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1 **Novel brominated flame retardants relevant for European aquatic environments: ranking of analytes to**
2 **monitor and focus on the French Eastern Mediterranean coastline.**

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7 **Abstract**

8 Around a hundred of novel brominated flame retardants are currently being used to replace those regulated in the
9 2000s. However, data about their production, usage and toxicity is still scarce, as well as their levels of
10 contamination in the Mediterranean Sea and the subsequent risk. Our goal was to select the relevant novel
11 brominated flame retardants to monitor and to apply it along the northeastern Mediterranean Sea. We proposed a
12 ranking for novel brominated flame retardants based on their production or import, occurrence and ecotoxicology,
13 yielding to a selection of 21 priority molecules. From this list, 16 compounds were analyzed in ten coastal
14 suspended matter samples, together with six related chemicals. To assess their occurrence in comparison to better
15 documented flame retardants, eight legacy polybromodiphenyl ethers, seven polychlorobiphenyls, and short- and
16 medium-chain chlorinated paraffins were also targeted. Novel brominated flame retardants and
17 polychlorobiphenyls were detected in all the samples. Polybromodiphenyl ethers and chlorinated paraffins were
18 detected in nine and seven samples respectively. Out of the 22 novel brominated flame retardants analyzed, nine
19 were detected, with total concentrations ranging from 0.4 to 18.5 ng.g⁻¹ d.w., which was often higher than that of
20 polybromodiphenyl ethers. A high risk for 2,4,6-tribromophenol and PCB 118 was assessed in two and six
21 samples, respectively. To our knowledge, this is the first priority ranking and screening of most of the novel
22 brominated flame retardants selected in the French Mediterranean Sea.

23 **Keywords:** Contaminants of emerging concern ; European regulation ; Mediterranean Sea ; Novel brominated
24 flame retardants (nBFRs) ; Pollutant ranking ; Polybrominated diphenyl ethers (PBDEs) ; Risk assessment ;
25 Suspended matter

26 Introduction

27 Flame retardants are used to reduce flammability, hence the risks of fire. They are added during the production of
28 many daily items or materials, like electronic devices, construction materials, transport vehicles, or furniture
29 (de Wit, 2002; Xiong et al., 2019). Very different compounds can be used as flame retardants, like inorganic or
30 organic molecules, with halogen heteroatoms or not. Among halogenated compounds, brominated flame retardants
31 (BFRs) and chlorinated flame retardants are the most widely used (European Chemicals Agency, 2023).

32 Since the 1960s, four main groups of BFRs were produced and used in large quantities worldwide, i.e.,
33 polybromodiphenyl ethers (PBDEs), polybromobiphenyls (PBBs), hexabromocyclododecane (HBCDD) and
34 tetrabromobisphenol A (TBBPA). Whereas TBBPA corresponds to one organic molecule, PBDEs and PBBs, are
35 chemical families grouping 209 theoretical congeners. PBDEs were widely used as flame retardants and produced
36 as three commercial mixtures (penta-, octa- and deca-BDE). Eight congeners are the major components of these
37 mixtures, namely PBDEs 28, 47, 99, 100, 153, 154, 183 and 209. HBCDD was produced in a commercial mixture
38 containing three main isomers (γ : 75-89%; α : 10-13%; β : 1-12%). In 1989, the global production of BFRs was
39 estimated at almost 106,700 tons (Alaee, 2003). In 1992, it had increased to 150,000 tons (de Wit, 2002), and it
40 reached 203,740 tons in 2001 (Birnbaum & Staskal, 2004). The latest data from 2019 estimated a global
41 consumption of BFRs of 406,300 tons per year (European Chemicals Agency, 2023).

42 However, since the beginning of the 2000s, concern was raised about environmental and health risks induced by
43 chemicals and international regulations were established. Some of these regulations target the above-mentioned
44 BFRs. First, the Stockholm Convention on Persistent Organic Pollutants was signed by 152 countries worldwide
45 in 2001 and enforced in 2004. It identified originally 12 compounds as persistent organic pollutants (POPs), but
46 the list has now been extended to 30 compounds or group of compounds sorted in three groups: elimination (annex
47 A), restriction (annex B) and unintentional production (annex C) (Stockholm Convention, 2017). In the European
48 Economic Area, other regulations were also applied. It is the case of the Restriction of Hazardous Substances in
49 Electrical and Electronic Equipment (RoHS) which has been adopted in 2003 (2002/95/EC, 2003) and amended
50 in 2011 (2011/65/EU, 2011). It lists ten compounds or group of compounds that must be restricted in electronic
51 and electrical devices. These compounds cannot be present at more than 0.1 % by weight of homogeneous material.
52 The Water Framework Directive (WFD), adopted in 2000 (2000/60/EC, 2000), aims to ensure good water quality
53 in Europe and provides a list of 45 priority substances. Their concentrations in aquatic environments (inland
54 surface waters, other surface waters and biota) must remain below environmental quality standards (EQS) given

55 in an amendment from 2013 (2013/39/EU, 2013). Also, 21 out of the 45 priority substances are considered as
56 dangerous and member states must stop their emission in aquatic environments.

57 BFRs are known to be harmful to human health, since they have been shown neurotoxic (Chao et al., 2011),
58 carcinogenic, toxic to reproduction and may disturb the thyroid function (Vauclin et al., 2021). They were thus
59 concerned by these new regulations. All PBDEs were included in the RoHS directive. In 2009, tetra-, penta-, hexa-
60 and hepta-PBDEs were listed as POPs to eliminate (annex A) by the Stockholm Convention, and the deca-PBDE
61 commercial mixture was added in 2017. Six congeners of PBDE (28, 47, 99, 100, 153, 154) were listed as
62 dangerous priority substances, according to the WFD. Since 2003, the use of PBBs was limited by the RoHS
63 directive. In 2013, HBCDD was added both to the Stockholm Convention (annex A) and to the WFD (dangerous
64 priority substances). TBBPA is the only legacy BFR still widely used, with a global production of 170,000 tons in
65 2004 (Covaci et al., 2009) and between 10,000 and 100,000 tonnes per year produced or imported nowadays to
66 the European Economic Area, according to the European Chemical Agency (ECHA).

67 Under pressure of all these new regulations, the massive production and use of a high number of new molecules
68 have emerged, to comply with fire safety standards. Many of them are also brominated organic molecules. Indeed,
69 among halogenated flame retardants, BFRs are considered as the most efficient, followed by the chlorinated ones
70 (European Chemicals Agency, 2023). Thus, the three well-known families of BFRs, taken off the market, have
71 been replaced by over a hundred of the so-called novel brominated flame retardants (nBFRs), as classified by the
72 United States Environmental Protection Agency (US EPA). The global production of BFRs therefore kept
73 increasing, reaching 410,000 tons in 2008 (Covaci et al., 2011). The nBFRs of current use, as reported by Bergman
74 et al., (2012), cover a wide range of physicochemical properties, with octanol-water partition coefficients between
75 $1.04 < \log K_{ow} < 15.11$, raising questions about their possible presence in different environmental compartments,
76 possible bioaccumulation and persistence. Some of them have chemical structures very close to legacy BFRs,
77 raising concerns about their likely toxic effect by similar mechanisms and their POP-like properties. However,
78 little is known about their environmental risks (Mahfoudhi et al., 2023). First toxicity studies realized at high
79 concentration showed that nBFRs could cause hormone or endocrine disruption, neurotoxicity, or DNA damage
80 (Xiong et al., 2019). NBFRs enter the environment after atmospheric release mainly from e-waste recycling sites,
81 but also from manufacturing sites, waste incineration plants and other industrial processes (McGrath et al., 2017;
82 Ameer et al., 2020) as well as from wastewater treatment plants (Covaci et al., 2011). Once released in the
83 environment, nBFRs can undergo bioaccumulation and biomagnification, biodegradation or photodegradation
84 (Xiong et al., 2019). Moreover, they can also be transported by the atmospheric route over long distances (Xiong

85 et al., 2019) and have therefore been detected in marine benthos from the Arctic (Carlsson et al., 2018) and in the
86 atmosphere from West Antarctica (Hao et al., 2022). Local structures all around the world are presently working
87 to collect data about these new molecules and to regulate them if necessary. In the United States, the US EPA
88 develops and enforces national environmental laws and has created a database of all ever-observed flame
89 retardants, including BFRs. In Europe, the ECHA controls chemicals, assesses their risks and ensures that
90 companies abide by the law. Since 2006, the REACH (Registration, Evaluation, Authorization and restriction of
91 CHemicals) regulation (REACH, 2006), administered by the ECHA, aims to register all chemicals produced or
92 imported inside the European Economic Area in quantities above one ton per year.

93 Facing the large number of newly produced synthetic molecules and the persistence of numerous legacy pollutants
94 in the environment, it becomes over-challenging to monitor all of them and to properly assess the quality of water
95 bodies, which is one of the final environmental receptacles of all these pollutants. The aim of this work was to
96 identify, among the hundreds of nBFRs now in use, the most relevant compounds to search for in the European
97 aquatic environments based on production, occurrence and toxicity criteria, using data available from the US EPA,
98 the ECHA and the literature. Out of the 125 papers reviewed for this study, only six evaluated the presence of
99 nBFRs in the Mediterranean Sea (Munsch et al., 2015; Aznar-Alemany et al., 2018, 2021; Mekni et al., 2019,
100 2020) and only three of them were dealing with suspended matter or sediments along Tunisian, Spanish or Italian
101 coastlines (Aznar-Alemany et al., 2018; Mekni et al., 2019, 2020), highlighting the need for further studies. The
102 French Mediterranean coast was not previously studied. However, in the 1990s, nearly 1/3 of PBDEs used in
103 Europe was produced on the continent and France was an important producer (International Program on Chemical
104 Safety, 1994). One of the factories was located near the industrial area of Fos-sur-Mer. Nowadays, little is known
105 about the production of nBFRs in France, but the ECHA assessed the consumption to 28 thousand tons/year in
106 2019 in Western Europe (European Chemicals Agency, 2023). Hence, we carried out a first screening of 16 of the
107 hereby pointed-out nBFRs, combined with six additional bromobenzenes and bromophenols or derivatives, in
108 coastal suspended matter samples from the northeastern Mediterranean Sea, near Marseille, which cumulates
109 urban, industrial and port activities. As the targeted molecules are mainly hydrophobic and the nBFRs are presently
110 in use, suspended matter was chosen to observe the current input over a known time period, that can impact the
111 endemic Mediterranean biodiversity at the sampling sites. Sampling periods lasted about three months, to integrate
112 the mean contamination over a given season. The measured concentration levels of nBFRs were finally compared
113 to better documented environmental pollutants, like the eight legacy polybromodiphenyl ethers (PBDEs), as well

114 as other halogenated flame retardants, namely short- and medium-chain chlorinated paraffins (CPs) and the seven
115 indicator polychlorobiphenyls (PCBs) listed by the International Council for the Exploration of the Sea (ICES).

116 I. Materials and methods

117 I.1. Methodology for relevance ranking of nBFRs in Europe

118 The complete list of molecules used as brominated flame retardants was elaborated according to the database
119 provided by the US EPA (<https://comptox.epa.gov/dashboard/chemical-lists/FLAMERETARD>) and to the
120 literature (Bergman et al., 2012). Current use BFRs in Europe, referred below as nBFRs, were ranked according
121 to three criteria. The first criterion considered the use of these nBFRs in Europe, with data available on the ECHA
122 website (<https://echa.europa.eu/fr/home>) for each compound registered under the REACH regulation, including
123 their annual volume of production or import inside the European Economic Area. The second criterion referred to
124 the occurrence of nBFRs in aquatic environments. An exhaustive literature study was performed on Web of
125 Science (WOS) to find articles written in English over the last ten years (between 2012 and 2022) and dealing with
126 the term “flame retardant*”. The research was narrowed by selecting four WOS categories, i.e., environmental
127 science, chemistry analytical, chemistry multidisciplinary and multidisciplinary sciences. As our study focuses on
128 aquatic environments, we selected papers containing at least one of the following keywords: “marine”, “estuary”,
129 “lake”, “river*”, “aquatic”, “sea*”, “ocean*”, “water*”, “sediment*”, “suspended matter”, “marine biota”, “fish”,
130 “mollusk*” or “passive sampling”. We excluded some research terms to discard toxicity reports and occurrence
131 studies in non-aquatic environments, such as “thyroid”, “milk”, “terrestrial”, “soil*”, “tree”, “sewage”,
132 “wastewater*”, “toxic*”, “serum”, “synth*”, “in vivo” and “in vitro”. The 2,664 results thus obtained were sorted
133 one by one based on their title and abstract, to finally keep only 125 papers actually analyzing nBFRs in natural
134 aquatic environments. The third criteria aimed at evaluating the ecotoxicological risk of nBFRs. It was assessed
135 with the ecological structure activity relationships (ECOSAR) predictive model ([https://www.epa.gov/tsca-](https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model)
136 [screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model](https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model)), and with published data
137 reporting the trophic magnification of some molecules (Liu et al., 2021).

138 I.2. Chemicals and materials

139 The surrogate standard BDE 189, the internal standard BDE 140 and a certified standard mixture of the 8 regulated
140 PBDE congeners (BDE 28, 47, 99, 100, 153, 154, 183 and 209) were purchased from Accustandard (Interchim,
141 Montluçon, France), as well as the 13 following nBFRs: di(2-ethylhexyl)tetrabromophthalate (EH-TBB),

142 hexachlorocyclopentadienyl-dibromocyclooctane (DBHCTD), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane
143 (DBE-DBCH), pentabromobenzylacrylate (PBB-Acr), pentabromobenzylbromide (PBBB), pentabromophenol
144 (PBP), pentabromotoluene (PBT), tetrabromobisphenol S bismethyl ether (TBBPS-BME), 2,4,6-tribromophenyl
145 allyl ether (TBP-AE), di(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), tris(2,3-dibromopropyl)isocyanurate
146 (TDBP-TAZTO), 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ). The nBFRs hexabromobenzene
147 (HBB) and decabromodiphenyl ethane (DBDPE), three surrogate standards (BDE 79, PCB 30-d₅, PCB 156-d₃),
148 and two internal standards (PCB 116-d₅ and ¹³C₆-hexachlorobenzene) were obtained from CIL Cluzeau
149 (Courbevoie, France). Tetrabromobisphenol A (TBBPA), 2,4-dibromophenol (2,4-DBP), 2,4,6-tribromophenol
150 (2,4,6-TBP), 2,3,4,5,6-pentabromoethylbenzene (PBEB), tetrabromobisphenol A bis(dibromopropyl ether)
151 (TBBPA-BDBPE), a mixture of the seven indicator PCB congeners (PCB 28, 52, 101, 118, 138, 153 and 180),
152 and a certified standard for short-chained chlorinated paraffins (SCCPs ; C₁₀₋₁₃, 63 % of chlorine by weight) were
153 purchased from LGC Standards (Dr. Ehrenstorfer, Molsheim, France). For the extraction and purification steps,
154 copper powder (< 63 μm, EMSURE®) and silica gel cartridges (SPE Supelclean™ LC-Si, 1 g, 6 mL) were
155 furnished by Sigma-Aldrich (Lyon, France). Finally, dichloromethane (DCM), methanol (MeOH) and n-hexane
156 (HEX) of HPLC grade were purchased from Sigma-Aldrich (Lyon, France).

157 I.3. Study area

158 The French Mediterranean coast can be very anthropized and industrialized at some points, like in Marseille (the
159 second biggest city in France) and could thus be burdened by legacy and emerging contaminants. Given the very
160 few data available along the Mediterranean coast, particularly in France, ten suspended matter (SM) samples were
161 collected in 2018 from SM traps installed along a *Posidonia oceanica* meadows surveillance network that was
162 established along the French Mediterranean coast (**Fig 1**).

163 The selected sampling sites cover various types and levels of anthropogenic activity. The site located in the Gulf
164 of Fos (FOS) is impacted by commercial activities, ore and oil terminals, various industrial activities and is subject
165 to a fraction of sedimentary deposits from the Rhône River. At the north of the Marseille Bay, Estaque and Niolon
166 (EST and NIO, respectively) were chosen as they are potentially impacted by commercial harbor and urban
167 activities to which superimposed microplastics and ionic pollution from the coastal stream Aygalade (Gérigny et
168 al., 2022; Fanton et al., 2023). At the south of the Marseille Bay, Samena (SAM), Maire (MAI) and Plateau des
169 Chèvres (CHE) were chosen as they are under the influence of urbanization, pollution from the coastal stream
170 Huveaune and from the wastewater from nearly 1.9 million population equivalent of the Cortiou outfall (Castro-

171 Jiménez et al., 2021; Schmidt et al., 2021). In the semi-closed Bay of Toulon, the sites of Saint-Mandrier North
172 and Headland (SMN and SMH), were chosen because they undergo important urban and harbor pressure. To
173 contrast with strong anthropization conditions, the site of Veyron (VEY) was chosen for its offshore location in
174 the Marseille Bay (about 14 km) and the site of Le Pradet (PRA) for its distant location from Toulon Harbor (about
175 7 km).

176 I.4. Sample preparation

177 I.4.1. Sampling and pre-treatment

178 The suspended matter was sampled with home-made passive collectors shown in Online Resource-Figure S1. After
179 recovering, the samples were freeze-dried and sieved under 500 μm , except for Estaque and Maire samples, which
180 were sieved at 250 μm , as described in Online Resource-Table S1, together with the collecting periods ranging
181 from two to five months to integrate the input of a season. The dried and sieved samples were stored at room
182 temperature until their extraction.

183 I.4.2. Extraction

184 The dried suspended matter was extracted by pressurized liquid extraction with an automated Dionex ASE 200
185 system (Thermo Scientific™ Dionex™, Sunnyvale, USA) with a mixture of HEX:DCM (1:1, v/v). Three
186 extraction cycles were realized at 100°C, 100 bars, for 7 min in static mode. Because of the small quantities of
187 suspended matter recovered, the sample mass used for analysis depended on the dry mass available (0.5 g d.w. to
188 10 g d.w.). The cell sizes (5 mL, 11 mL, 22 mL, 33 mL) were adjusted depending on the sample mass. A glass
189 fiber filter was disposed at the bottom of the cells, which were then filled with the sample mixed with pyrolyzed
190 Fontainebleau sand and activated copper. Copper powder was activated by acidification with hydrochloric acid
191 (3M) followed by rinses with ultrapure water, MeOH and DCM. Each cell was then spiked with the surrogate
192 standards (25 ng of BDE 79 and 189 and 50 ng of PCB 30-d₅, PCB 156-d₃). The extracts were then concentrated
193 near dryness under a gentle pressurized air flow and reconstituted in 1 mL of n-hexane before the clean-up.

194 I.4.3. Clean-up

195 Solid-phase extraction on silica gel cartridges was applied to clean up the extracts. The cartridges were first
196 conditioned with 6 mL DCM, 6 mL HEX:DCM (1:1, v/v) and 6 mL HEX. After that, the 1 mL extract was loaded.
197 The cartridges were then eluted with 6 mL HEX (F1) and 6 mL HEX:DCM (1:1, v/v ; F2). Both fractions were
198 collected in separate vessels, then concentrated and reconstituted in 200 μL of n-hexane, and 20 ng of the internal

199 standards were added (BDE 140, PCB 116-d₅, ¹³C₆-hexachlorobenzene). After the analysis of PCBs (F1) and CPs
200 (F2), both fractions were combined for the analysis of PBDEs and nBFRs.

201 I.5. Instrumental analysis

202 PBDEs and nBFRs were analyzed using gas chromatography in combination with electron capture negative ion
203 mass spectrometry (GC/ECNI-MS), with GC Clarus 600 AutoSystems XL coupled to MS Clarus 600C
204 (PerkinElmer, Waltham, USA). GC separation was performed on an RTX-1614 column (15 m x 0.25 mm i.d. x
205 0.10 µm film thickness; Restek, France) after pulsed splitless injection (1 µL). The temperature of the injector,
206 transfer line and source were set at 260°C, 280°C and 250°C, respectively. The oven temperature was programmed
207 to start at 70°C (hold 4 minutes), raised at 10°C/min until 220°C (hold 6 minutes), increased at 5°C/min until
208 230°C and then at 10°C/min until the final temperature of 315°C (hold 5 minutes). The acquisition was performed
209 in the single ion monitoring mode (SIM). All the compounds were monitored with ion fragments m/z 79 and 81
210 except for PBP (m/z = 406/408), PBB-Acr (m/z = 71), DBHCTD (m/z = 35/37) and BDE 209 (m/z = 487/489).

211 The analysis of PCBs and CPs was performed in two separate runs using a gas chromatography-tandem mass
212 spectrometry system with electron ionization (GC/EI-MS/MS). The analysis conditions were adapted from
213 (Godéré et al., 2022), as detailed in Online Resource-Table S2 and Table S3.

214 I.6. Quality assurance / Quality control

215 A procedural blank was performed using Fontainebleau sand. Only DBE-DBCH was detected in the blank and the
216 concentration of this compound was thus subtracted from the environmental samples. The mean recoveries of
217 surrogates in environmental samples were 85% ± 31% (BDE 79), 75% ± 12% (BDE 189), 46% ± 6% (PCB 30-d₅)
218 and 93 ± 18% (PCB 156-d₃). Limits of detection (LODs) and limits of quantification (LOQs) were calculated for
219 each compound using a signal-to-noise ratio (S/N) of 3 and 10, respectively. LODs ranged from 0.01 to
220 1.82 ng.g⁻¹ d.w. for nBFRs and from 0.01 to 4.85 ng.g⁻¹ d.w. for PBDEs, based on a sample mass of 10 g d.w.
221 LOQs ranged from 0.3 to 6.08 ng.g⁻¹ d.w. for nBFRs and from 0.04 to 16.15 ng.g⁻¹ d.w. for PBDEs, based on a
222 sample mass of 10 g d.w. All LODs and LOQs are given in Online Resource-Table S4. Calibration curves were
223 constructed with 4 to 9 levels and all coefficients of determination R² (linear regression) were above 0.99, except
224 for PBP (R² = 0.986) and BDE 209 (R² = 0.988).

225 I.7. Data analysis and risk assessment

226 I.7.1. Statistical analysis

227 Statistical analysis was performed to determine whether some compounds have the same source of release. Since
228 data were not normally distributed, a non-parametric Spearman rank correlation was applied between the detected
229 compounds in the station network, using JMP 9.0 software (SAS Institute Inc.). The treatment of not detected and
230 not quantified values was as follows: a value of 0.001 ng.g⁻¹ d.w. was assigned to values below LOD and a value
231 of 0.005 ng.g⁻¹ d.w. was assigned to values below LOQ, corresponding respectively to the lowest LOD and LOQ
232 divided by ten. Significant correlations were displayed for p-values below 0.05.

233 I.7.2. Risk assessment

234 Despite the lack of methods for suspended matter, the risk assessment study was performed using sediments risk
235 assessment methods since suspended matter is made of settleable particles. When environmental quality standards
236 were available, these values were applied to assess the environmental risks caused by the studied halogenated
237 flame retardants. The OSPAR commission established Background Assessment Concentrations (BAC), and
238 Environmental Assessment Concentrations (EAC) for PCBs in sediments and biota. Concentrations below BACs
239 indicate that the contamination can be considered as near background, which is estimated as the concentration
240 occurring before industrial developments, or at remote sites, or close to zero for man-made substances. EACs are
241 estimated thresholds of contamination below which even sensitive marine species should not suffer from chronic
242 effects (OSPAR Commission, 2009). Values of BACs and EACs for PCBs in sediments are given in Online
243 Resource-Table S5. For CPs, the Canadian government states Federal Environmental Quality Guidelines (FEQGs)
244 in sediments based on the toxicity of the targeted molecules. The FEQGs in sediments were set at 1.8 mg.kg⁻¹ d.w.
245 for SCCPs and 5.4 mg.kg⁻¹ d.w. for MCCPs, with values normalized to 1% TOC (Canadian Environmental
246 Protection Act, 1999, 2016). FEQGs for PBDEs in sediments were also determined and are displayed in Online
247 Resource-Table S6 (Canadian Environmental Protection Act, 1999, 2013). However, such data is not yet available
248 in the literature for emerging compounds like nBFRs. For such compounds, risk quotients (RQ) are commonly
249 calculated in the literature, based on Equation 1, where MEC refers to the measured environmental concentration
250 and PNEC to the predicted no effect concentration (Cristale et al., 2013). The value of RQ indicates the level of
251 environmental risk, with $RQ < 0.01$ for very low risk, $0.01 \leq RQ < 0.1$ for low risk, $0.1 \leq RQ < 1$ for medium risk,
252 and $RQ \geq 1$ for high risk (Lin et al., 2018).

$$253 \quad RQ = \frac{MEC}{PNEC} \quad (\text{Equation 1})$$

254 Here, the MEC corresponds to the sample contamination, while the PNEC values are more often available in water
255 ($PNEC_{water}$) rather than in sediments ($PNEC_{sediments}$). A first approach is to determine the $PNEC_{sediments}$ from the
256 predicted no effect concentration in water ($PNEC_{water}$) thanks to the equilibrium partitioning method (EPM)
257 developed by the European Chemicals Bureau, 2003 that can be simplified as written in Equation 2 when using
258 common values for the parameters of the EPM (European Chemicals Bureau, 2003; ChemSafetyPRO, 2016; Zind,
259 2020).

$$260 \quad PNEC_{sediments} = (0,783 + 0,0217 * K_{OC}) * PNEC_{water} \quad (Equation 2)$$

261 A second approach consists in replacing the MEC in Equation 1 by the concentration in pore water (C_{PW}), to
262 compare it to $PNEC_{water}$. Di Toro et al., 1991 proposed a relationship between C_{PW} and the concentration found in
263 sediments (C_S), that depends on the fraction of organic carbon (f_{OC}) and the partition coefficient for sediment
264 organic carbon (K_{OC}), as given in Equation 3.

$$265 \quad C_{PW} = \frac{C_S}{f_{OC} * K_{OC}} \quad (Equation 3)$$

266 Both methods require nevertheless a value for $PNEC_{water}$ that can be derived from known ecotoxicological
267 parameters such as lethal or effect concentrations (LC_{50} and EC_{50} , respectively), by dividing them with a security
268 factor (f) of 1,000 as shown in Equation 4 (Rodil et al., 2019).

$$269 \quad PNEC_{water} = LC_{50} \text{ or } EC_{50} / f \quad (Equation 4)$$

270 The main challenge to assess the risk of these emerging pollutants is the dramatic lack of related toxicity data. The
271 values of LC_{50} or EC_{50} were found in the literature for only three compounds out of the 12 nBFRs quantified in
272 our samples. The risk assessment was established with both methods for these three molecules, namely 2,4,6-TBP,
273 DBDPE and HBB, and the highest RQ value was chosen, considering the worst-case scenario. Among the nine
274 remaining nBFRs, $PNEC_{water}$ could be predicted by the ECOSAR only for 2,4-DBP since its values of K_{OW} and
275 water solubility were included in the range of validity of the model, while the other compounds were too
276 hydrophobic.

277 II. Results and discussion

278 II.1. Selection of relevant nBFRs to analyze in Europe

279 II.1.1. Identification of molecules used as BFRs

280 The US EPA database for flame retardants contains regulated BFRs, such as PBDEs, PBBs, HBCDD isomers, that
281 were discarded from the present study, since their use is now banned or highly restricted. Only TBBPA, which is
282 still widely used nowadays was processed with the other nBFRs more recently launched. The 139 organic nBFRs
283 extracted from this database, together with nine additional compounds identified as nBFRs in the literature
284 (Bergman et al., 2012), were compiled into a complete list of 148 nBFRs of emerging concern that is given in
285 Online Resource-Table S7. Out of this list, 114 were registered by the ECHA and were thus further ranked
286 according to their production, occurrence and ecotoxicological risk.

287 II.1.2. Production or import inside the European Economic Area

288 The 114 ECHA nBFRs were first sorted according to their annual quantity of production or import inside the
289 European Economic Area (EEA). Noticeably, five compounds, namely DBDPE, TBBPA, TBBPA-BDBPE,
290 1,2-dibromoethane (CAS N°106-93-4) and benzene, ethenyl-, ar-bromo derivatives. (CAS N°125904-11-2) are
291 produced or imported over 1,000 tons per year (t/y). Nevertheless, most of the compounds are produced or
292 imported in relatively small quantities, below 1 t/y for 27% of the nBFRs and between 1 and 10 t/y for 59% of the
293 nBFRs (**Fig 2**). One compound was even classified as confidential without further information (CAS
294 N°109678-33-3).

295 II.1.3. Occurrence through literature review

296 A literature review of 125 papers published between 2012 and 2022 was performed. All of them aimed at looking
297 for various nBFRs in biotic or non-biotic matrices from aquatic environments all around the world. **Fig 3** presents
298 the number of studies in which each compound was analyzed and detected in. It enables to highlight the most
299 frequently targeted and detected nBFRs in environmental studies. It reveals that most studies focus on the same
300 contaminants, with seven nBFRs studied in more than half of the articles, while many others were rarely or even
301 never analyzed. However, it reveals that some of these orphan compounds can be detected in aquatic environments,
302 whereas they are rarely studied.

303 II.1.4. Ecotoxicology

304 Only few studies have been carried out to assess the ecotoxicity of nBFRs, but the available data are not easy to
305 compare since parameters and organisms can noticeably vary between studies. To overcome these discrepancies,
306 predictive models like ECOSAR can be applied, since they enable to calculate values of toxicity based on the
307 chemical structure of the targeted molecules. The acute toxicity (LC_{50} in fish after 96 hours) of all nBFRs was then
308 predicted by ECOSAR (**Fig 4**). Four molecules could not be found by the predictive model (CAS N°58495-09-3,
309 59789-51-4, 75795-16-3 and 168434-45-5). For nBFRs with several chemical functions, the model predicted
310 several concentrations for LC_{50} , and the lowest value has been selected in this study. To select thresholds of toxicity
311 for relevance ranking, we first looked on ECOSAR for the LC_{50} (fish, 96 hours) of the 8 regulated PBDE
312 congeners, which ranged from $0.0007 \mu\text{g.L}^{-1}$ (BDE 209) to $110 \mu\text{g.L}^{-1}$ (BDE 28). Considering that the molecules
313 replacing the regulated ones should be less toxic, the threshold was set at $110 \mu\text{g.L}^{-1}$. A security factor of 10 was
314 applied as it is classically done in ecological or health risk assessment, thus extending the present study to
315 molecules with $110 \mu\text{g.L}^{-1} < LC_{50} < 1,100 \mu\text{g.L}^{-1}$. Compounds with $LC_{50} < 1 \mu\text{g.L}^{-1}$ were considered as especially
316 relevant.

317 However, predictive models can only be approximative, and have some limits. The ECOSAR model was created
318 for molecules with a molecular weight below 1,000, while some nBFRs are heavier. Also, it is based on the
319 chemical functions of the compounds, so it gives several values for toxicity if the molecule has several chemical
320 functions. An experimental parameter was thus additionally chosen to avoid these calculation limits. This
321 additional ecotoxicological parameter was the trophic magnification factor (TMF), which was previously
322 determined for 14 nBFRs registered by the ECHA in a zooplankton – invertebrate – fish – bird food chain (Liu et
323 al., 2021). A TMF higher than 1 means that the contaminant will biomagnify in the food chain, while a TMF lower
324 than 1 shows trophic dilution.

325 II.1.5. Relevance ranking

326 For the production criterion, 15 nBFRs were given the score of 1 (≥ 10 to < 100 t/y, one molecule), 2 (≥ 100 to
327 $< 1,000$ t/y, nine molecules), 3 ($\geq 1,000$ to $< 10,000$ t/y, three molecules) or 4 ($\geq 10,000$ to $< 100,000$ t/y, two
328 molecules). Three additional compounds were given a score between 1 and 4 despite their current low production
329 inside EEA. Indeed, data given in 2021 by the ECHA for the same molecules was higher than nowadays and due
330 to the persistence of BFRs in the environment, we decided to take the older values into account. Thus, TTBP-TAZ
331 (CAS N°25713-60-4) and DBPT (CAS N°3296-90-0) were scored 2 (production ≥ 1 to < 10 t/y in 2023, but ≥ 100

332 to < 1000 t/y in 2021) and TTBNPP (CAS N°19186-97-1) was scored 1 (production < 1 t/y in 2023, but ≥ 10 to
333 < 100 t/y in 2021). Finally, the production/import scores ranged from 0 to 4.

334 For the occurrence criterion, the 89 nBFRs analyzed in only five papers or less were all given the score of 1, as it
335 was judged that data are dramatically insufficient for these compounds in the environment. The compounds
336 analyzed in more than six papers were ranked according to the ratio between the number of studies in which it was
337 detected divided by the number of studies in which a compound was targeted. According to the more or less
338 confirmed presence of a given molecule in the aquatic environment, a score of 0 to 3 was given. A ratio lower than
339 25% led to the score of 0, because of a lack of relevance in the environment. For a ratio ≥ 0.25 and < 0.5, a score
340 of 2 was given (six nBFRs). For a ratio ≥ 0.5, a score of 3 was given (18 nBFRs). Only one compound, namely
341 PBBB, was scored 0.

342 For the ecotoxicological criterion, depending on their LC_{50} , nBFRs were assigned the score of 3 ($LC_{50} < 1 \mu\text{g.L}^{-1}$),
343 2 ($1 \leq LC_{50} < 110 \mu\text{g.L}^{-1}$), 1 ($110 \leq LC_{50} < 1,100 \mu\text{g.L}^{-1}$) or 0 ($LC_{50} \geq 1,100 \mu\text{g.L}^{-1}$). An extra point was added to
344 the previous score for nBFRs with a reported TMF > 1 or subtracted for nBFRs with a TMF < 1. Hence, the
345 ecotoxicological scores ranged from -1 to 4.

346 All scores were summed up for each compound to get a final score ranging theoretically between -1 and 11. All
347 details and scores are given in Online Resource-Table S7.

348 The scores obtained ranged from 1 to 9, and nBFRs with a score of 5 or higher were considered as relevant to
349 analyze in European aquatic environments, as shown in **Fig 5**. The highest ranked molecules were DBDPE (CAS
350 N°84852-53-9), TBBPA (CAS N°79-94-7) and TBBPA-BDBPE (CAS N°21850-44-2), with a score of 9.
351 BEH-TEBP (CAS N°26040-51-7) was scored 8. BTBPE (CAS N°37853-59-1), TDBP-TAZTO (CAS
352 N°52434-90-9) and PBB-Acr (CAS N°59447-55-1) were scored 7. Then nine compounds were scored 6, including
353 four bromobenzenes: PBBz (CAS N°608-90-2), PBEB (CAS N°85-22-3), HBB (CAS N°87-82-1) and PBT (CAS
354 N°87-83-2), as well as DBHCTD (CAS N°51936-55-1), EHTEBPI (CAS N°32588-76-4), EH-TBB (CAS
355 N°183658-27-7), TTBP-TAZ (CAS N°25713-60-4) and TBP-DBPE (CAS N°35109-60-5). Finally, five
356 compounds were scored 5, namely 2,4,6-TBP (CAS N°118-79-6), TBBPA-BGE (CAS N°3072-84-2),
357 DBE-DBCH (CAS N°3322-93-8), HCTBPH (CAS N°34571-16-9) and TBCT (CAS N°39569-21-6).

358 II.2. Occurrence of legacy and novel brominated flame retardants in suspended 359 matter from the French Eastern-Mediterranean coastline

360 Among the 21 previously selected nBFRs, three were both brominated and chlorinated (DBHCTD, HCTBPH and
361 TBCT), thus in this preliminary study, we decided to keep only one of them (DBHCTD). Three other nBFRs were
362 discarded, namely TBP-DBPE because it was not commercially available, and EHTEBPI and TBBPA-BGE
363 because they cannot be analyzed by GC/ECNI-MS. The list of target analytes was thus gathering 16 nBFRs. In
364 addition, six nBFRs with chemical structures close to those of the already targeted nBFRs were also added, more
365 especially four bromophenols or derivatives (2,4-DBP, PBP, TBBPS-BME and TBP-AE) and two bromobenzenes
366 (TBX, PBBB). The final list of the 22 compounds analyzed in coastal suspended matter samples and their
367 physicochemical properties are given in Online Resource-Table S8.

368 Among the 22 analyzed nBFRs, three have been detected and quantified in all suspended matter samples, namely
369 2,4-DBP, 2,4,6-TBP and DBE-DBCH. Six other compounds (PBB-Acr, DBDPE, PBBB, BTBPE, HBB, TBP-AE)
370 have been detected and quantified in at least one sample. Finally, TBBPA-BDBPE, PBT and PBEB have been
371 detected in four, three and one samples respectively, but were below LOQs. Mean, lower and higher concentrations
372 obtained, as well as detection frequencies for the 12 nBFRs detected in this study are given in **Tab 1**.

373 The sum of quantified nBFRs ranged from 0.4 ng.g⁻¹ d.w. (SAM) to 18.5 ng.g⁻¹ d.w. (SMN) (**Fig 6a**). The most
374 contaminated sites were SMN, SMH, MAI and EST, off the coast of Marseille and Toulon, which house dense
375 population, urban and port activities and are commonly considered as anthropized areas. All concentrations are
376 detailed in Online Resource-Table S9. Eight regulated PBDE congeners were analyzed as well. In most sampling
377 sites, the sum concentrations of nBFRs were higher than that of PBDEs, except in FOS, MAI and PRA. Moreover,
378 lighter PBDE congeners (i.e., BDE 47 and BDE 100) were mainly found, except in FOS and MAI, where
379 decabromodiphenyl ether (BDE 209) was predominant, and the sum of PBDE concentrations exceeds the ones of
380 nBFRs.

381 Only few studies deal with nBFRs in sediments or suspended matters of the Mediterranean Sea or similar
382 environments. The contamination levels measured in these studies were compared with the present results in
383 **Tab 2**. DBDPE, HBB and PBEB were the most often targeted compounds in previous works. Most of the time,
384 these three compounds were not detected or at low concentrations, which is consistent with our results in French
385 coastal Mediterranean SM. However, in the Rhône River samples, higher concentrations of these three compounds
386 were reached, as well as for PBBz, PBT and TBBPA, which were not detected or could not be quantified in our

387 study. This could be explained by the dilution of contaminants coming from this river into the marine environment,
388 or by the fact that most studies have focused on sediments, which accumulate pollution over a longer period than
389 SM.

390 Eleven of the analyzed compounds have not been previously reported in environmental studies dealing with nBFRs
391 in sediments or SM from this geographic area. Among them, DBE-DBCH was detected in all of our samples,
392 whereas it has not been detected previously in sediments from other parts of Europe, despite its screening in river
393 sediments from the United Kingdom (UK) (Ganci et al., 2019) and in river and marine sediments from Germany
394 (Sühring et al., 2016). In China however, its concentrations could reach 109.0 ng.g⁻¹ d.w. (Zhu et al., 2018). The
395 study of Sühring et al., (2016) in Germany also targeted TBP-AE, PBB-Acr, 2,4,6-TBP, PBBBB and
396 TDBP-TAZTO, but none were detected. On the contrary, TBP-AE, PBB-Acr, 2,4,6-TBP, PBBBB were detected in
397 our samples, especially 2,4,6-TBP present in all the sites. In the River Thames, the UK, 2,4,6-TBP ranged from
398 not detected (n.d.) to 0.4 ng.g⁻¹ d.w. (Ganci et al., 2019) and in the South China Sea it reached 22.33 ng.g⁻¹ d.w.
399 (Feng et al., 2021). The same study in the South China Sea also reported concentrations ranging from n.d. to
400 0.22 ng.g⁻¹ d.w. and from not detected to 1.52 ng.g⁻¹ d.w. for TDBP-TAZTO and TTBP-TAZ respectively,
401 whereas neither molecule was detected in the present study. But our LODs (for 10 g d.w. of sample) were equal
402 to 0.37 and 1.05 ng.g⁻¹ d.w. for TDBP-TAZTO and TTBP-TAZ respectively, which might be too high to detect
403 such low concentrations.

404 II.3. Discussion and comparison with regulated halogenated flame retardants

405 In addition to legacy and nBFRs, two families of regulated chlorinated flame retardants, namely
406 polychlorobiphenyls and short and medium chain chlorinated paraffins were analyzed in the present work. The
407 seven regulated PCBs were detected in all samples, with a total concentration ranging from 1.0 to 26.8 ng.g⁻¹ d.w.,
408 dominated by highly chlorinated congeners. The detection frequency for chlorinated paraffins was 70%, with
409 concentrations ranging from 42 to 323 ng.g⁻¹ d.w. Several nBFRs were detected in the ten samples, with 12
410 compounds detected at least once, and nine compounds quantified in one sample or more, while four congeners of
411 PBDEs (BDE 28, 47, 100, 209) were detected and quantified in nine samples. All concentrations are given in
412 Online Resource-Table S9.

413 CPs concentrations, representing the sum of the concentrations of thousand congeners, were higher than any other
414 halogenated flame retardant and had to be represented ten times lower in **Fig 7**. On the other hand, PCBs, PBDEs
415 and nBFRs were one decade lower and covered similar concentration ranges. The boxplot (**Fig 7**) exhibits skewed

416 distributions, mainly negative except for CPs. However, the contamination pattern of PCBs was homogeneous
417 between the different sites except in SAM, with the predominance of penta- and hexa-chlorinated congeners, while
418 PBDEs and nBFRs profiles were more heterogeneous depending on the site (**Fig 6b and c**). It could be explained
419 by more local and recent inputs of these contaminants, which are currently used or were regulated more recently
420 (i.e., BDE 209). Among the nBFRs, the bromophenols 2,4-DBP and 2,4,6-TBP were predominant in nearly all
421 samples and represented 42% to 90% of the total load of nBFRs. Their occurrences are of interest and their sources
422 remain somehow unclear. Besides their use as flame retardants, bromophenols can be formed through the
423 photodegradation of other BFRs like PBDEs or BTBPE (Bendig & Vetter, 2013; Zhang et al., 2016). They were
424 also reported as disinfection by-products (Dron et al., 2022), and they can occur naturally (Hassenklöver &
425 Bickmeyer, 2006).

426 Some specific areas in the Mediterranean Sea are especially contaminated with PCBs, like in Tunisia where a
427 study from 2023 reported concentrations in sediments ranging from 28.6 to 230.6 ng.g⁻¹ d.w. for the seven
428 indicator PCBs in Bizerte Lagoon (Barhoumi et al., 2023). However, our results are consistent with most of the
429 studies performed on Mediterranean sediments. In 2013, Salvadó et al., (2013) found concentrations (Σ_7 PCBs)
430 ranging from 1.3 to 38 ng.g⁻¹ d.w. in the Gulf of Lion. In the Spanish Mediterranean Sea, a total concentration of
431 1.8 ng.g⁻¹ d.w. for the seven congeners was reported in 2017 (Robinson et al., 2017), and in Egypt, the sum of the
432 same contaminants ranged from 0.18 to 35.04 ng.g⁻¹ d.w. in 2016 (El Nemr & El-Sadaawy, 2016).

433 Recent data concerning the contamination levels of the Mediterranean Sea by PBDEs and CPs are scarce. In
434 Tunisia in 2019, only BDE 209 was detected (n.d. to 6.86 ng.g⁻¹ d.w.) (Mekni et al., 2019), while in the Rhône
435 River in France, the sum of the eight regulated congeners ranged from 7.00 to 131.99 ng.g⁻¹ d.w. in sediment cores,
436 which covered time-periods between 1968 and 2020 (Vauclin et al., 2021). In the Persian Gulf, Iran, CPs were
437 quantified both in suspended matter (17.8 to 71.9 ng.g⁻¹ d.w.) and sediments (22.7 to 71.1 ng.g⁻¹ d.w.) (Ranjbar
438 Jafarabadi et al., 2021). The concentrations detected in Mediterranean suspended matter were closer to
439 concentrations observed in sediments sampled in the Bohai Sea in 2017 where short-chain CPs ranged from 64.14
440 to 452.9 ng.g⁻¹ d.w. (Zhao et al., 2019).

441 A Spearman correlation table given in Online Resource-Table S10 shows very strong correlations between all PCB
442 congeners. At first glance, this could be interpreted as a common source for all these contaminants. However, it
443 could also mean that concentrations have been homogenized over the years, since these pollutants have been
444 regulated for decades, creating a contamination continuum and making source identification nearly impossible.

445 CPs were positively correlated with the most chlorinated PCBs (congeners 118, 138, 153), probably due to similar
446 physicochemical properties. 2,4,6-TBP was strongly correlated with DBE-DBCH ($p = 0.8788$) and PBB-Acr
447 ($p = 0.8909$). These compounds thus should have the same sources. These sources must be different from those of
448 PBT, BDE 28 and BDE 209, since these three compounds are strongly correlated together, but negatively
449 correlated with the first group of nBFRs (2,4,6-TBP, DBE-DBCH, PBB-Acr). Also, TBBPA-BDBPE was
450 correlated with DBDPE ($p = 0.825$) and 2,4-DBP ($p = 0.6396$). Finally, PCB 28 was correlated with one nBFR,
451 namely PBB-Acr ($p = 0.6848$). However, it can be challenging to explain these correlations with the data available
452 about BFRs uses (Covaci et al., 2011), and further studies would be necessary to elucidate the sources of nBFRs
453 in the environment.

454 II.4. Risk assessment

455 Most PCBs were above the BACs determined by the OSPAR commission, except for PCB 28 in two samples
456 (SAM and SMH) and PCB 52 in three samples (VEY, SMH, PRA). Tetra- to hepta-chlorinated biphenyls exceeded
457 the BACs up to 35 times, except in one sample (SAM) where concentrations could be considered close to zero.
458 Even though they were mostly above background levels, most PCB congeners did not represent an environmental
459 risk since the observed concentrations were lower than the EACs. The only exception was for the dioxin-like
460 PCB 118, that showed concentrations up to five times higher than its EAC in six samples, which can raise concern
461 because its toxicity mechanisms are similar to those of dioxins (Fiolet et al., 2022). When observed above LOQs,
462 CPs were at least ten times below the FEQGs set by the Canadian government after being normalized to 1% TOC.
463 PBDEs were also unlikely to represent an environmental risk in this study. Indeed, only BDE 99 at one site (CHE)
464 was higher than its FEQGs of $0.4 \text{ ng}\cdot\text{g}^{-1} \text{ d.w.}$, with a concentration of $0.68 \text{ ng}\cdot\text{g}^{-1} \text{ d.w.}$ when normalized to 1%
465 TOC. Risk quotients were calculated both with the EPM method (calculation of $\text{PNEC}_{\text{sediments}}$) and with the C_{PW}
466 method (calculation of C_{PW} according to Di Toro et al., 1991). Higher risks were observed when using the first
467 method. DBDPE and HBB, that could be quantified in Maïre (MAI) sample only showed a very low environmental
468 risk ($\text{RQ} = 0.002$ and $\text{RQ} = 0.00001$ respectively). 2,4-DBP and 2,4,6-TBP showed very low to medium
469 environmental risk, as represented by the RQ given in Online Resource-Table S11. However, 2,4,6-TBP presented
470 a high risk in EST ($\text{RQ} = 1.2$) and in SMH ($\text{RQ} = 1.6$). Nevertheless, for these increasingly diverse mixtures of
471 compounds, produced and used in smaller tonnage than other historical compounds, determining a risk on the basis
472 of individual molecules seems unsuitable. It is necessary to be able to sum up these risks or consider the effects of
473 mixtures.

474 Conclusion

475 This study enabled to point out 21 nBFRs for their relevance to monitor in European aquatic environments, based
476 on a ranking of 114 nBFRs according to criteria of production or import in Europe, occurrence in water
477 environments worldwide and ecotoxicology. Out of the 21, 16 nBFRs together with six additional nBFRs were
478 analyzed by GC/ECNI-MS in suspended matter from ten sampling points covering various types and levels of
479 anthropic activities along the French Mediterranean coast. To our knowledge, there was no previous study about
480 the contamination of suspended matter or sediments from the French Mediterranean Sea by all these nBFRs.

481 Ten compounds were not detected in any sample, namely TBX, PBBz, PBP, DBHCTD, EH-TBB, TBBPS-BME,
482 TDBP-TAZTO, BEH-TEBP, TTBP-TAZ and TBBPA. Three compounds were detected but not quantified, namely
483 TBBPA-BDBPE (four samples), PBT (three samples) and PBEB (one sample). Mean concentrations for the nine
484 quantified nBFRs (2,4-DBP, 2,4,6-TBP, TBP-AE, DBE-DBCH, HBB, PBBBB, PBB-Acr, BTBPE, DBDPE) ranged
485 between 0.1 (HBB) and 12.5 (2,4-DBP) ng.g⁻¹ d.w. Three nBFRs, i.e., 2,4-DBP, 2,4,6-TBP and DBE-DBCH,
486 observed in all the samples analyzed. Other studies in Europe reveal that nBFRs are rarely detected, or at low
487 levels, which is consistent with our results. Other regulated halogenated flame retardants were also analyzed in the
488 present work. CPs, representing a group of thousands of congeners, were detected in seven samples and had
489 concentrations about ten times higher than the other groups of contaminants. PCBs, although banned for decades,
490 were still detected in all samples, with similar profiles. PBDEs were detected in nine samples, with different
491 contributions of the eight congeners according to the sample. PBDEs (sum of the eight congeners), nBFRs (sum
492 of the 22 molecules) and PCBs (sum of the seven indicator congeners) had similar concentration ranges.

493 As future work, the two chlorinated and brominated compounds ranked in our list of relevant nBFRs but not
494 analyzed in this study (HCTBPH and TBCT) should be targeted as well, especially since DBHCTD analyzed in
495 the present work was successfully separated on the GC/ECNI-MS method developed. The further analysis of
496 sediments from the same study area would be interesting since this compartment act as a sink for hydrophobic
497 contaminants. Moreover, with a higher sample mass available, LODs and LOQs could be driven down, which is
498 necessary for such ultratraces of contamination.

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717 Supplementary Information

718 Supplementary material is provided in a supplementary file available online.

719 Author Contributions

720 Camille Rigal, Pierre Doumenq and Laure Malleret contributed to the study conception and design. The study area
721 was instrumented and sampled by Pascal Mirleau. Formal analysis and investigation were carried out by Camille
722 Rigal, with the assistance of Laurence Asia and Stéphanie Lebarillier, and under the supervision of Laure Malleret
723 and Pierre Doumenq. Laure Malleret and Pascal Mirleau contributed to funding acquisition and administration of
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725 Malleret. All authors have read, commented and approved the final version of the manuscript.

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732 **Data availability:** All data generated and analyzed during our study are included in this article.

733 Declarations

734 Ethical approval: The authors declare research did not involve human participants and/or animals. The submitted
735 manuscript complies with all the ethical requirements of the journal following the rules of good scientific practice:
736 No part of this paper has been previously published or is being considered for publication elsewhere. We report
737 results from original completed research. No data, text, or theories by others are presented as if they were the
738 author's own ("plagiarism"). We provide referenced information from studies from the authors' own works as
739 background to the study carried out.

740 Consent to participate: All authors agreed with the content that all gave explicit consent to participate and that they
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