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Vertical fluxes and organic composition of settling material from the sewage impacted Buenos Aires coastal area, Argentina

J.C. Colombo [a,b,*], N. Cappelletti [a,b], E. Speranza [a], M.C. Migoya [a,c], J. Lasci [a], C.N. Skorupka [a]

[a] *Laboratorio de Química Ambiental y Biogeoquímica, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Av. Calchaqui km 23500 (1888) Florencio Varela, Buenos Aires, Argentina*
[b] *Comisión de Investigaciones Científicas, Provincia de Buenos Aires, Argentina*
[c] *Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina*

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Abstract

Settling particulates collected upstream and downstream of Buenos Aires main sewer in the Río de la Plata were analyzed for total organic carbon (TOC), nitrogen (TN), resolved aliphatic hydrocarbons (ALI), unresolved complex mixture (UCM), terpane biomarkers, linear alkylbenzenes (LABs) and PCBs to evaluate the composition, sources and variability of anthropogenic fluxes. Sediment traps collected a substantial amount of material (19.9 ± 13.5 g cm^{-2} yr^{-1}) with relatively high organic contents (TOC: 7.7 ± 5.5%; TN: 0.65 ± 0.34%; C/N: 13 ± 3.2) and contaminant loads (UCM: 949 ± 737, ALI: 115 ± 111, LABs: 18 ± 12; PCBs: 0.07 ± 0.04 μg g^{-1}). The resulting vertical fluxes are very large (TOC: 1.9 ± 2.5 g cm^{-2} yr^{-1}; total hydrocarbons: 21 ± 23 mg cm^{-2} yr^{-1}; LABs: 0.42 ± 0.62 mg cm^{-2} yr^{-1}; PCBs: 1.6 ± 1.8 μg cm^{-2} yr^{-1}). The settling material showed a clear organic enrichment downstream the sewer and during rainy, warm months. A variance component analysis revealed that spatial differences were less significant (13–27%) than the seasonal trend (30–63% total variability) which is inversely related to compound stabilities. The organic composition indicated slightly altered inputs of petrogenic hydrocarbons, detergents and Aroclor 1242:1254:1260 residues, with limited contribution of terrestrial plant waxes and negligible from plankton. The seasonal variation of individual compounds revealed a summer enrichment of labile components inversely correlated to molecular weight, with terpane biomarkers showing an opposite pattern. Rainy, warm months showed higher total mass fluxes and C/N ratios with signatures enriched in $<n$-C_{22} alkanes, external LABs, less chlorinated PCBs and $>C_{30}$ hopanes suggesting a more efficient washout of fresher organic residues. Conversely, cold months showed more degraded signatures depleted of low molecular weight components and enriched in UCM, internal LABs and tricyclic terpanes.

1. Introduction

The settling of organic matter in aquatic environments transfers biogenic and anthropogenic signals to underlying sediments where the intense microbial

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[*] Corresponding author. Address: Laboratorio de Química Ambiental y Biogeoquímica, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Av. Calchaqui km 23500 (1888) Florencio Varela, Buenos Aires, Argentina.
E-mail address: laqab@intervar.com.ar (J.C. Colombo).

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metabolism results in a rapid depletion of labile components. The organic signature of sediments is thus biased towards more persistent compounds such as terrestrial long chain *n*-alkanes, aromatic hydrocarbons and sterols (Prahl et al., 1980; Colombo et al., 1997). Sediment traps allow an estimation of fresh organic inputs normally enriched in labile biogenic components from algae, zooplankton and higher level biota fecal material (Prahl and Carpenter, 1979; Meyers et al., 1980; Colombo et al., 1996). In urbanized coastal environments affected by industrial and sewage discharges the downward flux of material is dominated by anthropogenic organic matter containing a variety of relatively labile components such as petrogenic aliphatic hydrocarbons, fatty acids, intermediate stability compounds such as linear alkylbenzenes (LABs) and fecal sterols and more recalcitrant pollutants like PCBs and hopanes (Barrick, 1982; Eganhouse and Kaplan, 1982; Bates et al., 1984; Broman et al., 1987; Eganhouse and Sherblom, 2001; Mudge and Duce, 2005).

The Río de la Plata (RLP) is a funnel-shaped (300 km long and 30–220 km wide), coastal plain turbid estuary with a freshwater discharge of 16–28 × 10^3 m^3 s^{-1} and a suspended particulate matter load of 90 million tons yr^{-1} (Esteves et al., 2000). The upper freshwater sector is dominated by a vast delta in front of Buenos Aires City which concentrates one third of the total Argentinean population. The main Buenos Aires sewer serves 5 million inhabitants and discharges ~2 million m^3 per day of untreated effluents including domestic and industrial inputs 2.5 km offshore Berazategui (Fig. 1). In addition, the Port of Riachuelo and several polluted channels (e.g. Sarandi, Santo Domingo, Gimenez; Fig. 1) discharge an unknown amount of chemicals to the coastal ecosystem. The organic load from these sources has been estimated at ~410 tons BOD_5 day^{-1}, 45% corresponding to the sewer and 32% to Riachuelo Port (FREPLATA, 2005). The combination of high particulate load and crude anthropogenic discharges in the coastal area results in large fluxes of pollutants which accumulate in underlying sediments (Colombo et al., 2005a,b, 2006).

In this paper we report data on vertical fluxes, elemental and trace organic composition of settling material collected upstream and downstream of Buenos Aires main sewer in the Río de la Plata. The fluxes, sources and temporal variability are evaluated with a 20 sediment trap data set.

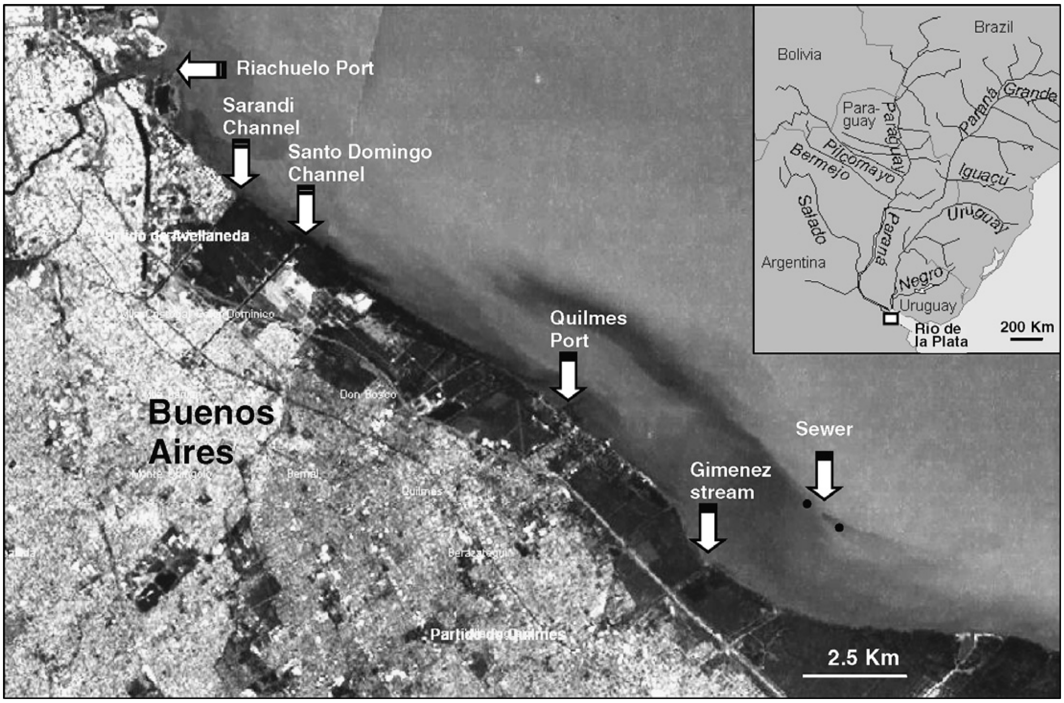

Fig. 1. Study area and sampling sites in Metropolitan Buenos Aires coast (NASA World Win image). The arrows indicate different point source discharges. Main tributaries of the Río de la Plata are shown in the upper right figure.

2. Methods

Settling particles were collected in the coastal area of Berazategui affected by industrial and sewage discharges (Fig. 1), 1.5 m below the surface in a 5–6 m water column during eleven trap deployments covering 2004–2006. Two fixed 10 cm diameter bi- and tricylindrical traps (total surface: 157–235 cm^2) were deployed 500 m upstream and downstream from the sewer for 20–48 h. To minimize the capture of resuspended bottom material in this shallow coastal area, storm events were specifically avoided in the sampling scheme. The consistently fresher aliphatic signature of the trap material relative to bottom sediments suggests no significant capture of degraded bottom material (Colombo et al., 2005b).

The material collected by the traps was immediately centrifuged and split for total organic carbon and nitrogen analysis (Thermo Finnigan, CE FlashEA 1112 elemental analyzer) and for the determination of trace organics (Colombo et al., 2005a,b). Briefly, the analytical method included ultrasonic extraction of the wet material with acetone:dichloromethane:petroleum ether (1:2:2), nitrogen concentration, activated copper treatment, silica gel fractionation and analysis by HRGC-FID-ECD (Agilent 6890N) and HRGC-MSD (Agilent 6850 – 5973N; EI 70 eV, 2.94 scans/seg, 50–550 amu). Quantification was performed by an external standard of 31 individual aliphatic hydrocarbons (*n*-C_{10} to *n*-C_{38} plus pristane and phytane; AccuStandard Inc.), 41 individual PCB congeners (IUPAC N^o: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199–201, 205, 206, 208, 209; Quebec Ministry, AccuStandard Inc.), and a linear alkylbenzene (LABs) mixture provided by a local petrochemical company. Deuterated C_{16} and C_{24} (Absolute Standards Inc.) and PCB 103 and 198 (ULTRA) were added to control recovery yields. C_{29} norhopane and C_{30} hopane identified at *m*/*z* 191 were quantified based on the FID response factor of *n*-C_{31} eluting between them (Fig. 2). The unresolved complex mixture (UCM) was quantified based on the total surface area and the response factor of overlying peaks. MSD data was used to confirm the aliphatic identities (*m*/*z*: 71, 85), to correct the possible co-elution of pristane and phytane with LABs (*m*/*z*: 91 and 105), and to characterize the

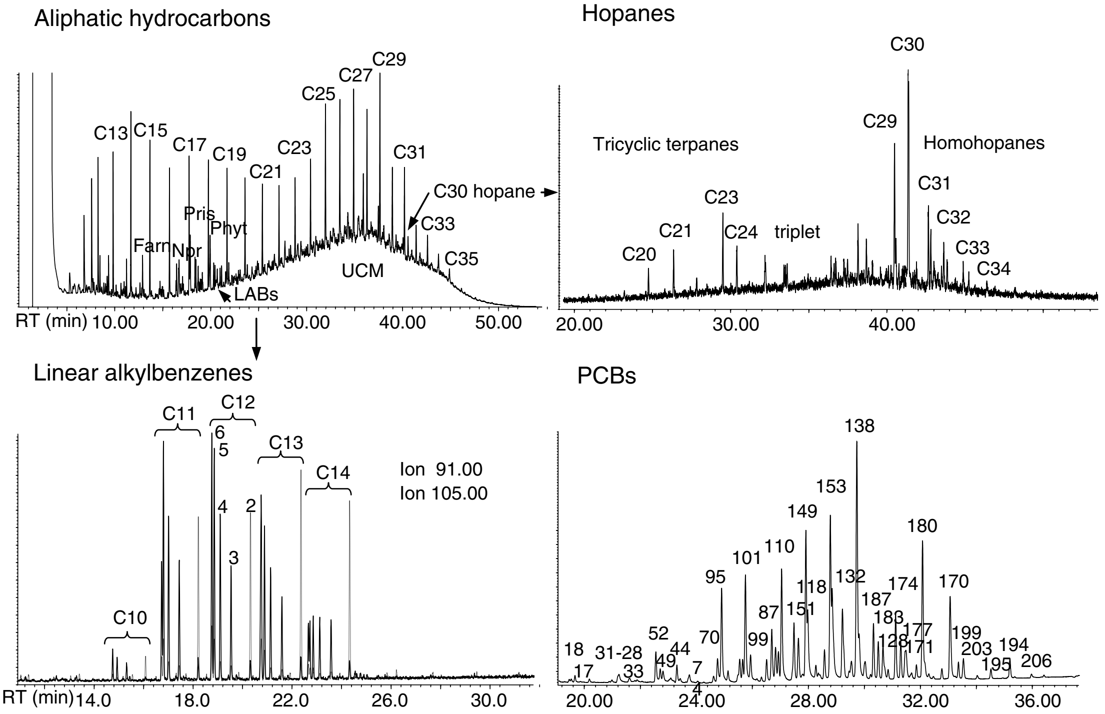

Fig. 2. Gas chromatograms of aliphatic hydrocarbons, hopanes, LABs and PCBs in the settling material (traps from December 2004).

profile of tri- and pentacyclic terpane biomarkers (*m*/*z* 191). Repeated analysis of an internal reference sediment from La Plata harbor in the Río de la Plata (aliphatic hydrocarbons: 2.7 ± 0.60 μg g^{-1}; PCBs: 21 ± 3.6 ng g^{-1}) indicated an average reproducibility of 17–22%. Method accuracy evaluated through the analysis of certified sediment samples (NIST 1944) averaged 75 ± 12% for 24 individual PCB congeners ($n = 8$).

3. Results and discussion

3.1. Vertical fluxes and general organic composition of settling particulates

Table 1 summarizes the total mass flux and organic composition of settling particulates collected upstream and downstream of Buenos Aires main sewer in the Río de la Plata. The traps collected a substantial amount of material averaging a total flux of 14.5 ± 5.6 g cm^{-2} yr^{-1} (~0.4 kg m^{-2} day^{-1}) and a sedimentation rate of 5.5 ± 2.1 cm yr^{-1} (density: 2.65 g cm^{-3}). These high total mass fluxes reflect the anthropogenic discharges but also the natural high turbidity of the estuary mostly derived from rainy Andean food plains through the muddy Bermejo River discharge (suspended solids ~6000 mg l^{-1}) to the Paraná River, 1300 km north of Buenos Aires (Fig. 1).

The total carbon and nitrogen content of the settling material is relatively high averaging 7.7 ± 5.5% and 0.65 ± 0.34%, respectively. The carbon content is in the same range as that reported for Boston Harbor combined sewer over-

Table 1
Total mass flux and organic composition of settling particulates collected upstream (Up) and downstream (Dw) of Buenos Aires main sewer in the Río de la Plata.

Date	Position	Mass Flux (g cm^{-2} yr^{-1})	Sed Rate (cm yr^{-1})	Organic composition							
				TOC (%)	TN (%)	C/N	ALI (μg g^{-1})	UCM (μg g^{-1})	HOP (μg g^{-1})	LABs (μg g^{-1})	PCBs (ng g^{-1})
23 February 04	Up	14.1	5.3	8.9	0.70	14.8	72.0	408	1.18	8.6	76.3
23 February 04	Dw	14.3	5.4	12.3	0.92	15.5	88.7	597	1.40	10.3	74.9
29 March 04	Up	19.1	7.2	3.3	0.36	10.7	108.9	1131	2.95	8.4	61.9
29 March 04	Dw	6.0	2.3	6.1	0.69	10.3	222.4	2691	6.26	32.3	115.7
13 May 04	Up	22.6	8.5	2.1	0.24	10.2	15.3	291	0.77	2.7	14.4
13 May 04	Dw	14.0	5.3	2.3	0.25	10.6	16.6	368	0.82	2.4	13.0
12 June 04	Up	15.7	5.9	1.6	0.16	11.6	20.3	858	2.34	7.7	71.7
14 September 04	Dw	5.0	1.9	7.6	0.81	10.9	227.6	2118	5.23	24.2	77.4
24 November 04	Up	11.9	4.5	6.3	0.46	16.0	73.2	963	2.19	7.9	56.3
24 November 04	Dw	17.8	6.7	18.5	1.08	20.0	435.9	2445	6.80	34.2	154.1
31 May 05	Up	9.1	3.4	3.0	0.37	9.5	35.1	299	1.42	8.8	42.8
31 May 05	Dw	10.1	3.8	3.3	0.42	9.1	24.2	244	0.89	10.6	33.3
8 July 05	Up	9.2	3.5	3.3	0.39	9.7	28.5	405	1.56	24.0	84.2
8 July 05	Dw	10.7	4.0	3.3	0.37	10.3	32.3	439	1.82	21.5	84.3
17 October 05	Up	24.0	9.0	9.6	0.92	12.3	103.5	600	2.21	21.9	67.8
17 October 05	Dw	11.8	4.5	14.7	1.30	13.2	119.3	588	2.34	23.7	66.0
20 December 05	Up	17.0	6.4	8.7	0.83	12.2	109.4	686	2.55	15.5	80.1
20 December 05	Dw	23.9	9.0	20.1	1.19	19.7	303.3	1514	3.93	51.4	151.3
21 February 06	Up	13.5	5.1	5.3	0.48	12.7	75.9	804	1.55	16.3	58.4
21 February 06	Dw	20.9	7.9	13.1	1.00	15.2	199.0	1522	3.12	20.0	81.5
Grand mean		14.5	5.5	7.7	0.65	12.7	115.6	949	2.57	17.6	73.3
SD		5.6	2.1	5.5	0.34	3.2	110.8	737	1.74	12.1	36.4
Mean Up		15.6	5.9	5.2	0.49	12.0	64.2	645	1.87	12.2	61.4
SD		5.1	1.9	3.0	0.25	2.1	37.0	293	0.68	6.9	20.6
Mean Dw		13.4	5.1	10.1	0.80	13.5	166.9	1253	3.26	23.1	85.2
SD		6.1	2.3	6.5	0.36	4.0	136.7	926	2.21	14.0	45.3
Mean warm		16.2	6.1	10.6	0.83	14.4	159.3	1163	3.04	20.9	87.0
SD		5.3	2.0	5.3	0.30	3.1	112.6	749	1.80	13.1	34.4
Mean cold		12.0	4.5	3.3	0.38	10.3	50.0	628	1.86	12.7	52.6
SD		5.3	2.0	1.8	0.20	0.8	72.1	632	1.47	9.2	30.4

Sed rate: sedimentation rate; TOC: total organic carbon; TN: total nitrogen; ALI: resolved aliphatic hydrocarbons; UCM: unresolved complex mixture; HOP: hopanes; LABs: linear alkylbenzenes; PCBs: polychlorinated biphenyls.

flow discharge (TOC: 5.8–22%) while the nitrogen content is lower (TN: 0.69–3.28%; Eganhouse and Sherblom, 2001). Underlying sediments contain seven times lower carbon concentrations (1.1%) reflecting the intense organic matter alteration at the sediment water interface (Colombo et al., 2005b). The C/N ratio of the settling material (13 ± 3.2) is in the range of values reported for sewage which are highly variable (4–38) depending on the contribution of domestic and mixed industrial inputs (Rosenani et al., 2004). The main Buenos Aires sewer receives street runoff, domestic as well as crude industrial inputs from a densely populated urban area. The combination of high particle fluxes and organic loads from crude effluents results in large organic carbon fluxes which average 1.2 ± 1.2 g cm^{-2} yr^{-1}.

The concentrations of organic contaminants in settling particulates are moderate averaging 949 ± 737 and 116 ± 111 μg g^{-1} for UCM and resolved aliphatic hydrocarbons, respectively (∼1.1 mg g^{-1} total hydrocarbons), 18 ± 12 μg g^{-1} for LABs and 73 ± 36 ng g^{-1} for PCBs. These values are lower than those reported for Boston Harbor combined sewer overflow discharge (total hydrocarbons: 12–150 mg g^{-1}, LABs: 8.7–55 μg g^{-1}, PCBs: 0.9–18 μg g^{-1}; Eganhouse and Sherblom, 2001). The combination of very high total mass and carbon fluxes with moderate contaminant concentrations results in large contaminant fluxes totaling 15 ± 14 mg cm^{-2} yr^{-1} for total hydrocarbons, 0.26 ± 0.27 mg cm^{-2} yr^{-1} for LABs and 1.1 ± 0.8 μg cm^{-2} yr^{-1} for PCBs. These fluxes are 10–1000 times higher than those reported for less turbid and impacted deeper marine environments (Colombo et al., 2005a,b). Applying the concentrations measured in the trap material to the total solid load of the sewer (180 tons day^{-1}; FREPLATA, 2005), the discharges amount to ∼14 tons TOC day^{-1}, ∼193 kg hydrocarbons day^{-1}, ∼3 kg LABs day^{-1} and ∼13 g PCBs day^{-1}.

3.2. Upstream downstream and seasonal variability

The total mass, TOC, TN and contaminant average concentrations discussed above include 38–96% variability related to spatial and temporal components. The relative standard deviation (RSD) ranges from 38–72% for total mass, TOC and TN, and decreases from resolved aliphatic hydrocarbons (96%) > UCM (78%) > LABs (69%) ∼ hopanes (68%) > PCBs (50%), suggesting a relationship with compound stabilities. The C/N ratio is more conservative (RSD = 25%) indicating a relatively homogeneous gross organic matter composition.

Fig. 3 presents the variation of total mass fluxes, TOC and contaminant contents of settling particulates. A clear organic enrichment downstream from the sewer and during warm, rainy months (October–March: 17–23 °C and 105–134 mm, mean monthly temperature and precipitation) relative to the cold, dry period (April–September: 12–15 °C and 63–74 mm, respectively) is observed. This pattern is followed by TOC and all organic pollutants which are significantly ($p = 0.05$) correlated with TOC ($R^2 = 0.63$, 0.52, 0.50, 0.25, 0.21 for ALI, PCBs, LABs, hopanes and UCM, respectively), indicating a higher organic particulate load in summer. The significant correlation between sewage tracers as LABs with PCBs ($R^2 = 0.76$), ALI ($R^2 = 0.60$) and UCM ($R^2 = 0.39$) confirms that mixed sewage-industrial inputs are a significant source of pollutants in this coastal area. The total mass flux ranged between 5 and 24 g cm^{-2} yr^{-1} with normally higher values in warm months (average increase ∼35%), but the differences are not significant ($p = 0.05$). TOC, TN and organic pollutants suggest a positive association with the total flux but the correlations are not significant ($p = 0.05$).

A variance component analysis performed considering seasonal (warm vs. cold period) and spatial differences (upstream vs. downstream) revealed that the seasonal component is more significant (ALI: 63% > TN: 56% ∼ C/N: 55% > TOC: 49% > UCM: 33% > PCBs: 30% > HOP: 25% of the total variability; $p < 0.05$). Spatial differences explain a lower amount of variability for fewer parameters (LABs: 27% > TOC: 25% > TN: 22% > ALI: 13% total variability; $p < 0.05$). The seasonal variability follows a decreasing trend related to the compound stabilities (i.e. highest for aliphatics and lowest for hopanes), whereas only the upstream downstream differences are significant for LABs. These results confirm that the seasonal pattern has some relationship with a microbially mediated decay of organic matter. The detailed analysis of aliphatic hydrocarbons, LABs and PCBs effectively indicate more degraded pollutant signatures with relative enrichment of recalcitrant components in cold months when concentrations are lower (see general composition of organic pollutants).

During the cold–dry season C/N ratios display significantly lower values (10.3 ± 0.8 vs. 14.4 ± 3.1 in warm months; Table 1), suggesting either reduced

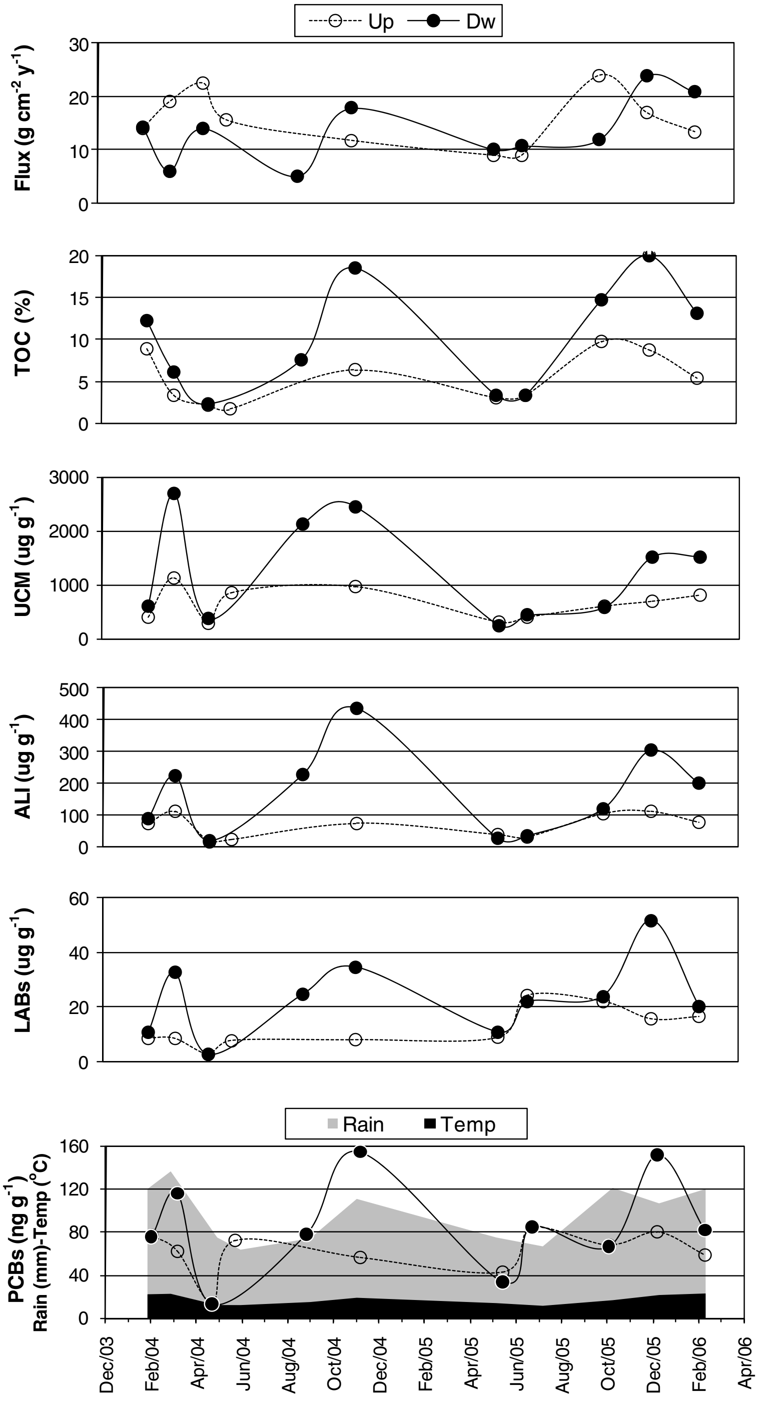

Fig. 3. Total mass fluxes, organic carbon (TOC), unresolved (UCM) and resolved aliphatic hydrocarbons (ALI), linear alkylbenzenes (LABs) and polychlorinated biphenyls (PCBs) in settling material collected upstream (Up) and downstream (Dw) of Buenos Aires main sewer. The monthly average precipitation and temperature are shown as shaded grey and black areas, respectively.

input of terrestrial material or enhanced decay of sewage organic matter which is normally accompanied by decreasing C/N ratios (Margesin et al., 2006). The higher C/N ratios during the rainy, warm season could be associated with a more efficient washout of terrestrial plant debris from

Buenos Aires. However, the *n*-alkane C_{26-31} preference index, typical indicator of terrestrial plant biowaxes, is low and does not show seasonal differences (see general composition of organic pollutants). Thus, the increase of C/N ratios in rainy, warm months is compatible with a lower alteration of organic matter associated with increased overflow discharges from industry treatment plants, small reservoirs and streets to the sewage system. A similar rain-driven contaminant pulse originating from polluted Riachuelo Port and nearby channels may also contribute influencing our sampling sites (Fig. 1).

An increase of primary production and biogenic fluxes during warm months could be discarded since the high turbidity of the estuary severely limits light penetration and algal growth. A spectrophotometric analysis of chlorophyll contents of trap material collected in spring effectively showed low and mostly degraded pigment levels (15 and 42 $\mu g\,g^{-1}$ chlorophyll a and phaeopigments, respectively), representing an algal input of 1.1–3.8% of TOC. In addition, other algal indicators such as C_{15} or C_{17} *n*-alkanes (see composition) or C/N ratios consistently suggest a negligible contribution of algae to the prevailing anthropogenic carbon pool.

3.3. General composition of organic pollutants

Fig. 4 presents the general composition of organic pollutants in the settling material compared with fresh sources such as a local crude oil, a LAB formulation and an Aroclor 1242:1254:1260 mixture. Aliphatic hydrocarbons show a consistent petrogenic pattern of C_{12-35} *n*-alkanes with a bimodal distribution maximizing at C_{13-18} and C_{25-31} over a UCM which peaks at C_{27-29} (Fig. 2). The low molecular weight carbon preference index ($CPI_{15-20} = \sum n\text{-}C_{15,17,19} / \sum n\text{-}C_{16,18,20}$) is uniformly low ($1.20 \pm 0.06$) comparable to the local crude oil value (1.16). However, the composition of settling particles denotes an incipient decay with loss of low molecular weight *n*-alkanes and isoprenoids ($\leqslant n\text{-}C_{22} = 34 \pm 11\%$; $\geqslant n\text{-}C_{23} = 57 \pm 12\%$; isoprenoids $= 8.6 \pm 2.4\%$) relative to crude oil ($\leqslant n\text{-}C_{22} = 65\%$; $\geqslant n\text{-}C_{23} = 20\%$; isoprenoids $= 16\%$). This is also indicated by the C_{17}/pristane and C_{18}/phytane ratios which are lower (1.4 ± 0.5 and 1.3 ± 0.5) than crude oil values (1.9 and 1.7, respectively). The enrichment of the more refractory UCM relative to resolved components (UCM/ALI $= 12 \pm 8.6$ in the traps vs. 1.02 in crude oil) further supports the alteration of the hydrocarbon signature.

The high molecular weight carbon preference index ($CPI_{26-31} = \sum n\text{-}C_{27,29,31} / \sum n\text{-}C_{26,28,30} = 1.19 \pm 0.19$) of the settling material is slightly higher than in crude oil (0.89) reflecting a limited contribution of terrestrial plant biowaxes enriched in $n\text{-}C_{27,29,31}$ (Fig. 2). The decay of oil hydrocarbons and preferential preservation of this terrestrial suite during early diagenetic processes is indicated by the higher CPI_{26-31} values of underlying sediments (1.9–3.4; Colombo et al., 2005b). The aliphatic composition shows a clear seasonal trend of more degraded signatures in cold, dry months with reduced abundance of lower molecular weight components and lower C_{17}/pristane (0.9 ± 0.3 vs. 1.8 ± 0.3) and C_{18}/phytane ratios (0.7 ± 0.3 vs. 1.7 ± 0.3, cold vs. warm). The increase of UCM/resolved aliphatic ratios in cold months (7.8 ± 2.9 to 17 ± 11) confirms an enhanced alteration. In contrast, the CPI_{26-31} presents more uniform values (1.1 ± 0.1 and 1.3 ± 0.2 in cold and warm months; Fig. 4), indicating a minor, background terrestrial plant input.

Persistent petrogenic biomarkers (m/z 191) include C_{20-26} tricyclic terpanes maximizing at C_{23}, and pentacyclic αβ hopanes maximizing at C_{29} norhopane and C_{30} hopane (Fig. 2) with a general prevalence of 22*S* over the 22*R* C_{31-32} homohopane epimers (mean $S/(S+R)$ ratio: 0.59 ± 0.05 and 0.62 ± 0.08 for $C_{31,32}$). The average composition of settling particulates is rather homogeneous ($C_{20-26} = 28 \pm 6.5\%$, $C_{27} = 12 \pm 2.3\%$, $C_{29} = 16 \pm 2.2\%$, $C_{30} = 22 \pm 2.8\%$, $C_{31-32} = 22 \pm 3.6\%$), comparable to a fresh crude oil but depleted of lower molecular weight terpanes and enriched in homohopanes (Fig. 4). A similar low to high molecular weight terpane shift has been observed with distance offshore in underlying sediments and attributed to selective decay (Colombo et al., 2005b). However, the seasonal pattern of the traps suggests that C_{20-26} terpanes are more persistent. Within the αβ hopane series, diagnostic ratios also indicate an early alteration of the trap material which shows consistently higher C_{29}/C_{30} (0.70 ± 0.05) and C_{31S}/C_{30} ratios (0.39 ± 0.05) relative to fresh crude oil (0.60 and 0.28, respectively) suggesting selective loss of C_{30} which is further intensified in offshore sediments (Colombo et al., 2005b). Consistent with the lower incidence of temporal and upstream–downstream variability, tricyclic and pentacyclic terpanes show subtle but still perceptible seasonal changes (Fig. 4), i.e. a higher proportion of tricyclic C_{20-26} terpanes during cold, dry months.

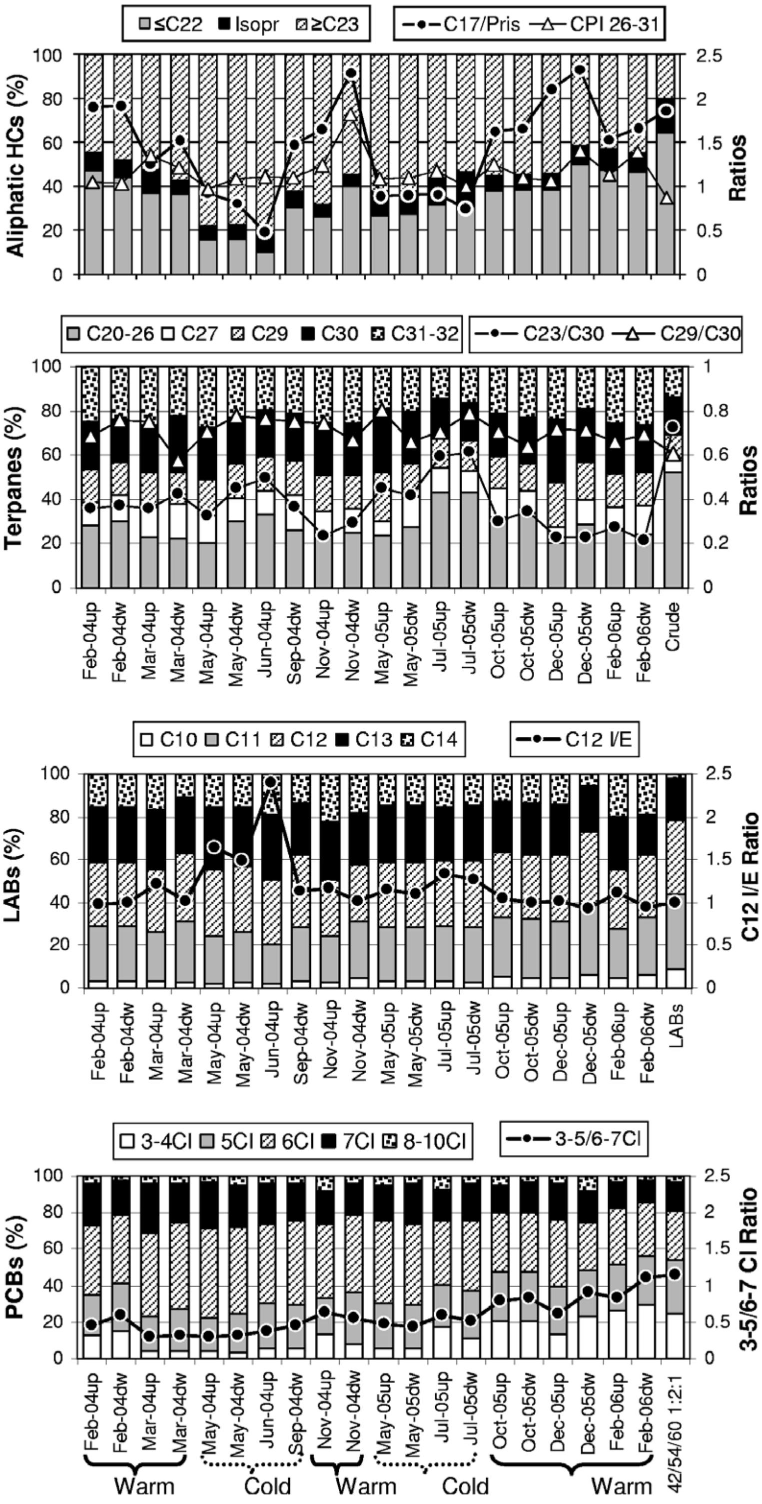

Fig. 4. Relative composition and ratios of aliphatic hydrocarbons, terpanes, LABs and PCBs in the settling material compared to fresh crude oil, a LAB formulation and a 1:2:1 Aroclor 1242:1254:1260 mixture.

This is captured by the C_{23}/C_{30} ratio which increases in cold months (0.46 ± 0.10 vs. 0.30 ± 0.07 in the warm period). In contrast, the C_{29}/C_{30} and C_{31S}/C_{30} ratios do not show significant differences between warm (0.68 ± 0.05 and 0.39 ± 0.05) and cold months (0.73 ± 0.05 and 0.38 ± 0.05, respectively). The C_{31} $S/(S+R)$ ratios are also quite conservative (0.58 ± 0.06 and 0.59 ± 0.04) but the C_{32} $S/(S+R)$ ratio suggests an increase in cold months (from 0.61 ± 0.08 to 0.64 ± 0.07), which in view of the higher susceptibility to biodegradation of R epimers, appear to support a higher alteration.

The composition of LABs shows a fairly homogeneous contribution of isomers with 11–13 carbons which accounts for a grand mean average of 81% ($C_{11} = 25 \pm 2.9\%$, $C_{12} = 30 \pm 2.0$, $C_{13} = 25 \pm 2.5\%$), followed by C_{14} ($15 \pm 3.5\%$) and minor amounts of C_{10} LABs ($3.7 \pm 1.3\%$). Compared to a local fresh LABs mixture, low molecular weight LABs (i.e. C_{10}) appear depleted, whereas C_{14} components are enriched (Fig. 4), suggesting an incipient decay. However, the average LAB profile of settling particulates is similar to that reported for laundry detergents (Eganhouse et al., 1983), suggesting that the alteration is only minor. The ratio of internal to external C_{12} isomers ($I/E = \sum 6C_{12}–5C_{12}/\sum 4C_{12}, 3C_{12}, 2C_{12}$; Fig. 2), indicative of LABs biodegradation due to more rapid attack of external isomers, is slightly higher in the trap material (1.2 ± 0.3) relative to the fresh LAB formulation ($I/E = 1.0$), supporting an incipient alteration. Bacterial decomposition in sewage sludges from primary or secondary treatment plants usually results in much higher I/E ratios (1.4–9.4; Jardé et al., 2005). On a temporal basis, the I/E ratio provides a good record of higher values (i.e. decay) during cold months (1.5 ± 0.4) with an extreme of 2.4 in June 2004, whereas in warm periods it is very close to the fresh LABs mixture (1.1 ± 0.1). These results are very consistent with those from hydrocarbons supporting a higher decay in cold months. However, LABs appear more conservative than hydrocarbons as indicated by the decrease of the resolved aliphatic/LABs ratios in cold months (8.0 ± 2.9 to 4.2 ± 2.9) suggesting an enhanced aliphatic decay and more uniform LAB inputs.

As observed for the other organic compounds the composition of PCBs in the trap material is relatively homogeneous and is dominated by penta–heptachlorobiphenyls which collectively account for an average 83% of total PCBs ($5\ Cl = 24 \pm 2.9\%$, $6\ Cl = 39 \pm 6.8\%$, $7\ Cl = 20 \pm 3.6\%$), followed by tri–tetra ($3–4\ Cl = 12 \pm 8.1$) and octa–decachlorobiphenyls ($8–10\ Cl = 4.3 \pm 1.5\%$). The average trap composition is similar to a 2:1 Aroclor 1254:1260 mixture. However, the proportion of lower chlorinated congeners displays some variability and insinuate an enrichment in warm months and a rising trend in the last trap deployments when the composition resembles a 1:2:1 Aroclor 1242:1254:1260 mixture (Fig. 4). Following the reduction of the seasonal difference with increasing compound stability (see upstream–downstream and seasonal variability), PCBs show only minor seasonal changes. The proportion of tri–tetra chlorobiphenyls and the 3–5/6–7 PCB ratio ($\sum 31, 52, 101, 110, 118/\sum 149, 153, 138, 180, 170$) appear to decrease in cold relative to warm months (0.48 ± 0.10 vs. 0.70 ± 0.24), which may reflect an enhanced decay of less chlorinated PCBs.

3.4. Seasonal variation of individual compounds

The most significant seasonal trends of individual compounds are illustrated in Fig. 5 by representative gas chromatograms of aliphatic hydrocarbons, terpanes, LABs and PCBs for warm and cold-season traps. The aliphatic chromatograms show a depletion of lower molecular weight *n*-alkanes with concurrent relative increase of the UCM and LABs in cold months. At the same time, biomarkers present a relative increase of tricyclic vs. pentacyclic terpanes whereas LAB signatures show depletion of C_{10} isomers and of most external LABs with the phenyl ring in positions 3 and specially 2. The chromatograms of PCBs show a reduction of lower chlorinated tri–tetrachlorobiphenyls in the cold season. The molecular weight dependence of these changes is presented in Fig. 6 which shows the average warm to cold trap relative enrichment of individual compounds against molecular weight. This has been calculated as the average warm/cold trap ratios of the relative abundances of individual components for each organic pollutant class.

Except for terpanes, there is a clear pattern of exponential reduction of the warm trap enrichment with increasing molecular weight. This reflects the normally higher recalcitrance of larger molecules confirming the seasonal variability as directly related to the discharge of residues with a different degree of alteration in warm–wet (fresher) and cold–dry (more degraded) periods. The exponential decrease is most significant for aliphatic hydrocarbons ($R^2 = 0.96$) which show 2.5–1.3 times higher relative abundances of n-C_{12} to n-C_{23}, respectively,

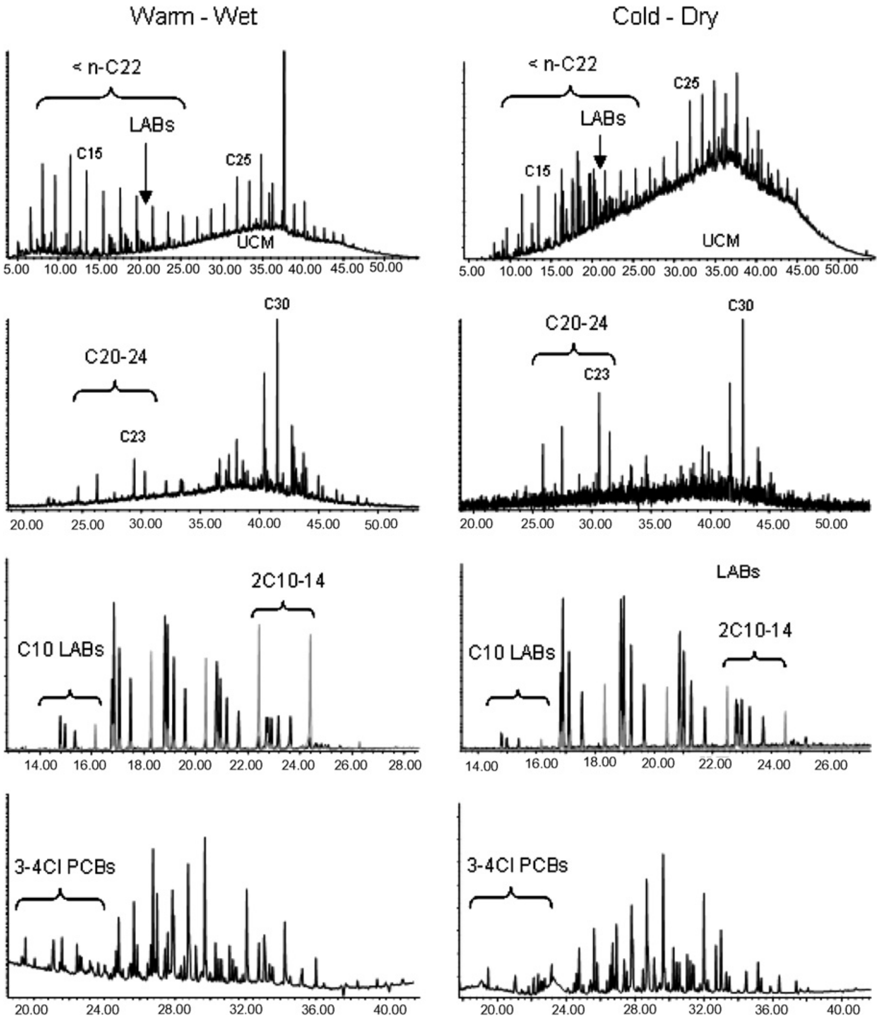

Fig. 5. Representative gas chromatograms of aliphatic hydrocarbons, terpanes, LABs and PCBs showing main compositional changes in warm and cold-season traps.

in warm months, with lower proportions of more conservative higher molecular weight *n*-alkanes. The relative abundance of more resistant isoprenoids does not show such marked warm–cold differences but still displays the exponential pattern ($R^2 = 0.87$), basically due to a slight summer enrichment of lower molecular weight farnesane. A similar behavior is observed for LABs with the phenyl ring in position 6, 5 and 4 (i.e. more internal isomers) which show more comparable proportions in warm and cold-season traps and exponential functions ($R^2 = 0.87$–0.89) very similar to isoprenoids (Fig. 6), suggesting that they are as reactive as these compounds. In contrast, the most external 3 and especially 2 LAB isomers are significantly enriched in the warm period, reflecting their higher susceptibility to microbial attack. The summer enrichment of $2C_{10}$ LAB is highest (2.5 times), similar to that of C_{12} *n*-alkane. PCBs show a poorer exponential fit ($R^2 = 0.44$) basically due to very homogeneous relative abundances of penta- to decachlorobiphenyls (MW: 326–499) with an apparent warm-season enrichment for tri- and tetrachlorobiphenyls.

In contrast to most organic pollutants, terpane biomarkers follow exactly the opposite pattern; the proportions are more conservative (i.e. warm–cold differences: 0.6–1.4) and show a significant increasing trend with molecular weight ($R^2 = 0.46$–0.89 for C_{27-32}–$C_{20-26,}$ or 0.82 for the whole group). Lower molecular weight tricyclics are enriched in degraded cold traps whereas pentacyclic hopanes, and specially C_{32} homohopanes, show a relative

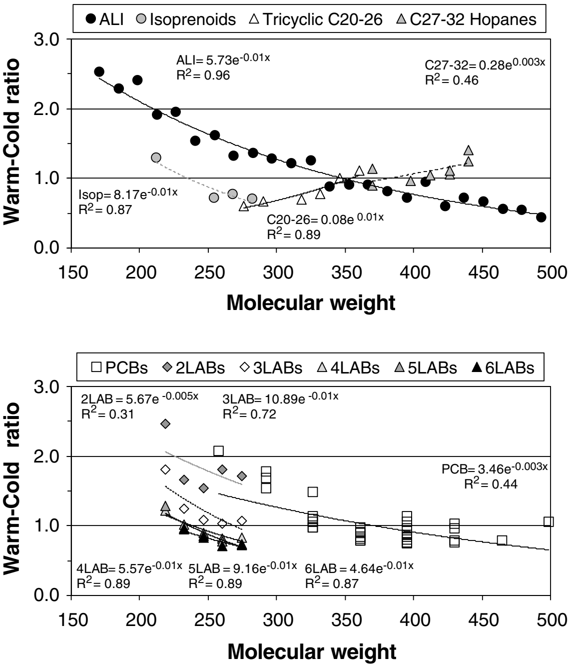

Fig. 6. Average warm to cold trap enrichment in the proportion of individual components for each pollutant class plotted against molecular weight.

increase in warm samples. As indicated previously, this is reflected by the warm–cold difference of C_{23}/C_{30} (0.30 ± 0.07–0.46 ± 0.10) and C_{32}/C_{30} ratios (0.36 ± 0.12–0.29 ± 0.07), indicating selective preservation of tricyclics and decay of C_{32} homohopanes in cold, dry months. The biodegradation pattern of terpanes has been controversial concerning lower vs. higher molecular weight susceptibility. Tricyclic terpanes are recognized as very resistant to biodegradation surviving even when hopanes are removed (Peters and Moldowan, 1993; Alberdi et al., 2001), but the opposite pattern, i.e. lower persistence than C_{29} and C_{30} hopanes has been also reported (Wang et al., 2001). Similar contradicting low vs. high molecular weight degradation sequences have been reported for the αβ hopane series (Peters and Moldowan, 1993; Wang et al., 2001). The changes of the terpane signature with distance offshore in Río de la Plata sediments indicated a preferential loss of tricyclics, a lower stability of C_{30} relative to C_{29} norhopane or C_{31} homohopane, and enhanced decay of higher homohopane members (Colombo et al., 2005b). Differences in environmental conditions and bacterial assemblages could possibly explain these contradicting results. Río de la Plata settling material corresponds to the degradation of mixed sewage plus industrially derived organic matter under anaerobic conditions as indicated by the dark-black color and strong sulfur smell of the samples, whereas superficial sediments present an offshore anoxic–oxic gradient related to the impact of effluent discharges. A selective preservation of tricyclic terpanes in anoxic conditions and a more efficient decay in oxic offshore sediments could explain the patterns observed in settling material and underlying sediments of the Río de la Plata. Alternatively, different fossil fuel sources or physical processes such as progressive offshore shift between two signals or a differential tricyclic mobilization need to be invoked to conciliate both observations.

References

Alberdi, M., Moldowan, J.M., Peters, K.E., Dahl, J.E., 2001. Stereoselective biodegradation of tricyclic terpanes in heavy oils from the Bolivar coastal fields, Venezuela. Organic Geochemistry 32, 181–191.

Barrick, R.C., 1982. Flux of aliphatic and polycyclic aromatic hydrocarbons to Central Puget Sound from Seattle (Westpoint) primary sewage effluent. Environmental Science & Technology 16, 682–692.

Bates, T., Hamilton, S., Cline, J.D., 1984. Vertical transport and sedimentation of hydrocarbons in the central main basin of Puget Sound, Washington. Environmental Science & Technology 18, 299–305.

Broman, D., Colmsjo, A., Ganning, B., Naf, C., Zebuhr, Y., Ostman, C., 1987. Fingerprinting petroleum hydrocarbons in bottom sediment, plankton, and sediment trap collected seston. Marine Pollution Bulletin 7, 380–388.

Colombo, J.C., Silverberg, N., Gearing, J.N., 1996. Lipid biogeochemistry in the Laurentian Trough: 1 – fatty acids, sterols and aliphatic hydrocarbons in rapidly settling particles. Organic Geochemistry 25, 211–225.

Colombo, J.C., Silverberg, N., Gearing, J.N., 1997. Lipid biogeochemistry in the Laurentian Trough: II – Changes in composition of fatty acids, sterols and aliphatic hydrocarbons during early diagenesis. Organic Geochemistry 26, 257–274.

Colombo, J.C., Cappelletti, N., Barreda, A., Migoya, M.C., Skorupka, C., 2005a. Vertical fluxes and accumulation of PCBs in coastal sediments of the Río de la Plata estuary, Argentina. Chemosphere 61, 1345–1357.

Colombo, J.C., Cappelletti, N., Lasci, J., Migoya, M.C., Speranza, E., Skorupka, C.N., 2005b. Sources, vertical fluxes and accumulation of aliphatic hydrocarbons in coastal sediments of the Río de la Plata estuary. Environmental Science & Technology 39, 8227–8234.

Colombo, J.C., Cappelletti, N., Lasci, J., Migoya, M.C., Speranza, E., Skorupka, C.N., 2006. Sources, vertical fluxes and equivalent toxicity of aromatic hydrocarbons in coastal sediments of the Río de la Plata estuary, Argentina. Environmental Science & Technology 40, 734–740.

Eganhouse, R.P., Kaplan, I.R., 1982. Extractable organic matter in municipal wastewaters. 2. Hydrocarbons: molecular characterization. Environmental Science & Technology 16, 541–551.

Eganhouse, R.P., Sherblom, P.M., 2001. Anthropogenic organic contaminants in the effluent of a combined sewer overflow: impact on Boston Harbor. Marine Environmental Research 51, 51–74.

Eganhouse, R.P., Ruth, E.C., Kaplan, I.R., 1983. Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography/high-resolution gas chromatography and gas chromatography/mass spectrometry. Analytical Chemistry 55, 2120–2126.

Esteves, J.L., Ciocco, N.F., Colombo, J.C., Freije, H., Harris, G., Iribarne, O., Isla, I., Nabel, P., Pascual, M., Penchaszadeh, P.E., Rivas, A., Santinelli, N., 2000. The Argentine Sea: the Southeast South American Shelf Marine Ecosystem. In: Sheppard, C. (Ed.), Seas at the Millennium: An Environmental Evaluation. Elsevier, pp. 749–771.

FREPLATA, 2005. Análisis Diagnóstico Transfronterizo del Río de la Plata y su Frente Marítimo. Documento Técnico. Proyecto PNUD/GEF/RLA/99/G31, p. 311.

Jardé, E., Mansuy, L., Faure, P., 2005. Organic markers in the lipidic fraction of sewage sludges. Water Research 39, 1215–1232.

Margesin, R., Cimadom, J., Schinner, F., 2006. Biological activity during composting of sewage sludge at low temperatures. International Biodeterioration & Biodegradation 57, 88–92.

Meyers, P.A., Edwards, S.J., Eadie, B.J., 1980. Fatty acids and hydrocarbon content of settling sediments in Lake Michigan. Journal Great Lakes Research 6, 331–337.

Mudge, S.M., Duce, C.E., 2005. Identifying the source, transport path and sinks of sewage derived organic matter. Environmental Pollution 136, 209–220.

Peters, K.E., Moldowan, J.M., 1993. The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall.

Prahl, F.G., Carpenter, R., 1979. The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. Geochimica et Cosmochimica Acta 43, 1959–1972.

Prahl, F.G., Bennett, J.T., Carpenter, R., 1980. The early diagenesis of aliphatic and organic matter in sedimentary particulates from Dabob Bay, Washington. Geochimica et Cosmochimica Acta 44, 1967–1976.

Rosenani, A.B., Kala, D.R., Fauziah, C.I., 2004. Characterization of Malaysian sewage sludge and nitrogen mineralization in three soils treated with sewage sludge. In: SuperSoil 2004: Third Australian New Zealand Soil Conference, pp. 1–7.

Wang, Z., Fingas, M., Owens, E.H., Sigouin, L., Brown, C.E., 2001. Long-term fate and persistence of the spilled Metula oil in a marine salt marsh environment. Degradation of petroleum biomarkers. Journal of Chromatography A 926, 275–290.