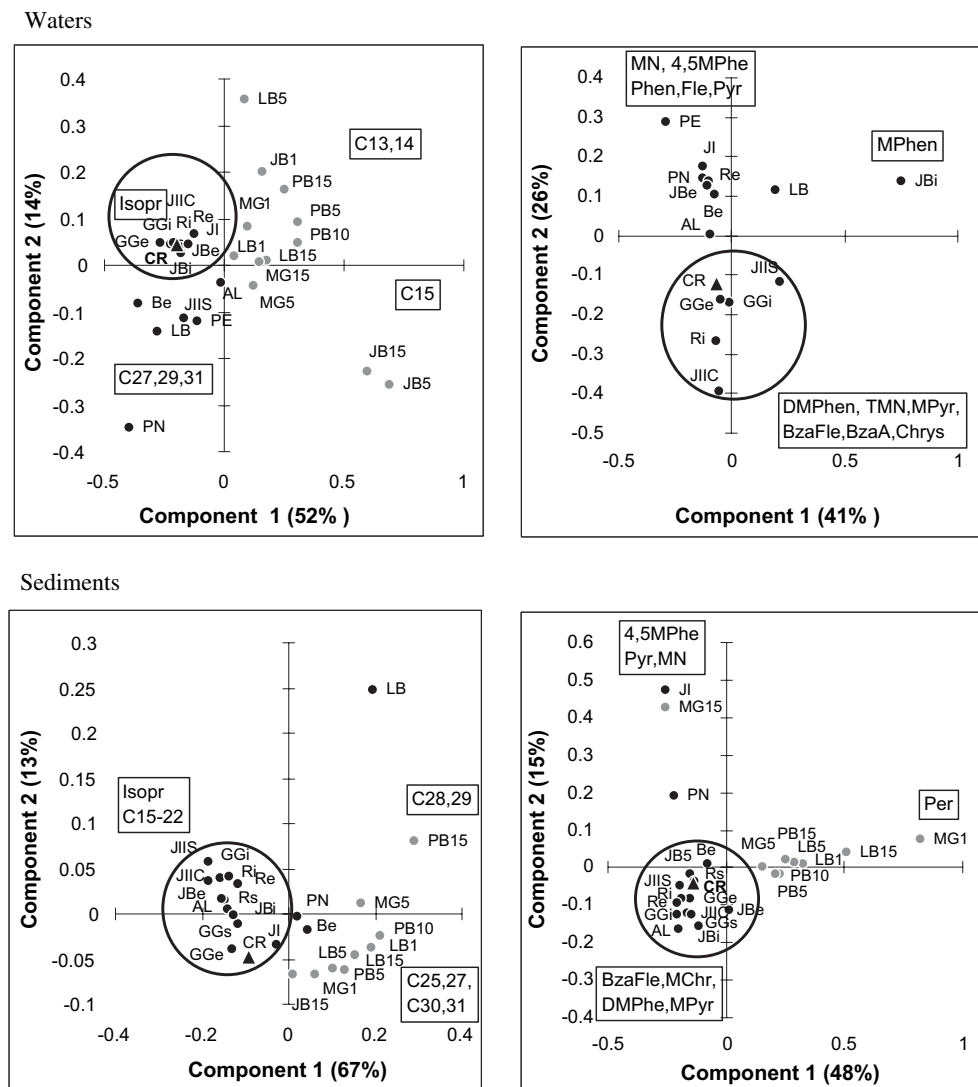


Fig. 5. Principal component analysis of the composition of aliphatic and aromatic hydrocarbons in waters and sediments (see text for explanation). Samples are coastal (black circles), offshore (gray circles) and a fresh crude oil (CR, triangle). The circle groups most contaminated samples. The original variables with stronger contribution to both components are indicated. Isopr, isoprenoids (farnesane, norpristane, pristane, phytane); C13–31, *n*-alkanes with 13–31 carbons; M, DM, TM, methyl, dimethyl, trimethyl; N, naphthalene; Phen, phenanthrene; Fle, fluorene; Pyr, pyrene; BzaFle, benzo[*a*]fluorene; BzaA, benzo[*a*]anthracene; Chrys, chrysene; Per, perylene; IndPyr, indeno[123*cd*]pyrene.

related to higher proportions of 4,5-methylene phenanthrene and pyrene.

Tacking together the information on total hydrocarbon concentrations and composition, these results confirm that offshore waters and sediments were little affected by the spill as opposed to the littoral fringe around Magdalena which was heavily oiled.

3.4. Hydrocarbon composition in biotic compartments

The PCA results of aliphatic and aromatic hydrocarbons in macrophytes and clams (Fig. 6) are less conclusive than those of sediments, probably due to the interference of the stronger and variable biogenic

signal and the averaging effect of long-term residue bioaccumulation. The first two components of the aliphatic PCA of macrophytes explains 83% of the total variability, 70% the first and 13% the second. A large portion of this variability is explained by the contribution of petrogenic isoprenoids and low molecular weight *n*-alkanes, and high molecular weight odd carbon *n*-alkanes from cuticular waxes. The relative abundance of some intermediate chain length components (*n*-C21–26) complete the sources of variability. In this context, less contaminated plants plot on the positive side of component 1 according to their higher contents in *n*-C23–31, whereas polluted samples are discriminated on the negative side by their higher proportion of isoprenoids and lower molecular weight components.

Macrophytes

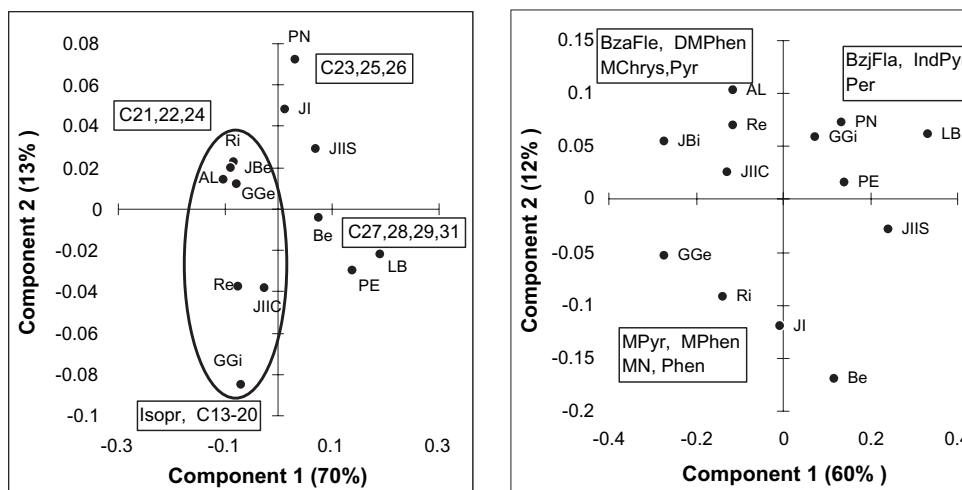


Fig. 6. Principal component analysis of the composition of aliphatic and aromatic hydrocarbons in macrophytes and asiatic clams. Legends as in Fig. 5.

The contribution of biogenic inputs from algae is also apparent in the data. This is indicated by the *n*-C17/pristane ratio which is very high in less polluted samples such as JI, JIIS, PN, PE (6.1 ± 1.6) indicating the contribution of *n*-C17 from periphytic algae, whereas it is much lower in oiled plants, e.g. JIIC, GG, JB, AL, R (0.9 ± 0.6) denoting the selective decay of *n*-alkanes. As there are no significant biogenic sources for *n*-C18 its ratio to phytane indicates partially degraded petrogenic residues in almost all samples (1.1 ± 0.5). Due to the abundance of natural hydrocarbons, the petrogenic/biogenic ratio is low in the plants (average 0.4 ± 0.3), but still discriminates most contaminated from less polluted sites (0.6 – 0.8 vs. 0.1 at LB and PE; Table 2).

The aromatic PCA is more difficult to interpret and does not supply much additional information. It explains 72% of total variability basically due to the contribution

of methylated species ($-PC1$) and high molecular weight PAH ($+PC1$) and discriminates some polluted from uncontaminated plants according to the abundance of methylated PAHs. As most PAHs do not have biogenic sources, the petrogenic/pyrogenic ratio is not biased in the plants which shows similar values to soils and sediments (0.4 ± 0.2 ; Table 2) suggesting some degree of impact in all samples. The ratios are highest in polluted sites JIIC, Ri, GGe, and JBe (0.5 – 0.7) compared to the crude (1) and previous baseline macrophyte values (0.1).

The aliphatic PCA of clams explains 85% of the total variability, 73% the first component and 12% the second. Most of the scatter is explained by the opposition between some biogenic *n*-alkanes predominant in algae (*n*-C15, 17) plus a series of even low molecular chain components of uncertain origin on negative PC1, and pristane, phytane and C21, 22, 24

n-alkanes most probably derived from petrogenic sources. Samples are widely spread in the PCA with apparently combined natural and petrogenic contributions for most of them. This is probably related to the long-term bioaccumulation of detrital hydrocarbons. The petrogenic/biogenic ratio in the clams are high (5.5 ± 3.3 ; Table 2), principally because biogenic components are restricted to algae inputs (C15, 17). Higher molecular weight *n*-alkanes were difficult to detect in bivalves due to their low abundance and interference of some unremoved high molecular weight lipid derivatives. The highest petrogenic/biogenic values are observed in the central most contaminated area (6–13). The *n*-C17/pristane and *n*-C18/phytane ratios are low (0.23 ± 0.29 and 0.27 ± 0.19 , respectively), denoting the decay of petrogenic residues. The advanced decay of residues is also evidenced by the abundance of UCM hydrocarbons (see total hydrocarbons concentrations), supporting the incorporation of detritus-associated recycled hydrocarbons. The first two components of the aromatic PCA explain 76% of the total variability, 57% the first and 19% the second. The higher contribution of methyl chrysenes and benzo[a]fluorene appear to discriminate most contaminated clams whereas less polluted samples show higher proportions of phenanthrene, acenaphthene and pyrene. The petrogenic/pyrogenic ratios are lower and homogeneous (0.2 ± 0.1), thus do not provide any additional information on spatial trends. This is probably related to the long-term integration of environmental signals by the clams.

4. Conclusions

The quantitative and qualitative assessment of aliphatic and aromatic hydrocarbons in waters, sediments, soils and biota indicated that offshore waters and sediments were little affected by the spill of ~1000 tons oil in the Río de la Plata. In contrast, the coast was severely oiled and 6 months after the spill coastal waters, sediments, soils and biota still presented very high hydrocarbon levels, exceeding baseline concentrations by 1–3 orders of magnitude, specially in low-energy stream embouchures and bays which acted as efficient oil traps. UCM/resolved aliphatic ratios showed a clear trend of increasing decay: coastal waters (3.3) < macrophytes (6.7) < soils (9.4) < offshore sediments (13) < coastal sediments (17) < clams (52). The evaluation of hydrocarbon composition by PCA indicated biogenic (algae, higher plants), background anthropic, pyrogenic and diagenetic hydrocarbons, offshore and in non-impacted coastal sites, and petrogenic signatures characterized by isoprenoids, low molecular weight *n*-alkanes and methylated aromatics in polluted stations. The petrogenic/biogenic ratio ($<n$ -C22 +

isoprenoids/*n*-C15 + *n*-C17 + $>n$ -C23) and petrogenic/pyrogenic relationship (methylated/unsubstituted PAH) discriminated the samples according to the different degrees of impact.

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