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# Temporal trends of legacy and novel brominated flame retardants in sediments along the Rhône River corridor in France

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### Highlights :

- Time trends of legacy BFRs in sediments along the Rhône River are similar.
- Legacy BFRs reached their peak between the 1970s and the 2000s, and are now stable.
- nBFRs concentrations are two to four times lower than that of legacy BFRs.
- Some nBFRs appeared along the Rhône River as early as the 1970s-1980s.
- No decreasing trend in nBFRs concentrations has been observed, so far.

1 **Keywords:** Brominated flame retardants; contamination trend; polychlorinated biphenyls; Rhône  
2 River; sediment core.

### 4 **Abstract**

5 Brominated flame retardants (BFRs) are anthropogenic compounds that are ubiquitous in most  
6 manufactured goods. Few legacy BFRs have been recognised as persistent organic pollutants (POPs)  
7 and have been prohibited since the 2000s. However, most BFRs continue to be used despite growing  
8 concerns regarding their toxicity; they are often referred to as novel BFRs (nBFRs). While  
9 environmental contamination due to chlorinated POPs has been extensively investigated, the levels  
10 and spatiotemporal trends of BFRs are comparatively understudied. This study aims to reconstruct the  
11 temporal trends of both legacy and novel BFRs at the scale of a river corridor. To this end, sediment  
12 cores were sampled from backwater areas in four reaches along the Rhône River. Age-depth models  
13 were established for each of them. Polychlorinated biphenyls (PCBs), legacy BFRs (polybrominated  
14 diphenyl ethers - PBDEs, polybrominated biphenyls - PBBs and hexabromocyclododecane - HBCDDs)  
15 and seven nBFRs were quantified. Starting from the 1970s, a decreasing contamination trend was  
16 observed for PCBs. Temporal trends for legacy BFRs revealed that they reached peak concentrations  
17 from the mid-1970s to the mid-2000s, and stable concentrations by the mid-2010s. Additionally,  
18 individual concentrations of nBFRs were two to four orders of magnitude lower than those of legacy  
19 BFRs. Their temporal trends revealed that they appeared in the environment in the 1970s and 1980s.  
20 The concentrations of most of these nBFRs have not decreased in recent years. Thus, there is a need  
21 to comprehend the sources, contamination load, repartition in the environment, and toxicity of nBFRs  
22 before their concentrations reach hazardous levels.

### 23 **1. Introduction**

24 Brominated flame retardants (BFRs) are a group of anthropogenic molecules that are manufactured to  
25 prevent or slow down the development of fire (WHO, 1997). Their production began in the 1960s and  
26 1970s (Prevedouros et al., 2004; Jinhui et al., 2017). Since then, they have been incorporated in a wide

27 range of industrial processes and applications, including electronics, transportation, furniture (foams  
28 and carpets), textiles, and construction (Alaee et al., 2003). Certain BFRs, namely polybrominated  
29 diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecanes (HBCDDs) and  
30 tetrabromobisphenol A (TBBPA) are regarded as “established” or “legacy” BFRs. This is because they  
31 have been identified in environmental matrices worldwide (De Wit, 2002; Law et al., 2003; Law et al.,  
32 2006; De Wit et al., 2010; Guerra et al., 2012; Li et al., 2015), and their persistence and toxicity have  
33 been assessed and acknowledged. They generally exhibit low acute toxicity but significant chronic  
34 toxicity, leading to liver, kidney, and thyroid disorders (PBDEs and HBCDDs), development and  
35 neurobehavioral issues in children (PBDEs and HBCDDs), reproductive disorders, digestive system  
36 cancer, and lymphoma (mainly PBBs) (Darnerud et al., 2003; Kim et al., 2014). As a result, most legacy  
37 BFRs have been progressively classified as persistent organic pollutants (POPs) in the Stockholm  
38 Convention. Tetra and penta-BDE (commercial penta-BDE mixture) was classified in 2009, whereas  
39 deca-BDE commercial mixture was classified in 2017 (Annex A of the Stockholm Convention, 2018).  
40 This delay in addition is because legacy BFRs are not as well-studied as other pollutants, such as  
41 chlorinated compounds (e.g. polychlorinated biphenyls [PCBs], dioxins, furans, and organochlorine  
42 pesticides), which are regulated in Europe through the Water Framework Directive (2000/60/EC). The  
43 global production of BFRs has reached the same order of magnitude as some of the chlorinated  
44 compounds, such as PCBs. The production of PCBs reached its peak in the late 1960s at approximately  
45 80 kt year<sup>-1</sup> (Breivik et al., 2002a), the global production of PBDEs global production peaked in 2002,  
46 also around 80 kt (Abbasi et al., 2019). Nevertheless, health and environmental concerns linked to  
47 legacy BFRs have led to a steady decline in their production and use over time. PBBs were produced  
48 up until 1976 in the USA, 1977 in Germany, 1985 and the United Kingdom, and 2000 in France (IARC,  
49 2016). Most commercial mixes of PBDEs have been prohibited by the European Union (EU) in the  
50 electronic and electric industries from 2002 (2002/95/CE). Furthermore, the global production of  
51 HBCDDs reportedly peaked in 2006 at 22 kt, most of the produced HBCDDs being used in the EU;  
52 however, their production has seen a decline ever since (Koch et al., 2015).

53 As a result, numerous brominated compounds have replaced legacy BFRs and have gained attention  
54 from the scientific community. According to Bergman et al. (2012), these replacement BFRs should be  
55 referred to as “emerging BFRs” if they are present in the environment and/or in wildlife, humans or  
56 other biological matrices, and as “novel BFRs” (nBFRs) if they are documented as potential flame  
57 retardants in materials or products. Although the term “emerging BFRs” is rarely used in the literature,  
58 the term “nBFRs” is commonly used (Poma et al., 2014; McGrath et al., 2017; 2018; Ganci et al., 2019;  
59 Xiong et al., 2019). Therefore, this paper uses the term “novel BFRs” to designate BFRs which are new  
60 to the market or have recently been observed in the environment, as defined by Covaci et al. (2011).  
61 The European Food Safety Authority (EFSA, 2013) has identified twenty-seven nBFR compounds,  
62 including pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), and tetrabromo-o-  
63 chlorotoluene (TBCT). Similar to legacy BFRs, nBFRs are used in many products such as textiles, plastics,  
64 foams, and electrical cable coatings (Xiong et al., 2019). Furthermore, they have been identified in  
65 many environmental matrices including air (Möller et al., 2011; Yu et al., 2015), wastewater (Cristale  
66 et al., 2015; Li et al., 2018), indoor dust (Hassan et Shoeib, 2015; McGrath et al., 2018), sediments and  
67 soils (Shi et al., 2009; La Guardia et al., 2013), and biota (Vetter et al., 2017; Vénisseau et al., 2018).  
68 Additionally, nBFRs have been shown to bioaccumulate in some species (Wu et al., 2011; Zhang et al.,  
69 2011). Existing toxicological studies suggest that they may cause various adverse effects (endocrine  
70 disruption, neurotoxicity, DNA damage) at high exposure; however, information on their effects due  
71 to chronic exposure at low concentrations is still scarce (Xiong et al., 2019).

72 It is essential to investigate the temporal trends of anthropogenic chemicals in environmental matrices  
73 in order to evaluate their potential risks and to assess the need to regulate their production and use.  
74 If a regulation is already in place, it is imperative to comprehend its lag time and effectiveness in  
75 reducing the concentrations of contaminants in the environment. For this purpose, sediment deposits  
76 are valuable natural archives of the anthropogenic contamination of hydrosystems. They are especially  
77 relevant when investigating lipophilic contaminants (i.e., POPs), such as BFRs that tend to accumulate  
78 in sediments (de Wit, 2002). Numerous sediment records have been successfully used to reconstruct

79 the temporal trends of PCBs. Moreover, various studies have shown that their worldwide prohibition  
80 in the 1980s led to a significant decrease in their environmental concentrations (Chi et al., 2007;  
81 Desmet et al., 2012; Bigus et al., 2014 Cui et al., 2016; Dendievel et al., 2020). However, their stocks  
82 might continue to persist in sediments and could pose a risk of intermittent contaminant releases in  
83 hydrosystems. As compared to PCBs, studies on the temporal trends of BFRs in sediments uncommon.  
84 Most studies on BFRs focus on PBDEs (Baltic Proper: Nylund et al., 1992; Tokyo Bay: Minh et al., 2007;  
85 Scotland: Muir and Rose, 2007; Switzerland: Kohler et al., 2008; Japan and Southern China coasts:  
86 Tanabe, 2008; Sydney Estuary: Drage et al., 2015; Seine River: Lorgeoux et al., 2016), as they are often  
87 the predominant BFRs in terms of concentrations detected in the environment (Law et al., 2006; 2014).  
88 Sediment records of HBCDDs (Kohler et al., 2008; Tanabe et al., 2008; Poma et al., 2014; Law et al.,  
89 2014) and temporal trends of PBBs (Zhu and Hites, 2005) are even more scarce in the literature. So far,  
90 most temporal records of BFRs are thus derives from cores from a single location; however, no  
91 temporal study has been attempted at the scale of a whole river corridor. To the best of our  
92 knowledge, among nBFRs, temporal trends of just decabromodiphenyl ethane [DBDPE] and 1,2-  
93 Bis(2,4,6-tribromophenoxy)ethane [BTBPE] have been published to date (Yang et al., 2012; Poma et  
94 al., 2014). The scarcity of recorded temporal evolution of nBFRs in environmental matrices is especially  
95 concerning because they continue to be manufactured. Given the growing evidence of their hazardous  
96 effect (e.g., persistence, bioaccumulation, and toxicity), their increasing concentrations in the  
97 environment is not ideal.

98 Therefore, this study aims to fill knowledge gap in the literature regarding both legacy and novel BFRs  
99 by 1) characterising the temporal and spatial trends of PCBs and legacy BFRs (PBDEs, PBBs, HBCDDs)  
100 and 2) comparing the trends of legacy and novel BFRs in sediments over time, along the highly  
101 anthropized Rhône River corridor. To this end, sediment cores were retrieved from secondary channels  
102 as well as a dam reservoir in four distinct areas along the Rhône River. The cores were characterised  
103 in terms of grain size and total organic carbon, and dated. Moreover, concentrations of PCBs, legacy

104 BFRs (PBDEs, PBBs, and HBCDDs), and seven nBFRs were quantified, allowing for the robust  
105 reconstruction of temporal trends for both legacy and novel brominated flame retardants.

## 106 2. Geographic settings

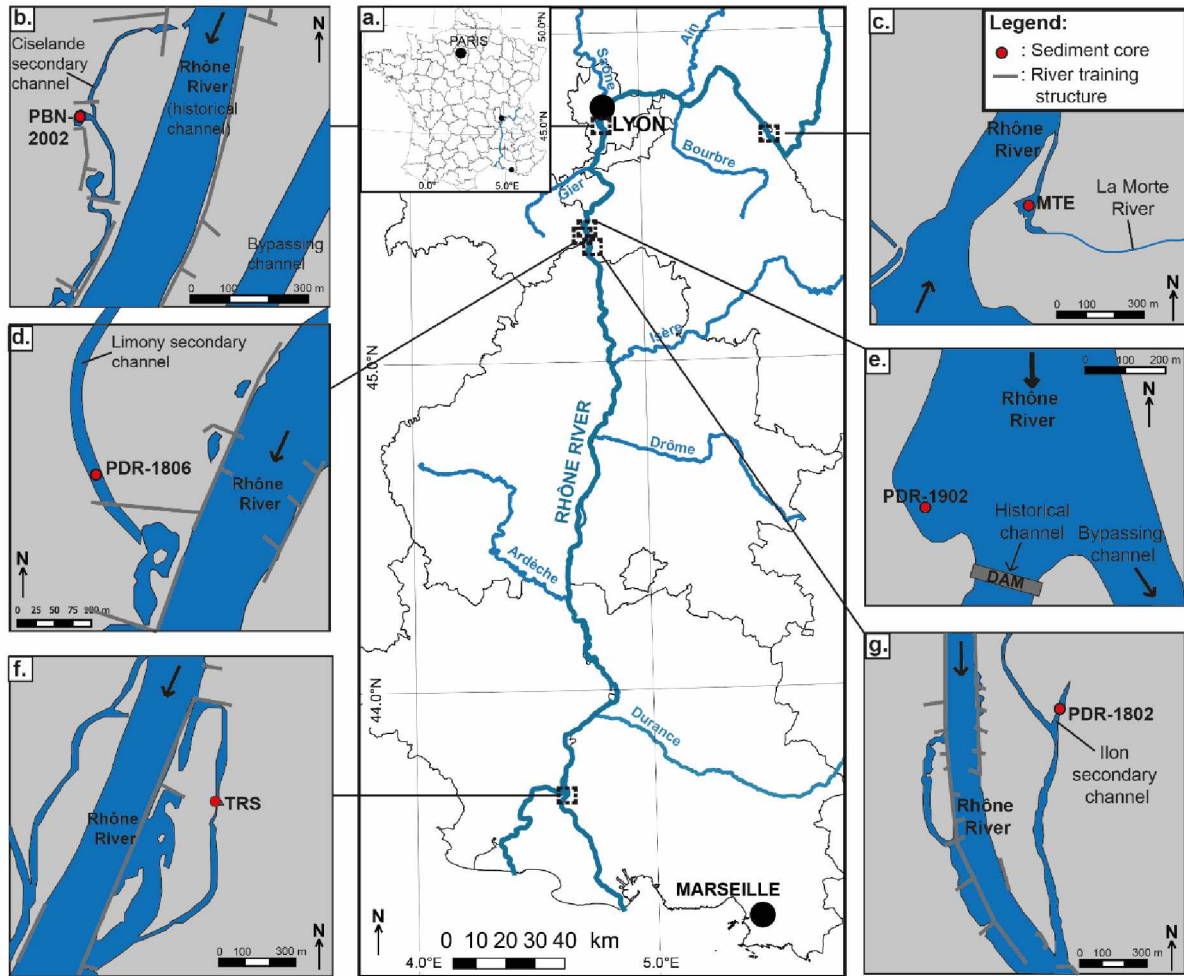
### 107 2.1. Geographic context

108 The Rhône River is 812 km; it runs from the Valais region in Switzerland to the Mediterranean Sea in  
109 France (Fig. 1.a). Its catchment covers an area of 98 500 km<sup>2</sup>, of which 92 % is in France, and is mostly  
110 mountainous (Olivier et al., 2009). With an average annual discharge of 1 690 m<sup>3</sup> s<sup>-1</sup> close to its delta  
111 (Arles), the Rhône is the largest river in France; moreover, in terms of discharge, it ranks eight in  
112 Europe. It is also the most active river in France in terms of sediment transport, with a long-term mean  
113 annual sediment load of approximately 6.6 x 10<sup>6</sup> tons (Poulier et al., 2019) and a conveying speed of  
114 approximately 2 km year<sup>-1</sup> (Pont et al., 2002).

115 The Rhône River catchment is highly anthropized. It supports a population of approximately 15.5  
116 million that is mostly distributed along the river corridor. The river runs through major cities, including  
117 Geneva (~1 million inhabitants) and Lyon (~1.4 million inhabitants), and through several industrial  
118 areas. The largest industrial area in the region is the “Chemical Valley”, which is a 10 km-long reach  
119 directly downstream of Lyon, comprising of numerous pharmaceutical, chemical, and petrochemical  
120 industries. The river course has also been extensively engineered to facilitate navigation and to  
121 produce hydroelectricity. There are numerous dykes and groynes constraining the river bed as well as  
122 19 hydroelectric dams along the French section of the river, with one dam every 30 km on average  
123 (Bethemont and Bravard, 2016).

### 124 2.2. Sampling sites





125

126 *Figure 1: a. Rhône River catchment with localisation of the study sites; b. PBN study site; c. MTE study site; d. PDR-1806 study*  
 127 *site; e. PDR-1902 study site; f. TRS study site; g. PDR-1802 study site. [IN COLOUR]*

128 Six study sites located in four distinct areas were identified for this study (Fig. 1). Secondary channels,  
 129 that is channels that are partly or entirely disconnected from the main channel most of the year, were  
 130 selected as they represented steady waters environments (oxbow lakes, backwater areas). Sediment  
 131 sequences in such environments are usually characterised by good preservation potential and  
 132 continuity as well as high stratigraphic resolution (Bábek et al., 2008; Van Metre et al., 2008; Mourier  
 133 et al., 2014), indicating that they might offer a reliable and high-resolution sediment record. The sites  
 134 are described from upstream to downstream, as follows:

135 - MTE (Fig. 1.c), located approximately 415 km from the estuary, consists of a secondary channel  
136 along the right bank, which is connected to the Rhône River at its downstream end and to a  
137 small river (“La Morte”) at its upstream end (Fig. 1.c).

138 - PBN (Fig. 1.b): the area of Pierre-Bénite (PBN) is located 319 km away from the estuary and a  
139 few kilometres downstream of the confluence of the Rhône and Saône rivers in Lyon. It is a  
140 highly anthropized bypassed reach that runs along the “Chemical Valley”. The historical  
141 channel is constrained by numerous groynes and dykes.

142 The site is selected for the study is an oxbow lake that was formed over time between two  
143 groynes as they were progressively filled with sediments (Fig. 1.b). Under high discharge  
144 conditions, it is connected to a secondary channel that was partly restored in 2000. The oxbow  
145 lake has never been dredged.

146 - PDR (Fig. 1.d, e, g): the area of Péage-de-Roussillon (PDR) is located 278 km from the estuary  
147 and approximately 50 km downstream of Lyon. It is a 12 km-long reach organised in a bypassed  
148 configuration that is typical of the Rhône River: an artificial canal equipped with a hydroelectric  
149 power plant has been dug out to improve navigation and produce electricity, while the  
150 historical channel has been dammed to obtain most of the discharge in the canal. The old  
151 channel is also equipped with river training infrastructures (dykes and groynes) that were built  
152 in the 1880s to facilitate navigation on the Rhône River.

153 Additionally, three sites from the historical channel were studied to include diverse  
154 depositional environments, and therefore varying time periods and contamination patterns  
155 recorded in the sediments:

- 156 ○ The dam reservoir (core PDR-1902, located 278 km from the estuary; Fig. 1.e) was built  
157 between 1974 and 1978. It is a run-of-river dam, implying that it can be removed  
158 during floods to allow high discharges. However, a small recess zone on the right bank  
159 has allowed continuous accumulation of sediment since the construction of the dam,  
160 as proved by bathymetric surveys of the reservoir over time (Vauclin et al., 2020).

- 161           ○ The Limony secondary channel is located on the right bank (core PDR-1806, located  
162                   273 km from the estuary; Fig. 1.d). It was disconnected due to the implementation of  
163                   artificial embankments in the 1880s. Currently, it is mostly supplied by groundwater  
164                   and is occasionally connected to the main channel during floods.
- 165           ○ The Ilon secondary channel (core PDR-1802, located 272 km from the estuary; Fig. 2.g)  
166                   is located on the left bank of a larger secondary channel. Its upstream end was  
167                   disconnected following the drastic discharge reduction caused by the implementation  
168                   of the dam in 1978. However, the channel is still underwater throughout the year,  
169                   supplied by its downstream end.

170           To decipher the variations in temporal concentrations, the results from this area are site-  
171                   specific. However, to understand spatial trends, they are studied from an overarching  
172                   perspective, as sites are located only a few kilometres apart.

- 173           - TRS (Fig. 1.f): this site is located approximately 275 km downstream from Lyon and 54 km  
174                   upstream from the estuary into the Mediterranean Sea, therefore it represents the river  
175                   catchment as a whole. It consists of a secondary channel, wherein the entrances were barred  
176                   by a combination of dykes and groynes in the late 19<sup>th</sup> century (Fig. 1.f). Consequently,  
177                   sediments accumulation led to migrating sandbars in the secondary channel.

178

### 179           3. Material and methods

#### 180                   3.1. Sediment cores sampling and general characterisation

181           One core was sampled from each study site (Fig. 1). Characteristics of all the cores, except PBN-2002,  
182                   have already been published in other papers, although the data on BFR contamination from these  
183                   cores are mostly original. Furthermore, data on MTE and TRS were published by Morereau et al. (2020),  
184                   and those for PDR-1802, PDR-1806, and PDR-1902 were published by Vauclin et al. (2020).

185 The core locations were systematically chosen after conducting on-site ground penetrating radar (GPR)  
186 surveys and analysing them. The cores were positioned to include a significant layer of sediments as  
187 well as interesting subsurface structures identified on the GPR profiles. All cores, except PDR-1806 (Fig.  
188 1.d) and TRS (Fig. 1.f) were sampled underwater from a flat-bottomed polyethylene boat using a  
189 UWITEC® gravity corer (Uwitec, Mondsee, Austria) fitted with a 2 m long and 63 mm diameter plastic  
190 liner. Cores PDR-1806 and TRS were sampled when their respective secondary channels were in a  
191 dewatered state. A Cobra TT percussion driller equipped with a 40 mm-diameter transparent PVC liner  
192 was used in the case of PDR-1806, and a 90 mm-diameter liner was used in the case of TRS.

193 The position and characteristics of the six cores are summarised in the Supplementary Material (SI-1).  
194 Grain size was measured in all cores every 0.5 cm (PDR-1902), 1 cm (PDR-1806, PDR-1802, PBN-2002),  
195 or 4–8 cm (TRS and MTE) in the LEHNA laboratory (Lyon, France) with a Mastersizer 2000© (Malvern  
196 Panalytical) particle size analyser mounted with a hydro SM small volume dispersion unit. Descriptive  
197 grain-size statistics (D50, mode, D10, D90, skewness, etc.) were computed using the Gradistat v.8  
198 software (Blott and Pye, 2001). To represent the grain-size distributions, heatmaps of each core were  
199 plotted; for each measured sample, the percentage of each grain-size class was represented using a  
200 colour scale (SI-4).

201 Rock-Eval pyrolysis was used to analyse the total organic carbon (TOC) in all the studied cores with a 4  
202 cm step (SI-4). The analyses were carried out in the ISTO laboratory (Orléans, France) using a Turbo 6  
203 Rock-Eval pyrolyser (Vinci Technologies).

### 204 3.2. Contaminants analysis

205 The following organic contaminants were quantified in the LABERCA laboratory (ONIRIS Nantes,  
206 France):

207 - Seven indicator polychlorinated biphenyl (PCB) congeners: PCB 28, 52, 101, 118, 138, 153, and 180;  
208 their sum is  $\sum 7\text{PCBi}$ .

209 - Eight polybrominated diphenyl ether (PBDE) congeners: PBDE 28, 47, 99, 100, 153, 154, 183, and 209,  
210 with their sum being  $\Sigma$ 8PBDE.

211 - Three polybrominated biphenyl (PBB) congeners: PBB 52, 101, and 15; their sum is  $\Sigma$ 3PBB.

212 - Three hexabromocyclododecane (HBCDD) stereoisomers:  $\alpha$ ,  $\beta$ , and  $\gamma$ ; their sum is  $\Sigma$ 3HBCDD.

213 - Seven novel BFRs (nBFRs): 1,2,3,5,4-pentabromobenzene (PBBz), pentabromotoluene (PBT), 2, 3, 5,  
214 6-tetrabromo-p-xylene (TBX), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB),  
215 tetrabromo-o-chlorotoluene (TBCT), and octabromotrimethylphenylindane (OBTMPI). Note that the  
216 nBFRs presented in this paper are abbreviated according to the harmonised list of abbreviations  
217 proposed by Bergman (2012), except for PBBz, which does not appear in the list.

218 PCBs, PBDEs, and PBBs were quantified in all the cores, HBCDDs were quantified in all the cores except  
219 PDR-1902 and PBN-2002, and nBFRs were quantified only in PDR (three cores) and PBN (one core)  
220 areas.

221 The samples were collected at a 4–8 cm steps, packaged in amber glass vials and sent to the LABERCA  
222 laboratory for further analysis. For each sample, pressurised liquid extraction was performed on 2 g of  
223 sediment, using a Büchi system (Büchi, Rungis, France) and a mixture of toluene/acetone as solvent  
224 (70/30, v/v) (Liber et al., 2019). Three purification steps were performed using acidic silica, Florisil®,  
225 and celite/carbon columns, successively (Liber et al., 2019). HBCDD stereoisomers were analysed using  
226 liquid chromatography with tandem mass spectrometry (LC-MS/MS). All the other persistent organic  
227 pollutants (POPs) analyses were simultaneously carried out by gas chromatography coupled with high-  
228 resolution mass spectrometry (GC/HRMS) using a 7890A gas chromatograph (Agilent) coupled with a  
229 JMS 800D double-sector high-resolution mass spectrometer (JEOL, Tokyo, Japan) with three injections:  
230 (1) PCBs, (2) deca-BDE and OBTMPI, and (3) PBBs, the remaining 7 PBDEs, and the remaining 6 nBFRs.  
231 Quantification was ensured by isotopic dilution of seven  $^{13}\text{C}$ -labeled internal PCB standards, eight  $^{13}\text{C}$ -  
232 labeled internal PBDE standards, and three  $^{13}\text{C}$ -labeled internal HBCDD standards added to the  
233 samples before the extraction step. For the nBFRs,  $^{13}\text{C}$ -labeled internal standards were used for HBB

234 and PBBz, while PBT, TBX, PBEB, and TBCT were quantified with regard to the PBBz standard. Finally,  
235 the OBTMPI was quantified with respect to the BDE-209 standard as both compounds were in the  
236 same elution fraction during purification and were injected in the same chromatographic column. A  
237 thorough description of the protocol can be found in Vénisseau et al. (2015) and Liber et al. (2019).

238 A procedural blank (consisting of a celite matrix) and an internal quality control (QC) standard were  
239 included in each batch of the ten samples. The associated in-house charts were in accordance with the  
240 acceptable limits fixed for these QC runs, that is, set at  $\pm 2\sigma$  of the average value. The analytical  
241 methods were conducted according to ISO 17025 standards; the QA/QC requirements were fulfilled  
242 throughout the study. Furthermore, the laboratory has continuously participated in proficiency tests  
243 on PCBs and PBDEs with acceptable results (Z-score  $b \pm 2$ ). The limits of detection (LODs) ranged from  
244 0.049 (PCB 118) to 0.109 (PCB 28)  $\mu\text{g kg}^{-1}$  dry weight (DW) for PCBs, 0.00002 (PBDE 28) to 0.05 (PBDE  
245 183)  $\mu\text{g kg}^{-1}$  DW for PBDEs, 0.00005 (PBB 52) to 0.0062  $\mu\text{g kg}^{-1}$  DW (PBB 101) for PBBs, 0.002 to 0.136  
246  $\mu\text{g kg}^{-1}$  DW for HBCDDs, and 0.00001 (TBCT and PBT) to 0.0482 (OBTMPI)  $\mu\text{g kg}^{-1}$  DW for nBFRs.

### 247 3.3. Sediment core dating

248 The age-depth models of MTE and TRS cores have been published by Morereau et al. (2020) and  
249 Dendievel et al. (2020). Furthermore, the age-depth models of cores PDR-1802, PDR-1806, and PDR-  
250 1902 were published by Vauclin et al. (2020). The model for core PBN-2002 is original but based on the  
251 multi-proxy methodology developed by Vauclin et al. (2020). Details regarding the modelling inputs  
252 and parameters for PBN-2002 are provided in the Supplementary Material (SI-3).

## 253 4. Results and discussion

### 254 4.1. Sediment characteristics and dating

#### 255 4.1.1. Grain-size characteristics

256 Grain-size characteristics as well as the TOC content of the six sediment cores are available in the  
257 Supplementary Information (SI-3). Grain-size distributions in cores MTE, PBN-2002, and PDR-1902 are

258 comparable: the sediments are silty (D50 ranging between 20 and 50  $\mu\text{m}$ ), poorly sorted (i.e., the  
259 distribution is widely spread around the D50), and vertically homogeneous. This type of grain size is  
260 optimal for studying contamination as POPs tend to bind strongly to fine particles (Karickhoff et al.,  
261 1979). Furthermore, uniformity indicates that the grain size is unlikely to be a confounding factor  
262 regarding vertical contamination trends. The top 50 and 80 cm of cores PDR-1806 and PDR-1802  
263 displayed similar grain size characteristics (silty, poorly sorted and homogeneous), respectively, but  
264 the bottom parts of these cores were composed of very fine to medium sands (D50 ranging from 100  
265 to 500  $\mu\text{m}$ ). These differences in grain size reflect the evolution of the channels in which the cores are  
266 sampled, ranging from a river channel (bottom part, coarser sediments) to an abandoned channel (top  
267 part, finer sediments), as established by Vauclin et al. (2020). Finally, the grain size in the TRS core  
268 constantly fluctuated between silt and fine sand (D50 mostly ranging from 10 to 100  $\mu\text{m}$ ).

#### 269 4.1.2. Total Organic Carbon content

270 Total Organic Carbon content (TOC) ranged from 0 to 5% in the studied cores. It was vertically  
271 homogeneous in MTE (2–3%), PBN-2002 (2–3%), PDR-1902 (~2%), and TRS (1–2%). It was slightly more  
272 variable in the PDR-1802 core, such that it was around 1% at the bottom of the core where the  
273 sediments were sandy; furthermore, it quickly increased to 3% at a depth of 60 cm, decreased, and  
274 finally remained stable at approximately 2%. Finally, the most significant TOC variation was observed  
275 in the PDR-1806 core, where the TOC was significantly low (< 1%) at the bottom of the core (up to 60  
276 cm) in the presence of sandy sediments. Then, it increased steadily up to 4–5% close to the surface.  
277 Organic carbon content is known to influence the affinity of organic contaminants for sediments;  
278 additionally, because of their hydrophobic properties, POPs tend to bind to organic matter (Karickhoff  
279 et al., 1979). As a result, TOC can be a confounding factor when examining vertical contamination  
280 trends. Spearman correlation matrices were computed between the POP concentrations, the TOC and  
281 the grain size (SI-8). They showed no significant relation between the TOC and the POP concentrations  
282 for all cores except PDR-1806. The PDR-1806 core exhibited strong correlations between the TOC and

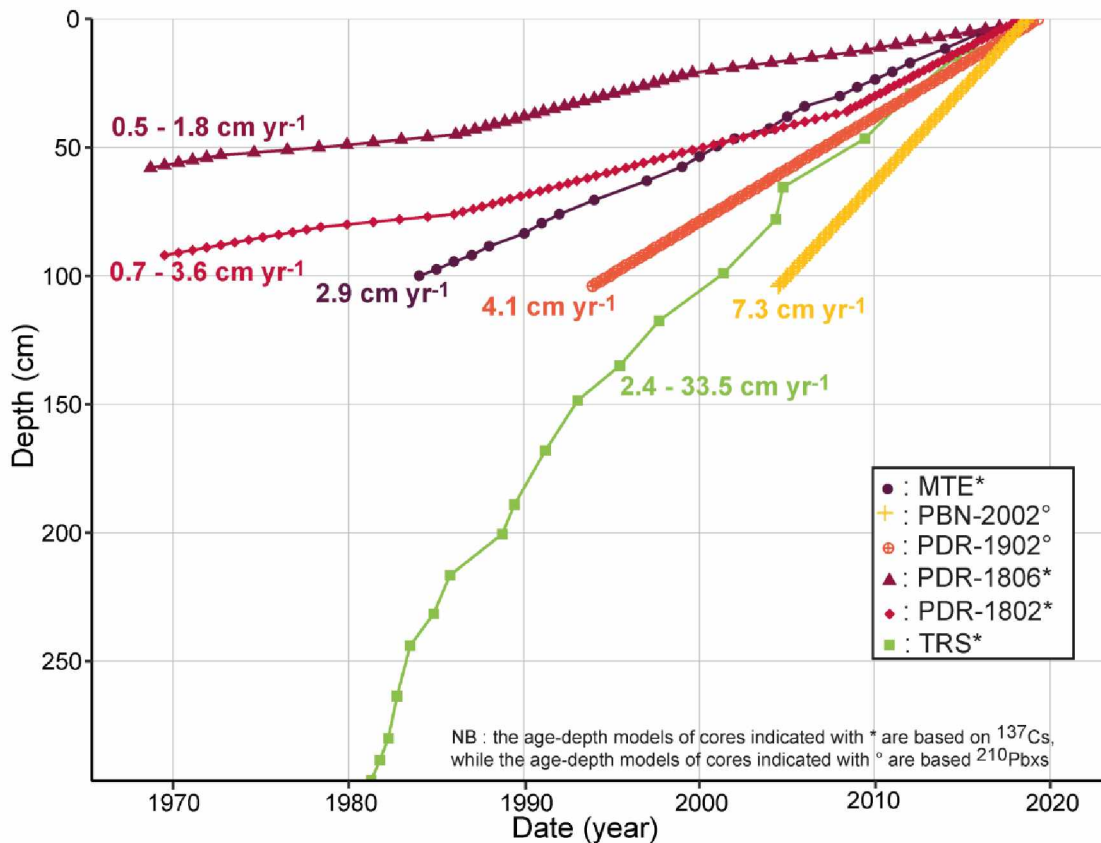
283 several contaminant concentrations (PBDEs, HBCDDs, HBB, PBBz, and TBX). Therefore, only the top 60  
284 cm of the core was used for analysis, where variations in TOC were less.

#### 285 4.1.3. Age-depth models

286 The age-depth models built for each core (Fig. 2) covered a time period ranging from 1970 to 2020.  
287 PDR-1806 in its entirety had sediments from the 1930s, but the top 60 cm used for the contamination  
288 trend comparison corresponds to a period ranging from 1968 to 2018. The different cores display  
289 variable sedimentation rates related to the type of depositional environment they were sampled in.  
290 PDR-1806 and PDR-1802 have the lowest accumulation rate, that is 0.5–1.8 cm yr<sup>-1</sup> and 0.7–3.6 cm yr<sup>-1</sup>,  
291 respectively, which is consistent with the fact that their filling mechanisms are characteristic of a  
292 passive channel fill (Vauclin et al., 2020); moreover, they cover the longest time-period (1970–2018).  
293 MTE displays a similar filling dynamic, that is a consistent sedimentation rate of around 2.9 cm yr<sup>-1</sup>. It  
294 covers a time-period ranging from 1985–2018. As PDR-1902 was sampled in an undisturbed dam  
295 reservoir, it exhibited a stable and slightly higher sedimentation rate of approximately 4.1 cm yr<sup>-1</sup>,  
296 covering a time period from the early 1990s to 2019. PBN-2002 dated back to the early 2000s and  
297 displayed a high accumulation rate of around 7.3 cm yr<sup>-1</sup>. This sedimentation is probably linked to the  
298 reactivation (dredging and reconnection in the early 2000s) of the secondary channel, which is  
299 connected to the oxbow lake where the sediment core was sampled (refer to Section 2.1). Finally, TRS  
300 had the highest and most fluctuating sedimentation rate out of the six cores, ranging from 2.4 to 33.5  
301 cm yr<sup>-1</sup>, with an average rate of 7.9 cm yr<sup>-1</sup>. A sedimentation rate of 33.5 cm yr<sup>-1</sup> is extremely high. The  
302 rates reported in the literature in similar hydromorphological contexts are usually lower: 0.65–2.4 cm  
303 yr<sup>-1</sup> along the Ain River, France (Piégay et al., 2008), 0–2.6 cm yr<sup>-1</sup> in small rivers from the south-east  
304 of France (Citterio and Piégay, 2009), 0.5–5.2 cm yr<sup>-1</sup> along the Wurm River, Germany (Hagemann et  
305 al., 2019), and up to 7.7–8 cm yr<sup>-1</sup> along the Morava River, Czech Republic (Bábek et al., 2008; Sedláček  
306 et al., 2016). However, the average sedimentation rate of core TRS (7.9 cm yr<sup>-1</sup>) is consistent with some  
307 of the reported values. In addition, most examples from the literature are from small or medium rivers,



308 while the TRS core is located close to the estuary of a major river known for its important sediment  
 309 transport, and downstream of the confluence of the Rhône River with the Durance River, which has a  
 310 high sediment load (Chapuis, 2012). In such a setting, dozens of centimetres of sediment can be  
 311 deposited in a short amount of time during floods, which explains the occasionally high sedimentation  
 312 rates.



313  
 314 *Figure Error! No text of specified style in document.2: Age-depth models for the six studied sediment cores. Models for TRS*  
 315 *and MTE were first published in Dendievel et al., 2020 and Morereau et al., 2020 while the models for PDR-1802, PDR-1806*  
 316 *and PDR-1902 were first published in Vauclin et al., 2020. [IN COLOUR]*

## 317 4.2. Legacy BFRs in the Rhône River sediments

### 318 4.2.1. Contamination levels and congeners repartition

319 In this study, PCBs were selected as the “reference” POPs, as their levels and spatiotemporal trends in  
 320 the Rhône River were extensively studied (Desmet et al., 2012; Mourier et al., 2014; Dendievel et al.,  
 321 2020). They were quantified in 100% of the samples (Table 1). Their concentrations range from 0.22

322  $\mu\text{g kg}^{-1}$  DW in PDR to  $194.72 \mu\text{g kg}^{-1}$  DW in TRS. Furthermore, based on the study area, their median  
323 concentrations ranged from  $10.20 \mu\text{g kg}^{-1}$  DW in MTE, which is the most upstream site, to  $41.13 \mu\text{g kg}^{-1}$   
324  $\text{DW}$  in TRS, which is the most downstream site. A comprehensive PCB contamination study (Dendievel  
325 et al., 2020) showed that its median concentrations in the Upper Rhône (upstream of Lyon) was  
326  $15 \pm 10 \mu\text{g kg}^{-1}$  (consistent with MTE concentrations) and the Middle Rhône section (between Lyon and  
327 the Isère River confluence) was  $32 \pm 24 \mu\text{g kg}^{-1}$  DW. This was consistent with the concentrations  
328 obtained in this study with respect to PBN and PDR. The seven congeners repartitions were similar in  
329 the six cores, with PCB-153 consisting of the highest proportion of  $\sum 7\text{PCBi}$  (with an average of  $\sim 28\%$   
330 for all six cores) and PCB-28 consisting of the lowest proportion ( $\sim 4\%$  on average). The three highly  
331 chlorinated congeners (PCB-138, PCB-153, and PCB-180) represented approximately 70% of the total  
332 concentration, on average. This repartition is consistent with other observations from the Rhône River  
333 sediments (Desmet et al., 2012), given that lighter congeners are more prone to volatilization or  
334 microbial degradation than highly chlorinated compounds (Barriault and Sylvestre, 1993).

335 *Table 1: Occurrence, mean and median concentrations of PCBs and legacy BFRs according to the study area, in  $\mu\text{g kg}^{-1}$  dry*  
336 *weight. The statistics were computed using all the values. DR = Detection rate; SD = standard deviation. LOD = limit of*  
337 *detection; NM = not measured.*

Contaminants	MTE (n = 25)			PBN (n = 27)			PDR (n = 72)			TRS (n = 20)		
	DR	Mean (SD)	Median (min-max)	DR	Mean (SD)	Median (min-max)	DR	Mean (SD)	Median (min-max)	DR	Mean (SD)	Median (min-max)
$\sum 7\text{PCBi}$	100%	<b>12.07</b> (5.54)	<b>10.20</b> (4.78– 23.96)	100%	<b>21.83</b> (11.89)	<b>19.0</b> (10.21– 62.27)	100%	<b>32.55</b> (24.72)	<b>30.79</b> (0.22– 114.60)	100%	<b>73.21</b> (63.88)	<b>41.13</b> (4.62– 194.72)
$\sum 8\text{PBDE}$	100%	<b>7.00</b> (6.65)	<b>4.94</b> (0.57– 30.11)	100%	<b>136.18</b> (78.63)	<b>131.99</b> (23.94– 287.87)	100%	<b>84.78</b> (76.16)	<b>108.11</b> (0.077– 376.73)	100%	<b>28.99</b> (38.15)	<b>13.33</b> (0.15– 125.15)

<b>Σ3PBB</b>	24%	<b>0.0018</b> (0.003)	<LOD (<LOD – 0.0098)	89%	<b>0.0043</b> (0.003)	<b>0.0037</b> (<LOD– 0.013)	42%	<b>0.0077</b> (0.014)	<LOD (<LOD– 0.075)	85%	<b>0.016</b> (0.015)	<b>0.0097</b> (<LOD– 0.048)
<b>Σ3HBCD</b> <b>D</b>	92%	<b>0.60</b> (1.05)	<b>0.29</b> (<LOD–5.3)	NM	NM	NM	71%	<b>5.5</b> (8.96)	<b>1.95</b> (<LOD– 41.95)	60%	<b>0.84</b> (1.71)	<b>0.13</b> (<LOD– 5.56)

338 PBDEs were also quantified in 100% of the samples, with concentrations ranging from 0.0077 µg kg<sup>-1</sup>

339 DW (PDR) to 376.73 µg kg<sup>-1</sup> DW (PDR); their median concentrations per study area ranged from 5 µg

340 kg<sup>-1</sup> DW in MTE to 132 µg kg<sup>-1</sup> DW in PBN. These concentrations were significantly higher than those

341 reported by Liber et al. (2019), wherein the median Σ8PBDE concentration was found to be 3.8 µg kg<sup>-1</sup>

342 DW in the five cores obtained from the Rhône River, and by Lorgeoux et al. (2016), where the

343 maximum Σ8PBDE concentration in a core located downstream the Paris megacity was 60 µg kg<sup>-1</sup> DW.

344 However, similar or higher PBDE concentrations in sediments have been observed in Europe, mainly

345 in estuaries. The average PBDE concentration in the Scheldt estuary in the Netherlands and in the

346 Clyde estuary in the UK was 115 µg kg<sup>-1</sup> DW (Van Ael et al., 2012) and 287 µg kg<sup>-1</sup> DW (Vane et al.,

347 2010) respectively. The congener distribution was dominated by BDE-209, which represented 97% of

348 the total concentration on average. This is a very common observation in PBDE congener profiles all

349 over the world (Law et al., 2014). Moreover, it is consistent with the extensive worldwide use of the

350 commercial mixture “deca-BDE” (mostly composed of congener 209), which was prohibited after 2008

351 in the European Union, after the prohibition of other PBDE mixtures/congeners.

352 PBBs were quantified in 24%, 89%, 42%, and 85% of the samples in MTE, PBN, PDR, and TRS,

353 respectively. The concentrations were significantly lower than those of PCBs or PBDEs, ranging from

354 values below LOD to a maximum of 0.075 µg kg<sup>-1</sup> DW in PDR. However, they are in the same order of

355 magnitude as PBB-153 concentrations observed in Lake Michigan (0.11 µg kg<sup>-1</sup> DW) and the Lake Erie

356 (0.06 µg kg<sup>-1</sup> DW) (Zhu and Hites, 2005). PBB-153 represented in average 56% of the Σ3PBB

357 concentrations in our samples, while PBB-101 and PBB-52 accounted for approximately 30% and 15%

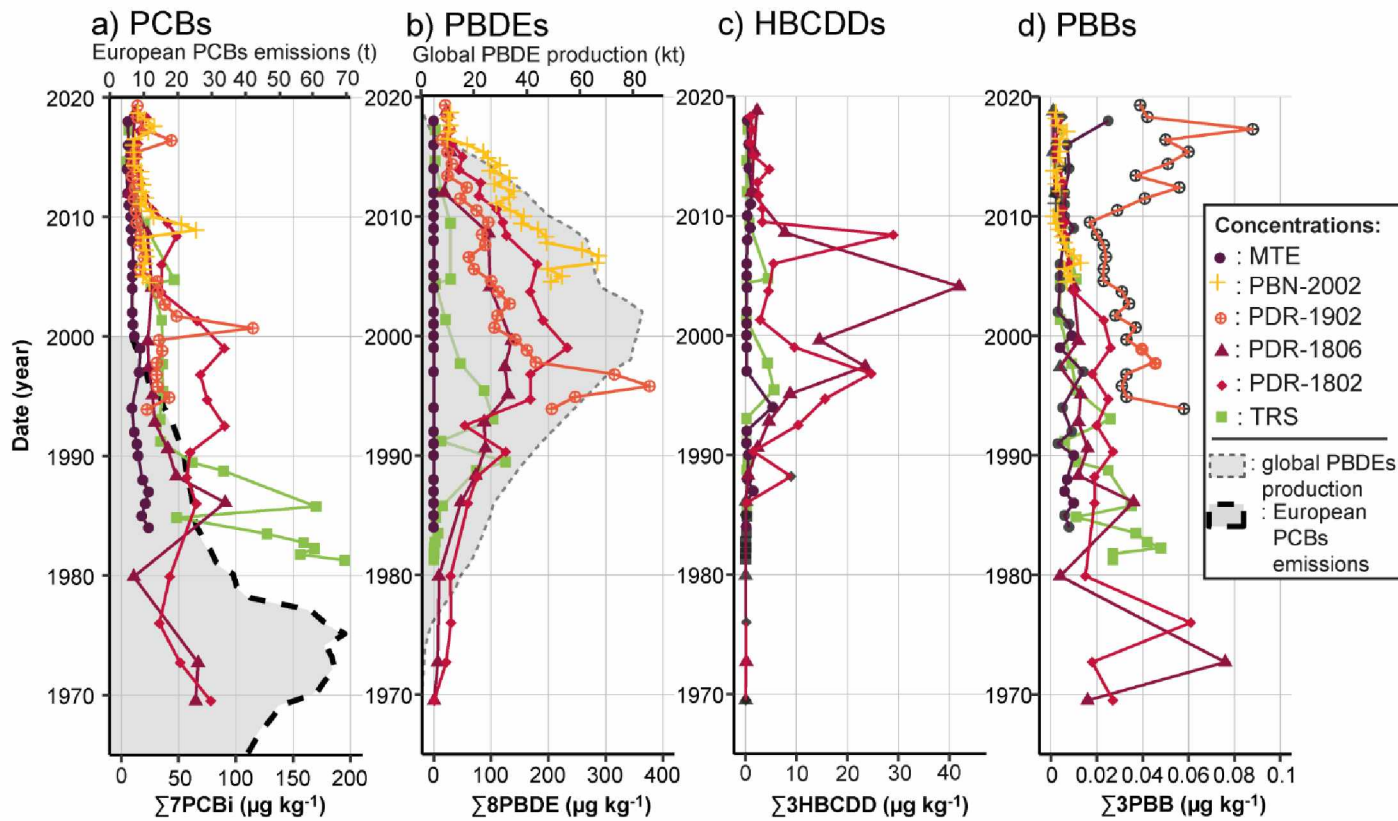
358 respectively. This is consistent with the fact that commercial PBB mixtures are mostly (60%–80%)  
359 composed of hexabromobiphenyls, such as PBB-153 (Sundström et al., 1976).

360 HBCDDs were quantified in 92%, 71%, and 60% of the samples in MTE, PDR, and TRS, respectively.  
361 Median concentrations per study area were relatively low, ranging from 0.13  $\mu\text{g kg}^{-1}$  DW in TRS to 1.95  
362  $\mu\text{g kg}^{-1}$  DW in PDR, with the maximum concentration being observed in PDR, that is 41.95  $\mu\text{g kg}^{-1}$  DW.  
363 Globally, these concentrations are of the same order of magnitude as those observed in the Garonne  
364 Estuary (maximum concentration of 0.09  $\mu\text{g kg}^{-1}$  DW; Lauzent, 2017), Brisbane estuary ( $1\pm 1.5$   $\mu\text{g kg}^{-1}$   
365 DW; Anim et al., 2017), the Sydney estuary (1.8–5.3  $\mu\text{g kg}^{-1}$  DW; Drage et al., 2015), Lake Ellasjøen in  
366 Norway (4  $\mu\text{g kg}^{-1}$  DW; Evenset et al., 2007) or even the Kuzuryu River in Japan, which receives effluents  
367 from the textile industry (0.087–7.8  $\mu\text{g kg}^{-1}$  DW; Oh et al., 2014). However, higher HBCDD  
368 concentrations were measured in the river and harbour of Tianjin in China (mean concentration: 31  $\mu\text{g}$   
369  $\text{kg}^{-1}$  DW; maximum: 634  $\mu\text{g kg}^{-1}$  DW; Zhang et al., 2013). On average, stereoisomer  $\gamma$ ,  $\alpha$ , and  $\beta$   
370 accounted for approximately 60%, 30%, and 10% of the total concentrations, respectively. This  
371 distribution is consistent with results in the literature (Oh et al., 2014; Anim et al., 2017) and the  
372 commercial HBCDD mixture formulation (Covaci et al., 2006; ANSES, 2017).

373 It should be noted that the legacy BFRs under consideration exhibited different levels of persistence in  
374 sediments, which could partially explain the variation in their concentration ranges. BDE-209 had the  
375 highest half-life of the three classes of BFRs, comprising approximately 2–4 years (Gerecke et al., 2005;  
376 2006). PBBs reportedly had half-lives ranging from 3 to 290 days (FAO, 2000). Although HBCDDs are  
377 classified as POPs, their half-lives in sediments ranged between 1 to 128 days (Davis et al., 2005; Marvin  
378 et al., 2011). This is below the regulatory 6 months for an organic pollutant to be considered as  
379 persistent. This may have enhanced the discrepancy between the concentration and detection rates  
380 of PBBs/HBCDDs and PBDEs. Moreover, for the three aforementioned compounds, the concentrations  
381 measured in the major part of the sediment cores were not representative of the full extent of the  
382 contamination at the time the sediments were deposited. However, the same can be stated for all the

383 other studies regarding BFRs in sediments. Thus, the comparisons based on the existing literature  
384 remain valid.

#### 385 4.2.2. Temporal trends



387 *Figure 3: Temporal trends of PCBs and legacy BFRs (PBDEs, PBBs, HBCDDs), in  $\mu\text{g kg}^{-1}$  dry weight. Points that are represented*  
388 *in black correspond to the limit of quantification in the sample. European PCBs emissions (Breivik et al., 2002b) and global*  
389 *PBDEs production (Abbasi et al., 2019) are provided as a comparison. Note that these graphs plotted with a logarithmic scale*  
390 *can be found in the Supplementary Information (SI-5). [IN COLOUR]*

391 The vertical trends of PCBs (Fig. 3.a) showed decreasing concentrations from the 1970s –1980s to 2019  
392 (PDR-1806, PDR-1802, TRS), and stable concentrations in more recent cores (MTE, PDR-1902, PBN-  
393 2002). In all the cores, there was a relatively constant concentration of approximately 10–30  $\mu\text{g kg}^{-1}$   
394 DW from the mid-2000s. These temporal trends are consistent with other observed trends of the  
395 Rhône River (Desmet et al., 2012; Dendievel et al., 2020) and with the data from Breivik et al. (2002b),  
396 which showed that PCB emissions peaked in the 1970s in the European Union and then decreased  
397 steadily.

398 The vertical trends of PBDEs (Fig. 3.b) showed that although the contaminants were detected at very  
399 low concentrations in the sediment from the 1970s, the concentrations increased significantly after  
400 the mid-1980s. Maximum concentrations were observed in the early 1990s in TRS and MTE. This is not  
401 apparent in the graph in Fig.3 because the concentration range in MTE is significantly lower than in the  
402 other cores. Additionally, maximum concentrations were observed in the late 1990s in PDR-1902, and  
403 in the early 2000s for PDR-1806 and PDR-1802. Decreasing trends were recorded in PBN-2002 from  
404 the mid-2000s, which coincided with the decreasing trends observed in the other cores. The temporal  
405 trends of cores PDR-1802 and PDR-1806 were found to be the most consistent with PBDE global  
406 emissions data from Abbasi et al. (2019); however, all cores showed reasonably good coherence with  
407 the temporality of the emissions.

408 HBCDD concentrations were mostly below the LOD before 1990 (Fig. 3.c), and then increased relatively  
409 quickly in cores PDR-1806 and PDR-1802. With respect to PDR-1806, the maximum concentration was  
410 observed in the mid-2000s, which was consistent with the fact that global HBCDD production peaked  
411 in 2006 (Koch et al., 2015). Afterwards, their concentrations decreased quickly and stabilised around  
412 1–5  $\mu\text{g kg}^{-1}$  DW from 2010 onwards. While a clear concentration peak was observed only in PDR-1806,  
413 HBCDDs in the Rhône River sediments had a clearly defined period of occurrence, that is comprised  
414 between 1990 and 2010, based on the results obtained from the four cores.

415 The vertical trend of PBB concentration for cores PDR-1806 and PDR-1802 (Fig. 3.d) showed that  
416 maximum PBB concentrations were recorded in the 1970s, followed by a steady decrease. The  
417 decreasing trend from 1980 in core TRS also suggested that an earlier peak concentration was not  
418 recorded. This is consistent with the fact that PBB production was stopped in 1976 in the USA and from  
419 1977 to 2000 in Europe following the accidental contamination of animal feed supplements by PBBs in  
420 Michigan (USA). This event highlighted the toxicity of the compounds (Darnerud, 2003). From the mid-  
421 2000s, PBB concentrations were low and stable in all three aforementioned cores as well as in PBN-  
422 2002. Most PBB concentrations in cores MTE and PDR-1902 were below the LOD (PBN-2002 was

423 characterised by remarkably high limits of quantification), and therefore could not be used for  
424 interpretation.

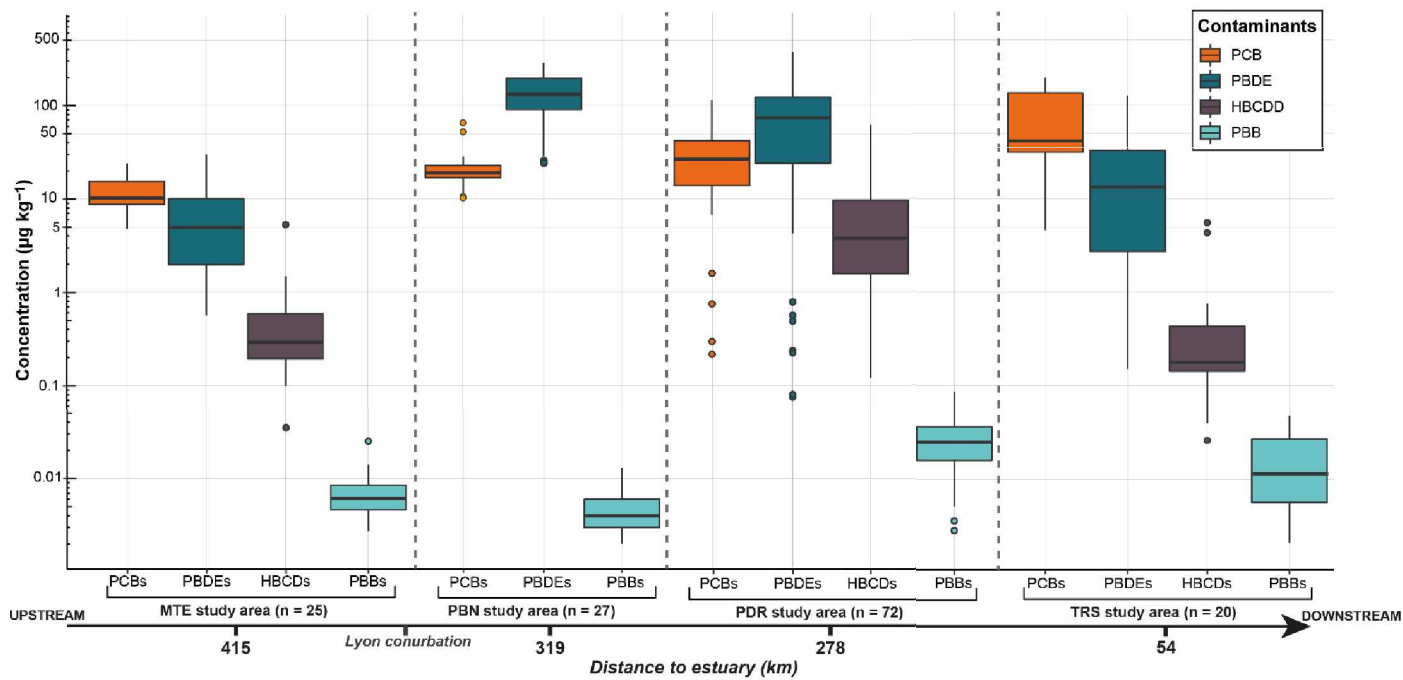
425 Overall, Fig. 3 shows the successive contamination trends of PCBs and legacy BFRs from 1970 to 2000.  
426 PCb concentrations decreased in the 1970s as there was a rapid increase and peak of PBB  
427 concentrations. In the 1980s, PBDE concentrations increased significantly and peaked in the late 1990s  
428 to the early 2000s. Finally, HBCDD concentrations increased in the 1990s and peaked in the mid- to  
429 late-2000s. While PBB and HBCDD concentrations rapidly returned to stable background values  
430 between 2005 and 2010, the decreasing trend of PBDEs was more gradual. This is likely because they  
431 were produced in larger volumes.

#### 432 4.2.3. Spatial trends along the river corridor

433 Boxplots with only quantified concentrations are presented in Fig. 4 for each study area, which allowed  
434 to differentiate broad spatial contamination trends along the Rhône River corridor. Three similar  
435 boxplots, which were plotted after dividing the concentration data into three groups based on the date  
436 of the sample (1969–1990, 1990–2010, and 2010–2019), are available in SI-4. These additional  
437 boxplots were constructed to verify whether the varying concentration levels over time would affect  
438 the spatial trend along the corridor. However, no significant differences were observed in the spatial  
439 trends of the four classes of contaminants between the three time periods (SI-4); therefore, we  
440 decided to present only the overall spatial trend over the entire study period (1969–2019; Fig. 4).

441 PCB concentrations steadily increased from the upstream area (MTE, 415 km from the estuary) to the  
442 most downstream area (TRS, 54 km from the estuary), although the median concentration range was  
443 relatively low (10 to 50  $\mu\text{g kg}^{-1}$  DW). These median concentrations accurately reflected the PCB stock  
444 estimated by Dendievel et al. (2020) for the period between 1945 and 2018 along the Rhône River. It  
445 should be noted that the time period covered by the different sediment cores also influenced the  
446 concentration ranges: for example, PBN-2002 is only for the last 16 years, which means that the peak  
447 PCB contamination has not been recorded. This explains the relatively low PCBs concentrations,

448 despite the core being located directly downstream of the Lyon conurbation.



449

450 *Figure 4: Boxplot representation of the concentrations of PCBs and legacy BFRs (PBDEs, PBBs, HBCDDD) in  $\mu\text{g.kg}^{-1}$  dry weight*  
451 *according to the study area localisation along the Rhône River corridor. [IN COLOUR]*

452 PBDEs followed a different spatial pattern than that of PCBs. While the most upstream area (MTE, 415  
453 km from the estuary) still displayed the lowest concentrations, the highest median concentration was  
454 found in PBN (319 km from the estuary) at  $150 \mu\text{g.kg}^{-1}$  DW; then the concentrations decreased in the  
455 next two downstream areas. This could indicate that Lyon and its surrounding urban and industrial  
456 areas (329 km from the estuary) are the main sources of PBDE contamination along the corridor, and  
457 that PBDEs originating from the metropolis tend to get diluted as they are transported downstream.  
458 Indeed, PBDE concentrations in soils and sediments have been shown to correlate positively with  
459 urban density (diffuse releases from houses, businesses, and vehicles) and industrial areas, even if the  
460 industries are not directly linked to the manufacture or disposal of flame retardants (McGrath et al.,  
461 2017). Although most of the Rhône River corridor is anthropized, the Lyon conurbation and the  
462 adjacent Chemical Valley represent the most heavily populated and industrialised areas, which could  
463 explain the observed spatial trend. In addition, PBDE point sources can be related to manufacturing  
464 industries, landfills, incinerators, and recycling facilities (especially e-waste landfills and recycling;



465 McGrath et al., 2017). However, no specific source of this kind was identified near the PBN area,  
 466 despite the fact that the Lyon conurbation entails many waste disposal and recycling facilities, which  
 467 might have also contributed to the PBDE contamination.

468 The same order of magnitude of HBCDD concentrations was found in the most upstream and  
 469 downstream sites, with median concentrations of approximately 0.3  $\mu\text{g kg}^{-1}$  DW in MTE and TRS.  
 470 Significantly higher concentrations were found in PDR, 278 km from the estuary (median around 4  $\mu\text{g}$   
 471  $\text{kg}^{-1}$  DW), which suggests that HBCDD spatial trends along the Rhône River corridor may be comparable  
 472 to PBDEs, although the lack of data in the PBN area makes the comparison difficult.

473 Finally, no clear spatial trend was observed regarding PBB contamination. The concentration variations  
 474 in the different areas were possibly related to the time period recorded in the sediment cores; for  
 475 example, PBN concentrations could be low because the core dates back to the early 2000s, while most  
 476 PBB contamination occurred in the 1970s.

#### 477 4.3. Novel BFRs in the Rhône River sediments

##### 478 4.3.1. Occurrence and contamination levels of nBFRs

479 *Table 2: Occurrence, mean, and median concentrations of nBFRs according to the sediment core, in ng kg<sup>-1</sup> dry weight.*

480 *Statistics were computed using all the values. DR = Detection rate; SD = standard deviation. LOD = limit of detection*

Contaminant	PBN-2002 (n = 27)			PDR-1902 (n = 27)			PDR-1806 (n = 21)			PDR-1802 (n = 24)		
	DR	Mean (SD)	Median (min- max)	DR	Mean (SD)	Median (min- max)	DR	Mean (SD)	Median (min- max)	DR	Mean (SD)	Median (min- max)
PBBz	100%	<b>14.59</b> (5.05)	<b>14.85</b> (6.65 - 26.29)	100%	<b>12.43</b> (5.96)	<b>12.38</b> (4.66 - 33.74)	100%	<b>13.03</b> (8.62)	<b>12.80</b> (3.34 - 31.01)	100%	<b>22.41</b> (9.14)	<b>24.51</b> (3.35 - 33.88)
PBT	100%	<b>5.6</b> (7.47)	<b>3.07</b> (0.8 - 37)	100%	<b>2.16</b> (2.36)	<b>1.18</b> (0.20 - 10.84)	100%	<b>25.08</b> (19.20)	<b>19.33</b> (4.74 - 87.2.6)	100%	<b>30.40</b> (16.76)	<b>24.15</b> (8.18 - 68.46)
TBX	100%	<b>0.7</b> (0.4)	<b>0.62</b> (0.27 - 2.18)	100%	<b>0.70</b> (0.31)	<b>0.62</b> (0.18 - 1.38)	71%	<b>1.11</b> (0.95)	<b>1.26</b> (<LOD - 3.72)	79%	<b>1.49</b> (2.35)	<b>1.01</b> (<LOD - 11.86)

<b>HBB</b>	100%	<b>8.97</b> (3.86)	<b>8.11</b> (3.14 - 19)	96%	<b>5.55</b> (3.37)	<b>5.04</b> (<LOD - 14.06)	100%	<b>27.16</b> (20.27)	<b>20.45</b> (7.26 - 68.10)	100%	<b>20.21</b> (17.31)	<b>15.89</b> (3.90 - 73.33)
<b>PBEB</b>	52%	<b>0.33</b> (0.42)	<b>0.044</b> (<LOD - 1.26)	67%	<b>0.54</b> (1.15)	<b>0.34</b> (<LOD - 6.08)	5%	<b>0.15</b> (0.71)	<b>&lt;LOD</b> (<LOD - 3.2)	13%	<b>1.90</b> (7.15)	<b>&lt;LOD</b> (<LOD - 34.67)
<b>TBCT</b>	48%	<b>0.3</b> (0.37)	<b>&lt;LOD</b> (<LOD - 1.15)	7%	<b>0.016</b> (0.071)	<b>&lt;LOD</b> (<LOD - 0.36)	0%	/	/	0%	/	/
<b>OBT</b> <b>MPI</b>	70%	<b>36.07</b> (32.63)	<b>30.91</b> (<LOD - 107.21)	56%	<b>23.34</b> (28.17)	<b>15.37</b> (<LOD - 99.15)	0%	/	/	8%	<b>5.72</b> (19.97)	<b>&lt;LOD</b> (<LOD - 85.23)

481 PBBz, PBT, and HBB were quantified in almost 100% of the samples in the four cores (PBN-2002, PDR-  
482 1902, PDR-1806, and PDR-1802) where nBFRs were analysed (Table 2). Out of the aforementioned  
483 compounds, PBBz displayed the highest concentrations, with their median concentrations ranging  
484 from 12.38 ng kg<sup>-1</sup> DW (PBN-1902) to 24.51 ng kg<sup>-1</sup> DW (PDR-1802). Maximum concentration was  
485 recorded in PDR-1802, that is 33.9 ng kg<sup>-1</sup> DW. These levels are similar to PBBz concentrations found  
486 in the surface sediments of the Great Lakes of the USA (maximum concentration of 50 ng kg<sup>-1</sup> DW; Guo  
487 et al., 2020). However, higher PBBz concentrations were found in the soils located inside an e-waste  
488 dismantling park in China (median concentrations of 47.9 µg kg<sup>-1</sup> DW in the park and 580 ng kg<sup>-1</sup> DW  
489 nearby; Ge et al., 2020) or around an e-waste recycling workshop in Vietnam (median concentration  
490 of 120 ng kg<sup>-1</sup> DW and maximum of 560 ng kg<sup>-1</sup> DW; Someya et al., 2016).

491 Significant levels of PBT were also found, with median concentrations ranging from 1.18 ng kg<sup>-1</sup> DW  
492 (PDR-1902) to 24.15 ng kg<sup>-1</sup> DW (PDR-1802). Furthermore, the maximum recorded concentration was  
493 in PDR-1806, that is 87.26 ng kg<sup>-1</sup> DW. These levels are similar to those found in the surface sediments  
494 of the Great Lakes, USA (maximum concentration of 90 ng kg<sup>-1</sup> DW; Guo et al., 2020), but lower than  
495 those found in an e-waste workshop in Vietnam (maximum concentration of 790 ng kg<sup>-1</sup> DW, Someya  
496 et al., 2016) or in the wetlands close to the industrialised Jiaozhou Bay in China (concentration range  
497 of 0.7-1887 µg kg<sup>-1</sup> DW; Wang et al., 2015).

498 Median HBB concentrations ranged from 5.04 ng kg<sup>-1</sup> DW (PDR-1902) to 20.45 ng kg<sup>-1</sup> DW (PDR-1806);  
499 the maximum measured concentration was 73.33 ng kg<sup>-1</sup> DW in PDR-1802. These levels were similar

500 to those found in surficial sediments in the Thames River of the UK (HBB concentrations  $<30 \text{ ng kg}^{-1}$   
501 DW; Ganci et al., 2019). However, significantly higher concentrations have been reported in sediments  
502 and soils around the world, that is up to  $5.56 \mu\text{g kg}^{-1}$  DW in the surface sediments of Lake Huron, USA  
503 (Guo et al., 2020) and  $8.94 \mu\text{g kg}^{-1}$  DW in the wetlands of the Jiaozhou Bay, China (Wang et al., 2015).

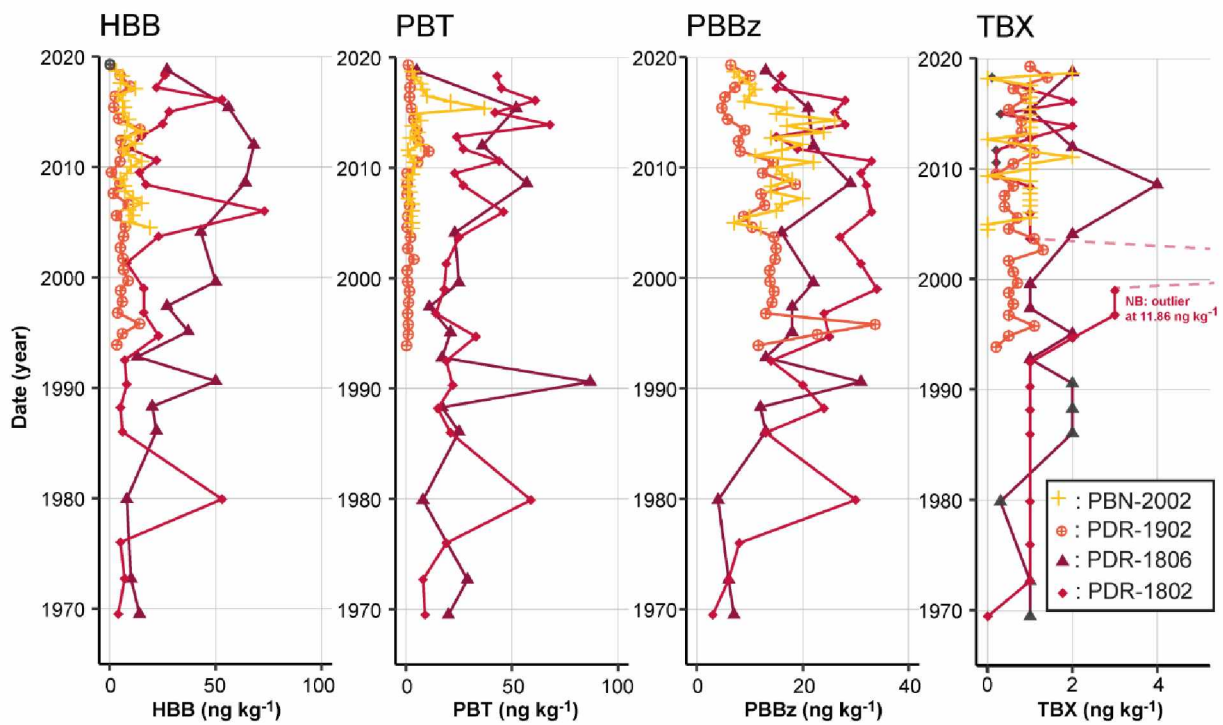
504 TBX was quantified in a majority of the samples, that is 100%, 100%, 71%, and 79% for PBN-2002, PDR-  
505 1902, PDR-1806 and PDR-1802, respectively. Moreover, its median concentrations ranged from 0.62  
506 to  $1.26 \text{ ng kg}^{-1}$  DW. Its maximum concentration was  $11.86 \text{ ng kg}^{-1}$  DW in PDR-1802. These  
507 concentrations were in the same order of magnitude as those found in the mangrove surface  
508 sediments of Shenzhen, China ( $9\text{--}50 \text{ ng kg}^{-1}$  DW; Hu et al., 2020), but significantly lower than those  
509 found in the wetlands of the Jiaozhou Bay, China ( $0.7\text{--}1.2 \mu\text{g kg}^{-1}$  DW; Wang et al., 2015).

510 PBEB, TBCT and OBTMPI were rarely detected, with detection rates ranging from 5% (PDR-1806) to  
511 52% (PBN-2002) for PBEB, 0% (PDR-1806 and 1802) to 48% (PBN-2002) for TBCT, and 0% (PDR-1806)  
512 to 70% (PBN-2002) for OBTMPI. While the measured concentrations of PBEB and TBCT are significantly  
513 low (median concentration  $<2 \text{ ng kg}^{-1}$  DW), the OBTMPI levels are similar to the well-quantified nBFRs  
514 measured in the four cores, with median concentrations being  $15.37 \text{ ng kg}^{-1}$  DW and  $30.91 \text{ ng kg}^{-1}$  DW  
515 in PDR-1902 and PBN-2002, respectively. Furthermore, the maximum concentrations in PDR-1902 and  
516 PBN-2002 were  $107.21$  and  $99.15 \text{ ng kg}^{-1}$  DW, respectively. For comparison, PBEB was measured in the  
517 sediments from the Shenzhen Mangrove, China, with concentrations ranging from 6 to  $60 \text{ ng kg}^{-1}$  DW  
518 (Hu et al., 2020) as well as in the sewage sludge in Catalonia, Spain, with concentrations as high as  $2.33$   
519  $\mu\text{g kg}^{-1}$  DW (Gorga et al., 2013). TBCT was rarely detected in the sediments and soils; however, its  
520 concentration was  $<30 \text{ ng kg}^{-1}$  DW in the San Francisco Bay, USA (Sutton et al., 2019). Similarly, OBTMPI  
521 levels in sediments/soils were rarely reported in the literature, but they were found in the soils close  
522 to an e-waste recycling workshop in Vietnam at a median concentration of  $190 \text{ ng kg}^{-1}$  DW (Someya et  
523 al., 2016).

524 Overall, the measured concentrations of nBFRs in the Rhône River sediments are of the same order of  
525 magnitude as PBBs, but two to four orders of magnitude lower than the concentrations of HBCDDs and  
526 PBDEs. While these relatively low concentrations are obviously not indicative of a massive nBFR  
527 contamination source along the Rhône River corridor, it is interesting to note that all the investigated  
528 compounds were detected and quantified to some extent, including PBEB, TBCT, and OBTMPI which  
529 were seldom detected in sediments/soils in previous studies. This might indicate a diffused but non-  
530 trivial nBFR contamination in the Rhône River. Additionally, the European Food Safety Authority  
531 identified 27 nBFRs in 2013 (EFSA, 2013), and at least 75 different BFRs have been commercialised  
532 (Alaee et al., 2003). This indicates that although the nBFRs concentrations are low when considered  
533 compound wise, the global contamination load related may be more significant.

#### 534 4.3.2. nBFRs temporal trends

535 Vertical contamination trends were plotted only for the four nBFRs that were detected in more than  
536 50% of the samples of the four sediment cores, that is HBB, PBT, PBBz, and TBX (Fig. 5). Although the  
537 temporal trends of the aforementioned compounds are vague as compared to the legacy BFRs, the  
538 concentrations of HBB, PBT, and PBBz are significant from the late 1970s to the early 1980s. This time  
539 period is similar to that of certain legacy BFRs, such as PBDEs. Of the three, PBBz is the only compound  
540 with a significantly decreasing trend in the 2010s in all the cores, after reaching its peak in the 1990s–  
541 2000s. PBT has showed gradual increase over the years in cores PDR-1806 and PDR-1802. On the other  
542 hand, the concentrations cores PBN-2002 and PDR-1902 were low and stable, without significant  
543 trends. A clear increase in HBB concentration was observed over time in PDR-1806, with a slight  
544 decrease in the 2010s. However, this observation was not corroborated by the three other cores. The  
545 concentrations in PDR-1902 and PBN-2002 were low, without significant trends. Additionally, PDR-  
546 1802 displayed several concentration peaks from 1980 to 2006, but no clear temporal trend.  
547 Meanwhile, TBX appeared in the early 1990s but remained moderate over the entire time period,  
548 except for a concentration peak ( $12 \text{ ng kg}^{-1} \text{ DW}$ ) in the early 2000s in PDR-1802.



550

551 *Figure 5: Temporal trends of novel BFRs (HBB, PBT, PBBz, TBX), in ng.kg<sup>-1</sup> dry weight. Points that are represented in black*  
 552 *correspond to the limit of quantification in the sample. Note that these graphs plotted with a logarithmic scale can be found*  
 553 *in the Supplementary Information (SI-7). [IN COLOUR]*

554 Although vertical plots of certain nBFRs were not plotted because they were not systematically  
 555 detected in this study, OBTMPI and PBEB were quantified in more than 50% of the samples in the two  
 556 most recent cores (PBN-2002 and PDR-1902, cf. Table 2). This indicates that these compounds have  
 557 recently appeared in the environment (possibly after 2000). This might be the reason that OBTMPI  
 558 and OBEB are among the least studied and the least detected in abiotic environmental matrices (Barón  
 559 et al., 2014; Ganci et al., 2019). Overall, although no clear and consistent temporal trends in sediments  
 560 for nBFRs were demonstrated in this paper, this first study proved that:

- 561 - Despite the “novel” BFRs appellation, most nBFRs may have been first produced and released
- 562 in the environment between the 1970s and the 1990s i.e., at the same time-period as “legacy
- 563 BFRs”. This is corroborative with the study by Hoh et al. (2005) that shows that PBEB was
- 564 mainly produced in the 1970s and the 1980s in the USA. Besides, while information on the

565 production period of other nBFRs studied in this paper are not readily available, 1,2-Bis(2,4,6-  
566 tribromophenoxy)ethane (BTBPE), another nBFR, is known to have been produced since the  
567 1970s (Covaci et al., 2011).

568 - However, nBFRs trends in the Rhône River sediments differ from legacy BFRs' because they do  
569 not display systematic and significant decreasing concentration trends in the 2010s.

570 Currently, the total number of nBFR molecules produced and released into the environment is  
571 unknown, and their screening is relatively uncommon in environmental matrices. However, promising  
572 advances in their analysis techniques might help promote their investigation (Bichon et al., 2018).  
573 Further research and monitoring efforts are required to ensure that nBFRs do not become a major  
574 environmental and sanitary threat as other POPs in the past.

## 575 5. Conclusion

576 In this study, legacy and novel brominated flame retardants were quantified in dated sediment cores  
577 from various locations along the Rhône River corridor in order to reconstruct the temporal trends of  
578 the compounds under consideration. A succession of legacy BFRs contamination trends from 1970 to  
579 2020 was highlighted: PBBs first appeared in the 1970s but decreased quickly. PBDEs were observed  
580 in the mid-1980s, reaching their peak in the late 1990s, and decreasing progressively in the early 2000s.  
581 Moreover, HBCDDs increased in the 1990s, peaked in the 2000s, and quickly decreased afterwards. By  
582 the late 2010s, following the regulation of their production and use, the aforementioned legacy BFRs  
583 reached relatively stable and low concentrations. Overall, legacy BFRs levels in the Rhône River  
584 sediments are within the same orders of magnitude as those reported in the literature with respect to  
585 other rivers or lakes. Furthermore, they seem to be indicative of diffused but non-trivial BFR  
586 contamination that is plausibly linked to the Lyon conurbation and its surrounding industrial areas.  
587 Seven nBFRs were also investigated; all of them were detected in the sediments, albeit at  
588 concentrations that were two to four orders of magnitude below those of legacy BFRs. While no clear  
589 or consistent temporal trends could be identified in our sediment archives, some nBFRs (HBB, PBBz,

590 PBT, and TBX) were estimated to appear in the environment between the 1970s and the 1990s, that  
591 is, at the same time period as legacy BFRs. In addition, no significant decrease was observed in their  
592 concentrations in recent years, thus emphasising the need for additional investigations regarding  
593 nBFRs. Compared to other historical POPs such as PCBs, legacy BFR contamination has been relatively  
594 overlooked in the Rhône River as well as worldwide. Furthermore, it is plausible that the contamination  
595 of nBFRs has been unnoticed due to their relatively low individual concentrations in the environment.  
596 However, the overall contamination load of the nBFRs molecules, which has not been estimated in  
597 environmental or ecotoxicological studies, may be more significant, given that not all nBFRs are known  
598 or quantifiable. Overall, the lack of knowledge regarding the total number of emerging BFRs, their  
599 individual and combined harmful effects, their volume and temporality of production, their sources in  
600 the environment, and the absence of regulations regarding their use and production could cause nBFRs  
601 to become environmental and health hazards in the near future.

602

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## 919 Supplementary Information

920 *SI-1: Coordinates and characteristics of the six studied sediment cores.*

Core	Study site typology	Total length (cm)	X coordinate (WGS 84)	Y coordinate (WGS 84)	Covered time-period
MTE	Secondary channel	101	5.554050	45.701585	1984-2018
PBN-2002	Owbow lake	108	4.824724	4.654604	2004-2020
PDR-1802	Secondary channel	94	4.76651	45.33100	1969-2018
PDR-1806	Secondary channel	82	4.760209	45.344806	1968-2018
PDR-1902	Dam reservoir	104	4.7552535	45.3821711	1993-2019
TRS	Secondary channel	300	4.618433	43.725261	1981-2017

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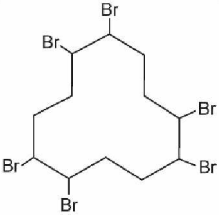
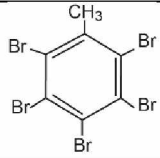
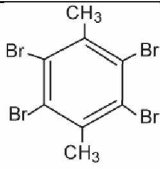
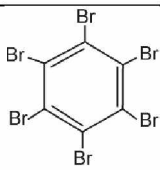
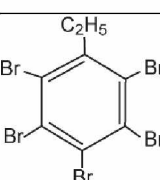

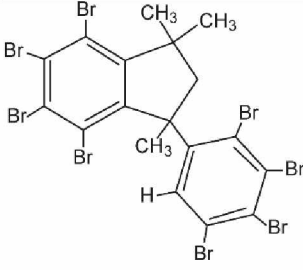
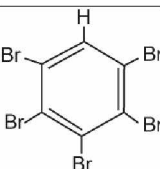
922

923 *SI-2: CAS number, abbreviations according to Bergman et al. (2012) and structure of the studied molecules. NB: molecules indicated with an asterisk (\*) were not listed in Bergman et al. (2012).*

924

CAS number	Practical abbreviation according to Bergman et al., 2012 (used in the manuscript)	Structural abbreviation according to Bergman et al., 2012	Chemical abstract name	Structure	13C-labeled internal standards used	Limits of detection ( $\mu\text{g kg}^{-1}$ )
1336-36-3	PCBs *	/	Polychlorinated biphenyls		13C-PCB28, 13C-PCB52, 13C-PCB101, 13C-PCB118, 13C-PCB138, 13C-PCB-153, 13CPCB-180	0.049 (PCB118) – 0.109 (PCB28)
/	PBDEs	/	Polybrominated diphenyl ethers		13C-BDE28, 13C-BDE47, 13C-BDE99, 13C-BDE100, 13C-BDE153, 13C-BDE154, 13C-BDE183, 13C-BDE209	0.00002 (BDE28) – 0.05 (BDE183)
/	PBBs	/	Polybrominated biphenyls		13C-PBB153	0.00005 (PBB52) – 0.0062 (PBB101)



3194-55-6	<b>HBCDD</b>	HxBcDD	Cyclododecane, 1,2,5,6,9,10- hexabromo-		13C- $\alpha$ HBCDD, 13C- $\beta$ HBCDD, 13C- $\gamma$ HBCDD	0.002- 0.136
87-83-2	<b>PBT</b>	PeBT	Benzene, 1,2,3,4,5- pentabromo-6- methyl		13C-PBBz	0.00001 - 0.00023
23488-38- 2	<b>TBX</b>	TeBDiMeBz	Benzene, 1,2,4,5- tetrabromo-3,6- dimethyl		13C-PBBz	0.00002 - 0.00019
87-82-1	<b>HBB</b>	HxBBz	Benzene, 1,2,3,4,5,6- hexabromo-		13C-HBB	0.00006 - 0.00258
85-22-3	<b>PBEB</b>	PeBEtBz	Benzene, 1,2,3,4,5- pentabromo-6- ethyl-		13C-PBBz	0.00004 - 0.00031
39569-21- 6	<b>TBCT</b>	TeBCMeBz	Benzene, 1,2,3,4- tetrabromo-5- chloro-6-mehtyl		13C-PBBz	0.00001 - 0.00041
1084889- 51-9- 1025956- 65- 3893843- 07-7	<b>OBTMPI</b>	OBTrMePhIn	1 H-Indene, 4,5,6,7- tetrabromo-2,3- dihydro- 1,1,3- trimethyl-3- (2,3,4,5- tetrabromophe nyl)-		13C-BDE209	0.00798 - 0.04782
608-90-2	<b>PBBz *</b>	/	Benzene, 1,2,3,4,5- pentabromo		13C-PBBz	0.00002 - 0.00041

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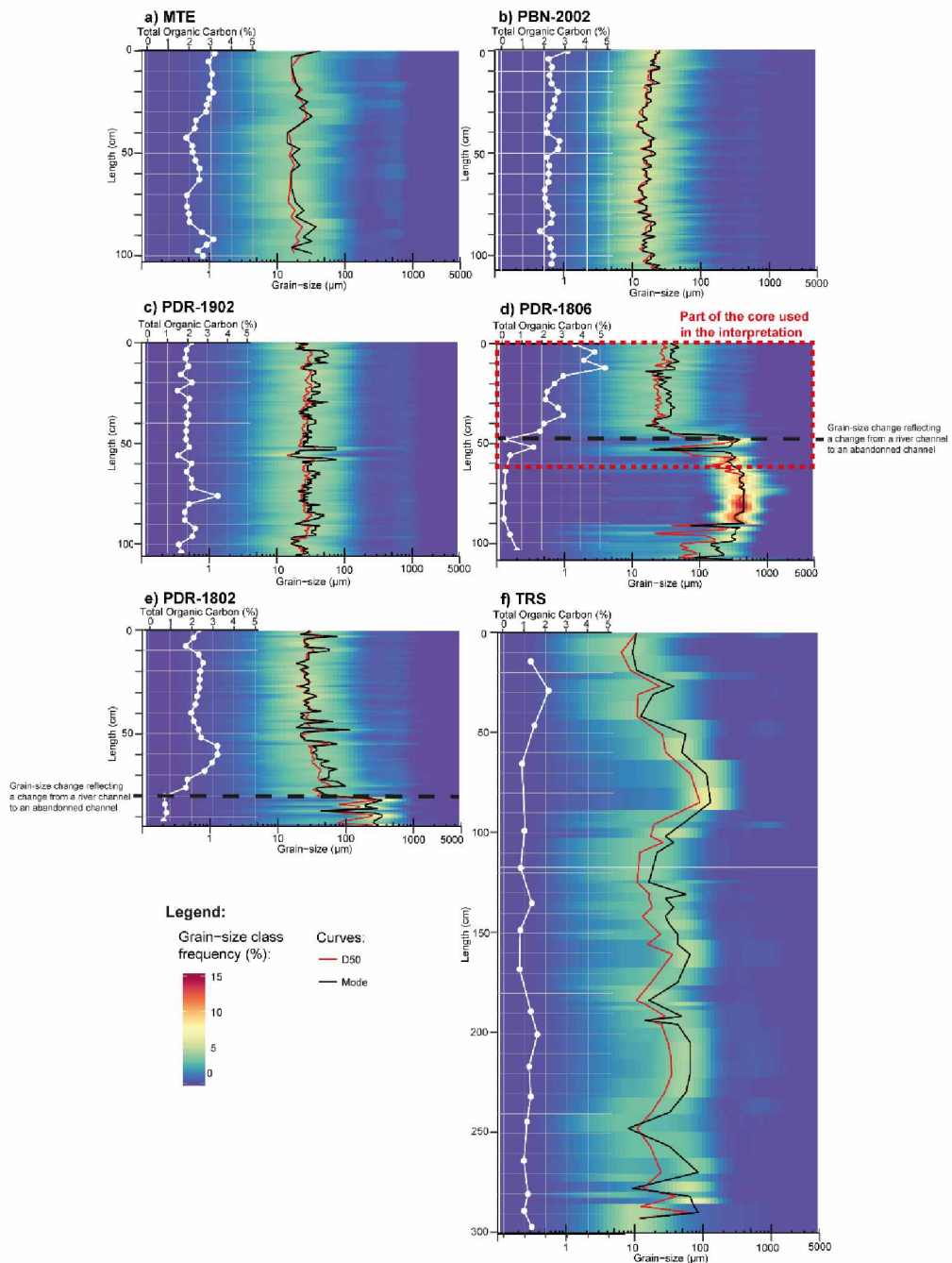
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929 *SI-3: Model type and parameters used to compute the age-depth model of core PBN-2002.*

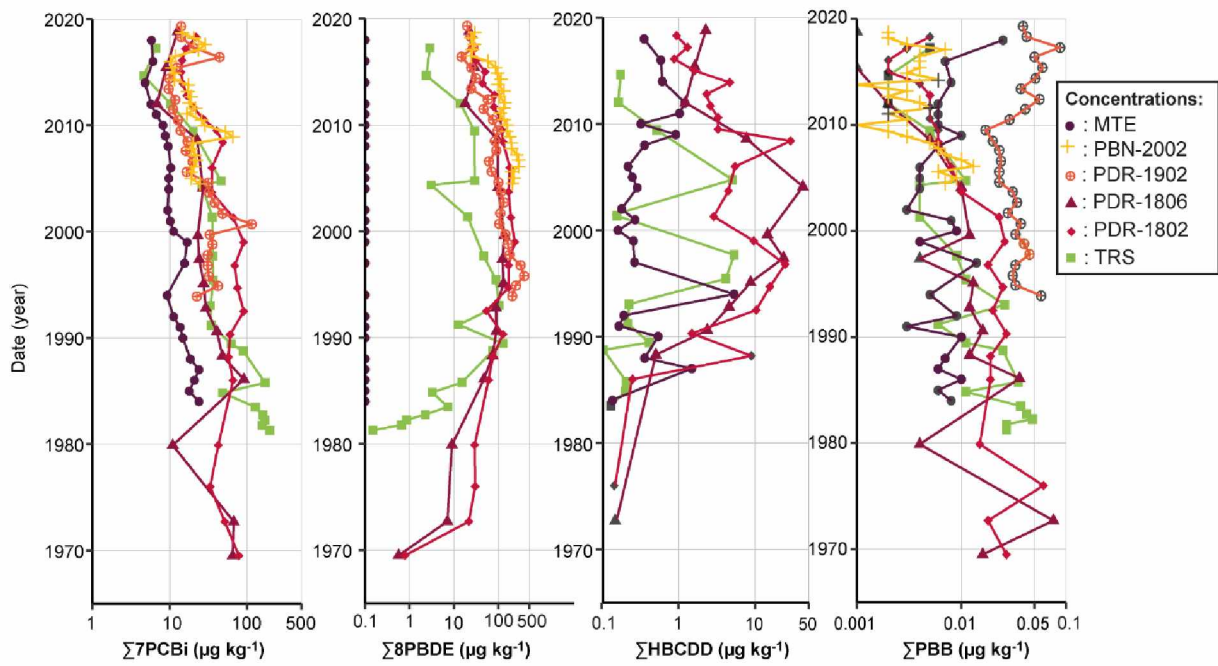
<b>PBN-2002 – Type of model: linear regression</b>			
<b>Time-marker</b>	<b>Date (years)</b>	<b>Depth (cm)</b>	<b>Standard error (years)</b>
Core sampling	2020	0	1
PBDE interdiction	2008	80	4
Date of the bottom of the core based on <sup>210</sup> Pbxs regression	2004	104	4

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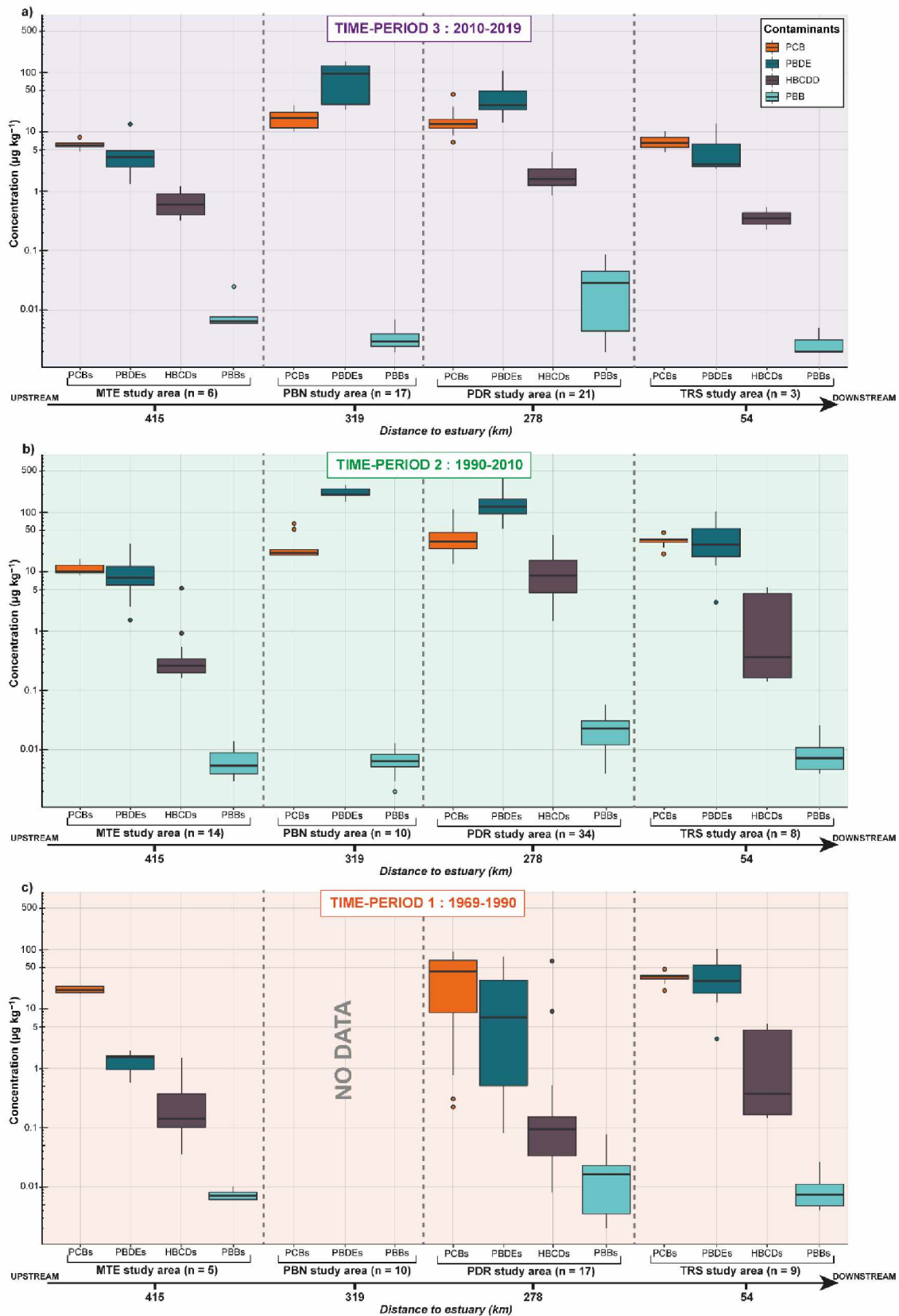
932 SI-4: Grain-size distribution and total organic carbon content of the six studied sediment cores.



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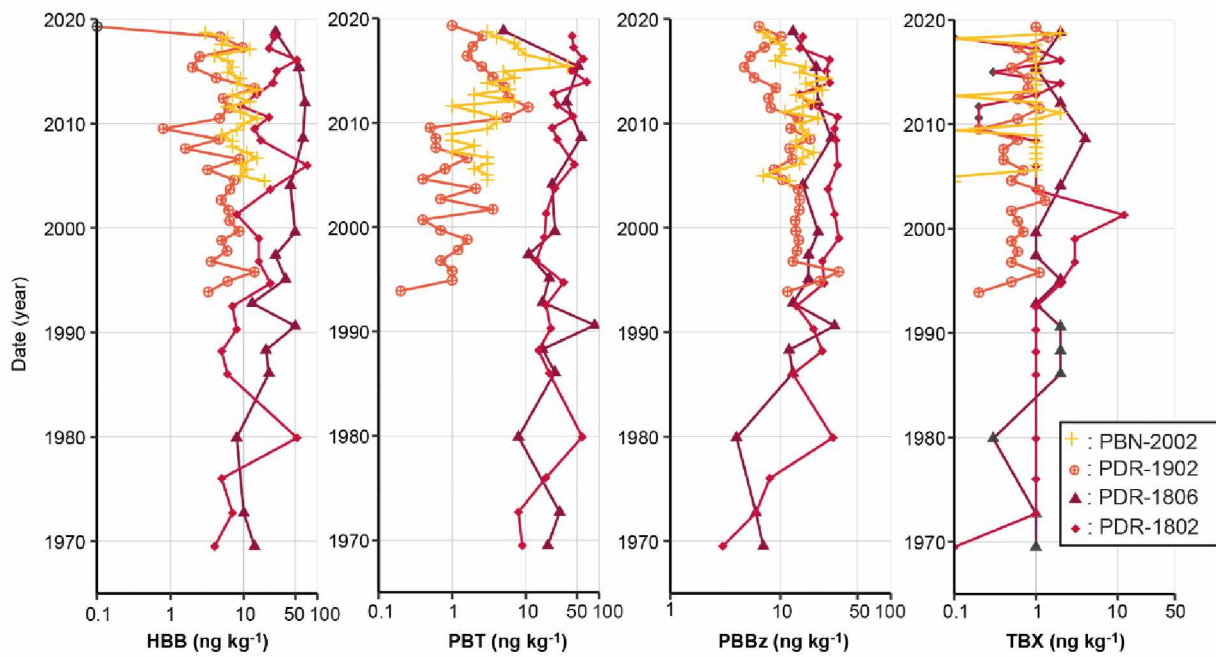
934 *SI-5: Temporal trends of PCBs and legacy BFRs (PBDEs, PBBs, HBCDDs) represented with a logarithmic scale in  $\mu\text{g kg}^{-1}$  dry*

935 *weight. Points that are represented in black correspond to the limit of quantification in the sample.*



936

937 *SI-6: Boxplot representation of the concentrations in PCBs and legacy BFRs (PBDEs, PBBs, HBCDDD) in µg kg<sup>-1</sup> dry weight*  
 938 *according to the study area localization along the Rhône River corridor. a) for the 2010-2019 time-period; b) for the 1990-*  
 939 *2010 time-period; c) for the 1969-1990 time-period.*

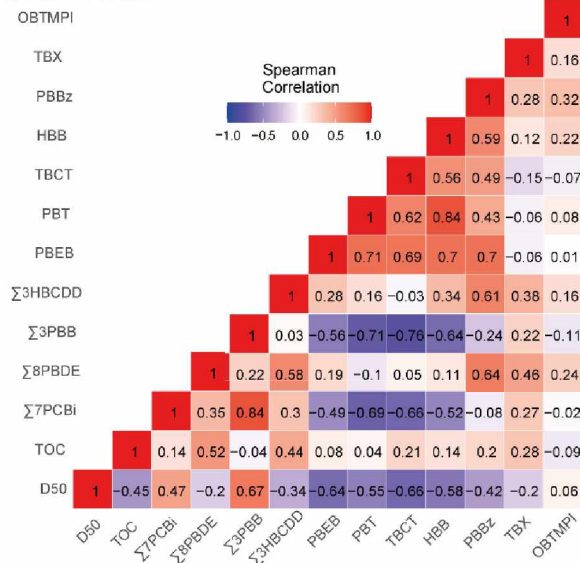


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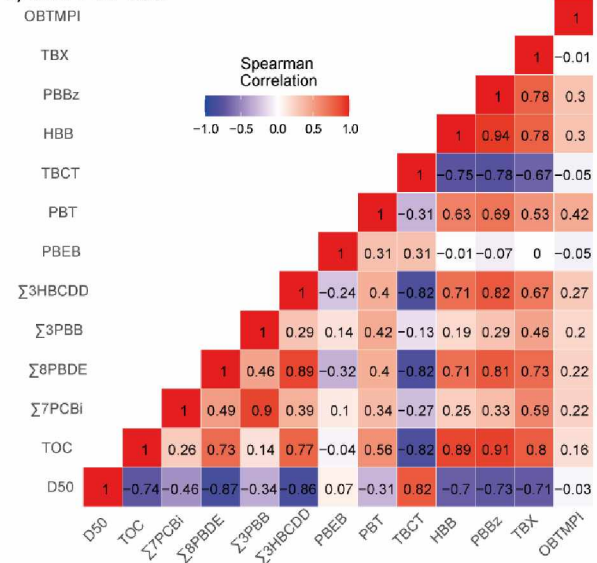
941 *SI-7: Temporal trends of novel BFRs (HBB, PBT, PBBz, and TBX) represented with a logarithmic scale in ng kg<sup>-1</sup> dry weight.*

942 *Points that are represented in black correspond to the limit of quantification in the sample.*

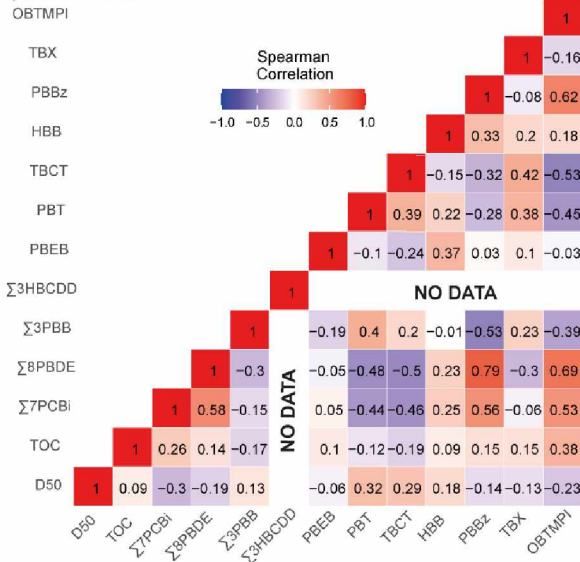
a) Core PDR-1802



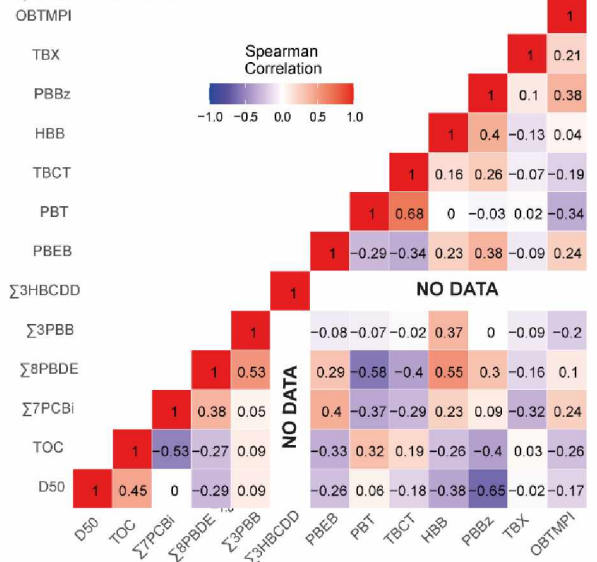
b) Core PDR-1806



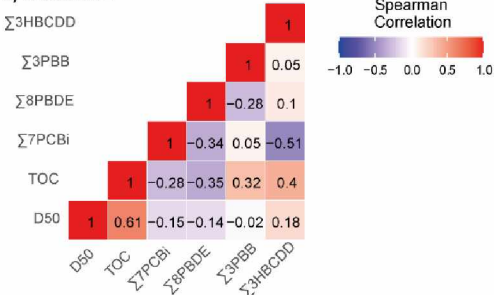
c) Core PDR-1902



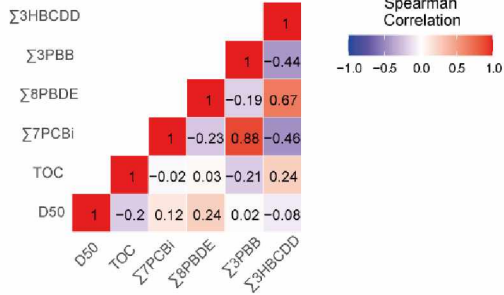
d) Core PBN-2002



e) Core MTE



f) Core TRS



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SI-8: Spearman correlations matrices between the analysed contaminants, Total Organic Carbon (TOC) and grain size (D50) for a) core PDR-1802, b) core PDR-1806, c) core PDR-1902, d) core PBN-2002, e) core MTE, f) core TRS.