



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

Camille Rigal<sup>1</sup> · Laurence Asia<sup>1</sup> · Stéphanie Lebarillier<sup>1</sup> · Pierre Doumenq<sup>1</sup> · Pascal Mirleau<sup>2</sup> · Laure Malleret<sup>1</sup>

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## Abstract

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

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

## Introduction

Flame retardants are used to reduce flammability, hence the risks of fire. They are added during the production of many daily items or materials, like electronic devices, construction materials, transport vehicles, or furniture (de Wit 2002; Xiong et al. 2019). Very different compounds can be used as flame retardants, like inorganic or organic molecules, with halogen heteroatoms or not. Among halogenated

compounds, brominated flame retardants (BFRs) and chlorinated flame retardants are the most widely used (European Chemicals Agency 2023).

Since the 1960s, four main groups of BFRs were produced and used in large quantities worldwide, i.e., polybromodiphenyl ethers (PBDEs), polybromobiphenyls (PBBs), hexabromocyclododecane (HBCDD), and tetrabromobisphenol A (TBBPA). Whereas TBBPA corresponds to one organic molecule, PBDEs and PBBs are chemical families grouping 209 theoretical congeners each. PBDEs were widely used as flame retardants and produced as three commercial mixtures (penta-, octa- and deca-BDE). Eight congeners are the major components of these mixtures, namely PBDEs 28, 47, 99, 100, 153, 154, 183, and 209. HBCDD was produced in a commercial mixture containing three main isomers ( $\gamma$ , 75–89%;  $\alpha$ , 10–13%;  $\beta$ , 1–12%). In 1989, the global production of BFRs was estimated at almost 106,700 tons (Alaee 2003). In 1992, it had increased

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✉ Laure Malleret  
laure.malleret@univ-amu.fr

<sup>1</sup> Aix Marseille Univ, CNRS, LCE, Marseille, France

<sup>2</sup> Aix Marseille Univ, Avignon Université, CNRS, IRD, IMBE, Marseille, France

to 150,000 tons (de Wit 2002), and it reached 203,740 tons in 2001 (Birnbau & Staskal 2004). The latest data from 2019 estimated a global consumption of BFRs of 406,300 tons per year (European Chemicals Agency 2023).

However, since the beginning of the 2000s, concern was raised about environmental and health risks induced by chemicals, and international regulations were established. Some of these regulations target the above-mentioned BFRs. First, the Stockholm Convention on Persistent Organic Pollutants was signed by 152 countries worldwide in 2001 and enforced in 2004. It identified originally 12 compounds as persistent organic pollutants (POPs), but the list has now been extended to 30 compounds or groups of compounds sorted in three groups: elimination (annex A), restriction (annex B), and unintentional production (annex C) (Stockholm Convention 2017). In the European Economic Area, other regulations were also applied. It is the case of the Restriction of Hazardous Substances (RoHS) in Electrical and Electronic Equipment which has been adopted in 2003 (Directive 2002/95/EC 2002) and amended in 2011 (Directive 2011/65/EU 2011). It lists ten compounds or groups of compounds that must be restricted in electronic and electrical devices. These compounds cannot be present at more than 0.1% by weight of homogeneous material. The Water Framework Directive (WFD), adopted in 2000 (Directive 2000/60/EC 2000), aims to ensure good water quality in Europe and provides a list of 45 priority substances. Their concentrations in aquatic environments (inland surface waters, other surface waters and biota) must remain below environmental quality standards (EQS) given in an amendment from 2013 (Directive 2013/39/EU 2013). In addition, 21 out of the 45 priority substances are considered as dangerous and member states must stop their emissions in aquatic environments.

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

Under pressure of all these new regulations, the massive production and use of a high number of new molecules have emerged, to comply with fire safety standards. Many of them are also brominated organic molecules. Indeed, among halogenated flame retardants, BFRs are considered as the most efficient, followed by the chlorinated ones (European Chemicals Agency 2023). Thus, the three well-known families of BFRs, taken off the market, have been replaced by over a hundred of the so-called novel brominated flame retardants (nBFRs), as classified by the United States Environmental Protection Agency (US EPA). The global production of BFRs therefore kept increasing, reaching 410,000 tons in 2008 (Covaci et al. 2011). The nBFRs of current use, as reported by Bergman et al. (2012), cover a wide range of physicochemical properties, with octanol–water partition coefficients between  $1.04 < \log K_{OW} < 15.11$ , raising questions about their possible presence in different environmental compartments, possible bioaccumulation, and persistence. Some of them have chemical structures very close to legacy BFRs, raising concerns about their likely toxic effect by similar mechanisms and their POP-like properties. However, little is known about their environmental risks (Mahfoudhi et al. 2023). First toxicity studies realized at high concentration showed that nBFRs could cause hormone or endocrine disruption, neurotoxicity, or DNA damage (Xiong et al. 2019). NBFRs enter the environment after atmospheric release mainly from e-waste recycling sites, but also from manufacturing sites, waste incineration plants, and other industrial processes (McGrath et al. 2017; Ameer et al. 2020), as well as from wastewater treatment plants (Covaci et al. 2011). Once released in the environment, nBFRs can undergo bioaccumulation and biomagnification, biodegradation, or photodegradation (Xiong et al. 2019). Moreover, they can also be transported by the atmospheric route over long distances (Xiong et al. 2019) and have therefore been detected in marine benthos from the Arctic (Carlsson et al. 2018) and in the atmosphere from West Antarctica (Hao et al. 2022). Local structures all around the world are presently working to collect data about these new molecules and to regulate them if necessary. In the United States of America, the US EPA develops and enforces national environmental laws and has created a database of all ever-observed flame retardants, including BFRs. In Europe, the ECHA controls chemicals, assesses their risks, and ensures that companies abide by the law. Since 2006, the REACH (Registration, Evaluation, Authorization and restriction of CHemicals) regulation (REACH 2006), administered by the ECHA, aims to register all chemicals produced or imported inside the European Economic Area in quantities above one ton per year.

Facing the large number of newly produced synthetic molecules and the persistence of numerous legacy pollutants in the environment, it becomes over-challenging to monitor

all of them and to properly assess the quality of water bodies, which is one of the final environmental receptacles of all these pollutants. The aim of this work was to identify, among the hundred of nBFRs now in use, the most relevant compounds to search for in the European aquatic environments based on production, occurrence, and toxicity criteria, using data available from the US EPA, the ECHA, and the literature. Out of the 125 papers reviewed for this study, only six evaluated the presence of nBFRs in the Mediterranean Sea (Munsch et al. 2015; Aznar-Alemayn et al. 2018, 2021; Mekni et al. 2019, 2020), and only three of them were dealing with suspended matter or sediments along Tunisian, Spanish, or Italian coastlines (Aznar-Alemayn et al. 2018; Mekni et al. 2019, 2020), highlighting the need for further studies. The French Mediterranean coast was not previously studied. However, in the 1990s, nearly 1/3 of PBDEs used in Europe was produced on the continent, and France was an important producer (World Health Organization & International Programme on Chemical Safety 1994). One of the factories was located near the industrial area of Fos-sur-Mer. Nowadays, little is known about the production of nBFRs in France, but the ECHA assessed the consumption to 28 thousand tons/year in 2019 in Western Europe (European Chemicals Agency 2023). Hence, we carried out a first screening of 16 of the hereby pointed-out nBFRs, combined with six additional bromobenzenes and bromophenols or derivatives, in coastal suspended matter samples from the northeastern Mediterranean Sea, near Marseille, which cumulates urban, industrial, and port activities. As the targeted molecules are mainly hydrophobic and the nBFRs are presently in use, suspended matter was chosen to observe the current input over a known time period that can impact the endemic Mediterranean biodiversity at the sampling sites. Sampling periods lasted about 3 months, to integrate the mean contamination over a given season. The measured concentration levels of nBFRs were finally compared to better documented environmental pollutants, like the eight legacy polybromodiphenyl ethers (PBDEs), as well as other halogenated flame retardants, namely short- and medium-chain chlorinated paraffins (CPs) and the seven indicator polychlorobiphenyls (PCBs) listed by the International Council for the Exploration of the Sea (ICES).

## Materials and methods

### Methodology for relevance ranking of nBFRs in Europe

The complete list of molecules used as brominated flame retardants was elaborated according to the database provided by the US EPA (<https://comptox.epa.gov/dashboard/chemical-lists/FLAMERETARD>) and to the literature (Bergman

et al. 2012). Current use BFRs in Europe, referred below as nBFRs, were ranked according to three criteria. The first criterion considered the use of these nBFRs in Europe, with data available on the ECHA website (<https://echa.europa.eu/fr/home>) for each compound registered under the REACH regulation, including their annual volume of production or import inside the European Economic Area. The second criterion referred to the occurrence of nBFRs in aquatic environments. An exhaustive literature study was performed on Web of Science (WOS) to find articles written in English over the last 10 years (between 2012 and 2022) and dealing with the term “flame retardant\*.” The research was narrowed by selecting four WOS categories, i.e., environmental science, chemistry analytical, chemistry multidisciplinary, and multidisciplinary sciences. As our study focuses on aquatic environments, we selected papers containing at least one of the following keywords: “marine,” “estuary,” “lake,” “river\*,” “aquatic,” “sea\*,” “ocean\*,” “water\*,” “sediment\*,” “suspended matter,” “marine biota,” “fish,” “mollusk\*,” or “passive sampling.” We excluded some research terms to discard toxicity reports and occurrence studies in non-aquatic environments, such as “thyroid,” “milk,” “terrestrial,” “soil\*,” “tree,” “sewage,” “wastewater\*,” “toxic\*,” “serum,” “synth\*,” “in vivo,” and “in vitro.” The 2664 results thus obtained were sorted one by one based on their title and abstract, to finally keep only 125 papers actually analyzing nBFRs in natural aquatic environments. The third criteria aimed at evaluating the ecotoxicological risk of nBFRs. It was assessed with the 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 reporting the trophic magnification of some molecules (Liu et al. 2021).

### Chemicals and materials

The surrogate standard BDE 189, the internal standard BDE 140, and a certified standard mixture of the 8 regulated PBDE congeners (BDE 28, 47, 99, 100, 153, 154, 183, and 209) were purchased from Accustandard (Interchim, Montluçon, France), as well as the 13 following nBFRs: di(2-ethylhexyl)tetrabromophthalate (EH-TBB), hexachlorocyclopentadienyl-dibromocyclooctane (DBHCTD), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBE-DBCH), pentabromobenzylacrylate (PBB-Acr), pentabromobenzylbromide (PBBB), pentabromophenol (PBP), pentabromotoluene (PBT), tetrabromobisphenol S bismethyl ether (TBBPS-BME), 2,4,6-tribromophenyl allyl ether (TBP-AE), di(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), tris(2,3-dibromopropyl)isocyanurate (TDBP-TAZTO), and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ). The nBFRs

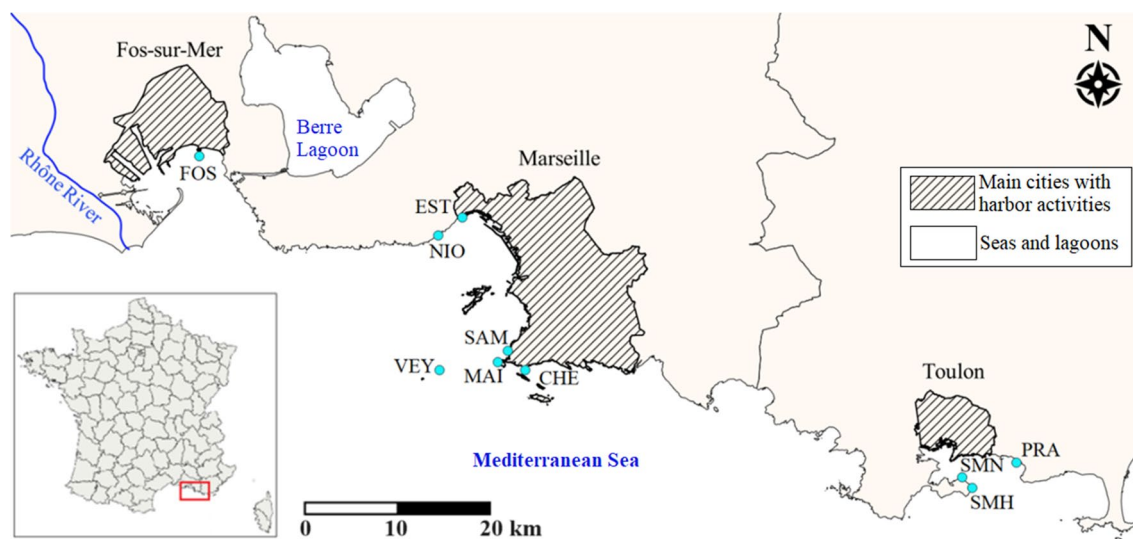
hexabromobenzene (HBB) and decabromodiphenyl ethane (DBDPE), three surrogate standards (BDE 79, PCB 30-d<sub>5</sub>, PCB 156-d<sub>3</sub>), and two internal standards (PCB 116-d<sub>5</sub> and <sup>13</sup>C<sub>6</sub>-hexachlorobenzene) were obtained from CIL Cluzeau (Courbevoie, France). Tetrabromobisphenol A (TBBPA), 2,4-dibromophenol (2,4-DBP), 2,4,6-tribromophenol (2,4,6-TBP), 2,3,4,5,6-pentabromoethylbenzene (PBEB), tetrabromobisphenol A bis(dibromopropyl ether) (TBBPA-BDBPE), a mixture of the seven indicator PCB congeners (PCB 28, 52, 101, 118, 138, 153, and 180), and a certified standard for short-chained chlorinated paraffins (SCCPs; C<sub>10-13</sub>, 63% of chlorine by weight) were purchased from LGC Standards (Dr. Ehrenstorfer, Molsheim, France). For the extraction and purification steps, copper powder (<63 μm, EMSURE®) and silica gel cartridges (SPE Supelclean™ LC-Si, 1 g, 6 mL) were furnished by Sigma-Aldrich (Lyon, France). Finally, dichloromethane (DCM), methanol (MeOH), and n-hexane (HEX) of HPLC grade were purchased from Sigma-Aldrich (Lyon, France).

## Study area

The French Mediterranean coast can be very anthropized and industrialized at some points, like in Marseille (the second biggest city in France), and could thus be burdened by legacy and emerging contaminants. Given the very few data available along the Mediterranean coast, particularly in France, ten suspended matter (SM) samples were

collected in 2018 from SM traps installed along a *Posidonia oceanica* meadows surveillance network that was established along the French Mediterranean coast (Fig. 1).

The selected sampling sites cover various types and levels of anthropogenic activity. The site located in the Gulf of Fos (FOS) is impacted by commercial activities, ore and oil terminals, and various industrial activities, and is subject to a fraction of sedimentary deposits from the Rhône River. At the north of the Marseille Bay, Estaque and Niolon (EST and NIO, respectively) were chosen as they are potentially impacted by commercial harbor and urban activities to which superimposed microplastics and ionic pollution from the coastal stream Aygalade (Gérigny et al. 2022; Fanton et al. 2023). At the south of the Marseille Bay, Samena (SAM), Maire (MAI), and Plateau des Chèvres (CHE) were chosen as they are under the influence of urbanization, pollution from the coastal stream Huveaune, and from the wastewater from nearly 1.9 million population equivalent of the Cortiou outfall (Castro-Jiménez et al. 2021; Schmidt et al. 2021). In the semi-closed Bay of Toulon, the sites of Saint-Mandrier North and Headland (SMN and SMH) were chosen because they undergo important urban and harbor pressure. To contrast with strong anthropization conditions, the site of Veyron (VEY) was chosen for its offshore location in the Marseille Bay (about 14 km) and the site of Le Pradet (PRA) for its distant location from Toulon Harbor (about 7 km).



**Fig. 1** Map of the study area, with ten sampling sites: FOS, Gulf of Fos; NIO, Niolon; EST, Estaque; VEY, Veyron; SAM, Samena; MAI, Maire Island; CHE, Plateau des Chèvres; SMN, Saint-Mandrier North; SMH, Saint-Mandrier Headland; PRA, Le Pradet

## Sample preparation

### Sampling and pre-treatment

The suspended matter was sampled with home-made passive collectors shown in Online Resource-Fig. S1. After recovering, the samples were freeze-dried and sieved under 500  $\mu\text{m}$ , except for Estaque and Maïre samples, which were sieved at 250  $\mu\text{m}$ , as described in Online Resource-Table S1, together with the collecting periods ranging from 2 to 5 months to integrate the input of a season. The dried and sieved samples were stored at room temperature until their extraction.

### Extraction

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

### Clean-up

Solid-phase extraction on silica gel cartridges was applied to clean up the extracts. The cartridges were first 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. The cartridges were then eluted with 6 mL HEX (F1) and 6 mL HEX:DCM (1:1, v/v; F2). Both fractions were collected in separate vessels, then concentrated and reconstituted in 200  $\mu\text{L}$  of n-hexane, and 20 ng of the internal standards were added (BDE 140, PCB 116-d<sub>5</sub>, <sup>13</sup>C<sub>6</sub>-hexachlorobenzene). After the analysis of PCBs (F1) and CPs (F2), both fractions were combined for the analysis of PBDEs and nBFRs.

## Instrumental analysis

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

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

### Quality assurance/quality control

A procedural blank was performed using Fontainebleau sand. Only DBE-DBCH was detected in the blank, and the concentration of this compound was thus subtracted from the environmental samples. The mean recoveries of surrogates in environmental samples were 85%  $\pm$  31% (BDE 79), 75%  $\pm$  12% (BDE 189), 46%  $\pm$  6% (PCB 30-d<sub>5</sub>), and 93  $\pm$  18% (PCB 156-d<sub>3</sub>). Limits of detection (LODs) and limits of quantification (LOQs) were calculated for each compound using a signal-to-noise ratio (S/N) of 3 and 10, respectively. LODs ranged from 0.01 to 1.82 ng.g<sup>-1</sup> d.w. for nBFRs and from 0.01 to 4.85 ng.g<sup>-1</sup> d.w. for PBDEs, based on a sample mass of 10 g d.w. LOQs ranged from 0.3 to 6.08 ng.g<sup>-1</sup> d.w. for nBFRs and from 0.04 to 16.15 ng.g<sup>-1</sup> d.w. for PBDEs, based on a sample mass of 10 g d.w. All LODs and LOQs are given in Online Resource-Table S4. Calibration curves were constructed with 4 to 9 levels, and all coefficients of determination  $R^2$  (linear regression) were above 0.99, except for PBP ( $R^2 = 0.986$ ) and BDE 209 ( $R^2 = 0.988$ ).

### Data analysis and risk assessment

#### Statistical analysis

Statistical analysis was performed to determine whether some compounds have the same source of release. Since data were

not normally distributed, a non-parametric Spearman rank correlation was applied between the detected compounds in the station network, using JMP 9.0 software (SAS Institute Inc.). The treatment of not detected and not quantified values was as follows: a value of 0.001 ng.g<sup>-1</sup> d.w. was assigned to values below LOD and a value of 0.005 ng.g<sup>-1</sup> d.w. was assigned to values below LOQ, corresponding respectively to the lowest LOD and LOQ divided by ten. Significant correlations were displayed for *p*-values below 0.05.

### Risk assessment

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

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

Here, the MEC corresponds to the sample contamination, while the PNEC values are more often

available in water (PNEC<sub>water</sub>) rather than in sediments (PNEC<sub>sediments</sub>). A first approach is to determine the PNEC<sub>sediments</sub> from the predicted no effect concentration in water (PNEC<sub>water</sub>) thanks to the equilibrium partitioning method (EPM) developed by the European Chemicals Bureau, 2003 that can be simplified as written in Eq. 2 when using common values for the parameters of the EPM (European Commission Institute for Health and Consumer Protection European Chemicals Bureau 2003; ChemSafetyPRO 2016; Zind 2020).

$$PNEC_{\text{sediments}} = (0.783 + 0.0217 * K_{OC}) * PNEC_{\text{water}} \quad (2)$$

A second approach consists in replacing the MEC in Eq. 1 by the concentration in pore water (C<sub>PW</sub>), to compare it to PNEC<sub>water</sub>. Di Toro et al. (1991) proposed a relationship between C<sub>PW</sub> and the concentration found in sediments (C<sub>S</sub>) that depends on the fraction of organic carbon (f<sub>OC</sub>) and the partition coefficient for sediment organic carbon (K<sub>OC</sub>), as given in Eq. 3.

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

Both methods require nevertheless a value for PNEC<sub>water</sub> that can be derived from known ecotoxicological parameters such as lethal or effect concentrations (LC<sub>50</sub> and EC<sub>50</sub>, respectively), by dividing them with a security factor (f) of 1000 as shown in Eq. 4 (Rodil et al. 2019).

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

The main challenge to assess the risk of these emerging pollutants is the dramatic lack of related toxicity data. The values of LC<sub>50</sub> or EC<sub>50</sub> were found in the literature for only three compounds out of the 12 nBFRs quantified in our samples. The risk assessment was established with both methods for these three molecules, namely 2,4,6-TBP, DBDPE, and HBB, and the highest RQ value was chosen, considering the worst-case scenario. Among the nine remaining nBFRs, PNEC<sub>water</sub> could be predicted by the ECOSAR only for 2,4-DBP since its values of K<sub>OW</sub> and water solubility were included in the range of validity of the model, while the other compounds were too hydrophobic.

## Results and discussion

### Selection of relevant nBFRs to analyze in Europe

#### Identification of molecules used as BFRs

The US EPA database for flame retardants contains regulated BFRs, such as PBDEs, PBBs, and HBCDD isomers,

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

### Production or import inside the European Economic Area

The 114 ECHA nBFRs were first sorted according to their annual quantity of production or import inside the European Economic Area (EEA). Noticeably, five compounds, namely DBDPE, TBBPA, TBBPA-BDBPE, 1,2-dibromoethane (CAS N°106-93-4), and benzene, ethenyl-, ar-bromo derivatives (CAS N°125,904-11-2), are produced or imported over 1000 tons per year (t/y). Nevertheless, most of the compounds are produced or 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 nBFRs (Fig. 2). One compound was even classified as confidential without further information (CAS N°109678-33-3).

### Occurrence through literature review

A literature review of 125 papers published between 2012 and 2022 was performed. All of them aimed at looking for various nBFRs in biotic or non-biotic matrices from aquatic environments all around the world. Figure 3 presents the number of studies in which each compound was analyzed and detected in. It enables to highlight the most frequently targeted and detected nBFRs in environmental studies. It reveals that most studies focus on the same contaminants, with seven nBFRs studied in more than half of the articles,

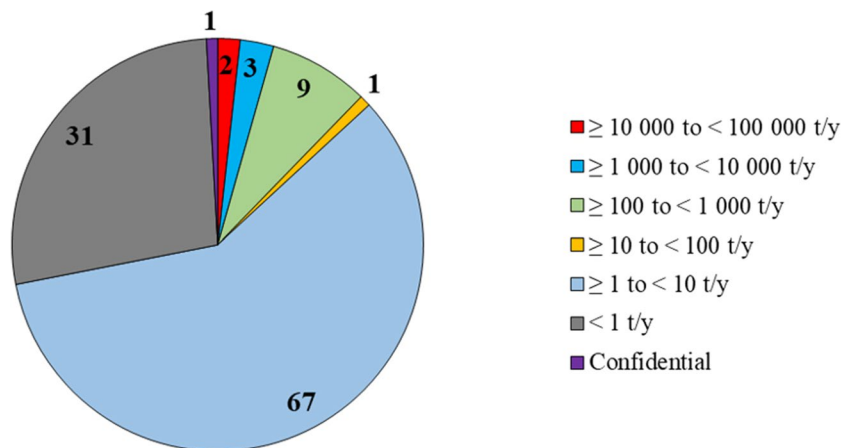
while many others were rarely or even never analyzed. However, it reveals that some of these orphan compounds can be detected in aquatic environments, whereas they are rarely studied.

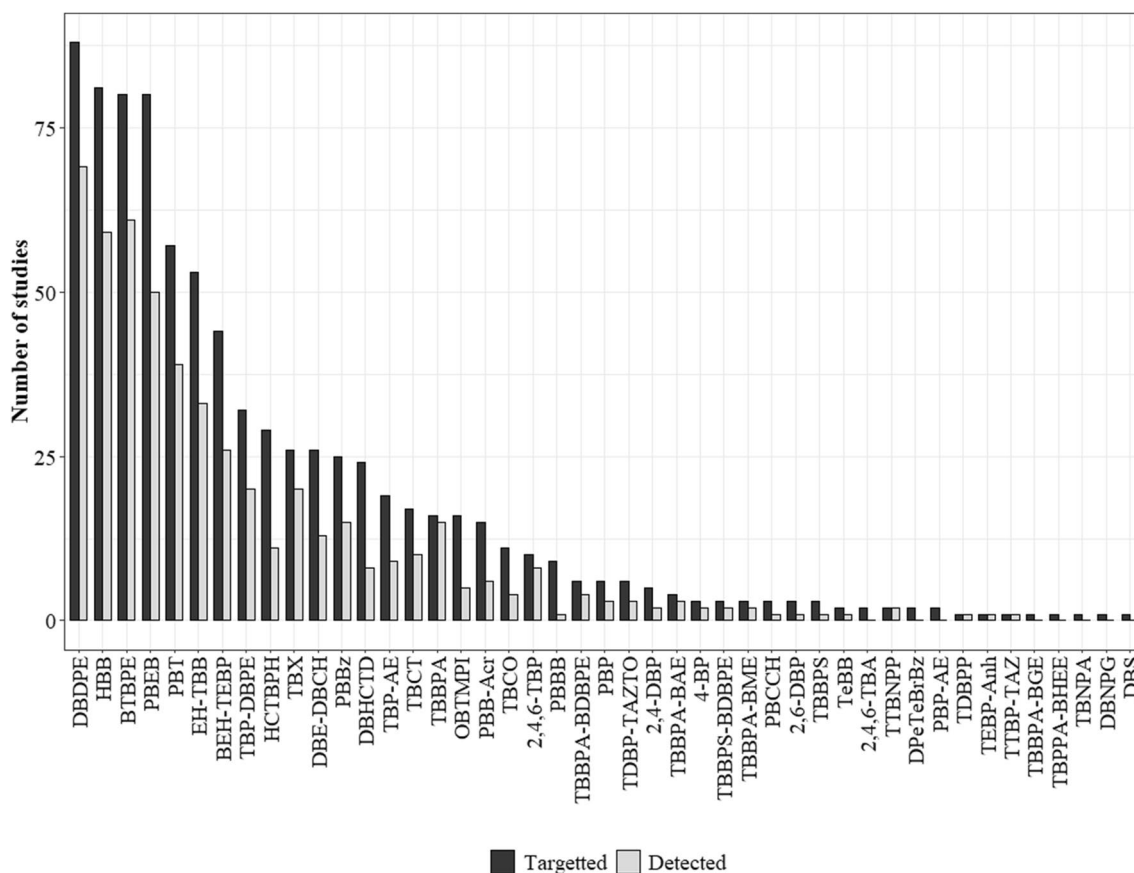
### Ecotoxicology

Only few studies have been carried out to assess the ecotoxicity of nBFRs, but the available data are not easy to compare since parameters and organisms can noticeably vary between studies. To overcome these discrepancies, predictive models like ECOSAR can be applied, since they enable to calculate values of toxicity based on the chemical structure of the targeted molecules. The acute toxicity ( $LC_{50}$  in fish after 96 h) of all nBFRs was then predicted by ECOSAR (Fig. 4). Four molecules could not be found by the predictive model (CAS N°58495-09-3, 59789-51-4, 75795-16-3, and 168434-45-5). For nBFRs with several chemical functions, the model predicted several concentrations for  $LC_{50}$ , and the lowest value has been selected in this study. To select thresholds of toxicity for relevance ranking, we first looked on ECOSAR for the  $LC_{50}$  (fish, 96 h) of the 8 regulated PBDE 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 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 applied as it is classically done in ecological or health risk assessment, thus extending the present study to molecules with  $110 \mu\text{g.L}^{-1} < LC_{50} < 1100 \mu\text{g.L}^{-1}$ . Compounds with  $LC_{50} < 1 \mu\text{g.L}^{-1}$  were considered as especially relevant.

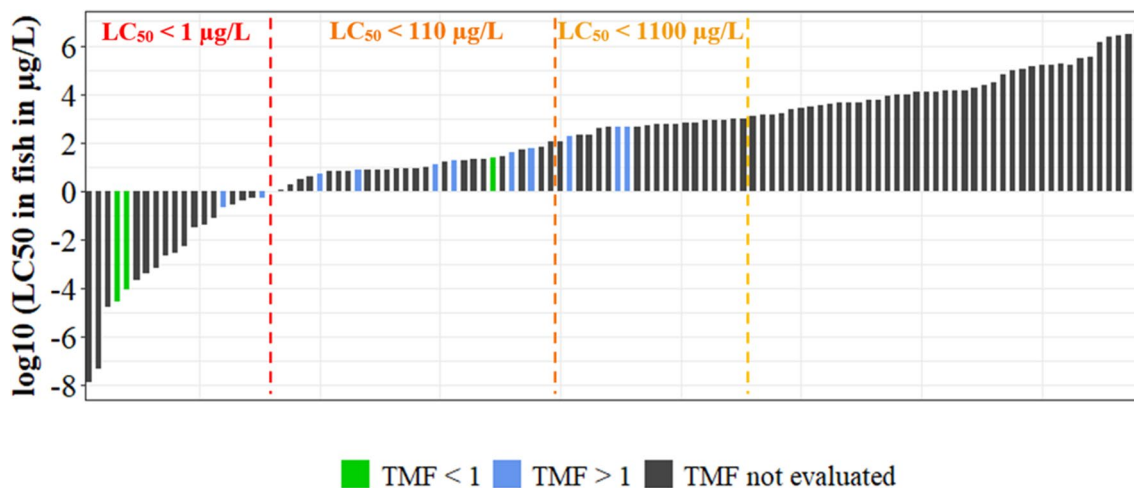
However, predictive models can only be approximative and have some limits. The ECOSAR model was created for molecules with a molecular weight below 1000, while some nBFRs are heavier. Also, it is based on the chemical functions of the compounds, so it gives several values for toxicity if the molecule has several chemical functions. An experimental parameter was thus additionally chosen to

**Fig. 2** Quantities of novel brominated flame retardants produced or imported inside the European Economic Area according to the European Chemical Agency (data from October 2023)





**Fig. 3** Occurrence of novel brominated flame retardants in aquatic environments according to a literature review ( $n=125$  studies, 2012–2022, Web of Science, methodology and keywords selection as described in materials and methods)



**Fig. 4** Ecotoxicology of novel brominated flame retardants registered by the European Chemical Agency:  $LC_{50}$  in fish after 96 h determined by the ECOSAR predictive model and trophic magnification factor (TMF) determined by Liu et al. (2021)

avoid these calculation limits. This additional ecotoxicological parameter was the trophic magnification factor (TMF), which was previously determined for 14 nBFRs registered by the ECHA in a zooplankton–invertebrate–fish–bird food

chain (Liu et al. 2021). A TMF higher than 1 means that the contaminant will biomagnify in the food chain, while a TMF lower than 1 shows trophic dilution.



## Relevance ranking

For the production criterion, 15 nBFRs were given the score of 1 ( $\geq 10$  to  $< 100$  t/y, one molecule), 2 ( $\geq 100$  to  $< 1,000$  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 molecules). Three additional compounds were given a score between 1 and 4 despite their current low production inside EEA. Indeed, data given in 2021 by the ECHA for the same molecules was higher than nowadays, and due to the persistence of BFRs in the environment, we decided to take the older values into account. Thus, TTBP-TAZ (CAS N°25713-60-4) and DBPT (CAS N°3296-90-0) were scored 2 (production  $\geq 1$  to  $< 10$  t/y in 2023, but  $\geq 100$  to  $< 1000$  t/y in 2021) and TTBNPP (CAS N°19186-97-1) was scored 1 (production  $< 1$  t/y in 2023, but  $\geq 10$  to  $< 100$  t/y in 2021). Finally, the production/import scores ranged from 0 to 4.

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

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

or subtracted for nBFRs with a TMF  $< 1$ . Hence, the ecotoxicological scores ranged from  $-1$  to 4.

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

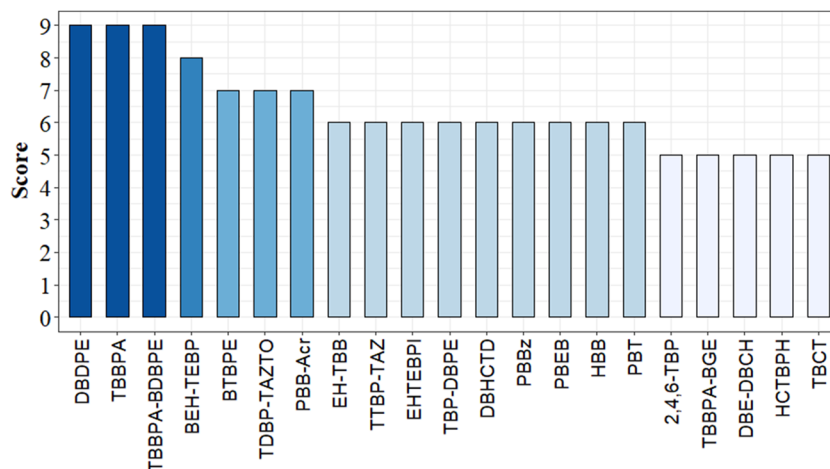
The scores obtained ranged from 1 to 9, and nBFRs with a score of 5 or higher were considered as relevant to analyze in European aquatic environments, as shown in Fig. 5. The highest ranked molecules were DBDPE (CAS N°84852-53-9), TBBPA (CAS N°79-94-7), and TBBPA-BDBPE (CAS N°21850-44-2), with a score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

## Focus on the French Eastern Mediterranean coastline

### Occurrence of legacy and novel brominated flame retardants in suspended matter from the French Eastern-Mediterranean coastline

Among the 21 previously selected nBFRs, three were both brominated and chlorinated (DBHCTD, HCTBPH, and TBCT); thus, in this preliminary study, we decided to keep only one of them (DBHCTD). Three other nBFRs were discarded, namely TBP-DBPE because it was not commercially

**Fig. 5** The twenty-one novel brominated flame retardants having a score of 5 or more



available and EHTEBPI and TBBPA-BGE because they cannot be analyzed by GC/ECNI-MS. The list of target analytes was thus gathering 16 nBFRs. In addition, six nBFRs with chemical structures close to those of the already targeted nBFRs were also added, more especially four bromophenols or derivatives (2,4-DBP, PBB, TBBPS-BME and TBP-AE) and two bromobenzenes (TBX, PBBB). The final list of the 22 compounds analyzed in coastal suspended matter samples and their physicochemical properties are given in Online Resource-Table S8.

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

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

Only few studies deal with nBFRs in sediments or suspended matters of the Mediterranean Sea or similar

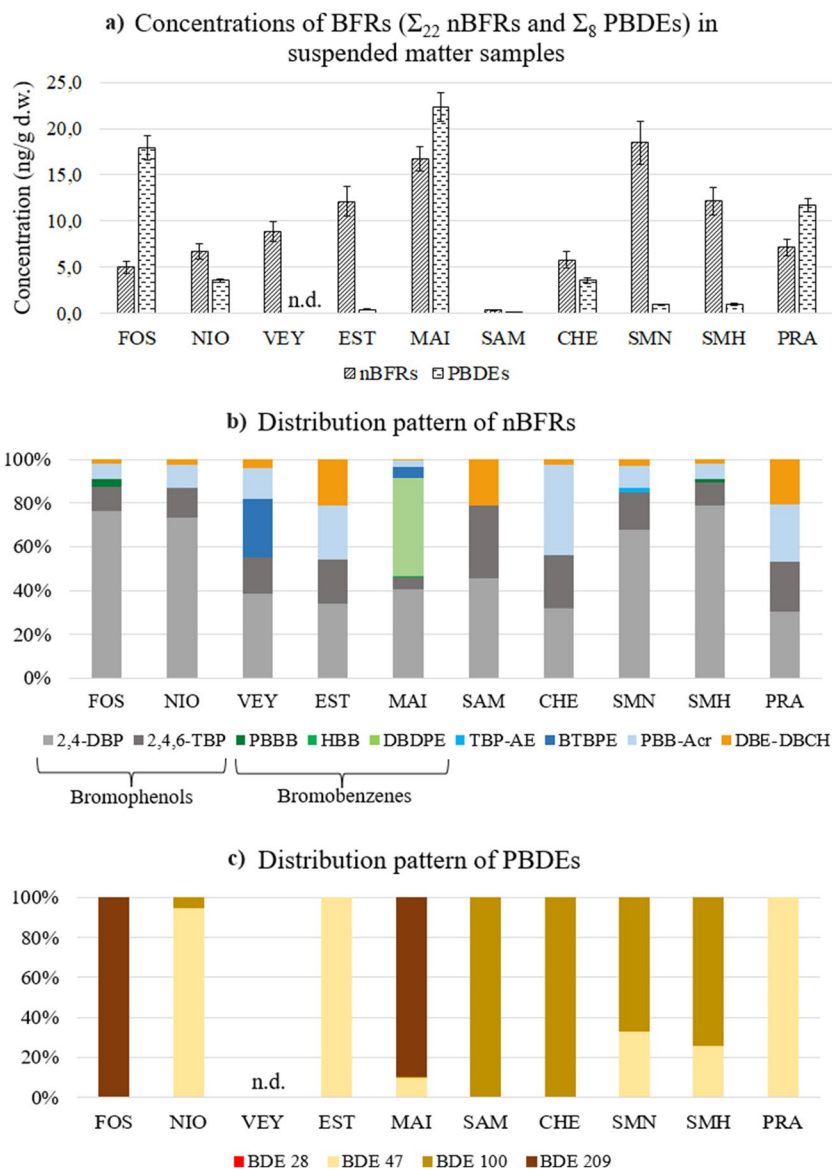
environments. The contamination levels measured in these studies were compared with the present results in Table 2. DBDPE, HBB, and PBEB were the most often targeted compounds in previous works. Most of the time, these three compounds were not detected or at low concentrations, which is consistent with our results in French coastal Mediterranean SM. However, in the Rhône River samples, higher concentrations of these three compounds were reached, as well as for PBBz, PBT, and TBBPA, which were not detected or could not be quantified in our study. This could be explained by the dilution of contaminants coming from this river into the marine environment, or by the fact that most studies have focused on sediments, which accumulate pollution over a longer period than SM.

Eleven of the analyzed compounds have not been previously reported in environmental studies dealing with nBFRs in sediments or SM from this geographic area. Among them, DBE-DBCH was detected in all of our samples, whereas it has not been detected previously in sediments from other parts of Europe, despite its screening in river sediments from the United Kingdom (UK) (Ganci et al. 2019) and in river and marine sediments from Germany (Sühling et al. 2016). In China, however, its concentrations could reach 109.0 ng.g<sup>-1</sup> d.w. (Zhu et al. 2018). The study of Sühling et al. (2016) in Germany also targeted TBP-AE, PBB-Acr, 2,4,6-TBP, PBBB, and TDBP-TAZTO, but none were detected. On the contrary, TBP-AE, PBB-Acr, 2,4,6-TBP, and PBBB were detected in our samples, especially 2,4,6-TBP present in all the sites. In the River Thames, the UK, 2,4,6-TBP ranged from not detected (n.d.) to 0.4 ng.g<sup>-1</sup> d.w. (Ganci et al. 2019) and in the South China Sea, it reached 22.33 ng.g<sup>-1</sup> d.w. (Feng et al. 2021). The same study in the South China Sea also reported concentrations ranging from n.d. to 0.22 ng.g<sup>-1</sup> d.w. and from not detected to 1.52 ng.g<sup>-1</sup> d.w. for TDBP-TAZTO and TTBP-TAZ, respectively, whereas neither molecule was detected in the present study. But

**Table 1** Mean values of concentrations above limits of quantification, lower and higher concentrations, and detection rate of the 12 nBFRs out of the 22 targeted, found in at least one sample

Compound	Mean concentration (ng.g <sup>-1</sup> d.w.)	Lower concentration (ng.g <sup>-1</sup> d.w.)	Higher concentration (ng.g <sup>-1</sup> d.w.)	Detection rate
2,4-DBP	4.9	0.2	12.5	100%
2,4,6-TBP	1.4	0.1	3.2	100%
BTBPE	1.6	<LOD	2.4	20%
DBDPE	7.5	<LOD	7.5	50%
DBE-DBCH	0.6	0.1	2.6	100%
HBB	0.1	<LOD	0.1	20%
PBB-Acr	1.4	<LOD	3.0	90%
PBBB	0.2	<LOD	0.2	30%
PBEB	-	<LOD	<LOQ	10%
PBT	-	<LOD	<LOQ	30%
TBBPA-BDBPE	-	<LOD	<LOQ	40%
TBP-AE	0.4	<LOD	0.4	20%

**Fig. 6** Concentrations of brominated flame retardants (a) and distribution patterns of the 22 novel brominated flame retardants (b) and the 8 legacy polybromodiphenyl ethers (c) in suspended matter from ten sampling stations along the French Eastern Mediterranean coastline



our LODs (for 10 g d.w. of sample) were equal to 0.37 and 1.05 ng.g<sup>-1</sup> d.w. for TDBP-TAZTO and TTBP-TAZ, respectively, which might be too high to detect such low concentrations.

**Discussion and comparison with regulated halogenated flame retardants**

In addition to legacy and nBFRs, two families of regulated chlorinated flame retardants, namely polychlorobiphenyls and short and medium chain chlorinated paraffins were analyzed in the present work. The seven regulated PCBs were detected in all samples, with a total concentration ranging from 1.0 to 26.8 ng.g<sup>-1</sup> d.w., dominated by highly chlorinated congeners. The detection frequency for chlorinated paraffins was 70%, with concentrations ranging from 42

to 323 ng.g<sup>-1</sup> d.w. Several nBFRs were detected in the ten samples, with 12 compounds detected at least once, and nine compounds quantified in one sample or more, while four congeners of PBDEs (BDE 28, 47, 100, 209) were detected and quantified in nine samples. All concentrations are given in Online Resource-Table S9.

CPs concentrations, representing the sum of the concentrations of thousand congeners, were higher than any other halogenated flame retardant and had to be represented ten times lower in Fig. 7. On the other hand, PCBs, PBDEs, and nBFRs were one decade lower and covered similar concentration ranges. The boxplot (Fig. 7) exhibits skewed distributions, mainly negative except for CPs. However, the contamination pattern of PCBs was homogeneous between the different sites except in SAM, with the predominance of penta- and hexa-chlorinated congeners, while PBDEs and

**Table 2** Comparison of concentrations of novel brominated flame retardants (ng.g<sup>-1</sup> d.w.) measured hereby with those reported in the literature for the Mediterranean Sea or immediate environments

Mekni et al. (2019)	Mekni et al. (2020)	Aznar-Alemaný et al. (2018)	Kotthoff et al. (2017)	Vauclin et al. (2021)	Cristale & Lacorte, (2013)	Poma et al. (2014)	This study
Tunisia <i>Med. Sea</i> <sup>1</sup>	Tunisia <i>Med. Sea</i> <sup>1</sup>	Italy, Spain <i>Med. Sea</i> <sup>1</sup>	France <i>Rhône River</i>	France <i>Rhône River</i>	Spain <i>Besòs River</i>	Italy <i>Lake Maggiore + rivers</i>	France <i>Med. Sea</i> <sup>1</sup>
Sediments	Sediments	Sediments	Suspended matter	Sediments	Sediments	Sediments	Suspended matter
DBDPE							
<LOD–45.0	<0.11 <sup>2</sup>	0.12–0.23	-	-	DF 40% ≈ 400 ng. g <sup>-1</sup> d.w. (median) <sup>4</sup>	<LOD–280.00	<1.72 <sup>2</sup> –7.51
HBB							
<0.03 <sup>2</sup>	<0.03 <sup>2</sup>	<0.03 <sup>2</sup> –<0.09 <sup>3</sup>	-	<LOD–73.33	<LOD	<LOD–0.22	<0.02 <sup>2</sup> –0.06
PBEB							
<0.04 <sup>2</sup>	-	<0.03 <sup>2</sup> –<0.09 <sup>3</sup>	-	<LOD–34.67	<LOD	<LOD–0.2	<0.01 <sup>2</sup> –<0.05 <sup>3</sup>
TBX							
-	-	-	-	<LOD–11.86	-	-	<0.01 <sup>2</sup>
PBBz							
-	-	-	-	3.34–33.88	-	-	<0.02 <sup>2</sup>
PBT							
-	-	-	-	0.2–87.26	<LOD	-	<0.01 <sup>2</sup> –<0.03 <sup>3</sup>
DBHCTD							
-	-	-	-	-	<LOD	-	<0.03 <sup>2</sup>
EH-TBB							
-	-	-	-	-	<LOD	-	<0.12 <sup>2</sup>
BEH-TEBP							
-	-	-	-	-	<LOD	-	<0.68 <sup>2</sup>
BTBPE							
-	-	-	-	-	<LOD	<LOD–0.895	<0.09 <sup>2</sup> –<2.37 <sup>3</sup>
TBBPA							
-	-	-	1.83–3.93	-	-	-	<0.59 <sup>2</sup>

<sup>1</sup> “Med. Sea” refers to the Mediterranean Sea

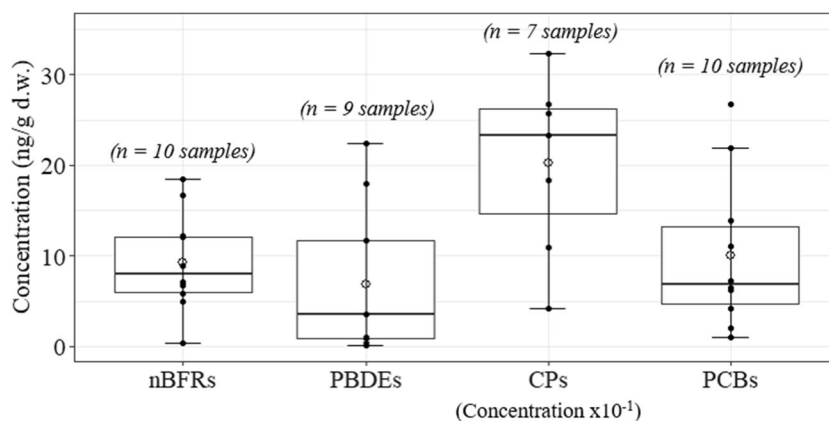
<sup>2</sup>LOD value, when given in the paper

<sup>3</sup>LOQ value, when given in the paper

<sup>4</sup>Approximative value taken deduced from a graph

nBFRs profiles were more heterogeneous depending on the site (Fig. 6b and c). It could be explained by more local and recent inputs of these contaminants, which are currently used or were regulated more recently (i.e., BDE 209). Among the nBFRs, the bromophenols 2,4-DBP and 2,4,6-TBP were predominant in nearly all samples and represented 42 to 90% of the total load of nBFRs. Their occurrences are of interest and their sources remain somehow unclear. Besides their use as flame retardants, bromophenols can be formed through the photodegradation of other BFRs like PBDEs or BTBPE (Bendig & Vetter 2013; Zhang et al. 2016). They were also reported as disinfection by-products (Dron et al. 2022), and they can occur naturally (Hassenklöver & Bickmeyer 2006).

Some specific areas in the Mediterranean Sea are especially contaminated with PCBs, like in Tunisia where a study from 2023 reported concentrations in sediments ranging from 28.6 to 230.6 ng.g<sup>-1</sup> d.w. for the seven indicator PCBs in Bizerte Lagoon (Barhoumi et al. 2023). However, our results are consistent with most of the studies performed on Mediterranean sediments. In 2013, Salvadó et al. (2013) found concentrations ( $\Sigma_7$ PCBs) ranging from 1.3 to 38 ng.g<sup>-1</sup> d.w. in the Gulf of Lion. In the Spanish Mediterranean Sea, a total concentration of 1.8 ng.g<sup>-1</sup> d.w. for the seven congeners was reported in 2017 (Robinson et al. 2017), and in Egypt, the sum of the same contaminants ranged from 0.18 to 35.04 ng.g<sup>-1</sup> d.w. in 2016 (El Nemr & El-Sadaawy 2016).



**Fig. 7** Boxplot of the concentrations of four groups of halogenated flame retardants: 22 novel brominated flame retardants (9 quantified), 8 legacy polybromodiphenyl ethers (4 quantified), short- and medium-chain chlorinated paraffins, and 7 indicator polychlorobiphenyls (7 quantified) measured in the ten suspended matter samples col-

lected along the French Mediterranean coast. The lines in the boxes represent from the bottom to the top the 25, 50 (median), and 75% percentiles. The mean values are displayed as empty dots. The black dots represent the sample concentrations

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

A Spearman correlation table given in Online Resource-Table S10 shows very strong correlations between all PCB congeners. At first glance, this could be interpreted as a common source for all these contaminants. However, it could also mean that concentrations have been homogenized over the years, since these pollutants have been regulated for decades, creating a contamination continuum and making source identification nearly impossible. CPs were positively correlated with the most chlorinated PCBs (congeners 118, 138, 153), probably due to similar physicochemical properties. 2,4,6-TBP was strongly correlated with DBE-DBCH ( $p=0.8788$ ) and PBB-Acr ( $p=0.8909$ ). These compounds thus should have the same sources. These sources must be different from those of PBT, BDE 28, and BDE 209, since these three compounds are strongly correlated together, but negatively correlated with the first group of nBFRs (2,4,6-TBP, DBE-DBCH, PBB-Acr). Also, TBBPA-BDBPE was correlated with DBDPE ( $p=0.825$ ) and 2,4-DBP ( $p=0.6396$ ). Finally, PCB 28 was correlated

with one nBFR, namely PBB-Acr ( $p=0.6848$ ). However, it can be challenging to explain these correlations with the data available about BFRs uses (Covaci et al. 2011), and further studies would be necessary to elucidate the sources of nBFRs in the environment.

### Risk assessment

Most PCBs were above the BACs determined by the OSPAR commission, except for PCB 28 in two samples (SAM and SMH) and PCB 52 in three samples (VEY, SMH, PRA). Tetra- to hepta-chlorinated biphenyls exceeded the BACs up to 35 times, except in one sample (SAM) where concentrations could be considered close to zero. Even though they were mostly above background levels, most PCB congeners did not represent an environmental risk since the observed concentrations were lower than the EACs. The only exception was for the dioxin-like PCB 118 that showed concentrations up to five times higher than its EAC in six samples, which can raise concern because its toxicity mechanisms are similar to those of dioxins (Fiolet et al. 2022). When observed above LOQs, CPs were at least ten times below the FEQGs set by the Canadian government after being normalized to 1% TOC. PBDEs were also unlikely to represent an environmental risk in this study. Indeed, only BDE 99 at one site (CHE) was higher than its FEQGs of 0.4 ng.g<sup>-1</sup> d.w., with a concentration of 0.68 ng.g<sup>-1</sup> d.w. when normalized to 1% TOC. Risk quotients were calculated both with the EPM method (calculation of  $PNEC_{\text{sediments}}$ ) and with the  $C_{PW}$  method (calculation of  $C_{PW}$  according to Di Toro et al. 1991). Higher risks were observed when using the first method. DBDPE and HBB, that could be quantified in Maïre (MAI) sample, only showed a very low environmental

risk (RQ=0.002 and RQ=0.00001, respectively). 2,4-DBP and 2,4,6-TBP showed very low to medium environmental risk, as represented by the RQ given in Online Resource-Table S11. However, 2,4,6-TBP presented a high risk in EST (RQ=1.2) and in SMH (RQ=1.6). Nevertheless, for these increasingly diverse mixtures of compounds, produced and used in smaller tonnage than other historical compounds, determining a risk on the basis of individual molecules seems unsuitable. It is necessary to be able to sum up these risks or consider the effects of mixtures.

## Conclusion

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

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

As future work, the two chlorinated and brominated compounds ranked in our list of relevant nBFRs but not analyzed in this study (HCTBPH and TBCT) should be targeted as well, especially since DBHCTD analyzed in the present work was successfully separated on the GC/

ECNI-MS method developed. The further analysis of sediments from the same study area would be interesting since this compartment acts as a sink for hydrophobic contaminants. Moreover, with a higher sample mass available, LODs and LOQs could be driven down, which is necessary for such ultratracés of contamination.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s11356-024-34607-w>.

**Author contribution** Camille Rigal, Pierre Doumenq, and Laure Malleret contributed to the study conception and design. The study area was instrumented and sampled by Pascal Mirleau. Formal analysis and investigation were carried out by Camille Rigal, with the assistance of Laurence Asia and Stéphanie Lebarillier, and under the supervision of Laure Malleret and Pierre Doumenq. Laure Malleret and Pascal Mirleau contributed to funding acquisition and administration of the project. Data treatment, visualization, and first draft writing were undertaken by Camille Rigal and Laure Malleret. All authors have read, commented, and approved the final version of the manuscript.

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

## Declarations

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

**Consent to participate** All authors agreed with the content that all gave explicit consent to participate and that they obtained consent from the responsible authorities at the institute/organization where the work has been carried out.

**Consent for publication** All authors agreed with the content and gave explicit consent to submit and publish, and that they obtained consent from the responsible authorities at the institute/organization where the work has been carried out.

**Competing interests** The authors declare no competing interests.

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