

Levels and trends of the emerging contaminants HBCDs (hexabromocyclododecanes) and PFCs (perfluorinated compounds) in marine shellfish along French coasts

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Abstract:

The levels and congener patterns of HBCDs (hexabromocyclododecanes) and PFCs (perfluorinated compounds) were determined in filter-feeding molluscs collected in 2008 and 2010 along the coasts of mainland France. α -HBCD and PFOS (perfluorooctane sulfonate) were detected in all samples, revealing widespread contamination of the coastal environment by these emerging contaminants. The spatial distribution of Σ -HBCD concentrations showed higher median levels in samples from the Mediterranean Sea and English Channel respectively, i.e. 0.19 ng g⁻¹ wet weight (ww) and 0.08 ng g⁻¹ ww, related to high anthropogenic pressure from urban and industrial activities, while the median concentration was 0.05 ng g⁻¹ ww in samples from the Atlantic coast. Among PFCs, PFOS was the only compound detected in all samples and PFDA (perfluorodecanoic acid) was the second most frequently-detected compound. PFOS median concentrations were 0.18 ng g⁻¹ ww, 0.09 ng g⁻¹ ww and 0.04 ng g⁻¹ ww in samples from the English Channel, the Atlantic coast and the Mediterranean coast respectively. The highest PFOS concentration was found in the Loire estuary, possibly related to local industrial activities. The Mediterranean samples showed a different pattern, with predominant long-chain PFCAs (perfluorocarboxylic acids), suggesting the presence of alternative sources on the Mediterranean coast.

The temporal trends studied in archived samples from the Seine estuary site showed a significant exponential increase in HBCD concentrations between 1981 and 2011, with a doubling time of 7 years, while PFOS levels underwent a significant linear decrease over time. These trends are coherent with current regulations on the use of these compounds. The results presented in this paper provide the first data on the contamination of the French coastal marine environment by the selected emerging compounds, and constitute a reference for the future monitoring of French coastal contamination by emerging contaminants.

Highlights

► Levels and trends of HBCDs and PFCs were studied in the French coastal environment. ► Results show widespread contamination of shellfish by α -HBCD and PFOS. ► Contamination by α -HBCD increased exponentially between 1981 and 2011. ► PFOS levels underwent a significant linear decrease over time.

Keywords: Persistent organic pollutants ; Environment specimen banking ; Coastal marine environment ; Concentrations ; Patterns ; Temporal trends

57 **1. Introduction**

58 Marine shellfish, and in particular filter-feeder bivalves, have been widely used to monitor
59 chemical contamination of the coastal environment by Persistent Organic Pollutants (POPs),
60 due to their broad geographical distribution, year-round availability and ability to
61 bioaccumulate contaminants without extensively degrading them. These monitoring efforts,
62 referred to as “Mussel Watch Programs”, have been implemented in numerous countries
63 worldwide (Beliaeff et al., 2002; O’Connor and Lauenstein, 2006; Ramu et al., 2007; Tanabe,
64 2008). Environmental specimen banking has been gaining interest since the 1960s and has
65 now become a recognized approach for regular environmental monitoring. Nineteen
66 Environmental Specimen Banks (ESB) currently exist on the 5 continents (Becker and Wise,
67 2010). In addition to the regular monitoring of historic contaminants, ESB samples can be
68 used to monitor emerging compounds and conduct retrospective surveys (Johansson et al.,
69 2006; Munschy et al., 2008; Esslinger et al., 2011; Kratzer et al., 2011; Reiner et al., 2011;
70 Tanabe and Ramu, 2012). Time-series studies of emerging contaminants are important in
71 order to assess variations in emissions, and evaluate the impact of legal restrictions on
72 environmental levels. In this study, the target emerging contaminants were
73 hexabromocyclododecanes (HBCDs) and perfluorinated compounds (PFCs). To our
74 knowledge, data on the occurrence and trends of both classes of contaminant in France is very
75 scarce, especially in relation to the coastal environment.

76 HBCD is mainly found in polystyrene insulation foam boards used for construction purposes,
77 in textiles for upholstered furniture, and in electrical and electronic equipment and appliances
78 (VECAP, 2009). World demand for HBCD has increased by nearly 32% since 2001 and

79 reached 22,000 tons in 2003, making it the third most widely-used brominated flame retardant
80 (BFR) on a global scale, and the second in Europe (de Wit et al., 2010). No global controls on
81 the production and use of HBCD have been reported to date (Lam et al., 2009), although
82 voluntary reductions in emissions have been reported in Europe (Law et al., 2008a), and
83 HBCD use has been banned in polystyrene building insulation under the European legislation
84 REACH (Registration, Evaluation, Authorization and Restriction of Chemical substances)
85 program since 2010 (Shaw et al., 2012).

86 Reportedly, HBCDs may be used as an alternative for polybrominated diphenyl ethers
87 (PBDEs) in some applications following restrictions on the usage of penta- and octa-BDE
88 commercial mixtures in Europe (Ramu et al., 2010; Ueno et al., 2010, Goscinnny et al., 2011).
89 HBCD recently came under consideration for inclusion in the Stockholm Convention POP list
90 due to its persistency, bioaccumulative character, potent long-range atmospheric transport and
91 toxicity (Marvin et al., 2011). HBCD presence has already been reported in various abiotic
92 and biotic environmental matrices all over the world (Law et al., 2005; Covaci et al., 2006;
93 Wu et al., 2012). Although commercial HBCD is mainly made up of γ -HBCD (75-89%), plus
94 lower amounts of the diastereoisomers alpha- and beta-HBCD (respectively 10-13% and 1-
95 12%) (Covaci et al., 2006), alpha-HBCD is the main diastereoisomer found in biota samples
96 due to its higher assimilation efficiency and/or slower degradation (Covaci et al., 2006;
97 Haukås et al., 2010).

98 PFCs are widely used as surfactants in industrial and consumer products and as additives for
99 fluoropolymer production (Ahrens, 2011). PFCs are extremely persistent, bioaccumulative
100 and toxic, and globally distributed in the environment. Among this vast class of chemical

101 products, the best known are perfluorosulfonates (PFSAs) and perfluorocarboxylic acids
102 (PFCAs), of which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are
103 recognized as widespread in the environment (Giesy and Kannan, 2001; Martin et al., 2004;
104 Nania et al., 2009; Houde et al., 2011). PFOS is often found to be the predominant compound
105 in biota, whereas PFOA has a lower assimilation efficiency and half-life (Martin et al., 2003).
106 PFOS has recently been included in the Stockholm Convention list of priority chemicals
107 (UNEP, 2009). Despite the phase-out in long-chain PFCA production since 2000, many PFCs
108 are still released into the environment through industrial and domestic activities and through
109 the release and degradation of their precursors (Prevedouros et al., 2006; Wang et al., 2012).
110 Waste Water Treatment Plants (WWTPs) and rivers are major pathways for their release into
111 the aquatic environment (Bossi et al., 2008; Clara et al., 2008; Sánchez-Avila et al., 2010).
112 However, data on their contamination levels in marine invertebrates and temporal trends
113 remains scarce, especially in Europe. Nonetheless, seafood (fish and shellfish) is recognised
114 as the primary dietary source of human exposure to PFCs (Falandysz et al., 2006; Haug et al.,
115 2010).

116 This study aims to investigate the contamination levels and spatial distribution of HBCDs and
117 PFCs in the French coastal marine environment and assess their temporal trends over the last
118 30 years. The samples (marine shellfish *Mytilus edulis*, *Mytilus galloprovincialis*, or
119 *Crassostrea gigas*) were obtained from specimens collected in the framework of the French
120 Mussel Watch Program (ROCCH –Réseau national d’Observation de la Contamination
121 CHimique) operated by IFREMER since 1979. The study provides new results on the
122 contamination of French coastal areas by emerging contaminants, thus filling the gaps as

123 regards knowledge of the past and present occurrence of these compounds on a national scale.
124 It also provides additional broad-interest data, aimed at increasing knowledge of the levels
125 and temporal trends of emerging organohalogen contaminants in Europe. This work is a
126 continuation of our previous study on polychlorinated biphenyls (PCBs), polychlorinated
127 dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and PBDEs in marine shellfish (Johansson
128 et al., 2006; Munschy et al., 2008).

129

130 **2. Materials and Methods**

131 *2.1. Sampling strategy*

132 The analysed samples were chosen from selected locations in the English Channel, Atlantic
133 and along Mediterranean coasts, as shown in Fig. 1. These locations cover main estuaries and
134 deltas (Seine, Loire, Gironde, Rhône), plus smaller tributaries. As no species-related
135 differences in POP accumulation in oysters and mussels have been reported in the literature
136 (Ueno et al., 2010), mussels (*Mytilus edulis* or *Mytilus galloprovincialis*) and oysters
137 (*Crassostrea gigas*) were used indifferently to monitor HBCD and PFC contamination levels.
138 HBCDs were analysed in samples collected in 2008 and 2010, while PFCs were analysed in
139 samples collected in 2010. Samples obtained from IFREMER's ESB between 1981 and 2011
140 were used for the temporal trend study.

141 The shellfish were collected and handled in accordance with international guidelines for the
142 monitoring of contaminants in biota (OSPAR, 2009). In order to avoid possible differences in
143 contaminant concentrations due to seasonal factors affecting the physiological state of the
144 shellfish (i.e., spawning), all samples were collected in the same manner and at the same time

145 of year (from late November to early December). In order to reduce inter-individual
146 variability, each composite sample consisted of at least 50 mussels of similar size (45–55 mm
147 shell length) collected from each sampling site. All samples were systematically depurated in
148 filtered water for 24 hours before freezing, to allow a natural clearance of particles from the
149 digestive tracts and mantle of the shellfish. The shellfish were shelled and their flesh (whole
150 soft body) was homogenized and stored at -20 °C prior to freeze-drying. The samples were
151 stored in a dry, cool and dark place until further analysis.

152 In order to check potential increase in water content during storage, gravimetric determination
153 of constant dry weight (dw) was systematically conducted on an aliquot of each sample before
154 sample extraction. This precaution was particularly important for the analysis of archived
155 samples, some of which had been stored for over 30 years. However, no increase in water
156 content (on average about 8%) was found in relation to sample storage duration.

157

158 *2.2. Chemicals*

159 Details on the solvents and standards used are provided in the Supplementary Material (SM).

160

161 *2.3. Sample preparation and analysis*

162 HBCD and PFC analyses were performed at the LABERCA laboratory as described below.

163 Further details on all analytical procedures are provided in the SM.

164 For HBCD analysis, the samples were extracted by Accelerated Solvent Extraction (ASE)
165 using toluene and acetone (70:30, v:v). The total amount of extractable lipids was determined
166 gravimetrically on this extract before further sample processing. Purification was performed

167 on a column comprising successive layers of anhydrous sodium sulfate, neutral silica gel, and
168 concentrated sulphuric acid acidified silica. HBCD stereoisomers were analyzed using
169 reverse-phase LC (Hypersil Gold column, 100 mm × 2.1 mm, 1.9 μm), and determined by
170 LC-MS/MS (Agilent 6410) fitted with an electrospray ion source, operating in the negative
171 ion mode.

172 For PFC analysis, the samples were extracted by liquid solid extraction using methanol. The
173 extracts were purified using dispersive solid phase extraction with Envicarb stationary phase,
174 according to a method described by Powley et al. (2005) followed by a hydrated silica
175 column. The purified extracts were separated using LC equipped with a C₁₈ reverse phase
176 column (50 mm x 2.0 mm, 3 μm) fitted with a guard column (10 mm x 2.0 mm, 3 μm) and
177 interfaced with a linear ion trap coupled to an orbital trap (LTQ-Orbitrap™) (Thermo
178 Scientific, Germany) operating in negative electrospray ionization mode.

179

180 2.4. QA/QC

181 LABERCA laboratory operates an ISO/IEC 17025:2005-certified Quality Assurance system
182 requiring strict controls as regards personnel, instrument conditions, and experimental
183 situations. The three HBCD isomers and various PFCs were quantified by isotopic dilution
184 using the corresponding ¹³C-labelled isomers, and real samples were quantified using internal
185 standard method. Laboratory blanks were simultaneously analysed and monitored in parallel
186 with the samples, and the signal of each compound in the blanks was checked to avoid
187 contamination throughout the analytical procedure. A reference fish sample (for HBCD
188 analysis) and egg sample (for PFC analysis) were included in each series of analysis to assure

189 repeatability. The results obtained for the fish and egg samples were used to set up a quality
190 control chart guaranteeing the robustness of the entire analytical procedure. In addition, our
191 laboratory regularly takes part in inter-laboratory comparison tests and achieves good results
192 for both of these methods. Moreover, our analytical methods have been approved and
193 accredited by the French accreditation body, with an overall uncertainty of between 24% and
194 29% depending on the compound.

195 The LOQ value was determined for each target compound in each analysed sample. LOQ was
196 between 0.0002 ng g⁻¹ ww and 0.002 ng g⁻¹ ww for each HBCD isomer, and between 0.02 ng
197 g⁻¹ ww and 0.2 ng g ww⁻¹ according to the PFC compound.

198

199 3. Results and discussion

200 *3.1. HBCD levels and patterns*

201 The geographical distribution of Σ -HBCD concentrations determined in shellfish is shown in
202 Fig. 2 for samples collected along the French coast in 2008 and 2010. Although HBCDs are
203 present in the technical mixture primarily in the form of three stereoisomers (α -, β - and,
204 predominantly, γ - HBCD), α -HBCD was shown to prevail in both mussels and oysters,
205 accounting for an average of 90% of the sum of three isomers. β -HBCD concentrations were
206 below the limit of detection in most of the samples. The prevalence of alpha-HBCD is usually
207 observed in aquatic biota due to its higher assimilation efficiency and/or slower degradation
208 (Haukås et al., 2009). A significant linear correlation ($r = 0.86$, $p < 0.05$) was observed
209 between γ - and α -isomer concentrations. No spatial trend was observed in HBCD patterns.

210 α -HBCD was detected in all samples, revealing the ubiquitous contamination of French
211 coasts by this BFR. In 2008, Σ -HBCD concentrations varied from 0.03 ng g⁻¹ wet weight
212 (ww) at the Etel estuary to 0.55 ng g⁻¹ ww at the Nivelle estuary, both located on the Atlantic
213 coast (Fig. 1). In 2010, minimum and maximum concentrations were found at the same sites,
214 ranging from 0.01 ng g⁻¹ ww to 0.36 ng g⁻¹ ww. As shown in Fig. 2, concentrations were
215 markedly lower in 2010 than in 2008 at all sites, on average by a factor of 0.7. The highest
216 concentrations in the English Channel were found at the Seine estuary site (0.41 ng g⁻¹ ww
217 and 0.31 ng g⁻¹ ww in 2008 and 2010 respectively) and Antifer site (0.26 ng g⁻¹ ww and 0.20
218 ng g⁻¹ ww in 2008 and 2010 respectively), the latter being under the influence of the Seine
219 estuary. Higher levels of various POPs (namely, PCBs, PCDD/Fs, and PBDEs) have
220 previously been reported related to high inputs from human activities via the Seine river
221 (Johansson et al., 2006; Munsch et al., 2008). Concentrations in samples from the
222 Mediterranean coast were generally in the high range too (0.07-0.41 ng g⁻¹ ww in both 2008
223 and 2010) versus the Atlantic. Samples from the Atlantic coast showed lower contamination
224 levels (0.01-0.06 ng g⁻¹ ww), except those originating from La Nivelle estuary in both 2008
225 and 2010, which were in a similar range to those found in samples from the Seine estuary.
226 This sampling site was revisited in November 2011, leading to a confirmation (0.45 ng g⁻¹
227 ww) of the high contamination level observed previously. This estuary also shows higher
228 PBDE contamination on the Atlantic coast (unpublished results), although no evidence of
229 major BFR local sources (i.e., industrial) could be found. Indeed, the Nivelle river is a small
230 coastal stream, which drains a mountainous catchment area before reaching the Bay of Biscay
231 (Atlantic Ocean).

232 The spatial distribution of HBCD concentrations varied according to the sampling site.
233 Median concentrations calculated in each coastal area decreased as follows: Mediterranean
234 coast > English Channel > Atlantic coast (Table 1). Distribution appears to correspond to
235 France's most highly-populated and/or industrialized areas. Human activities are obviously at
236 the origin of the presence of these chemicals in the environment, although a previous study
237 conducted in Japan showed that HBCD presence was related more to industrial activity than
238 to highly populated areas (Ueno et al., 2010).

239 To our knowledge, data on HBCD contamination of the French coastal environment is non-
240 existent. In the marine environment, most available data on HBCD contamination relates to
241 fish (Law et al., 2008b), related to HBCD biomagnification along trophic networks (Covaci et
242 al., 2006; Tomy et al., 2008; Haukås et al., 2010). Even on a worldwide scale, data on
243 shellfish contamination by HBCDs is limited versus PBDE data (Ueno et al., 2010). Table 1
244 presents available data on the contamination of shellfish by HBCDs in European countries.

245 The data available in the literature is usually reported as Σ -HBCD expressed in ng g^{-1} ww or
246 ng g^{-1} lipid weight (lw). Although HBCD concentrations showed no significant correlation
247 with lipid content in our samples (either in 2008 or in 2010), concentrations were also
248 expressed normalised to lipid content for comparison purposes (Table 1). Data from the
249 literature differs widely, i.e., from non-detected values to 329 ng g^{-1} ww depending on the
250 characteristics of the sampling area (i.e. proximity to sources). Data comparison on a
251 European scale shows levels determined in the French coastal environment to be in a similar
252 range to those reported in other European countries (i.e., Netherlands, Norway, UK), with the
253 exception of the much higher concentrations reported by Berge et al. (2006) on the West coast

254 of Norway, i.e., 55.4-329 ng g⁻¹ ww, related to the production of polystyrene polymer
255 products.

256

257 *3.2. PFC levels and patterns*

258 Among the various analysed PFCs, only PFOS was detected in all samples, indicating
259 widespread contamination of the French coastal environment by this chemical. PFOS was
260 found to be the predominant PFC in most samples collected from the English Channel and
261 Atlantic coast, while PFCAs prevailed in Mediterranean samples. PFOS is reportedly the
262 main PFC found in all species of aquatic biota throughout the world (Houde et al., 2011),
263 although some studies have reported PFOA as being the predominant compound, for example
264 in shellfish from Asia, related to direct sources (Nakata et al., 2006; Pan et al., 2010). The
265 spatial distribution of PFOS concentrations is presented in Fig. 3: these were in the 0.005-0.87
266 ng g⁻¹ ww range, with a median value of 0.08 ng g⁻¹ ww. Median concentrations were higher
267 in samples collected in the English Channel, followed by those from the Atlantic and
268 Mediterranean coasts (Table 1). As previously seen for HBCDs, the Seine estuary area (Seine
269 estuary and Antifer sites, Fig. 1) showed higher PFOS concentrations versus the other sites.
270 This is consistent with the results obtained by Labadie and Chevreuil (2011) in the Seine
271 river, where PFOS concentrations were found to be higher than in other European rivers. In
272 our study, the highest concentration (0.87 ng g⁻¹ ww) was found in one sample collected from
273 the Loire estuary site on the Atlantic coast (Fig. 3). The site was revisited in November 2011,
274 at which time the previously-observed high level of contamination was confirmed (0.68 ng g⁻¹
275 ww). This result is unexpected, as the Loire estuary catchment area is not particularly

276 industrialized or urbanized in comparison to the Seine river catchment area. As a result, the
277 Loire estuary does not show high concentrations of classic organic contaminants such as
278 PCBs or PCDD/Fs, or more recently-emerged compounds such as PBDEs (unpublished
279 results) and HBCDs (this study). PFOS has been identified in effluents from the paper and
280 metal industry and, in particular, at high concentrations in industrial effluents from
281 galvanising, nickel and chromium plating and metal anodising (Clara et al., 2008; Xiao et al.,
282 2012). The “Pays de la Loire” region, where the Loire estuary is located, is France’s foremost
283 region for the wood transformation and paper industry, and metal surface treatment industry,
284 both of which represent potential sources of PFOS. The higher PFOS concentrations found in
285 mussels at this site should therefore continue to be monitored in coming years.

286 Few studies report PFC presence in shellfish from the marine environment, and, to our
287 knowledge, none is available to date for France. Available data on PFOS concentrations in
288 shellfish is summarized in Table 1. PFOS was not detected or was found at low levels in
289 shellfish from most other European coastal areas (Bossi et al., 2008; Nania et al., 2009;
290 Fernández-Sanjuan et al., 2010; Gómez et al., 2011) with the exception of mussels from
291 north-central Portuguese estuaries crossing the country’s most industrialized areas, in which
292 high concentrations were detected (Cunha et al., 2005). Our data reveals a ubiquitous and
293 fairly high contamination of French coastal areas by PFOS versus other countries.

294 Although most data on biota reported in the literature concerns PFOS and PFOA, more recent
295 studies show evidence of the occurrence of other PFCs, for example in Asia (So et al., 2006;
296 Yoo et al., 2009; Naile et al., 2010; Pan et al., 2010; Wang et al., 2011) and Brazil (Quinete et
297 al., 2009). In our study, the second most-frequently detected compound (38% of samples,

298 Table SM-1), perfluorodecanoic acid (PFDA), was determined at lower levels than PFOS, i.e.
299 between 0.04 and 0.08 ng g⁻¹ ww (Table SM-1). PFDA occurrence in shellfish has barely
300 been reported in the literature and, to our knowledge, never in Europe. PFDA has been
301 identified at concentrations second to PFOS in sewage sludge from WWTPs in Denmark, but
302 it has not been detected in mussels (Bossi et al., 2008). It was identified in various
303 invertebrates from Korea at levels of between <MDL (method detection limit) and 2.08 ng g⁻¹
304 dw (Naile et al., 2010), and in mussels and oysters from the East Chinese Coast and Tokyo
305 Bay in Japan at <0.11-0.13 ng g⁻¹ ww and (So et al., 2006). Perfluoroundecanoic acid
306 (PFUnA) was detected in Mediterranean samples only, at levels of between 0.32 and 0.59 ng
307 g⁻¹ ww, i.e. slightly lower than the levels reported in mussels by Naile et al. (2010) (1.09-1.61
308 ng g⁻¹ ww). Perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA) and
309 perfluorotetradecanoic acid (PFTeDA) were detected at the Gulf of Fos site alone, at 0.51 ng
310 g⁻¹ ww, 0.44 ng g⁻¹ ww and 0.11 ng g⁻¹ ww respectively (Table SM-1). PFDoA levels were in
311 the same range as those found in mussels from Korea and oysters from Tokyo Bay (Naile et
312 al., 2010; So et al., 2006).

313 PFOSA (the main PFOS precursor) was detected in four samples (Antifer, Seine estuary,
314 Loire estuary and Gulf of Fos) influenced by urban and/or industrial activities. Concentrations
315 at three out of these four sites were higher than those of PFOS and found to be in the 0.36-
316 1.79 ng g⁻¹ ww range. No correlation between PFOS and PFOSA could be found: however,
317 only a small amount of data was obtained. These levels are comparable to those reported by
318 So et al. (2006) in mussels and oysters from the East China Coast and Tokyo Bay in Japan,
319 where the high levels of this compound have been associated with the extensive use of

320 insecticides to control termites and ants. In another study, PFOSA was not detected in
321 industrial effluents and barely detected in municipal WWTPs (Clara et al., 2008).

322 PFCs are used in a broad range of applications, such as surfactants, lubricants, paper and
323 textile coatings, polishes, food packaging and fire-retarding foams (Calafat et al., 2006). The
324 pattern observed in biota is the result of source exposure, assimilation and elimination, and
325 cannot therefore be used alone to track sources. In our study, several of the compounds
326 identified in shellfish, such as PFDA, PFDoA and PFOS, reportedly originate mainly from
327 industrial sources (Clara et al., 2008). In the Mediterranean samples, PFCAs prevailed over
328 PFOS (Fig. 4), with a PFCAs / PFOS ratio at the Gulf of Fos and Bay of Hérault of 11 and 14,
329 respectively. Among PFCAs, those with odd carbon number were present in higher
330 proportions versus the corresponding shorter even-chain length PFCAs (e.g., PFUnA >
331 PFDA). The predominance of odd-chain length PFCAs has previously been observed in fish
332 and partially explained by the degradation of fluorotelomer alcohols (FTOHs) (Ellis et al.,
333 2004; Martin et al., 2004). In Denmark, PFCAs have been identified at high concentrations in
334 effluent waters from the textile industry, but they may also originate from other industrial
335 activities (Bossi et al., 2008). Interestingly, the two patterns determined at the Hérault bay and
336 Gulf of Fos sites (Fig. 1) showed some dissimilarities: mainly shorter chain PFCAs (<
337 PFDoA) were observed in the former, while longer chain PFCAs (> PFUnA) prevailed in the
338 latter (Fig. 4). The Gulf of Fos is bordered by a heavily industrialized area, with chemical,
339 petroleum and steel-work plants, and receives freshwater inputs from the river Rhone, three
340 channels and the Berre Lagoon (Mille et al, 2007). The different patterns observed in
341 Mediterranean samples versus samples from the other coastal areas may indicate a variety of

342 sources. However, the reasons for the varying patterns we observed remains unclear and
343 difficult to link to specific industrial activities. More data on industrial activities together with
344 potential PFC sources would be needed in order to explain the patterns observed in shellfish.

345

346 *3.3. HBCD and PFC trends*

347 Both the temporal trends of HBCD and PFC concentrations were investigated at the Seine
348 estuary site between 1981 and 2011 using archived samples from the French ESB held by
349 Ifremer. This site is a French benchmark in terms of highly-contaminated estuaries.

350 Moreover, the data obtained in this study is complementary to the previous studies on POPs
351 (PCBs, PCDD/Fs, PBDEs) conducted by us at this site (Johansson et al., 2006; Munschy et
352 al., 2008).

353 The temporal trend of HBCD concentrations (α -isomer) in mussels from the Seine estuary
354 between 1981 and 2011 is presented in Fig. 5, with concentrations in the 0.01-0.39 ng g⁻¹ ww
355 range. Although concentrations decreased between 2008 and 2010 at all geographical sites
356 (see section 3.1), including the Seine estuary, the data obtained from the Seine estuary
357 samples between 1981 and 2011 reveal a significant exponential upward trend over the entire
358 study period, with a doubling time of 8 years. Similarly to our previous results on PCBs and
359 PBDEs, a concentration higher than that predicted by the exponential curve was observed in
360 the years 2000 and 2008, linked to higher flooding of the Seine River (Johansson et al., 2006;
361 Munschy et al., 2008).

362 Time trend studies published in the literature show diverging results, ranging from increasing
363 trends to insignificant or decreasing trends. Johansson et al. (2011) revealed a significant

364 increase of 11% per year in HBCD concentrations in Peregrine falcon in Sweden from the
365 mid-1980's until 2005, followed by an apparent levelling-off and decline after 2000. The
366 same trend was previously observed by Sellström et al. (2003) in guillemot eggs between
367 1969 and 2000, with a two-fold increase in concentrations over the study period followed by
368 levelling-off since the mid-1990s. An upward trend was detected in bird eggs from Northern
369 Norway between 1983 and 2003 (Covaci et al., 2006). Vorkamp et al. (2011) found a
370 statistically significant exponential time trend in ringed seals from East Greenland, with an
371 annual increase of 6.1%. Conversely, several recent studies have shown decreasing trends,
372 generally related to a local drop in production or industrial emissions, for example in the UK
373 and in Germany, with various time lags after production stoppage (Law et al., 2008a;
374 Esslinger et al., 2011). The results obtained in the Seine estuary did not suggest any recent
375 reductions in point source emissions.

376 HBCD trends contrast with those generally observed in PBDEs (except BDE-209) in Europe,
377 the levels of which have decreased or stabilised in recent years due to European regulations or
378 even voluntary withdrawal (Law et al., 2010; Johansson et al., 2011). Indeed, PBDEs (penta-
379 and octa-BDE products) have been banned since 2004 in Europe, while no regulations exist to
380 date for HBCD. de Wit et al (2010) reported that the global use of HBCD has increased
381 slightly since 2001, with 16,700 tons in 2001, 21,400 in 2002 and 22,000 tons in 2003.
382 However, total HBCD volumes sold in Europe have been relatively stable, with 9,500 tons in
383 2001, 10,897 tons in 2007 and 8913 tons in 2008 (de Wit et al., 2010; VECAP, 2009). This
384 obviously does not explain the increasing levels observed in the Seine estuary. The upward
385 trend observed in our study may suggest that HBCD is increasingly used as alternative to

386 PBDEs, as previously suggested by several authors (Lam et al., 2009; Wu et al., 2012).
387 However, additional studies may be required to monitor the evolution of concentrations at this
388 site and investigate trends in France on a wider scale.

389 The temporal variations in PFOS concentrations at the Seine estuary site showed a significant
390 linear decrease ($r = 0.89$, $\alpha = 0.05$) between 1990 and 2011 (Fig. 6). Although the observed
391 trend was significant over this time period, concentrations did not vary widely between 1990
392 and 2002 (1.42-2.58 ng g⁻¹ ww range), and lower concentrations were observed in the 2004-
393 2011 period (1.07-0.26 ng g⁻¹ ww range). The observed trend appears to be consistent with
394 other studies, which show an increase in PFOS levels in many industrialized countries until
395 the mid-1990s, followed by a decline, which may or may not be significant (Kwadjik et al.,
396 2010). More specifically, decreasing PFOS concentrations were found in Europe between
397 1999 and 2008 in harbour seals from the German Bight (Ahrens et al., 2009), although this
398 decrease was not significant. In ringed seals from the Baltic Sea, PFOS concentrations
399 showed a statistically significant increase between 1974 and 2008, although the trend
400 levelled-off after 1997 and no significant trend was observed after this date (Kratzer et al.,
401 2011). Eel samples from The Netherlands showed a PFOS increase from the end of the 1970s
402 to the mid-1990s, followed by a significant decrease from the late 1970s until 2008 (Kwadjik
403 et al., 2010). Galatius et al. (2011) reported no significant correlation in PFOS concentrations
404 in harbour porpoises from the Danish North Sea between 1980 and 2005, while decreasing
405 trends (although not significantly so) were found in harbour porpoises from Northern Europe
406 between 1991 and 2008 (Huber et al., 2012).

407 It therefore appears that the decline observed in the environment occurred before PFOS
408 manufacture was phased out by the company 3M between 2000 and 2002, although minor
409 PFOS production continued in Europe (< 42-82 t in 2003) for restricted applications (Ahrens
410 et al., 2009; Paul et al., 2009; Houde et al., 2011). In contrast, increasing PFCA
411 concentrations were reported, for example in harbour porpoises from Northern Europe,
412 suggesting continuous inputs of these compounds into the marine environment (Huber et al.,
413 2012).

414

415 4. Conclusions

416 Our study showed evidence of widespread contamination of the French coastal environment
417 by HBCDs and PFCs, and in particular PFOS, which is the most prevalent PFC. HBCD levels
418 were in the ranges reported in other European countries, while PFOS levels were
419 comparatively high, although very little data is available to date. Other PFCs, in particular
420 long-chain PFCAs, were also identified at some sites, especially in Mediterranean samples
421 where they were predominant, suggesting the existence of a variety of sources.

422 A significant exponential increase in HBCD levels was observed in the Seine estuary between
423 1981 and 2011, suggesting a regular input of this compound into the marine environment.
424 PFOS temporal trends showed opposite results, with a significant linear decrease since 1990.
425 These trends coincide with the global trends observed in Europe and with regulations on the
426 emission and use of these compounds.

427 The data obtained in this study is the first reported on a national scale. Further studies are now
428 required to assess French coastal contamination by emerging compounds and their temporal

429 trends. The French ESB is of major interest for this purpose.

430

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437

438

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1 **Figure captions**

2 Fig. 1: Sampling sites for study shellfish collected in 2008 and 2010 from the English
3 Channel, Atlantic coast and Mediterranean Sea

4

5 Fig. 2: Σ -HBCD concentrations (ng g^{-1} ww) in shellfish collected in 2008 and 2010 along
6 French coasts. nda= no data available

7

8 Fig. 3: PFOS concentrations (ng g^{-1} ww) in shellfish collected in 2010 along French coasts.
9 nda= no data available

10

11 Fig. 4: PFC concentrations (ng g^{-1} ww) in shellfish collected from the Seine estuary, Loire
12 estuary and Mediterranean coast (Hérault Bay and Gulf of Fos) in 2010

13

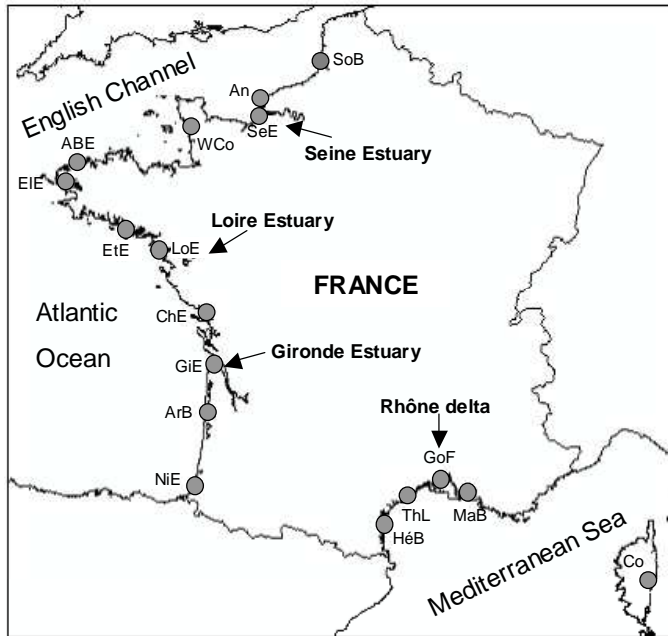
14 Fig. 5: Temporal trends of HBCD concentrations (α -isomer, ng g^{-1} ww) in mussel samples
15 (*Mytilus edulis*) from the English Channel (Seine estuary) between 1981 and 2011

16

17 Fig. 6: Temporal trends of PFOS concentrations (ng g^{-1} ww) in mussel samples (*Mytilus*
18 *edulis*) from the English Channel (Seine estuary) between 1981 and 2011

19

Fig. 1



ENGLISH CHANNEL

- SoB: Somme Bay
- An: Antifer
- SeE: Seine Estuary
- WCo: West Cotentin
- ABE: Aber Benoit Estuary

ATLANTIC

- EIE: Elorn Estuary
- EtE: Etel Estuary
- LoE: Loire Estuary
- ChE: Charente Estuary
- GiE: Gironde Estuary
- ArB: Arcachon Bay
- NiE: Nivelle Estuary

MEDITERRANEAN

- HéB: Hérault Bay
- ThL: Thau Lagoon
- GoF: Gulf of Fos
- MaB: Marseille Bay
- Co: Corsica

Fig. 2

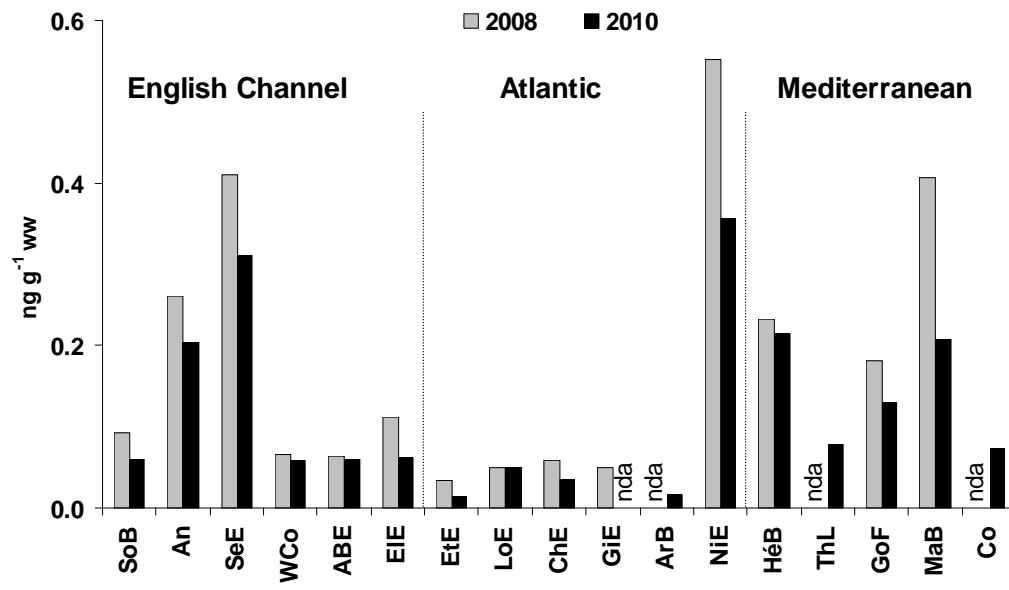


Fig. 3

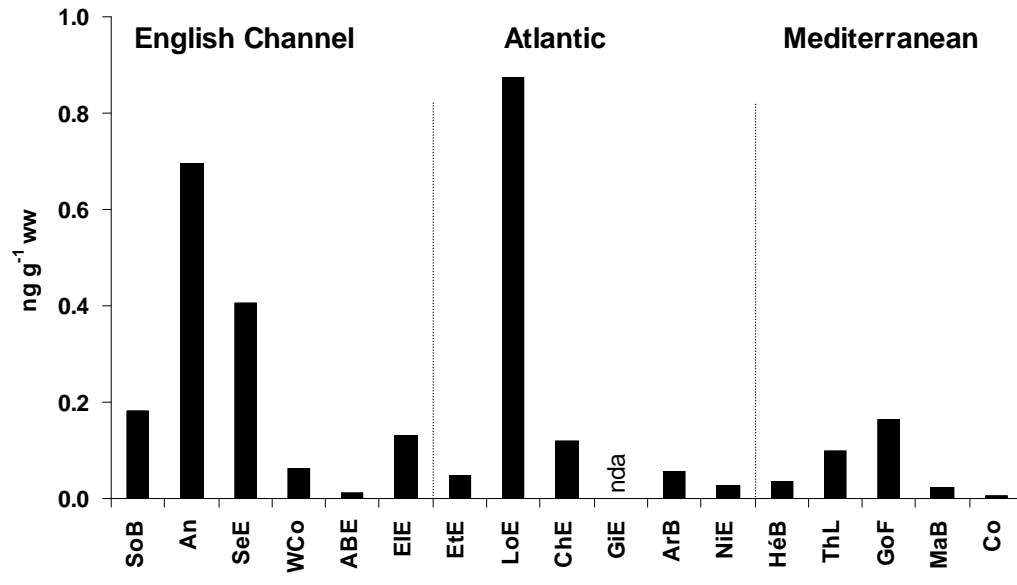


Fig. 4

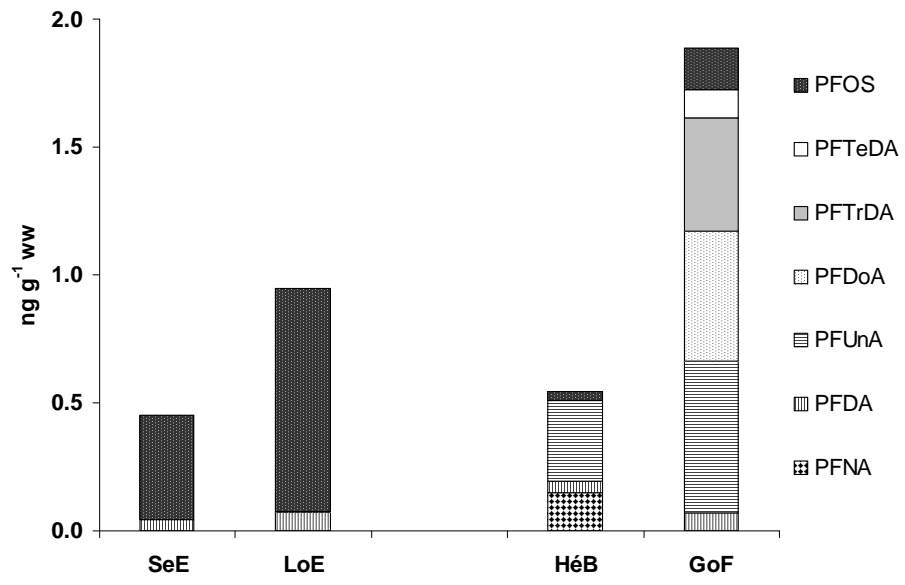


Fig. 5

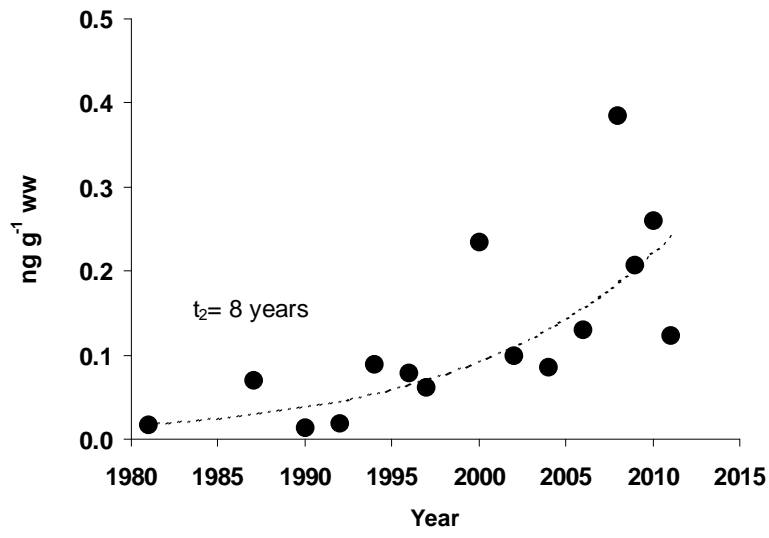


Fig. 6

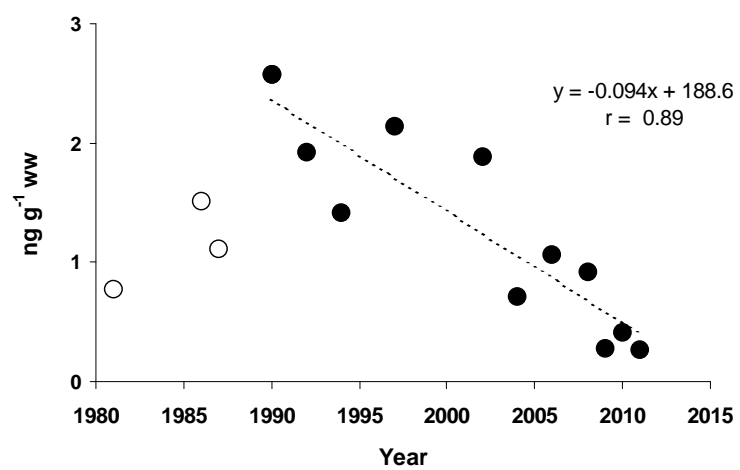


Table 1.

Σ -HBCD and PFOS concentration ranges (minimum–maximum/median or mean) in shellfish from various coastal locations in Europe (including this study). Results are expressed in ng g^{-1} ww unless otherwise stated.

Location	Sampling period	Concentrations min–max/median or mean	Organism	Reference
<i>Σ-HBCD</i>				
France (English Channel)	2008–2010	0.06–0.41/0.08	Mussels/oysters	This study
France (Atlantic coast)	2008–2010	0.01–0.55/0.04	Mussels/oysters	This study
France (Mediterranean coast)	2008–2010	0.07–0.41/0.18	Mussels	This study
France (all coasts)	2008–2010	0.67–30.7/3.4 ^a	Mussels/oysters	This study
Norway	2001	10–106/34 ^a	Mussels	Covaci et al. (2006)
Norway (North West coast)	2006–2007	nd ^b -109/48 ^a	Mussels	Haukås et al. (2010)
Norway (South coast)	2003–2004	<0.17–0.87/0.43	Mussels	Bethune et al. (2005)
Norway (West coast)	2004–2005	55.4–329	Mussels	Berge et al. (2006)
Netherlands (Scheldt/Wadden Sea)	2003	<0.1–0.9	Mussels	van Leeuwen and de Boer (2008)
UK (Scotland)	2006	0.192–12.1/0.56 ^c	Mussels/Oysters	Fernandes et al. (2008)
<i>PFOS</i>				
France (English Channel)	2010	0.01–0.7/0.2	Mussels/Oysters	This study
France (Atlantic coast)	2010	0.03–0.9/0.1	Mussels/oysters	This study
France (Mediterranean coast)	2010	0.005–0.2/0.04	Mussels	This study
UK	2006	1–10/2.5	Oysters	Clarke et al. (2010)
Denmark	–	nd ^b	Mussels	Bossi et al. (2008)
Spain (North)	2009	nd ^b -0.06	Mussels (caged)	Gómez et al. (2011)
Spain (North)	2006–2009	nd ^b	Oysters (caged)	Fernández-Sanjuan et al. (2010)
Portugal (North estuaries)	–	36.8–125.9/72.0 ^d	Mussels	Cunha et al. (2005)
Mediterranean Sea	–	<2–3/<2	Mussels/Clams	Nania et al. (2009)

a Values expressed in ng g^{-1} fw.

b nd: not detected.

c Median value recalculated from the data presented in Fernandes et al., 2008.

d Mean of means calculated from data presented in Cunha et al., 2005.

Table options ▼