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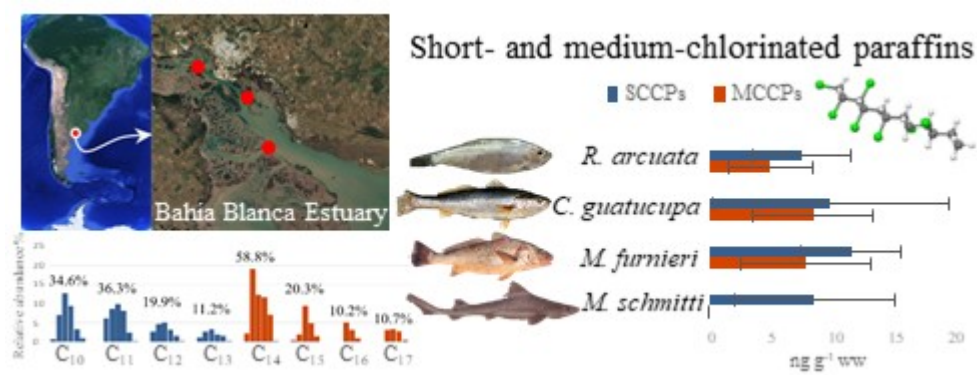
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1 **Short- and medium-chain chlorinated paraffins in fish from an**
2 **anthropized south-western Atlantic estuary, Bahía Blanca, Argentina**

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21 Abstract

22 Chlorinated paraffins (CPs) are synthetic organic compounds of growing environmental and
23 social concern. Short-chain chlorinated paraffins (SCCPs) were listed under the Stockholm
24 Convention on Persistent Organic Pollutants (POPs) in 2017. Further, in 2021, medium-chain
25 chlorinated paraffins (MCCPs) were proposed to be listed as POPs. We investigated SCCP and
26 MCCP amounts and homolog profiles in four wild fish species from Bahía Blanca Estuary, a
27 South Atlantic Ocean coastal habitat in Argentina. SCCPs and MCCPs were detected in 41% and
28 36% of the samples, respectively. SCCP amounts ranged from <12 to 29 ng g⁻¹ wet weight and
29 <750 to 5887 ng g⁻¹ lipid weight, whereas MCCP amounts ranged from <7 to 19 ng g⁻¹ wet
30 weight and <440 to 2848 ng g⁻¹ lipid weight. Amounts were equivalent to those found in fish
31 from the Arctic and Antarctic Oceans and from some North American and Tibetan Plateau
32 lakes. We performed a human health risk assessment and found no direct risks to human
33 health for SCCP or MCCP ingestion, according to present knowledge. Regarding their
34 environmental behaviour, no significant differences were observed among SCCP amounts,
35 sampling locations, species, sizes, lipid content, and age of the specimens. However, there
36 were significant differences in MCCP amounts across species, which might be attributed to fish
37 size and feeding habits. Homolog profiles in all fish were dominated by the less chlorinated (Cl₆
38 and Cl₇) and shorter chain length CPs were the most abundant, with C₁₀Cl₆ (12.8%) and C₁₁Cl₆
39 (10.1%) being the predominant SCCPs and C₁₄Cl₆ (19.2%) and C₁₄Cl₇ (12.4%) the predominant
40 MCCPs. To the best of our knowledge, this is the first study on the presence of CPs in the
41 environment in Argentina and the South Atlantic Ocean. CP occurrence in the environment,
42 particularly in the food chain, promotes the need for further research on their occurrence and
43 behavior, and the impact of CPs in marine ecosystems in Argentina.

44 **Keywords:** Environmental contamination; Chemical additives; Flame retardants; Plasticizers;
45 South America; Bioaccumulation

46 1. Introduction

47 Chlorinated paraffins (CPs) are synthetic mixtures of polychlorinated *n*-alkanes ($C_nH_{2n+2m}Cl_m$).
48 They have different carbon chain lengths and chlorination levels, typically between 30% and
49 70% by weight (Fiedler, 2010). In the scientific literature, they are generally classified as short-
50 chain (SCCPs, C_{10} – C_{13}), medium-chain (MCCPs, C_{14} – C_{17}), and long-chain CPs (LCCPs, $C_{\geq 18}$)
51 (Canadian Environmental Protection Agency, 2008; UNEP, 2016). Technical CP mixtures, on the
52 other hand, are frequently manufactured, labeled, and marketed solely based on their chlorine
53 content. These variations in carbon chain length and chlorine content provide a diverse set of
54 physical-chemical properties that may be used to a variety of industrial goods and processes
55 (Glüge et al., 2013).

56 CPs have been used as additives in paint, lubricants, metalworking fluids and fat-liquoring of
57 leather, as well as flame retardants and plasticizers in polymers as rubber and plastics (mostly
58 polyvinyl chloride - PVC) (Fiedler, 2010; Guida et al., 2020; Jiang et al., 2018).

59 From 1930 to 2014, the production and use of CP increased steadily, reaching a peak of more
60 than 1 million tons (0.44 Mt/year of SCCPs and 0.75 Mt/year of MCCPs), with most of it being
61 produced in China (Chen et al., 2022). Since then, production and use have remained stable,
62 totalling a global cumulative production of ~33 million tons since 1930 (Chen et al., 2022).

63 In South America, information on CP production and use is scarce. The available information
64 suggests that Brazil manufactured CPs from the 1980s until 1994, reaching a maximum annual
65 production of 360 tons (Guida et al., 2022a). Furthermore, Guida et al. (2022a) estimated that
66 between 5280 and 6125 tons of CPs were used in the last two decades in Brazil, whereas tens
67 of million tons of products containing CPs may have been imported into the country.
68 Meanwhile, Argentina reported having imported 474 tons of SCCPs between 2007 and 2010,
69 largely for the plastic industry (UMA, 2010).

70 Despite their widespread manufacture and use, CPs have received increased attention due to
71 their environmental fate and negative impacts on the environment and human health (Glüge
72 et al., 2018; Groh et al., 2019; UNEP, 2011; UNEP, 2015; Van Mourik et al., 2016). Short-chain
73 CPs have been shown to exhibit significant environmental persistence (Glüge et al., 2018; Yuan
74 et al., 2017), bioaccumulative capacity (Iozza et al., 2008; Ma et al., 2014; Zeng et al., 2017),
75 potential toxicity to animals (Cooley et al., 2001; UNEP, 2011; UNEP, 2015) and long-range
76 transport capacity (Li et al., 2016; 2017). Despite receiving less attention, recent research
77 reveals that medium-chain CPs, containing at least 45% chlorine by weight, exhibit similar
78 environmental behaviour and toxicity to SCCPs (Castro et al., 2018; Cooley et al., 2001; Glüge
79 et al., 2018; Yuan et al., 2017; Zeng et al., 2017).

80 SCCPs have been restricted or banned around the world. First in Europe (in 2002; Directive
81 2002/45/EC; Vetter et al., 2022), then in Japan (in 2005; Ministry of the Environment of Japan,
82 2017), Canada (in 2008; Canadian environmental Protection Agency, 2008), and the United
83 States (in 2009; USEPA, 2009), and, finally, globally, when it was listed in the Annex A (for
84 elimination) of the Stockholm Convention on Persistent Organic Pollutants (POPs) in May 2017
85 (UNEP, 2017). However, SCCPs were listed with specific exemptions for their major
86 applications (Guida et al., 2020) and the main producer of SCCPs, China, has not yet approved
87 a ban on these compounds (Vetter et al., 2022). Hence, SCCPs are still abundant in technical CP
88 mixtures (Xia et al., 2021) and used in several consumer goods (Chen et al., 2021). Therefore,
89 they are expected to impact any country importing CP-containing products or wastes (Chen et
90 al., 2022; Guida et al., 2022a, 2022b). Meanwhile, MCCPs are still globally unregulated. But, in
91 2021, the UK proposed MCCPs exceeding 45% chlorine by weight to be listed under the
92 Stockholm Convention on POPs (UNEP, 2021).

93 Consequently, various research on the environmental occurrence and fate of CPs have been
94 conducted (Glüge et al., 2018; Van Mourik et al., 2016). SCCPs and MCCPs can be considered

95 global contaminants due to their ubiquity. They were found in almost every environmental
96 compartment and locations investigated, including humans and biota (Basconcillo et al., 2015;
97 Harada et al., 2011; Zeng et al., 2015; 2017) and remote areas (Ma et al., 2014; Glüge et al.,
98 2018; Van Mourik et al., 2016).

99 Nevertheless, the map of the global distribution of CPs is incomplete and a huge information
100 gap remains for the global south, mainly for South America and the South Atlantic Ocean.
101 Moreover, estimating environmental concentrations is challenging due to the lack of detailed
102 information on the use and production of these chemicals in South America (Chen et al., 2022).
103 To the best of our knowledge, only two research on CPs in South American fish have been
104 published, both on fish from the Pacific Ocean. Krätschmer et al. (2019), investigated the
105 presence of CPs in salmon sold in Germany, including salmon farmed in Chile. In addition, Dong
106 et al. (2019) analyzed CPs in feed material sold in Chinese markets, including Chilean and
107 Peruvian fishmeal.

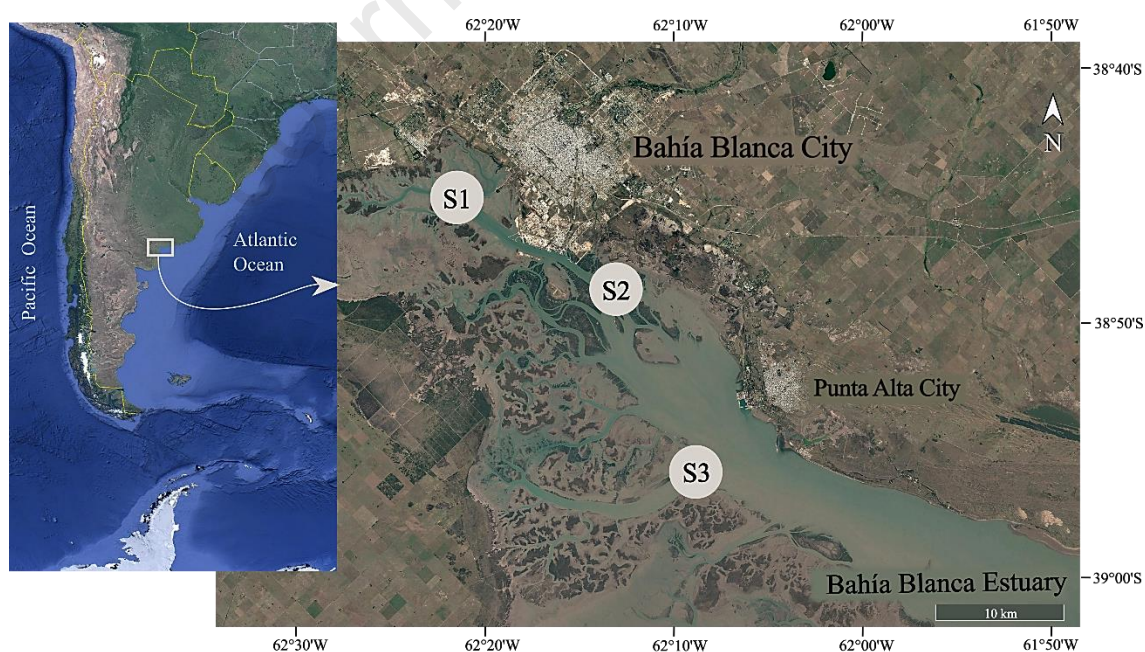
108 Consequently, our goal was to investigate the occurrence of SCCPs and MCCPs in four wild fish
109 species sampled in the Bahía Blanca estuary, an anthropized Argentinean coastal environment
110 in the South Atlantic Ocean. Furthermore, we assessed the influence of inter- (species) and
111 intra- (size/age) specific variations on CP amounts; investigated CP homolog profiles in fish;
112 compared the amounts found with those found in fish around the world; and assessed the
113 health risk associated with the ingestion of SCCP-containing fish, according to current
114 knowledge.

115 **2. Materials and methods**

116 **2.1 Study area**

117 This study analyzed CPs in fish from the Bahía Blanca estuary, a mesotidal system in the South
118 Atlantic Ocean and the southeast of South America (**Figure 1**; Perillo et al., 2001). This coastal

119 ecosystem has great environmental and local socioeconomic importance because it is a
120 reproduction, breeding, and feeding area for many species of fish, birds, and other animals and
121 plants. For this reason, in 1998, Bahía Blanca, Bahía Falsa and Bahía Verde were designated as
122 Natural Reserves (Provincial Law 12101). However, the economic development of the
123 influence area, as well as flaws in urban planning and environmental management, endangers
124 the health of this ecosystem. On its coasts, there is intense industrial and petrochemical
125 activity (for example, the production of fertilizers, PVC, polyethylene, and fuel); a settlement of
126 over 400,000 people (Bahía Blanca, General Cerri and Punta Alta cities) with poor sewage and
127 stormwater effluents treatment and irregular solid waste disposing (Streitenberger and
128 Baldini, 2016), as well as the main deep-water commercial port in Argentina. This ecosystem
129 has been the subject of numerous studies on chemical pollution, including POPs such as
130 polybrominated diphenyl ethers (PBDEs; Tombesi et al., 2017), organochlorine pesticides
131 (OCPs; Arias et al., 2011; Menone et al., 2004; Oliva et al., 2022; Tombesi et al., 2018), and
132 polychlorinated biphenyls (PCBs; Arias et al., 2013; Tombesi et al., 2017).



134 **Figure 1.** Satellite image of the Bahía Blanca estuary showing sampling sites (S1; S2; S3).

135 2.2. Sampling

136 Wild juvenile fish were caught by net between August and October 2017 at three sampling
 137 sites in the Bahía Blanca estuary, to ensure the representativeness of the estuary as a whole.
 138 The four fish species caught were Jenyn's sprat (*Ramnogaster arcuata*), narrownose smooth-
 139 hound (*Mustelus schmitti*), striped weakfish (*Cynoscion guatucupa*), and whitemouth croaker
 140 (*Micropogonias furnieri*). The fish were divided into classes according to their length. Only fish
 141 of the size/age that have been shown to have been in the estuary throughout their lives, i.e.,
 142 they were born there and have not yet left (Cazorla and Sidorkewicj 2009; Cazorla, 2018;
 143 Molina et al., 2021), were evaluated for the information to be an indicative of the local
 144 environmental quality. Each sample was a pool of a variable number of individuals classified by
 145 class, species, and location (**Table 1**).

146
 147 **Table 1.** Sample data, including species name, class, size range (cm), age (year), and number of
 148 individuals per composite sample grouped by sampling site.

Species	Class	Size (mm)	Age (year)	Individuals/sampling site		
				S1	S2	S3
<i>Mustelus schmitti</i>	C1	300-350	<1	-	3	-
<i>Mustelus schmitti</i>	C2	351-400	<1	3	3	4
<i>Mustelus schmitti</i>	C3	401-450	<1	2	2	2
<i>Micropogonias furnieri</i>	C1	40-70	<1	100	124	150
<i>Micropogonias furnieri</i>	C2	71-160	<1	60	61	-
<i>Cynoscion guatucupa</i>	C1	50-90	<1	-	-	150
<i>Cynoscion guatucupa</i>	C2	91-120	<1	14	46	62
<i>Ramnogaster arcuata</i>	C1	50-80	1-2	57	103	120
<i>Ramnogaster arcuata</i>	C2	81-110	2-3	33	32	60

149 2.3. Chemicals and standards

150 All cleaning and sample processing solvents (acetone, dichloromethane, isooctane, and *n*-
 151 hexane) were chromatographic grade, purchased from Dorwill (Buenos Aires, Argentina).

152 Sulfuric acid (95–97%; P.A. ACS), for acidified silica (44% w/w), was acquired from Cicarelli
153 (Santa Fe, Argentina) and sodium sulphate and silica gel (0.063–0.2 mm) were purchased from
154 Merck (Darmstadt, Germany). SCCP and MCCP chemical standards (C_{10-13} with 51.5%, 55.5%
155 and 63% of Cl content; and C_{14-17} with 42% 52% and 57% of Cl content) were acquired from Dr.
156 Ehrenstorfer (Augsburg, Germany). Surrogates PCB 103 and 198 and the internal standard 6'-
157 MeOH-BDE 66 (BCIS) were purchased from AccuStandard (New Haven, USA) and Dr. Vetter's
158 Lab (Germany; Vetter et al., 2011), respectively.

159 **2.4. Sample preparation**

160 Fish muscle samples were processed using a miniaturized analytical method optimized for the
161 simultaneous extraction and purification of organohalogenated contaminants from fatty
162 samples (Mello et al., 2016; Roscales et al., 2017) and adapted for fish muscle (Guida et al.,
163 2018). Briefly, 0.5 g of freeze-dried sample, 0.83 g of acidified silica gel (44% sulphuric acid,
164 w/w), and 0.5 g of anhydrous sodium sulphate were homogenized in a mortar for 5 min and
165 then surrogate standards (PCB 103 and 198, 20 ng) were added. The mixture was added on top
166 of a glass column filled with 14 mL of *n*-hexane/dichloromethane (9:1) and the following co-
167 sorbents (down to up): 1 cm of anhydrous sodium sulphate, 1.66 g of neutral silica gel, 5 g of
168 acid silica gel (44% w/w), and 0.83 g of neutral silica gel. The analytes were then eluted in
169 three 7-minute static extractions followed by dynamic steps with 7 mL of *n*-
170 hexane/dichloromethane (9:1, v/v) (21 mL total). Extract volume was reduced closed to
171 dryness and then washed 3 times with *n*-hexane into a glass insert for reduced vial volume.
172 Finally, extracts were dried and then reconstituted using 100 μ L of BCIS (100 ng mL⁻¹) in
173 isooctane as injection standard. Lipid content (on dry weight basis) was determined according
174 to Tölgyessy and Miháliková (2016).

175 **2.5. CP's Instrumental analysis**

176 Instrumental analysis was based on the procedure developed by Reth et al. (2005a) with
177 modifications described by Sprengel and Vetter (2019). The quantitative analysis was
178 performed in a gas chromatograph coupled with electronic chemical negative ionization mass
179 spectrometry (GC/ECNI-MS; 7890A-5975C, Agilent Technologies, Palo Alto, CA, USA), using
180 methane as the reagent gas. The column used was a DB-5MS fused silica capillary column (15
181 m, 0.25 mm ID, 0.1 μm thick) from Agilent Technologies (Palo Alto, CA, USA). The injector
182 temperature was 260 $^{\circ}\text{C}$, and the carrier gas was helium at a constant flow rate of 1.4 mL
183 min⁻¹. The temperature program for the oven was as follows: 80 $^{\circ}\text{C}$ for 1 minute, then raise to
184 270 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C min}^{-1}$ and held for 5 minutes.

185 CP homologs with different chlorine contents were used for the calibration curve (SCCP with
186 51.1%, 53.3%, 55.5%, 59.25%, and 63% Cl; MCCP with 42%, 47%, 52%, 54.5%, and 57% Cl). The
187 selected ion monitoring (SIM) mode was used for CP homolog monitoring. For quantification
188 and confirmation, the most abundant and second most abundant ion $[\text{M}-\text{Cl}]^{-}$ were utilized,
189 respectively (Reth and Oehme, 2004). To improve sensitivity and minimize interference, eight
190 SIM runs per sample and standard were performed, selecting the seven primary and seven
191 secondary ions from each group of homologs with the same chain length (C_{10} to C_{17}).

192 For the quantification, the procedure optimized by Reth et al. (2005a) was adopted. In brief,
193 the corresponding areas were integrated based on the retention times, signal shape, and
194 relationship between the primary and secondary ions, and the interferences were manually
195 subtracted. The amounts in the extract were calculated based on the relationship between the
196 relative area of each CP, the Cl content, and the calibration curve ($R^2 = 0.95$ for SCCPs and $R^2 =$
197 0.98 for MCCPs).

198 **2.6. Quality assurance and quality control (QA/QC)**

199 No plastic was used during the sampling or analytical procedure, and all material used was
200 exposed to 450 °C for 4 h and rinsed with *n*-hexane, dichloromethane, and acetone (3-times
201 each) before use to avoid CP contamination. A procedural blank was performed for every five
202 samples, to monitor contamination. CPs were detected in all blanks, especially SCCPs. For this
203 reason, the detection limit (DL) was calculated as the average sum of all blanks and three times
204 the standard deviation. The resulting DLs were 12.2 ng g⁻¹ wet weight (ww) for SCCPs and 7 ng
205 g⁻¹ ww for MCCPs. These detection limit values were similar to those shown in other studies
206 that also analyzed CP by low-resolution mass spectrometry (Jiang et al., 2013; Huang et al.,
207 2017; Reth et al., 2005a; Zeng et al., 2017; Zhou et al., 2018). Besides, the average CP amounts
208 in the analytical blanks were subtracted from those in samples. The method was previously
209 tested by spiking SCCP and MCCP standards into three triplicate samples and a triplicate blank
210 and analyzing them together with the same triplicate samples and blank without standard
211 fortification. The difference of SCCP and MCCP amounts between the enriched and non-
212 enriched samples resulted in a 80% ± 16% recovery of CPs. Furthermore, the recovery of the
213 surrogate standards, PCB 103 and 198, added to each sample was between 80 and 110%.

214 **2.7. Statistical analysis**

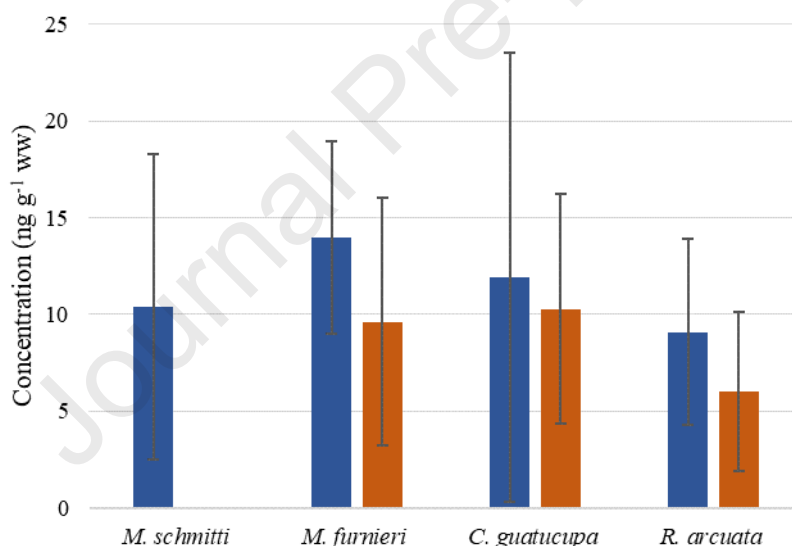
215 Data was tested for normal distribution by the Tuckey test. Since normality was not observed
216 in the dataset, the non-parametric Kruskal-Wallis test was used to analyze the significant
217 difference between groups ($p < 0.05$) and Spearman's correlation coefficient to evaluate the
218 association between multiple variables (Camacho-Sandoval, 2008). All statistical analyses were
219 performed using InfoStat 2018 software (InfoStat Group, Córdoba, Argentina). The moisture
220 content of each sample was used for the conversion of CP concentrations to wet weight basis;
221 firstly, because that represents fish consumption and secondly as a way of data normalization
222 to facilitate their comparison with other studies.

223 3. Results

224 3.1. SCCP and MCCP amounts

225 Total amounts of SCCPs and MCCPs grouped by species and size are summarized in **Table 1**
 226 and **Figure 2**, while the detailed information of all the samples is shown in **Table S1**.

227 SCCP amounts were below the detection limit ($12.2 \text{ ng g}^{-1} \text{ ww}$) in 13 samples and were
 228 detected in 9 samples, ranging from 12.7 ng g^{-1} to $29.4 \text{ ng g}^{-1} \text{ ww}$ and 889.5 to 5887.7 ng g^{-1}
 229 lipid weight (lw; **Table S1**). Meanwhile, MCCPs were below the detection limit ($7 \text{ ng g}^{-1} \text{ ww}$) in
 230 14 samples, including all *M. schmitti* samples, and were detected in 8 samples with levels
 231 ranging from 8.1 ng g^{-1} to $18.7 \text{ ng g}^{-1} \text{ ww}$ and 657.4 to $2848.5 \text{ ng g}^{-1} \text{ lw}$.



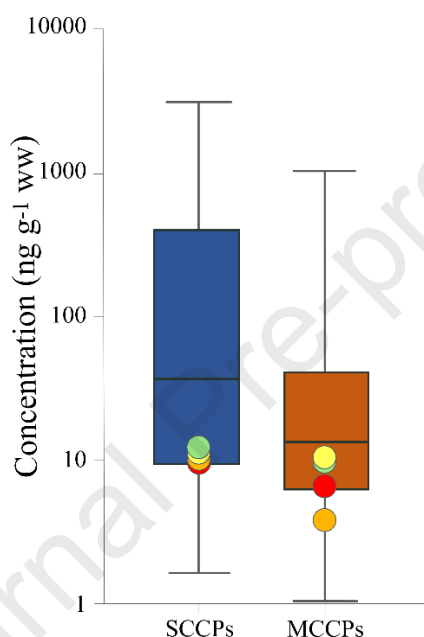
232

233 **Figure 2.** Levels (mean and SD) of SCCPs (blue bars) and MCCPs (orange bars) in fish grouped
 234 by species.

235 3.2. Comparison with worldwide CP amounts

236 Compared to fish from other regions, the CP amounts in this study were lower than the
 237 median and in the first or second quartile of the studies examined (**Table S2; Figure 3**). These
 238 levels were comparable to those found in fish from the Arctic (Dick et al., 2010) and Antarctica
 239 Oceans (Li et al., 2016), Great Lakes of North America (Basconcillo et al., 2015), and Chilean

240 and Scandinavian fisheries (Krätschmer et al., 2019). They were much lower than those found
 241 in fish from China (Du et al., 2018; Huang et al., 2017; 2019; Zhou et al., 2018) and Lake
 242 Michigan, North America (Basconcillo et al., 2015) and in fishmeal from different fisheries
 243 around the world (Dong et al., 2019). These results could be expected since there is no evident
 244 direct input of CPs into the studied environment nor Argentina is expected to be an important
 245 player regarding CP production and application.



246

247 **Figure 3.** Box plot for SCCP and MCCP amounts in fish worldwide based on data in Table S2.
 248 The middle hinge represents the median, the lower and upper hinges represent the first (Q1)
 249 and third (Q3) quartiles, and the whiskers reflect the minimum and maximum value. The
 250 colored circles represent the mean amount in each fish species in the Bahía Blanca estuary: *M.*
 251 *schmitti* (Orange), *M. furnieri* (Green), *C. guatucupa* (Yellow), and *R. arcuata* (Red).

252 3.3. Potential factors influencing CP accumulation in fish

253 Regarding capture sites, the innermost sampling site of the estuary (S1) showed higher
 254 average SCCP levels, followed by the outermost (S3) and middle (S2) sites, while MCCP average
 255 amounts were higher in S3, followed by S2 and S1 (**Figure S1**). However, there were no
 256 significant differences between the three sites ($p > 0.05$). This could be explained because the
 257 target fish circulate throughout the estuary and do not represent a punctual site (Cazorla,

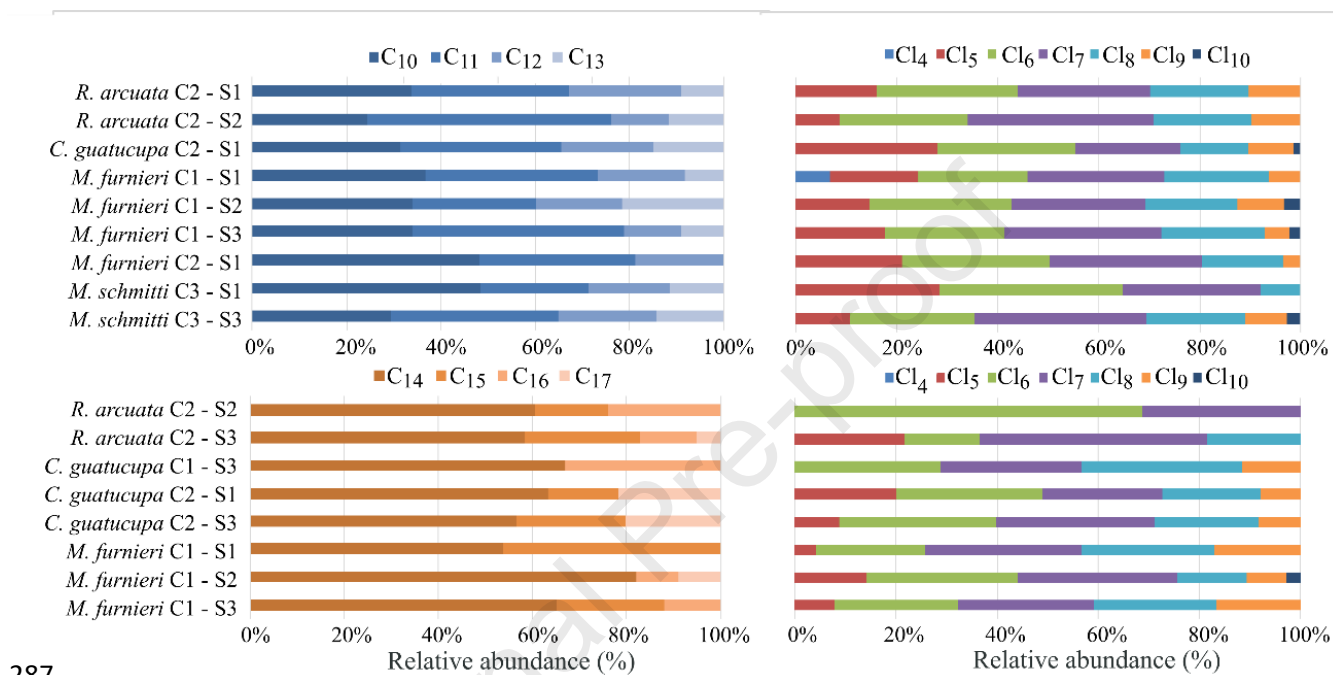
258 2018). Furthermore, the physical-chemical properties of the water in the study area are
259 relatively uniform (Arena et al., 2022; Piccolo and Perillo, 1990), as is the distance to pollution
260 sources. As a result, fish in the three sampling sites might be similarly exposed to CPs, but
261 further studies in this area should be conducted to confirm this.

262 Regarding the species, there were no statistically significant differences between SCCP
263 amounts in the four studied species ($p > 0.05$). Furthermore, Spearman's correlation analysis
264 showed no significant correlations between variables such as age, size, feeding habits, lipid
265 contents and SCCP amounts.

266 It has been well documented that lipid content is a key variable in the bioaccumulation of
267 chemicals with high octanol-water partition coefficients, such as SCCPs (Arnot and Gobas,
268 2006; Mackay and Fraser, 2000). Indeed, this trend has been documented in studies on SCCPs
269 in fish around the world (Du et al, 2018; Huang et al., 2017; Labadie et al., 2019; Ma et al.,
270 2014). In this study, we found no correlation between lipid content and SCPPs amounts;
271 however, the average levels of SCCPs were higher in the species with the highest lipid content,
272 *M. furnieri* (Table S1). Further, there were significant differences in MSCP amounts (on wet
273 weight basis) between species, particularly between *M. schmitti* and *M. furnieri* ($p < 0.05$).
274 These differences seem to be related to the size of the fish (Spearman's coefficients, $r = -0.6$, p
275 $= 0.018$, $n = 15$) and their feeding habits (i.e., zooplankton intake: Spearman's coefficients, $r =$
276 0.44 , $p = 0.10$, $n = 15$; crab intake: Spearman's coefficients, $r = -0.47$, $p = 0.08$, $n = 15$; Table S3).
277 In particular, between this two species, those differences could be explained by lipid content,
278 since *M. furnieri* showed a three times higher lipid content than *M. schmitti*. Regarding the rest
279 of the species, the concentrations did not correlate with the lipid content, which is consistent
280 with prior studies on these fish species (Huang et al., 2017; Labadie et al., 2019). Overall, these
281 results suggested that lipid content was not the main factor influencing the distribution of CPs
282 in fish of the BBE.

283 **3.4. CP homolog profiles**

284 Homolog profiles of SCCPs and MCCPs in fish from the Bahía Blanca estuary are provided in
 285 **Figure 4**. Regarding SCCPs, the most abundant alkane-chain length were C₁₁ and C₁₀, with
 286 averages of 36% and 35% and maximums of 53% and 48%, respectively (**Figure 4**).



287

288 **Figure 4**. SCCP and MCCP homolog profiles in the Bahía Blanca estuary fish. Size class: C1, C2,
 289 C3; sampling site: innermost site (S1), middle site (S2), outermost site (S3). The X-axes
 290 represent relative abundance (%).

291 The predominance of C₁₁-CPs has also been observed in animals from different parts of the
 292 world, including coastal, urban, and e-waste dismantling areas (Borgen et al., 2002; Houde et
 293 al., 2008; Ma et al., 2014; Reth et al., 2006; Sun et al., 2017; Yuan et al., 2017; Zeng et al.,
 294 2011). Other studies, however, found a higher abundance of the C₁₀-CP group, particularly in
 295 remote areas such as the Arctic (Li et al., 2017; Tomy et al., 2000) and Antarctic Oceans (Li et
 296 al., 2016) and Tibetan Plateau (Du et al., 2019). On the other hand, the highest relative
 297 abundance of C₁₂-CPs (e.g., Basconcillo et al., 2015, in Canada) or C₁₃-CPs (e.g., Du et al., 2018,
 298 in China) were common in other studies. Our findings were consistent with those reported in
 299 fish and fishmeal from Chilean and Peruvian fisheries in the Pacific Ocean (Dong et al., 2019;

300 Krätschmer et al., 2019) where shorter carbon chains predominated; however, in these
301 studies, C₁₀-CPs were more abundant.

302 Meanwhile, MCCPs were largely dominated by the C₁₄-CPs with relative abundances between
303 45% and 67% and an average of 59%, followed by the C₁₅-CP group with an average of 18%.
304 These patterns were consistent with studies on fish elsewhere (Basconcillo et al., 2015; Du et
305 al., 2018; Zeng et al., 2015; Reth et al., 2005b), including studies on Chilean and Peruvian fish
306 and fishmeal in the Pacific Ocean (Dong et al., 2019; Krätschmer et al., 2019). Some authors
307 suggested in the early 2000s that samples near urbanized and industrialized regions exhibit a
308 higher relative abundance of less volatile congeners and a pattern comparable to commercial
309 CP mixtures (Marvin et al., 2003; Reth et al., 2005b; Tomy et al., 2000). However, commercial
310 CP mixtures have diversified, and as a result, they contribute differently to the contamination
311 of environmental samples, making correlation of CP homolog profiles with commercial CP
312 mixtures extremely challenging (Vetter et al., 2022).

313 Concerning the Cl content, the SCCPs had between 58.5% and 61.4% (60.31% on average) and
314 the MCCPs had between 51.2% and 56.4% (54.1% on average). Moreover, the most abundant
315 homologs among the SCCPs were C₁₀Cl₆-CPs (12.8%) and C₁₁Cl₆-CPs (10.1%) and those among
316 the MCCPs were C₁₄Cl₆-CPs (19.2%) and C₁₄Cl₇-CPs (12.4%). Cl₆ and Cl₇ were the most abundant
317 groups overall, with averages of 27% and 29% for SCCPs and 31% and 31% for MCCPs,
318 respectively (Figure S2). The predominance of shorter chain groups (C₁₀-/C₁₁- and C₁₄-CPs) and
319 lower chlorinated groups (Cl₆ and Cl₇) is common in aquatic animals since those compounds
320 present the highest capacity for migration towards biological matrices. Finally, these results
321 matched with those reported by other researchers worldwide (Du et al., 2019; Guida et al.,
322 2020; Li et al., 2016; Lino et al., 2005; Ma et al., 2014; Reth et al., 2005b; Wang et al., 2018;
323 Yuan et al., 2017).

324 **3.5. Health risk assessment of CPs**

325 The health risk associated with consuming fish containing SCCPs and MCCPs from the BBE was
326 determined using the margins of exposure (MOEs). This is calculated as the ratio between the
327 no-observed-adverse-effect level (NOAEL) and the estimated daily intake (EDI) of CPs. NOAEL is
328 a limit of acceptable daily exposure determined by the European Chemicals Bureau based on
329 toxicity experiments in mammals (ECB, 2000; 2007), being 100 mg/kg/d and 6 mg/kg/d for
330 SCCPs and MCCPs, respectively (Wang et al., 2021). Meanwhile, EDI is calculated using the
331 following equation:

$$332 \textit{Estimated daily intake (EDI)} = \frac{C_i \times DFI}{BW}$$

333 Where, C_i is the SCCP or MCCP amounts in each fish sample ($\text{ng g}^{-1} \text{ ww}$), DFI is the daily fish
334 intake of Argentines (13 g/d; FAO, 2016), and BW is the average adult body weight in
335 Argentina (70kg).

336 MOE values >1000 are considered to indicate that exposure to SCCP and MCCP does not pose
337 significant risks to human health (Wang et al., 2018; Wang et al., 2021). This value was
338 determined as a total uncertainty factor for the NOAEL, given an uncertainty factor of 10 to
339 the interspecific, intraspecific and interannual differences (Lino et al., 2005).

340 The resulting EDI of SCCPs ranged from 1.14 to 3.70 ng/kg/d and the EDI of MCCPs from 0.65
341 to 3.24 ng/kg/d. While the MOEs of SCCPs ranged from 18,350 to 87,900 and those of MCCPs
342 ranged from 1,720 to 9,260. Consequently, all MOEs of SCCP and MCCP were >1,000,
343 suggesting no significant risk from consumption of fish from the BBE. However, these
344 parameters are calculated based on the average daily fish consumption of Argentines and may
345 be higher in populations linked to fishing and habitual fish consumers. In these cases, the
346 MOEs may be lower and consequently be close to the safety limits or even exceed them,
347 especially the MOEs of MCCPs.

348 **4. Conclusions**

349 This study demonstrates, for the first time, the environmental occurrence and bioavailability of
350 SCCP and MCCP in Argentina and the South Atlantic Ocean.

351 CP amounts found in this study were lower than in fish from highly industrialized/urbanized
352 areas of the world, such as Chinese estuaries or some North American Great Lakes, but
353 comparable to those found in fish from Chile, the Arctic and Antarctic Oceans, and some North
354 American and Tibetan Plateau lakes. Moreover, the consumption of the analysed fish would
355 not represent a health risk associated with the SCCPs and MCCPs. There were no significant
356 differences in CP amounts between sampling sites. SCCP amounts were similar between and
357 within species. Rather, there were significant differences in MCCP amounts between species,
358 which were related to feeding habits, fish size, and lipid content.

359 Regarding CP homolog profiles, C₁₀-CPs and C₁₁-CPs with Cl₆ and Cl₇ predominated among
360 SCCPs, whereas C₁₄-CPs with Cl₆ and Cl₇ predominated among MCCPs. These patterns matched
361 those found in other studies, particularly those conducted in urban/industrial areas.

362 Finally, the authors suggest that future research should be conducted to assess the
363 environmental occurrence, behavior, fate, and impacts of CPs in other South American
364 ecosystems influenced by humans where CPs may endanger ecosystems and human health.

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Highlights

- First report on the occurrence of SCCPs and MCCPs in fish from the South Atlantic Ocean in Argentina
- SCCP and MCCP amounts were considered low or moderate, compared to other studies
- Analysed fish are safe for human consumption regarding SCCP amounts
- SCCPs amounts showed no inter- or intra-specific significant differences
- MCCP interspecific differences were explained by feeding habits and fish size

Short- and medium-chain chlorinated paraffins in fish from an anthropized southwestern Atlantic estuary, Bahía Blanca, Argentina

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: