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Sophia Vauclin, Brice Mourier, André-Marie Dendievel, Philippe Marchand, Anaïs Vénisseau, et al.. Temporal trends of legacy and novel brominated flame retardants in sediments along the Rhône River corridor in France. *Chemosphere*, 2021, 271, pp.129889. 10.1016/j.chemosphere.2021.129889 . hal-03147392

**HAL Id: hal-03147392**

**<https://hal.science/hal-03147392>**

Submitted on 9 Apr 2021

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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.

3  
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



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

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

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

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

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

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

## 2. Geographic settings

### 2.1. Geographic context

The Rhône River is 812 km; it runs from the Valais region in Switzerland to the Mediterranean Sea in 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 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 (Arles), the Rhône is the largest river in France; moreover, in terms of discharge, it ranks eight in Europe. It is also the most active river in France in terms of sediment transport, with a long-term mean annual sediment load of approximately 6.6 x 10<sup>6</sup> tons (Poulier et al., 2019) and a conveying speed of approximately 2 km year<sup>-1</sup> (Pont et al., 2002).

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

### 2.2. Sampling sites

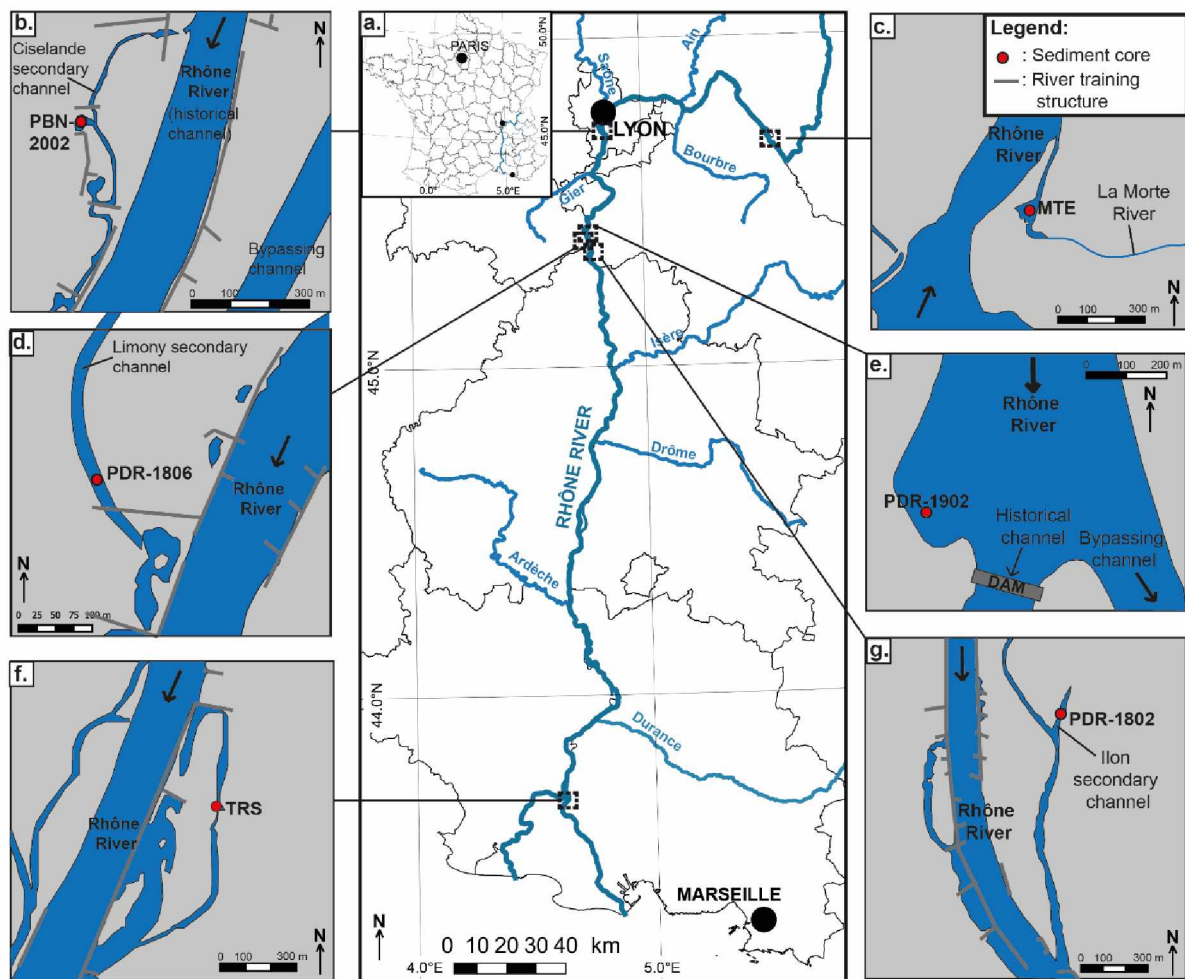


Figure 1: a. Rhône River catchment with localisation of the study sites; b. PBN study site; c. MTE study site; d. PDR-1806 study site; e. PDR-1902 study site; f. TRS study site; g. PDR-1802 study site. [IN COLOUR]

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

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

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

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

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

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

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

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

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

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

### 3. Material and methods

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

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



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

The position and characteristics of the six cores are summarised in the Supplementary Material (SI-1).

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

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

### 3.2. Contaminants analysis

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

- Seven indicator polychlorinated biphenyl (PCB) congeners: PCB 28, 52, 101, 118, 138, 153, and 180; 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

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

A procedural blank (consisting of a celite matrix) and an internal quality control (QC) standard were included in each batch of the ten samples. The associated in-house charts were in accordance with the acceptable limits fixed for these QC runs, that is, set at  $\pm 2\sigma$  of the average value. The analytical methods were conducted according to ISO 17025 standards; the QA/QC requirements were fulfilled throughout the study. Furthermore, the laboratory has continuously participated in proficiency tests on PCBs and PBDEs with acceptable results (Z-score  $b \pm 2$ ). The limits of detection (LODs) ranged from 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 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  $\mu\text{g kg}^{-1}$  DW for HBCDDs, and 0.00001 (TBCT and PBT) to 0.0482 (OBTMPI)  $\mu\text{g kg}^{-1}$  DW for nBFRs.

### 3.3. Sediment core dating

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

## 4. Results and discussion

### 4.1. Sediment characteristics and dating

#### 4.1.1. Grain-size characteristics

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

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

#### 4.1.2. Total Organic Carbon content

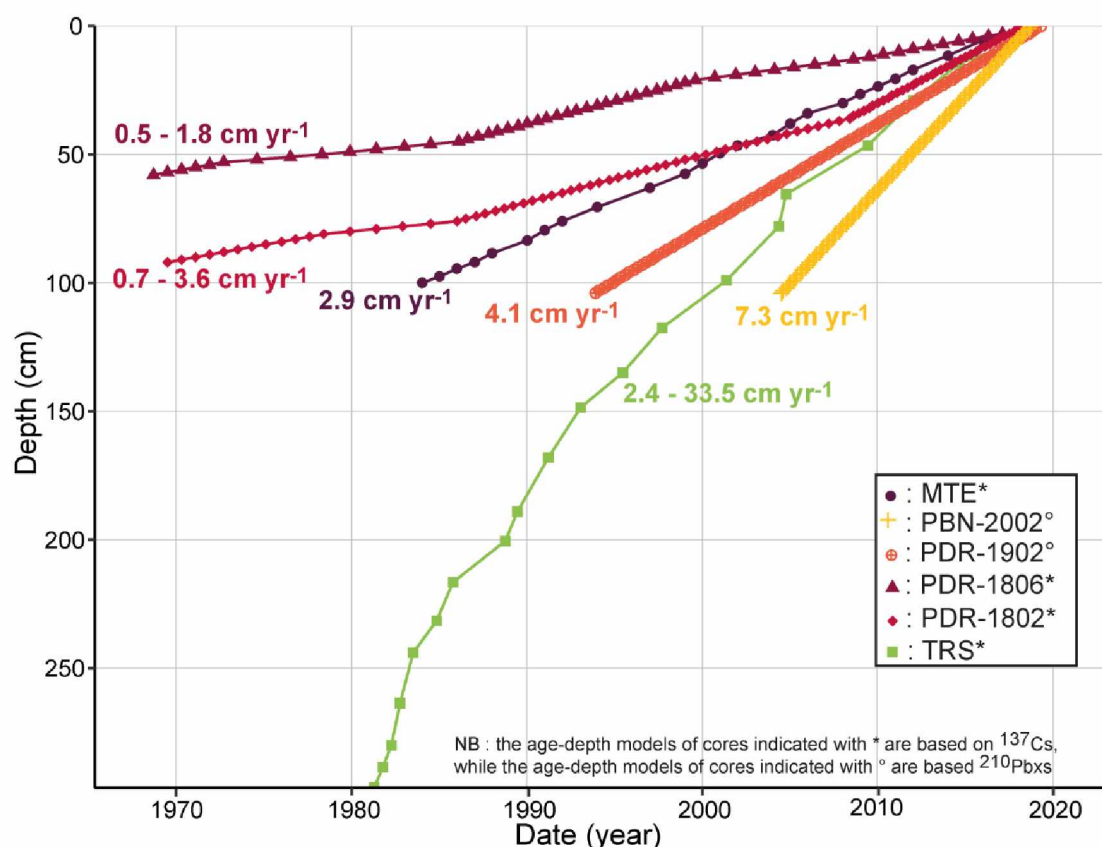
Total Organic Carbon content (TOC) ranged from 0 to 5% in the studied cores. It was vertically homogeneous in MTE (2–3%), PBN-2002 (2–3%), PDR-1902 (~2%), and TRS (1–2%). It was slightly more variable in the PDR-1802 core, such that it was around 1% at the bottom of the core where the sediments were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

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

#### 4.1.3. Age-depth models

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

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



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

## 4.2. Legacy BFRs in the Rhône River sediments

### 4.2.1. Contamination levels and congeners repartition

In this study, PCBs were selected as the “reference” POPs, as their levels and spatiotemporal trends in the Rhône River were extensively studied (Desmet et al., 2012; Mourier et al., 2014; Dendievel et al., 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  $\Sigma 7\text{PCBi}$  (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)
$\Sigma 7\text{PCBi}$	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)
$\Sigma 8\text{PBDE}$	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  $\mu\text{g kg}^{-1}$

339 DW (PDR) to 376.73  $\mu\text{g kg}^{-1}$  DW (PDR); their median concentrations per study area ranged from 5  $\mu\text{g}$

340  $\text{kg}^{-1}$  DW in MTE to 132  $\mu\text{g kg}^{-1}$  DW in PBN. These concentrations were significantly higher than those

341 reported by Liber et al. (2019), wherein the median  $\Sigma 8\text{PBDE}$  concentration was found to be 3.8  $\mu\text{g kg}^{-1}$

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

343 maximum  $\Sigma 8\text{PBDE}$  concentration in a core located downstream the Paris megacity was 60  $\mu\text{g kg}^{-1}$  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  $\mu\text{g kg}^{-1}$  DW (Van Ael et al., 2012) and 287  $\mu\text{g kg}^{-1}$  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  $\mu\text{g kg}^{-1}$  DW in PDR. However, they are in the same order of

355 magnitude as PBB-153 concentrations observed in Lake Michigan (0.11  $\mu\text{g kg}^{-1}$  DW) and the Lake Erie

356 (0.06  $\mu\text{g kg}^{-1}$  DW) (Zhu and Hites, 2005). PBB-153 represented in average 56% of the  $\Sigma 3\text{PBB}$

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

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

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

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



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

#### 4.2.2. Temporal trends

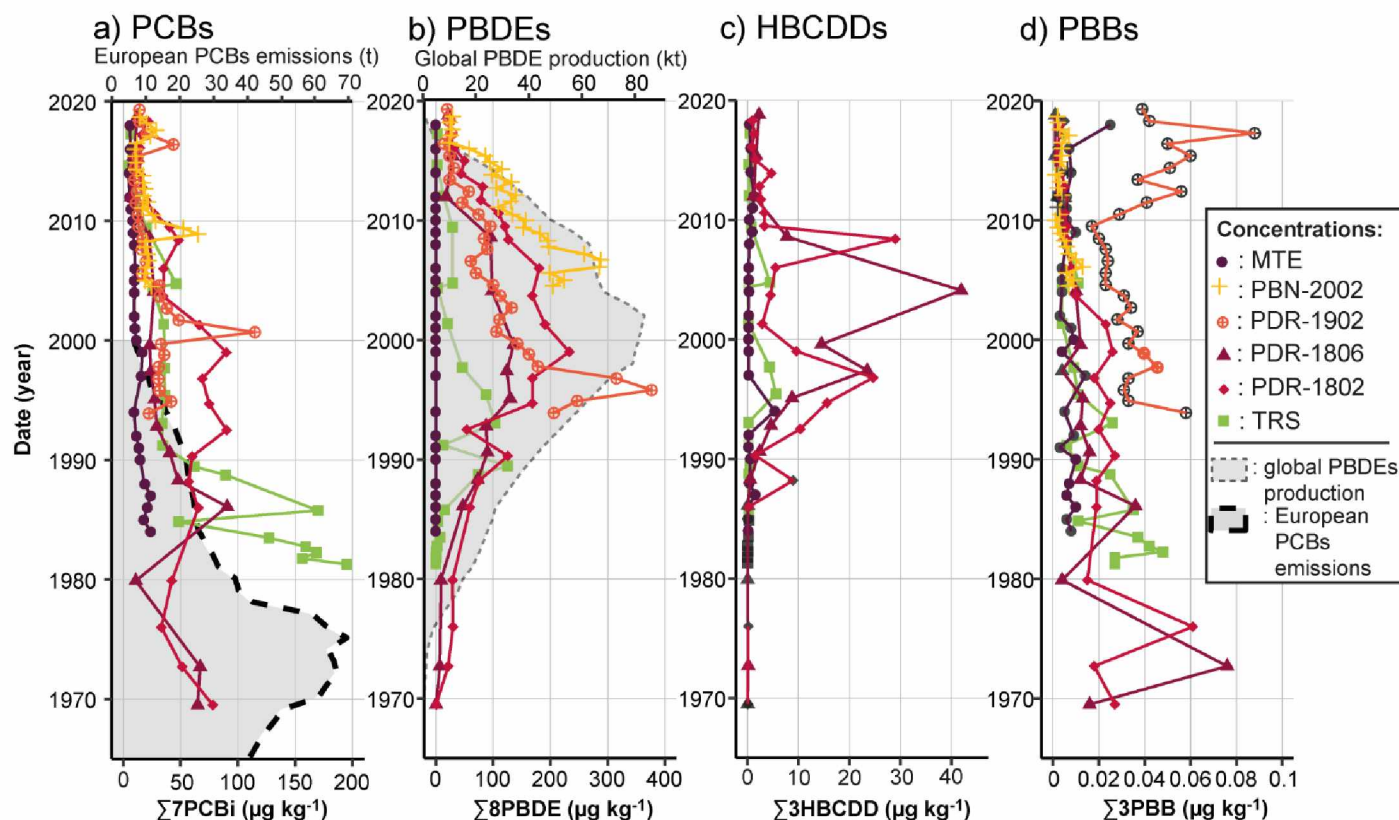


Figure 3: Temporal trends of PCBs and legacy BFRs (PBDEs, PBBs, HBCDDs), in  $\mu\text{g kg}^{-1}$  dry weight. Points that are represented in black correspond to the limit of quantification in the sample. European PCBs emissions (Breivik et al., 2002b) and global PBDEs production (Abbasi et al., 2019)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

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

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

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

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

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

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

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

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

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

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

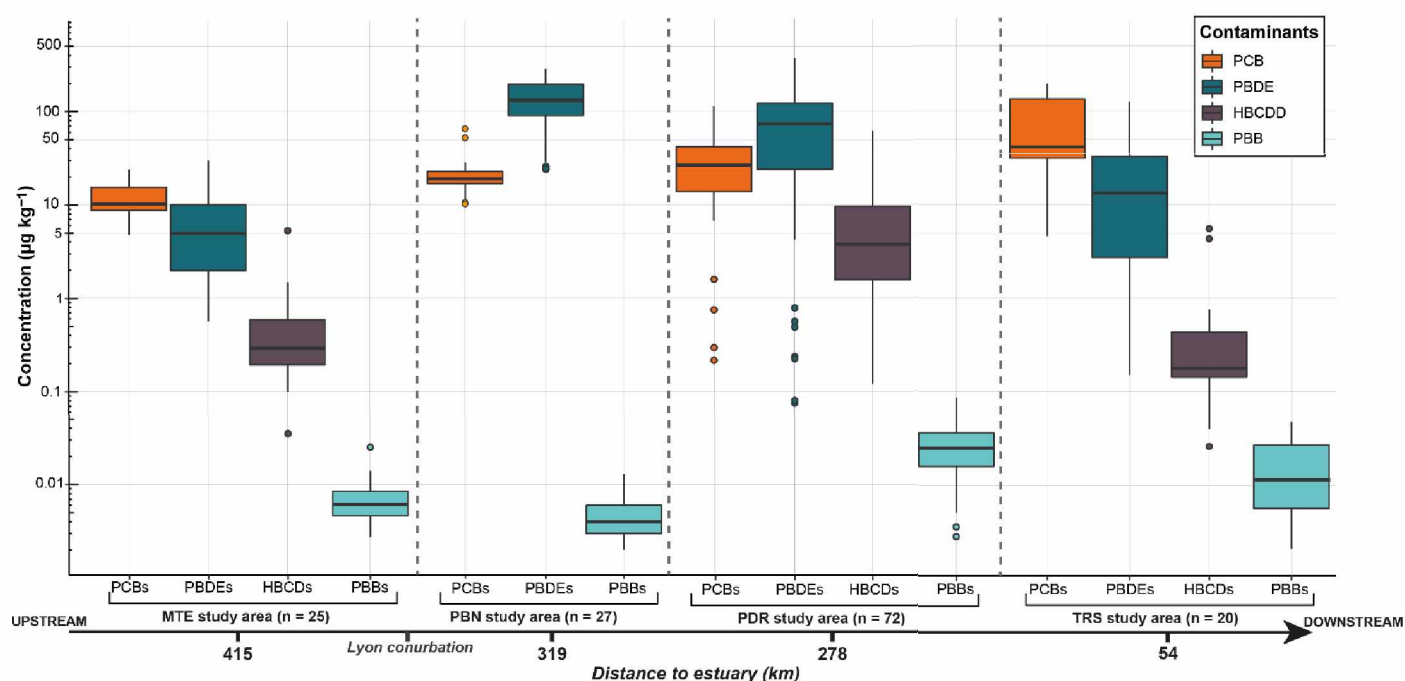


Figure 4: Boxplot representation of the concentrations of PCBs and legacy BFRs (PBDEs, PBBs, HBCDD) in  $\mu\text{g.kg}^{-1}$  dry weight according to the study area localisation along the Rhône River corridor. [IN COLOUR]

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

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

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

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

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

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

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

*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)
<b>PBBz</b>	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)
<b>PBT</b>	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 - 87.26)	100%	<b>30.40</b> (16.76)	<b>24.15</b> (8.18 - 68.46)
<b>TBX</b>	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>PBBB</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 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

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

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

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

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

#### 4.3.2. nBFRs temporal trends

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



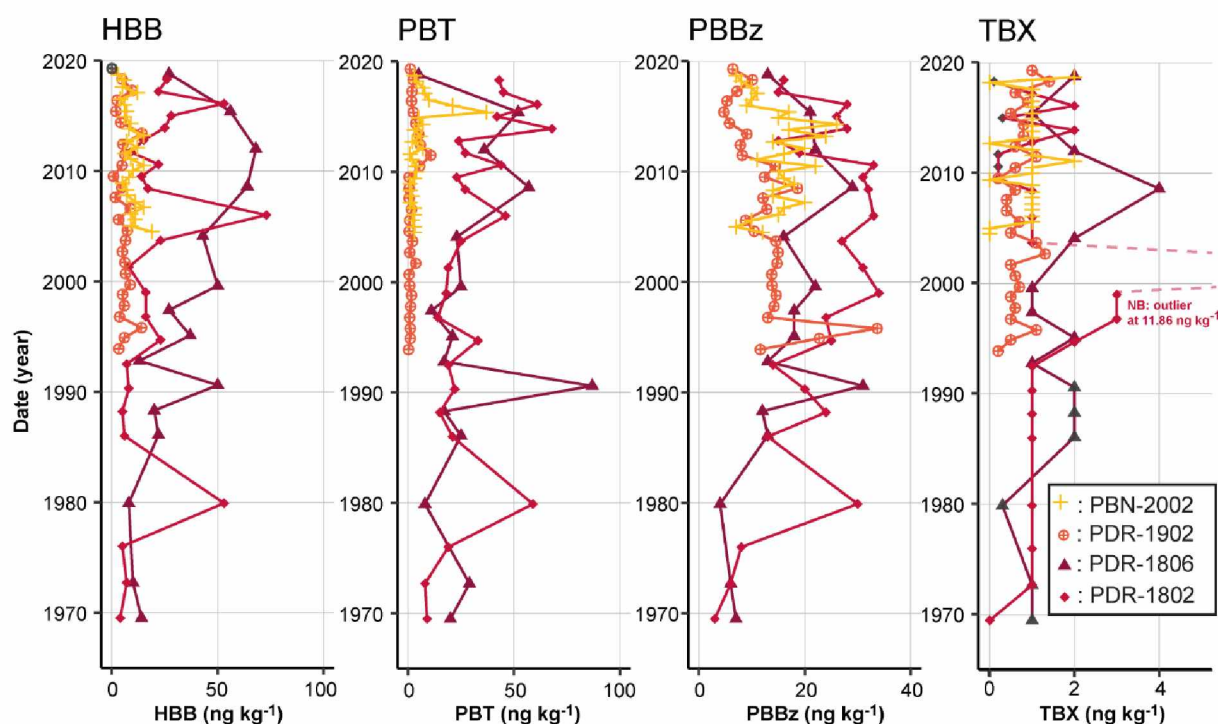


Figure 5: Temporal trends of novel BFRs (HBB, PBT, PBBz, TBX), in  $\text{ng.kg}^{-1}$  dry weight. Points that are represented in black correspond to the limit of quantification in the sample. Note that these graphs plotted with a logarithmic scale can be found in the Supplementary Information (SI-7). [IN COLOUR]

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

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

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

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

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

## 5. Conclusion

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

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

#### Acknowledgments:

Funding for the work was provided by the European Regional Development Fund (ERDF), Agence de l'eau RMC, CNR, EDF and three regional councils (Auvergne-Rhône-Alpes, PACA and Occitanie) in the context of the Rhône Sediment Observatory (OSR, <http://www.graie.org/osr>). These agencies had no role in the study design nor in the collection, analysis, or interpretation of the data and were not involved in the writing of the article. We confirm that all listed authors were involved in the study and read and approved the final submitted version of the manuscript.

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919 Supplementary Information

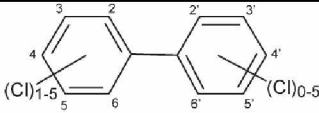
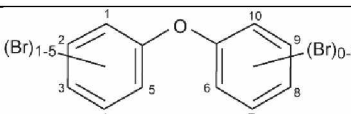
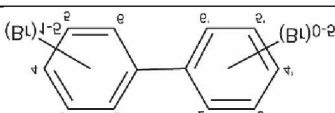
920 SI-1: Coordinates and characteristics of the six studied sediment cores.

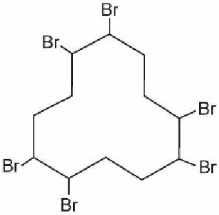
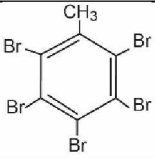


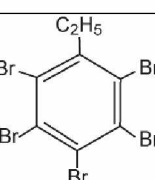
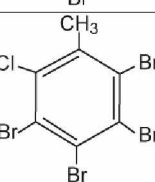
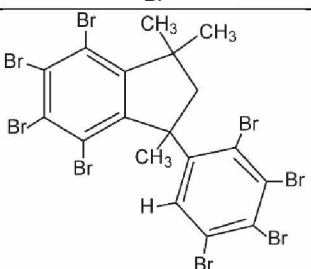

Core	Study site typology	Total length (cm)	X coordinate (WGS 84)	Y coordinate (WGS 84)	Covered time-period
MTE	Secondary channel	101	5.554050	45.701585	1984-2018
PBN-2002	Owbow lake	108	4.824724	4.654604	2004-2020
PDR-1802	Secondary channel	94	4.76651	45.33100	1969-2018
PDR-1806	Secondary channel	82	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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923 SI-2: CAS number, abbreviations according to Bergman et al. (2012) and structure of the studied molecules. NB: molecules  
924 indicated with an asterisk (\*) were not listed in Bergman et al. (2012).

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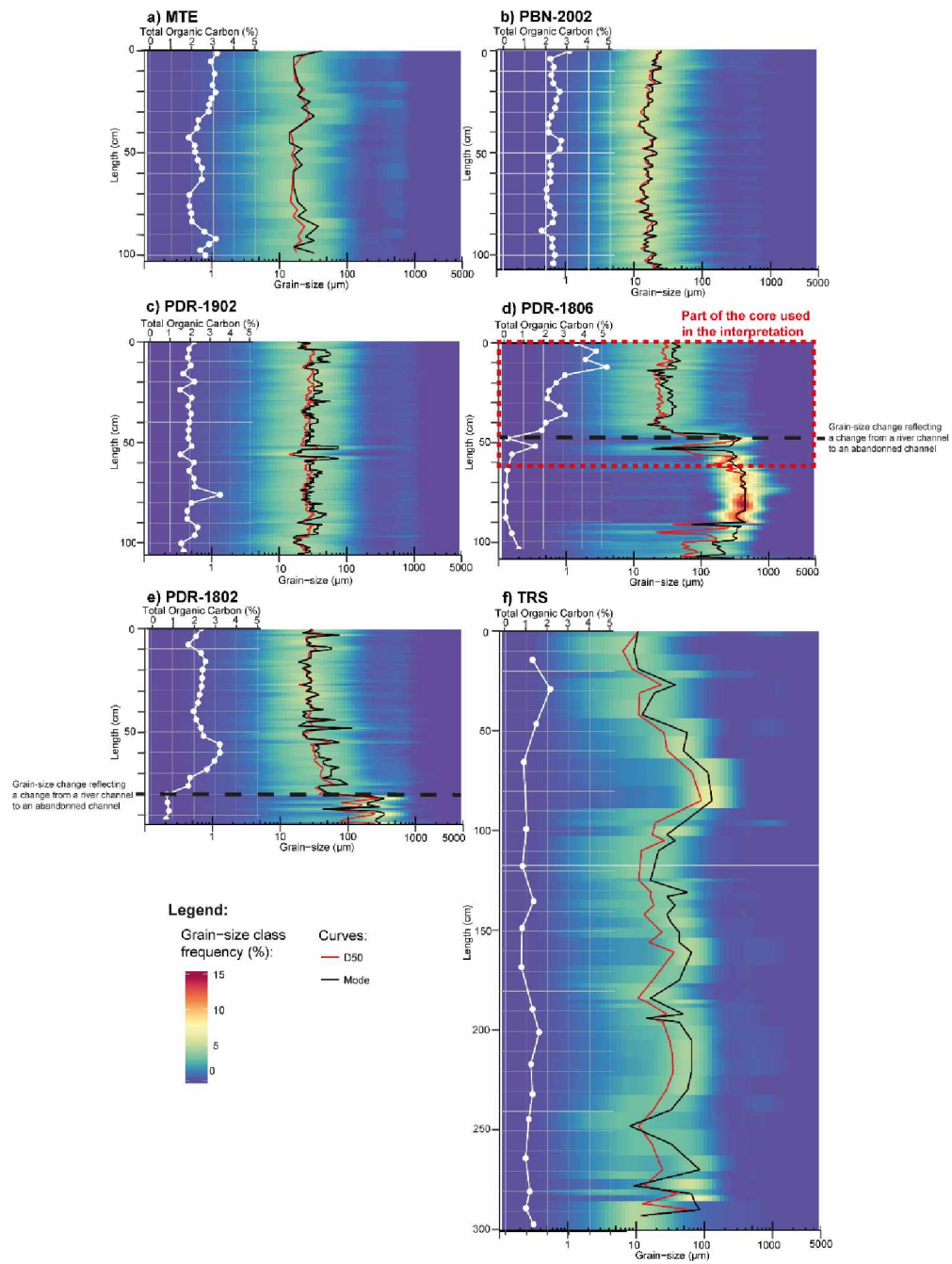
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929 SI-3: Model type and parameters used to compute the age-depth model of core PBN-2002.

PBN-2002 – Type of model: linear regression			
Time-marker	Date (years)	Depth (cm)	Standard error (years)
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

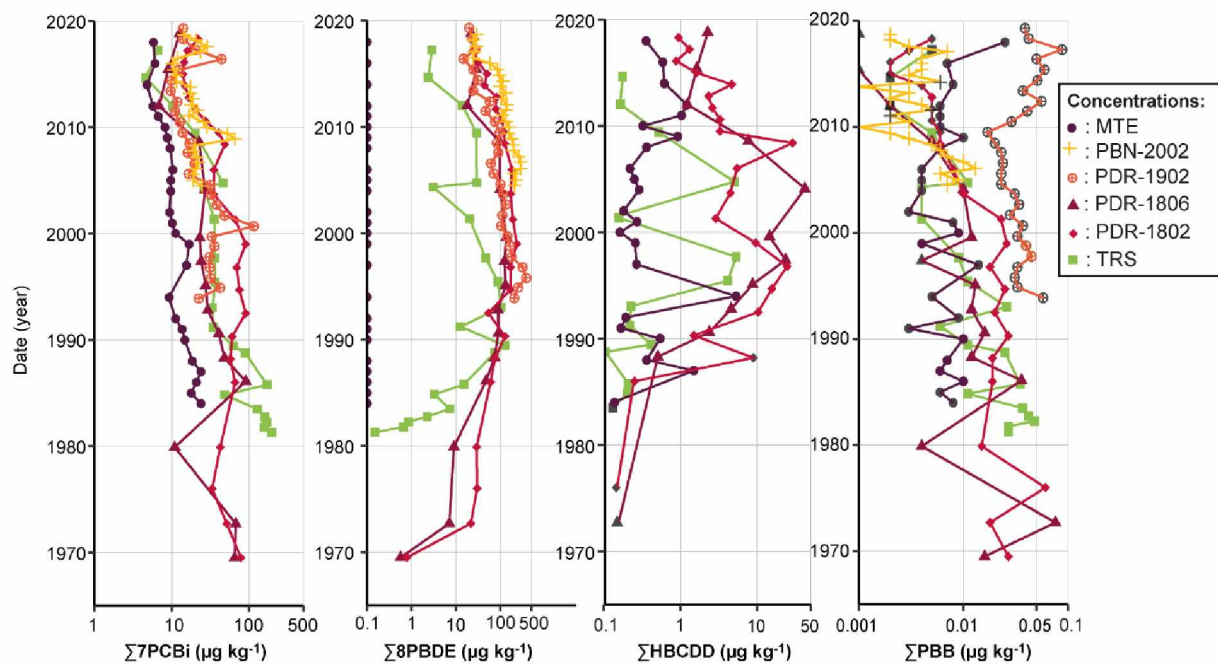
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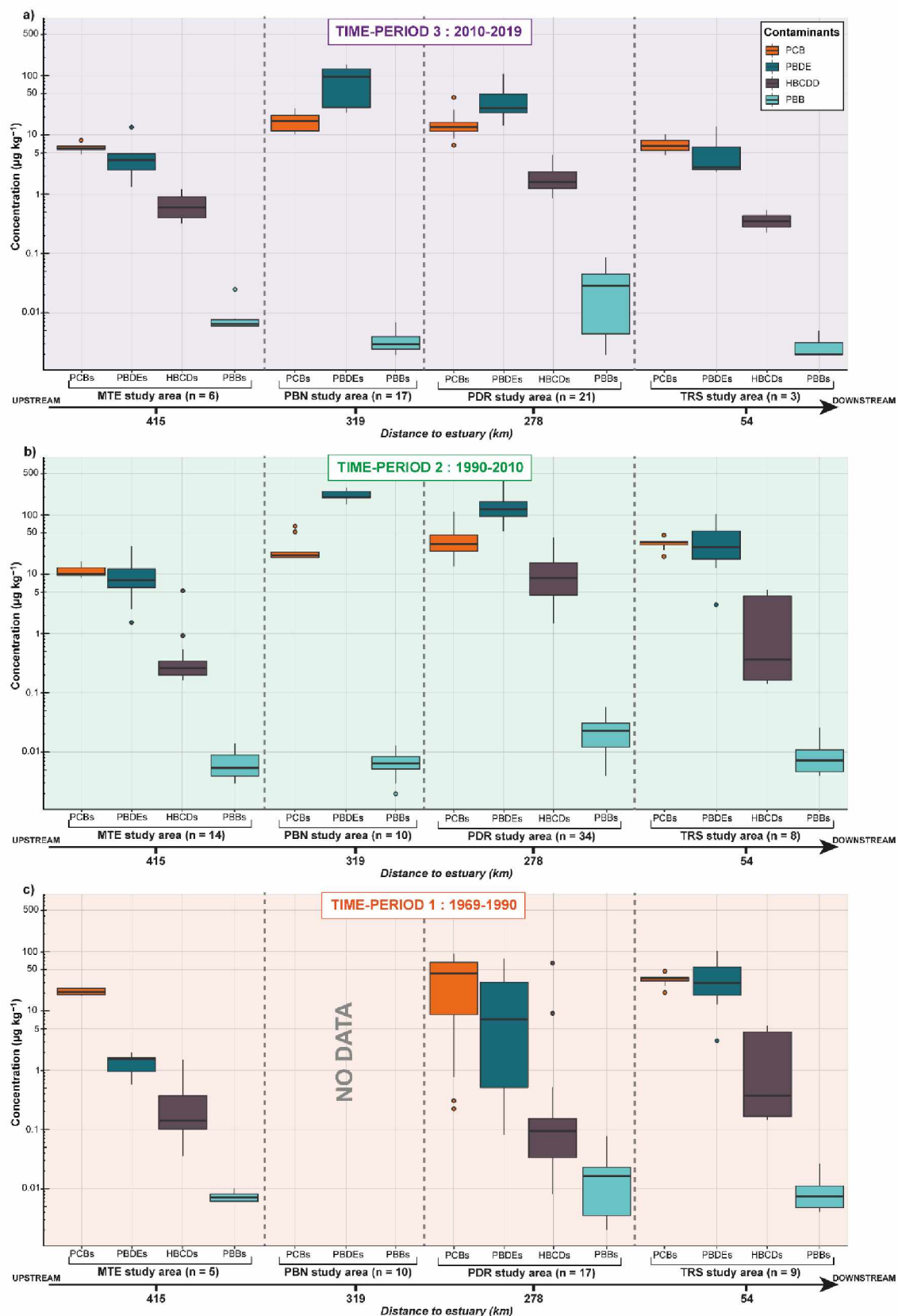
932 *SI-4: Grain-size distribution and total organic carbon content of the six studied sediment cores.*



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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.

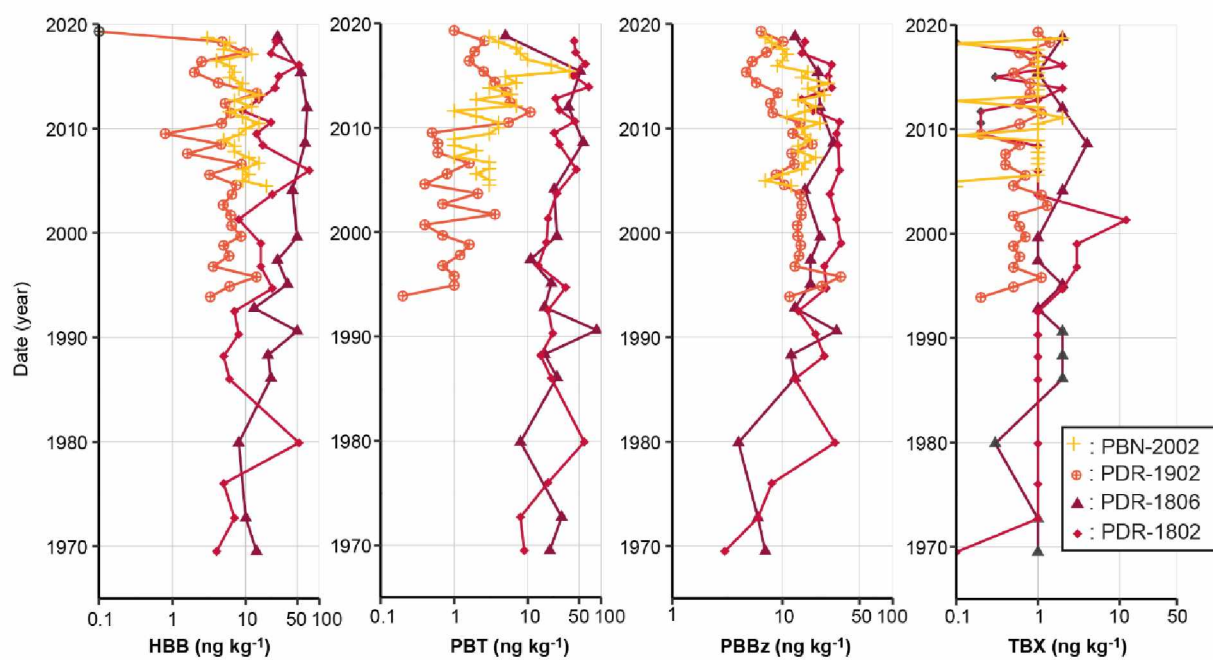


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937 SI-6: Boxplot representation of the concentrations in PCBs and legacy BFRs (PBDEs, PBBs, HBCDDD) in  $\mu\text{g kg}^{-1}$  dry weight

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.

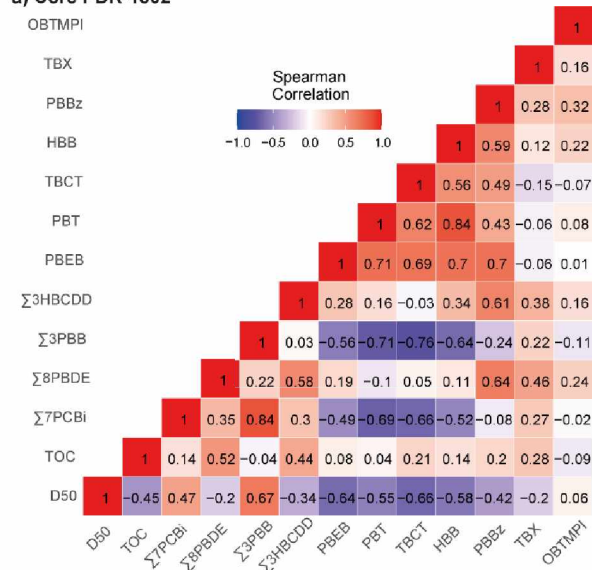


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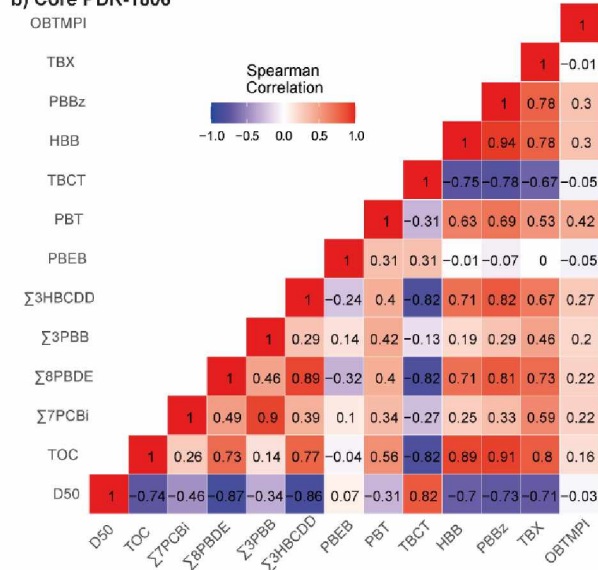
941 *SI-7: Temporal trends of novel BFRs (HBB, PBT, PBBz, and TBX) represented with a logarithmic scale in  $\text{ng kg}^{-1}$  dry weight.*

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

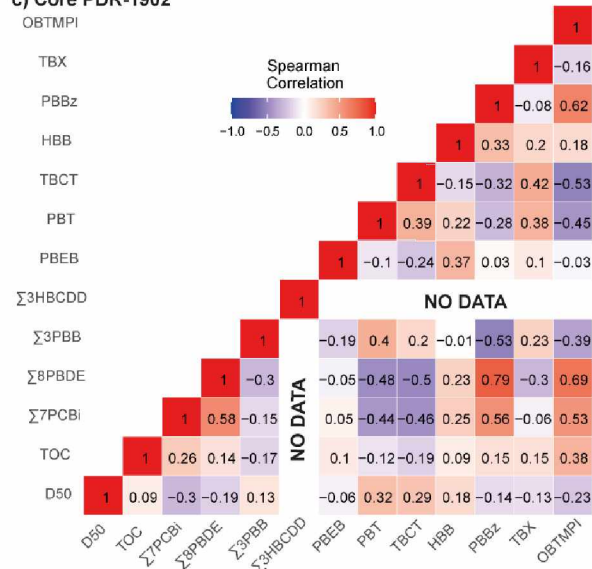
a) Core PDR-1802



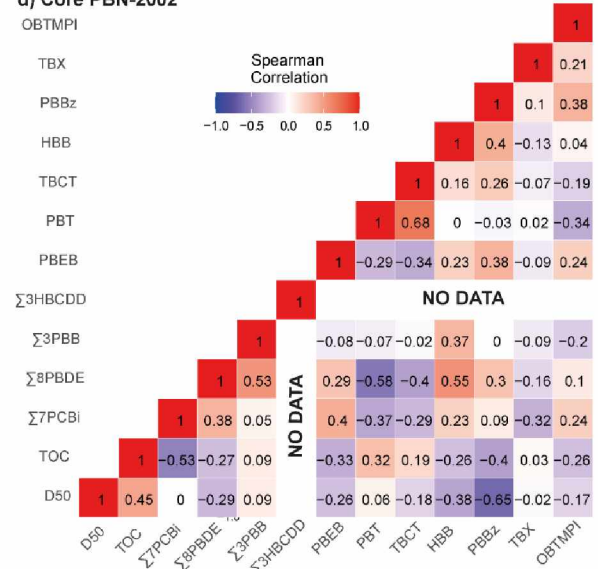
b) Core PDR-1806



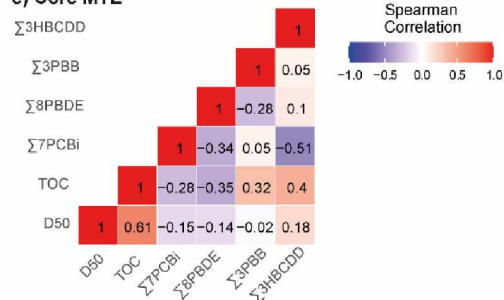
c) Core PDR-1902



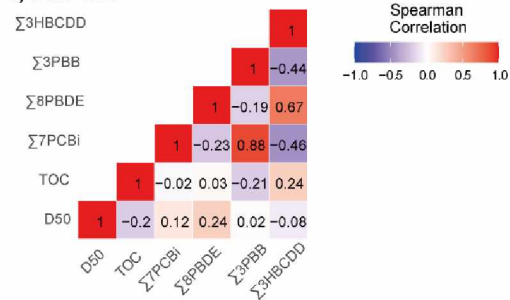
d) Core PBN-2002



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.