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Different carbon sources affect PCB accumulation by marine bivalves

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ABSTRACT

Pampean creeks were evaluated in the present study as potential land-based sources of PCB marine contamination. Different carbon and nitrogen sources from such creeks were analysed as boosters of PCB bioaccumulation by the filter feeder bivalve *Brachidontes rodriguezii* and grazer limpet *Siphonaria lessoni*. Carbon of different source than marine and anthropogenic nitrogen assimilated by organisms were estimated through their C and N isotopic composition. PCB concentration in surface sediments and mollusc samples ranged from 2.68 to 6.46 ng g^{-1} (wet weight) and from 1074 to 4583 ng g^{-1} lipid, respectively, reflecting a punctual source of PCB contamination related to a landfill area. Thus, despite the low flow of creeks, they should not be underestimated as contamination vectors to the marine environment. On the other hand, mussels PCB bioaccumulation was related with the carbon source uptake which highlights the importance to consider this factor when studying PCB distribution in organisms of coastal systems.

1. Introduction

Coastal areas pollution is generated not only from activities developed therein, but also from land-based sources. Large rivers reach the ocean through estuaries discharging vast amounts and diversity of contaminants to the marine environment (Gao and Chen, 2012; Yuan et al., 2001). Thus, contaminants come from different human activities like industries, farming, urbanization, among others (Miglioranza et al., 2013). Studies in this sense are very numerous which further state the consequences of such contamination to the receiving ecosystem (Farcy et al., 2013; Whitfield and Elliott, 2002). On the other hand, small estuaries, formed from small rivers, streams or creeks (with drainage basin <260 km^2; Strobel et al., 2000), are usually neglected as sources of marine pollution, maybe due to their small size and flow. However, attention on the influence of small estuaries discharge is increasing (Connolly et al., 2009; Gaston et al., 2006) and a seafloor imprint of export activity has been observed (Gaston et al., 2006). Still, the information on direct continental inputs from small creeks is very scarce.

Creeks may also carry terrestrial organic materials (TOM) in the form of dissolved organic matter (DOM), particulate organic matter (POM) (Hedges et al., 1997), and dissolved inorganic nutrients (i.e. N and P) to the coastal areas (Nixon et al., 1996). Both inputs (TOM and nutrients) may affect contaminants distribution at the receiving area through different processes. For instance, hydrophobic organic contaminants (HOC) present a great affinity to organic matter (Hassett and Anderson, 1979). Associations of these contaminants with DOM and POM according with their physicochemical characteristics are one of the main factors determining their distribution in the environment (Björk, 1995). Thus, different organic matter concentration and composition would lead to different HOC sorption processes and consequently a distribution pattern. In this sense, many studies reported the influence of organic matter source and composition on HOC distribution in coastal sediments (Edgar et al., 2003; Nouira et al., 2013), whereas studies of this process in marine organisms are scarce. There is

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evidence of differential HOC accumulation in aquatic organisms due to different sediment mineralogy (Edgar et al., 2006). On the other hand, nutrient input enhances POM concentration due to an increase in phytoplankton (Zhou et al., 2008), which may have consequences in HOC bioaccumulation. For instance, Björk and Gilek (1997) found that an increase in microalgae supply, enhanced PCB bioaccumulation by blue mussels due to physiological and behavioural adaptations to changes in food availability. Besides, Gunnarsson et al. (2000) reported that eutrophication (caused by abnormal enhanced nutrient concentration in an ecosystem) lead to high HOC concentrations in benthic organisms and sediments of the Baltic Sea. In this context, in coastal areas, terrestrial organic matter and nutrient input could affect HOC distribution and particularly lead to a high bioaccumulation in aquatic organisms, which is a key factor to consider in biomonitoring studies.

Both terrestrial organic matter and anthropogenic nitrogen input to a given environment can be estimated through carbon and nitrogen stable isotopes, respectively. Organism's isotopic composition of carbon varies according to the ultimate organic carbon source they consume (Post, 2002). Since the isotope end-members of the general marine and freshwater environments are fairly explored and well known (marine sources are ^{13}C enriched respect to terrestrial), stable isotope analysis can reveal riverine input to the marine environment (Connolly et al., 2009). Thus, the consumption of terrestrial organic material by marine organisms can be estimated by a shift in the C isotope signature (Schlacher and Connolly, 2009). On the other hand, nitrogen stable isotopes in marine organisms have been used to trace the fate and distribution of nutrients generated by human such as through residual waters discharge (Vizzini and Mazzola, 2006).

Polychlorinated biphenyls (PCBs) are synthetic HOC that have been mainly produced for industrial purposes. Although PCB production is actually globally banned, they are still found in toxicological relevant concentrations around the world (e.g. Lohmann and Belkin, 2014). Due to their physicochemical characteristics they are highly toxic and widely distributed in environmental compartments. The production and use of PCB has been phased out and they are included in the Annex A and C of the Stockholm Convention as Persistent Organic Pollutants (POPs). Therefore, the presence of PCBs at environmentally relevant levels and their bioaccumulation is of great concern (Beyer and Biziuk, 2009). Although banned in Argentina since 2005, PCB residues can still be found in freshwater (Ondarza et al., 2012, 2014), estuarine (Arias et al., 2013; Colombo et al., 2011) and marine (Commendatore et al., 2015) environments.

Mar del Plata city (Southwest Atlantic) is the most important beach resort of Argentina. Touristic activity is present almost all year round, being higher during summer when population increases more than 300%. The industrial activity (mainly fishing and textile, following by horticultural and metal working) is also well developed. In this context, the present study assessed the influence of creeks and different carbon and nitrogen sources in the distribution of PCB in sediments and molluscs from a Southwest Atlantic coastal environment. Although PCB are ubiquitously distributed due to atmospheric deposition, higher concentration at the marine ecosystem adjacent to creeks outfall are expected due to terrestrial sources (drainage) and because PCB specific distribution in organisms would be modified by the organic matter and nutrients inputs.

2. Materials and methods

2.1. Study sites

Sampling was carried out at the intertidal zones located at four creek outfalls on Mar del Plata coast (Southwest Atlantic) and one reference site (Fig. 1). La Tapera (LT) and Las Chacras (LC) creeks are under the influence of horticultural farming and very urbanized areas, and at their final stretch, they are used as pluvial drainages. Pesticides levels were reported both in the basin (Massone et al., 1998) and along (Miglioranza et al., 2004) LT creek. The final stretch of LC creek runs through a pipe and both heavy metals (Bocanegra et al., 2001) and pesticides (Massone et al., 1998) were found on its basin. Furthermore, illegal sewage connections to pluvial drainages have been detected in the area (Pérez Guzzi et al., 2006). In contrast, Seco (S) and Chapadmalal (Ch) creeks pass through extensive agricultural and slightly urbanized areas. There are no previous studies establishing the contamination status of these creeks. Their mouths have bath facilities for the beach-users, which is not the case for the LT and LC creeks. Finally, the reference site Barrera (B_{ref}) is an intertidal zone without direct influence of any creek outfall. An additional reference site was sampled for isotopic analysis, RCT_{ref}, which present the same characteristics than B_{ref} (without continental input).

2.2. Samples collection and preparation

The sampling was conducted in autumn 2012 during low tides. Sediment samples were taken both at the intertidal and 150 m upstream (except for LC), in order to determine the sediment particle size distribution, organic matter content and PCB analysis. Samples were dried in an oven at 60 °C until constant weight. Organic matter content was determined from the weight loss after incineration in a muffle at 500 °C during 4 h, whilst particle size distribution was determined through sieving (Carver, 1971).

For the PCBs analysis, six beach sediment samples were mixed and sieved to pass 300 μm, forming one composite sample. They were immediately placed on a glass flask and carried refrigerated to the laboratory. Then, sediments were dried in stainless steel plates at room temperature until constant weight. Three subsamples per site were stored in aluminium foil at − 20 °C until analysis.

Limpets *Siphonaria lessoni* (10–12 mm) and mussels *Brachidontes rodriguezii* (17–20 mm) were manually collected at the rocky intertidal area of each study area. Approximately 20 organisms from each site were carried refrigerated to the laboratory and kept on aerated tanks with seawater of the same area to depurate. After 24 h, shell length was measured and soft tissues were dissected, rinsed thoroughly with Milli-Q water and pooled. Subsamples of soft tissues were dried in an oven at 60 °C and then ground up with a mortar and pestle for the stable isotopes analysis. For PCB analysis, soft tissues were homogenized with a stainless steel blender and stored at −20 °C until analysis.

2.3. PCBs analysis

PCBs were extracted according to Metcalfe and Metcalfe (1997) with modifications of Miglioranza et al. (2003). Samples of dry sediments (10 g) and molluscs' soft tissues (3 g) were homogenized with anhydrous sodium sulphate and spiked with PCB #103 as surrogate standard. Organic compounds were Soxhlet extracted for 8 h with a 50:50 mixture of dichloromethane and n-hexane. The lipids of molluscs were removed from the extracts by gel permeation chromatography using Bio-Beads S-X3 (200–400 mesh) and evaporated to dryness to calculate the sample lipid content. The fractions containing PCB were further purified by column chromatography with activated silica gel (200 °C for 24 h). Extracts were concentrated to 1 mL and kept in vials at −20 °C prior to gas chromatography analysis. PCBs identification and quantification were performed using a Gas Chromatograph, Perkin Elmer Clarus 500, equipped with a ^{63}Ni Electron Capture Detector (GC-ECD) and

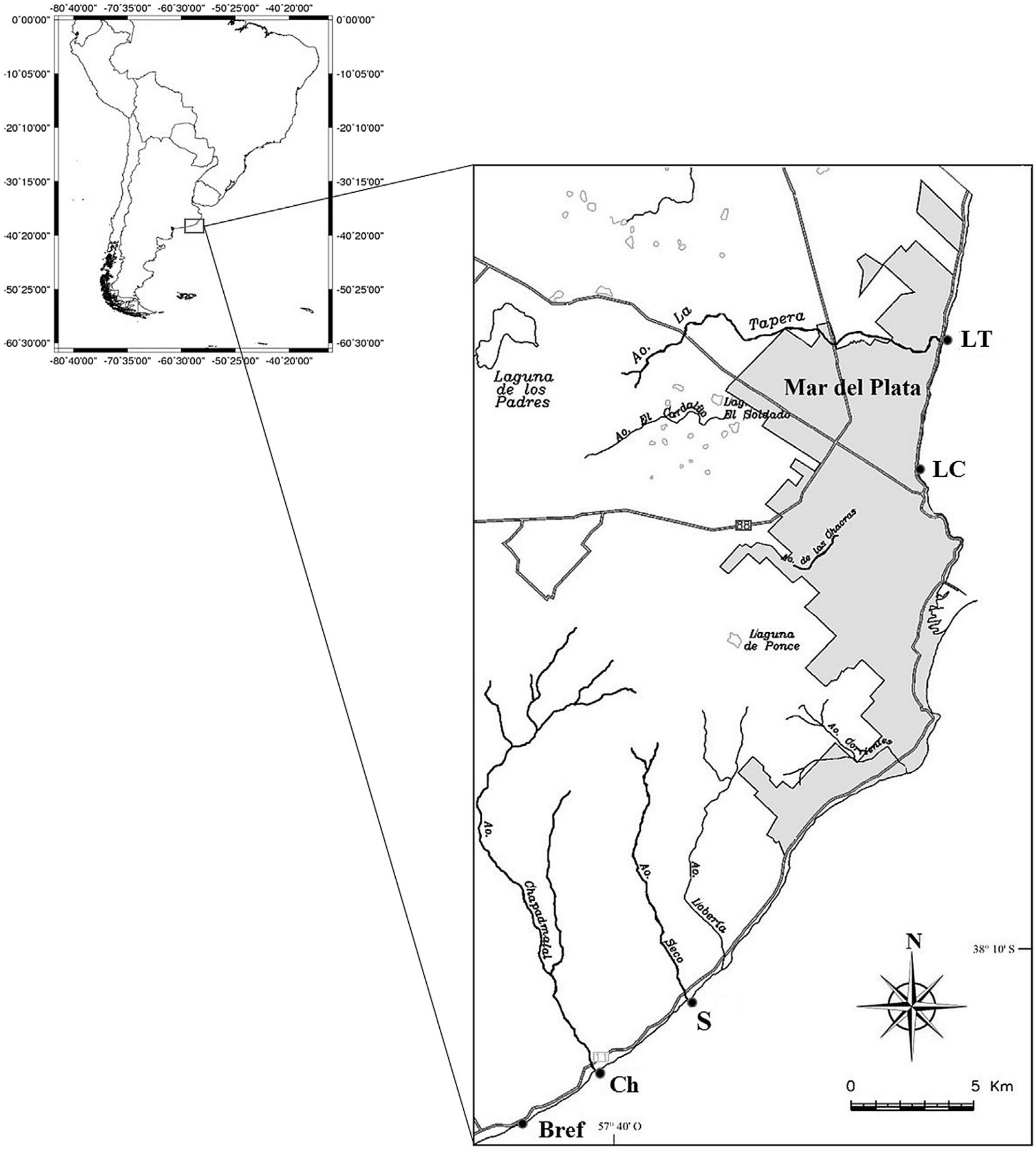

Fig. 1. Map showing sampling sites. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; B_{ref}: Barrera (reference site).

a capillary column DB-5 (30 m length, 0.25 mm i.d., 0.25 μm film thickness; Supelco Inc.). One μL was injected on a splitless mode (280 °C) and the detector was kept at 300 °C. The oven temperature program was: start at 40 °C and held for 1 min, followed by an increase of 20 °C min^{-1} up to 160 °C, held for 5 min, then 2 °C min^{-1} up to 260 °C, 0 min. Helium was used as carrier gas (1.5 mL min^{-1}) and nitrogen as make-up gas (30 mL min^{-1}) (Miglioranza et al., 2003). PCB #103 was used as internal standard while eleven PCB congeners were determined (IUPAC #18, 44, 52, 99, 101, 105, 110, 138, 149, 153, 180).

2.4. Stable isotopes analysis

Measurements of $\delta^{13}C$ and $\delta^{15}N$ for each sample were made on a CarloErba Elemental Analyzer (CHONS) coupled to a Finnigan MAT Delta V continuous-flow isotope ratio mass spectrometer (CF-IRMS) through a Thermo ConFlo IV interface using internal standards. These standards (caffeine: $\delta^{13}C = -39.33‰$, $\delta^{15}N = 7.02‰$; sugar: $\delta^{13}C = -11.41‰$; and collagen: $\delta^{13}C = -18.18‰$, $\delta^{15}N = 6.12‰$) were calibrated against VPDB and AIR reference standards for carbon (L-SVEC, NBS-19 and NBS-22) and nitrogen (IAEA N1 and IAEA N2) (Coplen et al., 1992, 2006; Gonfiantini, 1978). Replicates of internal standards showed analytical uncertainties to be on the order of ±0.2‰ for both $\delta^{13}C$ and $\delta^{15}N$ values.

2.5. Statistical analysis

ANOVA tests were used to compare among sites: i-surface sediment PCB concentrations and ii-mollusc carbon and nitrogen isotopic composition, after checking the normality and homoscedasticity, and transforming when necessary. When differences were found, a Tukey post hoc test was applied. Mollusc lipid content and PCB concentrations were compared between species through T-tests. The relation of sediment PCB concentration with sediments grain size and organic matter content was studied through a Pearson correlation test. The same test was used to determine whether PCB concentrations of molluscs were related with lipid content and carbon and nitrogen isotopic composition. All statistical analyses were conducted in R 2.13.0 (R Development Core Team, 2011).

3. Results and discussion

3.1. Sediments and molluscs PCB concentrations

In general, sediments from all sites were characterized by the predominance of medium and fine sand (Fig. 2) and low organic matter (OM) content (Table 1). Total PCB concentration in surface sediments ranged from 2.68 (±1.3) to 6.46 (±4.0) ng g^{-1} (dry weight basis) (Table 1), but there were no significant PCB concentration differences among sites ($p > 0.05$) or pattern regarding the presence of creek discharges. Indeed, the reference site (without a direct influence of any creek) presented the highest concentration of $\sum$PCB in sediments (6.46 ng g^{-1}). However, the distribution of the individual congeners showed that such concentration corresponds to tri and tetra-chlorinated homolog (Fig. 3). The dominance of such congeners in environmental samples would indicate an atmospheric origin of PCBs (Meijer et al., 2002), or the decomposition products of heavily chlorinated PCBs (Li et al., 2009). Given the absence of a point source at this site, the atmospheric source would be more likely.

Furthermore, PCBs concentrations were neither correlated with particle sizes nor with the OM ($p > 0.05$), even when congeners were analysed in separate. This finding agrees with results of other studies (Edgar et al., 2003; Zhao et al., 2010) and indicates that these features of the sediments are not important factors determining the distribution of PCBs in sediments of the studied area. Given the dynamics of this environment, other factors like hydrodynamic conditions, *in situ* input and degradation could be masking the interaction of particle size and OM with PCBs (Gao et al., 2013).

In general, PCB 18 (tri-chlorinated) was the most abundant (52.5–94.4% of total PCB) congener in sediments, except in LC (18.8%). Both LT and LC beaches presented 35.9% and 56.1%, respectively, of hexa-chlorinated homologue (Fig. 3). The commercial mixtures mainly used in Argentina were Aroclor 1260 and 1254, which were constituted principally by tetra, penta and hexa chlorinated and penta and hexa chlorinated biphenyls, respectively. Thus, many authors found a predominance of tetra, penta and hexa congener in different environmental samples of the region (Colombo et al., 2007, 2011; Menone et al., 2000; Miglioranza et al., 2013; Ondarza et al., 2010, 2011). In this context, the congener distribution in LT and LC indicates point sources, which could be from the horticultural farming and urbanization.

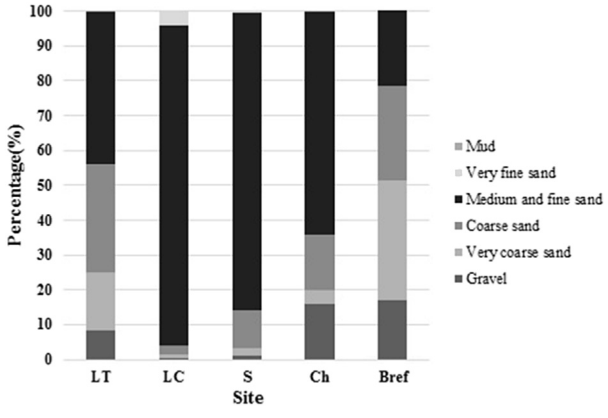

Fig. 2. Particle size distribution in beaches of LT: La Tapera, LC: Las Chacras, S: Seco, Ch: Chapadmalal and Bref: Barrera (reference site).

Regarding molluscs, PCB concentrations on a wet weight basis were significantly different between species and correlated with lipid percentage ($p < 0.05$); thus, PCBs concentrations in limpets *S. lessoni* and bivalves *B. rodriguezii* are presented on a lipid basis in Table 2. Mean concentrations of total PCB ranged from 1074 (±290) to 1894 ± (520) ng g^{-1} lipid wt in limpets *S. lessoni* and from 1903 (±580) to 4583 (±300) ng g^{-1} lipid wt in *B. rodriguezii*, being significantly higher in *B. rodriguezii* ($p < 0.05$). Zhao et al. (2005) suggested that different trophic habits could explain differential bioaccumulation in molluscs. This could be the case since *B. rodriguezii* are filter feeders while *S. lessoni* are grazers of micro and macroalgae. In addition, mussels would have higher uptake since they breathe through gills whilst limpets are pulmonated. However, different physiological mechanisms of each species such as contaminant biotransformation or depuration cannot be neglected (Barron, 1990).

On the other hand, when comparing sites in order to assess the contamination input by creeks outfalls, the highest PCB levels can be observed in *B. rodriguezii* collected at LC and S (Table 2). First, this result indicates that PCB distribution in the studied area is not regulated by the degree of urbanization, as LC flows through urbanized area and S does not. Instead, higher PCB levels and congener distribution pattern indicate the presence of point sources at LC and S. In most cases tri and hexa-chlorinated homologues predominated in mollusc samples (*S. lessoni*: 27–35% and 31–37%, respectively; *B. rodriguezii*: 32–44% and 30–39%, respectively) (Fig. 4). However, a deviation of such pattern was observed in *B. rodriguezii* of LC and S, being tetra (27%), penta (31%) and hexa (28%)-chlorinated and penta (31%) and hexa (30%)-chlorinated the predominant homologues, respectively (Fig. 4). This pattern coincides with the commercial mixtures used at this region. Las Chacras and Seco creek watersheds are under the influence of the municipal landfill, which could be related to such point source. Since PCB production and use are globally forbidden, landfills are one of the main sources of these compounds to the environment (Breivik et al., 2007). Since 1979, Mar del Plata city wastes are deposited in 3 landfills which cover an area of approximately 100 ha and accumulate about 450 tons of waste a day (Farenga et al., 2003). These wastes are deposited without appropriate sanitary landfill techniques (Massone et al., 1998). High PCB levels were previously found in soil (Miglioranza, unpublished data) and epiphytes of this site (Gonzalez et al., 2008). Therefore our results indicated that such contamination reaches the marine environment through creeks, although its flow is small. Placing the contamination in sediments and molluscs in perspective, total PCB concentrations are above those of pristine areas (Montone et al., 2001; Skarphedinsdottir et al., 2010) and comparable with sites considered low to moderately contaminated (Bayarri et al., 2001; Gao et al., 2013; Nouira et al., 2013; Tanabe et al., 2000).

3.2. Carbon and nitrogen isotopic analyses

Isotopic analysis revealed variation in carbon and nitrogen sources of molluscs along the studied area. Reference sites (B_{ref} and RCT_{ref}) presented values of $\delta^{13}C$ between −17.9‰ and −18.4‰ in mussels and between −13.9‰ and −15.1‰ in limpets. Botto et al. (2006) reported $\delta^{13}C$ of −17.9 ± 0.005‰ in scallops from a scallop bed located in front of Mar del Plata at approximately 100 m depth. Moreover, $\delta^{13}C$ values of −18.3 ± 0.3‰ and −17.96 ± 0.39‰ were found in filter-feeder bivalves from Samborombón Bay (González-Carman et al., 2014) and Nuevo Gulf (5–9 m depth; Zabala et al., 2013), respectively. Zabala et al. (2013) also reported $\delta^{13}C$ of −15.5 ± 0.24‰ in the grazer gastropod *Tegula patagonica*

Table 1
Organic matter content (%OM) and mean (±std deviation; n = 3) concentration of PCB congeners (ng g^{-1} dry weight) in surface sediments from creeks and beaches of each study site. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; B_{ref}: Barrera (reference site).

	Creeks			Beaches				
	LT	S	Ch	LT	LC	S	Ch	B_{ref}
%OM	6.95 ± 0.2	1.58 ± 0.1	6.8 ± 0.06	1.35 ± 0.2	0.77 ± 0.1	0.88 ± 0.2	0.7 ± 0.1	0.76 ± 0.08
18	3.26 ± 1	2.53 ± 1	3.26 ± 1.9	1.6 ± 1.9	1.21 ± 1.1	4.93 ± 5.8	2.53 ± 1.9	5.1 ± 2.9
52	0.1 ± 0.1	<LOD	0.03 ± 0.06	0.1 ± 0.1	1.39 ± 2.4	0.18 ± 0.2	<LOD	0.8 ± 0.7
44	<LOD	<LOD	0.38 ± 0.7	0.04 ± 0.08	0.22 ± 0.4	0.17 ± 0.1	<LOD	0.49 ± 0.5
101	0.1 ± 0.09	<LOD	0.26 ± 0.3	<LOD	<LOD	<LOD	<LOD	<LOD
99	<LOD	<LOD	<LOD	0.06 ± 0.1	<LOD	<LOD	0.23 ± 0.4	<LOD
110	<LOD	0.13 ± 0.23	0.16 ± 0.3	0.07 ± 0.1	<LOD	<LOD	<LOD	<LOD
149	<LOD	<LOD	<LOD	0.76 ± 0.01	<LOD	0.08 ± 0.1	<LOD	<LOD
153 + 105	0.2 ± 0.08	0.02 ± 0.02	0.16 ± 0.3	0.2 ± 0.1	3.38 ± 5.5	0.07 ± 0.1	0.03 ± 0.04	0.07 ± 0.07
138	<LOD	<LOD	<LOD	0.14 ± 0.02	0.2 ± 0.4	<LOD	<LOD	<LOD
180	<LOD	<LOD	<LOD	0.07 ± 0.1	0.01 ± 0.01	<LOD	<LOD	<LOD
∑PCBs	**3.66 ± 1**	**2.68 ± 1.3**	**4.25 ± 2.3**	**3.05 ± 2.1**	**6.42 ± 7.6**	**5.43 ± 5.9**	**2.8 ± 1.9**	**6.46 ± 4**

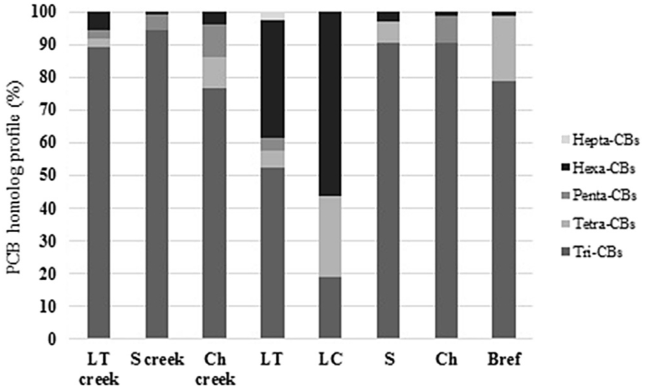

Fig. 3. PCB homolog profile in surface sediments from creeks and beaches of each study site. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; Bref: Barrera (reference site).

inhabiting the same gulf. Thus, reference $\delta^{13}C$ values of the present study are comparable with those reported in invertebrates from purely marine environments of the region confirming that these sites do not have freshwater influences.

Although molluscs from LT and Ch presented values similar to the reference sites B_{ref} and RCT_{ref}, significantly smaller values of $\delta^{13}C$ were found in limpets from LC (5‰ depleted) and mussels from S (2‰ depleted) ($p < 0.01$) (Fig. 5). Several works have reported this pattern in organisms inhabiting beaches under the influence of freshwater discharges, either of large (Schlacher and Connolly, 2009) or small rivers (Bergamino et al., 2012). Indeed, it is well established that marine organisms which feed partially on the terrestrial organic matter supplied by estuaries present depleted carbon isotopic signatures (Connolly et al., 2009). This is because terrestrial organic matter presents $\delta^{13}C$ depleted respect to marine organic matter (Peterson and Fry, 1987). Furthermore, Botto et al. (2011) found depleted carbon isotopic signature in benthic species of the great Río de La Plata estuary, located 400 km north, which reflected the consumption of marsh detritus by such species. Thus, although creek and/or marine end-members were not isotopically analysed in the present study, the observed pattern suggests an organic matter supply from creeks to the marine environment. Moreover, isotopic differences from the reference sites seen for the present study (5‰ and 2‰) are very similar to those found by many authors between river plume and non-plume influenced marine invertebrates. For instance, Connolly et al. (2009) and Schlacher and Connolly (2009) found a $\delta^{13}C$ depletion of 1.5‰ and 3‰, respectively, in organisms under the influence of river plumes respect to a marine reference site.

Respect to $\delta^{15}N$, limpets presented values between 7.8‰ and 16.3‰, whereas mussels ranged from 9.3‰ to 12.3‰ (Table 3). Since $\delta^{15}N$ values increase in ca. 3‰ between trophic levels (Peterson and Fry, 1987), results indicate that those two species occupy the same trophic level. Regarding isotopic variation due to site, reference sites presented $\delta^{15}N$ between 10.9‰ and 11.5‰ in mussels and between 9.9‰ and 12.1‰ in limpets (Table 3). These values are higher than the 8.9 ± 0.05‰ and the 9.5 ± 0.6‰ reported in bivalves inhabiting open sea areas in front of Mar del Plata (Botto et al., 2006) and in a great bay northwards (González-Carman et al., 2014), respectively. However, they are similar to those reported to filter-feeder bivalves and herbivorous gastropod from Nuevo gulf,

Table 2
Mean ± std deviation PCB concentrations (ng g^{-1} lipid weight) in *Brachidontes rodriguezii* (B.r.) and *Siphonaria lessoni* (S.l.) from each study site. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; B_{ref}: Barrera (reference site).

PCB	LT		LC		S		Ch		Bref	
	B.r.	S.l.	B.r.	S.l.	B.r.	S.l.	B.r.	S.l.	B.r.	S.l.
18	847 ± 240	301 ± 50	652 ± 43	239 ± 190	1002 ± 580	665 ± 330	840 ± 170	647 ± 130	929 ± 640	488 ± 104
52	121 ± 57	135 ± 149	827 ± 980	117 ± 99	192 ± 32	55 ± 29	80 ± 24	111 ± 7	50 ± 56	71 ± 12
44	82 ± 49	35 ± 4	407 ± 380	115 ± 69	199 ± 37	134 ± 130	27 ± 41	131.3 ± 19	133 ± 21	86 ± 26
101	29 ± 10	127 ± 200	840 ± 110	35 ± 34	871 ± 170	173 ± 190	17 ± 17	13 ± 13	33 ± 32	15 ± 10
99	282 ± 34	43 ± 75	460 ± 280	62 ± 26	322 ± 85	115 ± 32	146 ± 100	188 ± 24	184 ± 87	129 ± 28
110	207 ± 140	44 ± 76	117 ± 170	96 ± 23	190 ± 270	87 ± 59	104 ± 120	50 ± 10	238 ± 13	129 ± 27
149	606 ± 430	307 ± 120	722 ± 180	295 ± 53	856 ± 240	398 ± 52	549 ± 80	607 ± 12	672 ± 100	387 ± 82
153 + 105	16.4 ± 9	59 ± 63	408 ± 570	12 ± 19	340 ± 620	104 ± 170	14 ± 12	5.7 ± 5	320 ± 550	8.5 ± 13
138	119 ± 81	41 ± 38	142 ± 30	58 ± 8	76 ± 91	76 ± 11	83 ± 57	59 ± 68	141 ± 6	37 ± 44
180	144 ± 105	<LOD	9 ± 13	55 ± 40	225 ± 280	87 ± 58	43 ± 85	41 ± 82	194 ± 12	21 ± 42
∑ PCB	**2454 ± 480**	**1074.3 ± 290**	**4583 ± 300**	**1083 ± 91**	**4179 ± 340**	**1894 ± 520**	**1903 ± 580**	**1853 ± 330**	**2893 ± 110**	**1371 ± 250**

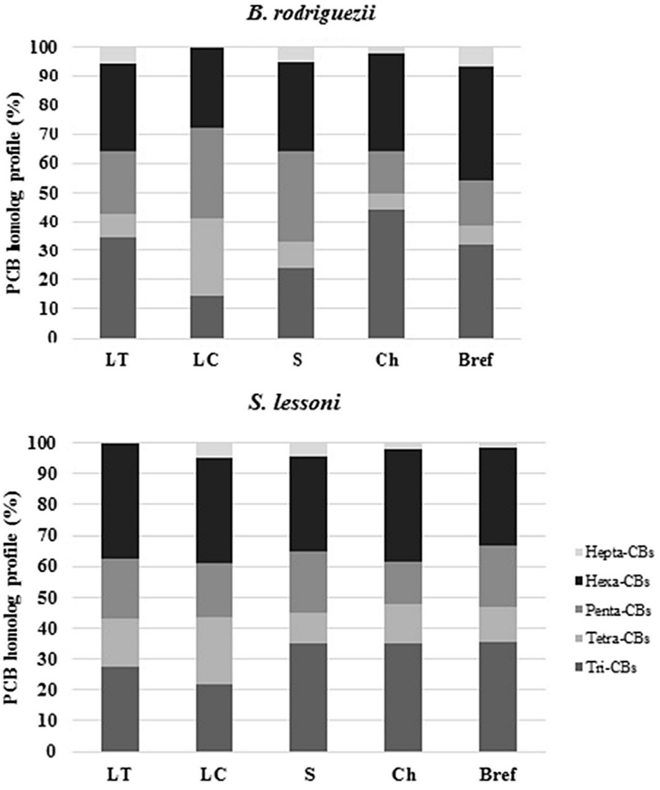

Fig. 4. PCB homolog profile in molluscs samples of each study site. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; Bref: Barrera (reference site).

1000 km south (Zabala et al., 2013). In general, more variable biogeochemical processes occur in coastal zones in comparison with the ocean (Wollast, 1998). Moreover, nitrogen cycle is one of the more complexes of all major elements cycles (Galloway et al., 2004), and biogeochemical processes lead to different N isotopic signatures in different environmental matrices due to fractionation (Peterson and Fry, 1987). For instance, denitrification fractionation in seawater lead to an enrichment of ^{15}N in the NO$_3^-$ pool and its depletion in the N$_2$ pool due to preferential reduction of ^{14}NO$_3^-$ over ^{15}NO$_3^-$. LC and Ch sites presented isotopic N values similar to the reference site. LT and S, however, showed significant differences ($p < 0.05$), indicating some creek influence. Limpets from S were 5‰ enriched, while limpets and mussels from LT were 3‰ and 1.4‰ depleted, respectively, respect to reference sites (Fig. 5). Two of the main anthropogenic nitrogen sources to the sea are farming activities, through the release of synthetic fertilizers, and the waste waters discharge (Howarth, 2008). Many studies report a decrease in δ^{15}N values in organisms as a consequence of the synthetic fertilizers input to the environment (Connolly et al., 2009; Valiela et al., 2000). Furthermore, an enrichment of δ^{15}N has been reported in both marine plants and invertebrates under the influence of sewage effluents (Costanzo et al., 2001; Dolenec et al., 2006). Therefore, results may suggest the presence of contamination by fertilizers in La Tapera creek, which, given the different farming activities affecting creeks of the area, would be related with the horticultural farming. Organic contamination in Seco creek could be associated with the direct discharge of sewage from the bathing facilities to the sea. Variations in biogeochemical processes among sites as an explanation of the deviation from the reference values in LT, LC and S should not be discarded. However, since the similar

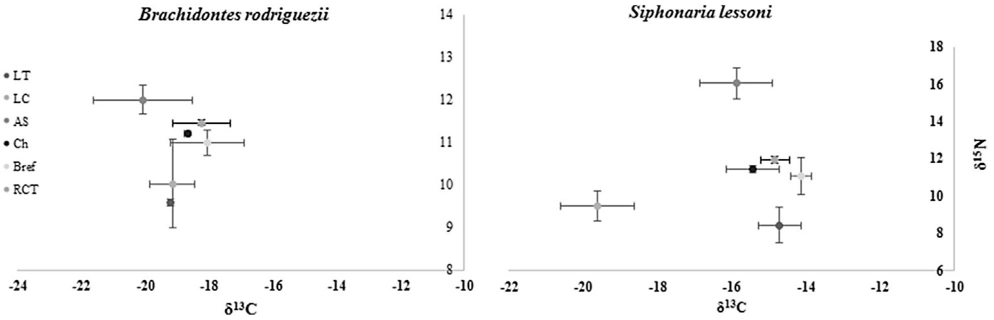

Fig. 5. Carbon and nitrogen stable isotopes ratios of molluscs. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; Bref: Barrera (reference site).

Table 3
Lipid content (%) and nitrogen (δ^{15}N) and carbon (δ^{13}C) stable isotopes (‰) in molluscs. LT: La Tapera; LC: Las Chacras; S: Seco; Ch: Chapadmalal; B$_{ref}$: Barrera (reference site); RCT$_{ref}$: RCT (reference site).

	Site	N	Lipids	δ^{15}N (‰)		δ^{13}C (‰)	
			% Wet weight	mean ± sd	Range	mean ± sd	Range
B. rodriguezii	LT	11 to 15	0.54 ± 0.01	9.58 ± 0.1	9.5–9.7	−19.22 ± 0.1	(−19.2)–(−19.3)
	LC	7	0.51 ± 0.03	10.02 ± 1	9.3–11.2	−19.15 ± 0.7	(−18.4)–(−19.7)
	S	9 to 18	0.455 ± 0.01	12 ± 0.3	11.6–12.3	−20.07 ± 1.5	(−18.8)–(−21.8)
	Ch	14 to 21	0.905 ± 0.2	11.2 ± 0.1	11.1–11.3	−18.68 ± 0.1	(−18.7)–(−18.8)
	B$_{ref}$	19 to 26	0.57 ± 0.03	10.99 ± 0.1	10.9–11.1	−18.05 ± 1	(−17.9)–(−18.2)
	RCT$_{ref}$	8 to 12	n.d.	11.4 ± 0.07	11.4–11.5	−18.2 ± 0.9	(−18.1)–(−18.4)
S. lessoni	LT	12 to 17	0.025 ± 0.01	8.44 ± 0.9	7.8–9.6	−14.71 ± 0.6	(−14)–(−15.1)
	LC	8 to 9	1.19 ± 0.1	9.45 ± 0.8	8.8–10.3	−19.62 ± 1.8	(−17.5)–(−21)
	S	7 to 12	0.895 ± 0.1	16.05 ± 0.8	15.1–16.3	−15.88 ± 0.9	(−14.9)–(−16.9)
	Ch	12 to 14	0.805 ± 0.1	11.42 ± 0.2	11.3–11.6	−15.44 ± 0.7	(−14.9)–(−16.3)
	B$_{ref}$	7 to 10	0.985 ± 0.3	11.07 ± 1	9.9–11.9	−14.13 ± 0.3	(−14)–(−14.4)
	RCT$_{ref}$	11 to 15	n.d.	11.9 ± 0.2	11.7–12.1	−14.8 ± 0.4	(−14.3)–(−15.1)

n.d.: not determined.

environmental conditions of the sampled zones, this can be considered unlikely. On the other hand, a combination of factors might take place since biogeochemical processes can be changed by anthropogenic influences, such as denitrificacion which is enhanced by nutrient inputs to the system (Seitzinger, 1988).

With the aim of assess whether creeks C and N input has influence in PCB bioaccumulation by marine molluscs, correlation tests were carried out between PCB concentrations and carbon and nitrogen stable isotopes ratios. PCBs levels were only correlated negatively with δ^{13}C of *B. rodriguezii* mussels ($p < 0.05$, rho: −0.68). This result indicates that at lower values of δ^{13}C, which would mean more creek influence, PCB concentration was higher. This would be produced due to an increase in organic matter quantity or due to changes in the metabolism of the organism generated by different organic matter features. It has been demonstrated that increases in organic matter reduce hydrophobic organic contaminants bioavailability since they are sequestered by the organic particles (Calberg et al., 1986; Thorsen et al., 2004). Bejarano et al. (2005) found that bivalves *Mercenaria mercenaria* accumulate between 25% and 86% more insecticide chlorpyrifos in dissolved organic matter (DOM)-free seawater than bivalves in the presence of various DOM forms. Thus, different composition of organic matter may result in differential PCB accumulation. In sediments, it has been suggested that the organic matter type and source influence PCB concentration due to differential sorption affinities (Edgar et al., 2003). Moreover, differential uptake of chlorinated congeners by *Mytilus edulis* has been related with sediment composition (sediment mineralogy) (Edgar et al., 2006). The terrestrial and marine organic materials are compositionally very different; abounding carbohydrates in terrestrial systems and proteins in marine systems (Baldock et al., 2004). This property, among others, is a crucial factor in the sorption process of hydrophobic compounds (Stangroom et al., 2000). Therefore, the relation between the origin of the consumed organic matter and PCB accumulation in mussel *B. rodriguezii* could be explained by the different composition of such organic matter, which would influence PCB sorption and hence, bioaccumulation. However, Bejarano et al. (2003) also found that the type of food particle ingested by estuarine clams influences elimination rates of the insecticide chlorpyrifos. Thus, it is necessary to take into account that the composition of the organic matter ingested by mussels could have effects in different processes which ultimately conduct to the net accumulation.

Finally, marine systems under the influence of freshwater inputs present specific physical, chemical and biological characteristics. Organic matter input and the consequent trophic subsidy to the marine food webs is one of the most studied issues in this sense (Peterson, 1999). The results of this study suggest that small creek inputs could also partially subsidize adjacent marine food webs. This influence is expected to be limited and confined close to the outfalls due to the small flow of the creeks (Connolly et al., 2009). However, the effects of the organic matter input in mollusc bioaccumulation could enhance the extent of creeks influence since the consumption of these organisms by mobile predators (Laitano et al., 2013) may lead to biomagnification process away the outfalls.

4. Conclusions

Creeks outfall affects not only PCB distribution in this coastal environment, due to their discharge of such compounds but also due to their input of carbon from different source. In the present study, PCB contamination from land based sources related to a landfill area has been found in an intertidal marine ecosystem of the south-eastern region of Buenos Aires Province, Argentina. These contaminants would reach the intertidal zone through creeks, which are so far poorly studied sources. Thus, although the studied creeks have small flow and despite the relatively high capacity of dispersion of the marine environment, PCB reached concentration of concern in the nearby coast. Finally, PCB accumulation in mussels *B. rodriguezii* was enhanced by the organic matter input from creeks, which highlights the importance to consider this factor when studying PCB distribution in organisms of coastal systems.

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