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## Combined spatial and retrospective analysis of fluoroalkyl chemicals in fluvial sediments reveal changes in levels and patterns over the last 40 years

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1 **Combined spatial and retrospective analysis of fluoroalkyl chemicals in fluvial**  
2 **sediments reveal changes in levels and patterns over the last 40 years**

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26 **Research Highlights**

27 1 - Upstream-downstream PFAS concentration gradient in bed sediments in the Rhône River

28 2- Reconstruction of temporal trends of PFAS contamination using a sediment core

29 3- Evidence of global PFSA background levels

30 4- Release of long-chain PFCAs from a point source into the river

31 5- Change of PFCA pattern through time likely reflects changes in production processes

32

## 33 **Abstract**

34 Bed sediments and a dated sediment core were collected upstream and downstream from the city of Lyon  
35 (France) to assess the spatial and temporal trends of contamination by per- and polyfluoroalkyl substances  
36 (PFASs) in this section of the Rhône River. Upstream from Lyon, concentrations of total PFASs ( $\Sigma$ PFASs) in  
37 sediments are low (between 0.19 and 2.6 ng g<sup>-1</sup> dry weight - dw), being characterized by a high proportion of  
38 perfluorooctane sulfonate (PFOS). Downstream from Lyon, and also from a fluoropolymer manufacturing plant,  
39  $\Sigma$ PFASs concentrations reach 48.7 ng g<sup>-1</sup> dw. A gradual decrease of concentrations is reported at the coring  
40 site further downstream (38 km). Based on a dated sediment core, the temporal evolution of PFASs is  
41 reconstructed from 1984 to 2013. Prior to 1987,  $\Sigma$ PFASs concentrations were low ( $\leq$  2 ng g<sup>-1</sup> dw), increasing  
42 to a maximum of 51 ng g<sup>-1</sup> dw in the 1990s and then decreasing from 2002 to the present day ( $\sim$ 10 ng g<sup>-1</sup> dw).  
43 In terms of the PFAS pattern, the proportion of perfluoroalkyl sulfonic acids (PFASs) has remained stable since  
44 the 1980s ( $\sim$ 10%), whereas large variations are reported for carboxylic acids (PFCAs). Long chain- (C>8)  
45 PFCAs characterized by an even number of perfluorinated carbons represent about 74% of the total PFAS  
46 load until 2005. However, from 2005 to 2013, the relative contribution of long chain- (C>8) PFCAs with an odd  
47 number of perfluorinated carbons reaches 80%. Such changes in the PFAS pattern likely highlight a major  
48 shift in the industrial production process. This spatial and retrospective study provides valuable insights into  
49 the long-term contamination patterns of PFAS chemicals in river basins impacted by both urban and industrial  
50 activities.

51

## 52 **Keywords**

53 Per- and polyfluoroalkyl substances, Rhône River, bed sediment, sediment core, temporal trend, spatial trend

54

## 55 **Capsule**

56 An extended spatial and temporal survey of PFAS chemicals in sediments provided valuable insights into the  
57 long-term contamination patterns in river basins impacted by both urban and industrial activities.  
58

## 59 **1. Introduction**

60 Over the past 50 years, per- and polyfluoroalkyl substances (PFASs) have been widely used in the production  
61 of fluoropolymer processing additives and surfactants in industrial processes, as well as in fire-fighting foams  
62 and many consumer applications (Paul et al., 2009; Prevedouros et al., 2006). Owing to their unique properties  
63 and widespread applications, some PFASs are ubiquitously distributed in the aquatic environment (Ahrens,  
64 2011; Ahrens and Bundschuh, 2014; Wang et al., 2015) and biota (Giesy and Kannan, 2001; Houde et al.,  
65 2011; Houde et al., 2006). This raises some concerns about the hazards PFASs might pose to wildlife or  
66 human health (Borg et al., 2013; Kannan, 2011; Naile et al., 2010; Peng et al., 2010). For PFASs currently  
67 observed in the environment, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA),  
68 sources include direct and indirect emissions (Prevedouros et al., 2006) as well as degradation of precursors  
69 (Stock et al., 2007; Wang et al., 2009). Sediments are identified as the ultimate sink (Prevedouros et al., 2006)  
70 for PFAS having eight carbon atoms or more. Accordingly, many authors have reported the occurrence of  
71 PFASs in sediments from marine/coastal systems (e.g. (Loi et al., 2013; Theobald et al., 2011; Thompson et  
72 al., 2011), lakes (e.g. (Clara et al., 2009; Guo et al., 2016; Zhou et al., 2012) or rivers (e.g. (Möller et al., 2010;  
73 Munoz et al., 2017b; Wang et al., 2013). Sediment cores allowing the assessment of temporal trends have  
74 been studied in several contexts, such as Tokyo Bay (Ahrens et al., 2009b; Zushi et al., 2010), or in Chinese  
75 urban rivers such as the Guangzhou and Huangpu (Bao et al., 2010) or the Haihe River (Zhao et al., 2014).  
76 These studies reported different temporal trends, with a decline of “legacy” PFASs (i.e. PFOS) since the late  
77 1990s (Ahrens et al., 2009b) or earlier (Zushi et al., 2010), while other compounds such as  
78 perfluoroundecanoate (PFUnDA) are still increasing. There is no consistent trend in Haihe river sediments,  
79 although PFOS concentrations are higher at the top of the cores than in deeper layers (Zhao et al., 2014),  
80 while cores from Guangzhou and Huangpu rivers both reveal increasing concentrations of PFOS and some  
81 perfluorocarboxylic acids (PFCAs) in the upper part of the sediment columns (Bao et al., 2010).

82 The Rhône is one of the largest rivers in France and represents a critical resource for agriculture and drinking  
83 water production. In Southeastern France, a peculiar PFAS molecular profile, dominated by long-chain PFCAs,  
84 is observed in fish (Miège et al., 2012) and sediments (Munoz et al., 2015) downstream from Lyon. This pattern  
85 is likely explained by an industrial source (Dauchy et al., 2012; Munoz et al., 2015).

86 In this context, the present study aims first to assess the spatial trends in PFAS contamination from surface  
87 sediments collected in the hydrological network around the city of Lyon, in order to identify and rank the current

88 PFAS sources in this urban-industrial area. Then, the time trends of PFAS levels and patterns downstream of  
89 the conurbation are reconstructed through the analysis of a sediment core.

90

## 91 **2. Material and methods**

### 92 **2.1 Study area**

93 The Rhône is one of the major rivers of Europe, with a length of 810 km and a catchment area of 97 800 km<sup>2</sup>  
94 and showing a remarkable climatic and geological diversity (Pekarova et al., 2006; Desmet et al., 2005). The  
95 mean daily discharge is 1 030 m<sup>3</sup> s<sup>-1</sup> (1966 to 2014) downstream from its confluence with the Saône River.  
96 Along its course in French territory, the Rhône has been intensively engineered since the end of the 19<sup>th</sup>  
97 century, with numerous embankments, groynes and 19 dams that have been implemented for purposes of  
98 navigation, flood protection or hydroelectric production (Bravard et al., 1999). These widely-developed  
99 anthropogenic pressures have profoundly modified the hydrology and geomorphology of the Rhone valley. In  
100 addition, the Rhone passes through many urban areas and industrial zones representing localized and  
101 potential sources of contamination.

102 The study area was chosen to evaluate the spatial distribution and temporal trends of PFAS-contaminated  
103 sediments upstream and downstream of the Lyon metropolitan area (Fig. 1). Sediment collection sites are  
104 located in the Rhône valley upstream of the Rhône-Saône confluence, in the Saône River upstream of the  
105 confluence and along a longitudinal transect of about 38 km downstream from the Rhône-Saône confluence.  
106 This area covers the industrial corridor extending to the south of the city of Lyon, as well as several tributaries:  
107 the Ain, Bourbre and Gier. Two potential point sources of PFASs within the studied area (Fig. 1) are  
108 represented by the waste water treatment plant (WWTP) at Saint-Fons, which was seriously under-capacity  
109 until the beginning of the 2010s, and a fluoropolymer manufacturing plant that has produced various fluorinated  
110 polymers including polyvinylidene fluoride (PVDF) since the 1980s (Dauchy et al., 2012).

111

### 112 **2.2 Sampling of surface sediments and flood deposits**

113 Twenty-five samples of surface sediments were collected in July 2013 along an upstream-downstream  
114 gradient that takes into account the main Rhône tributaries and industrial areas. Table S-1 reports the  
115 geographic coordinates of sampling points as well as some field notes. Fresh flood deposits were taken from  
116 the riverbank using a stainless steel scoop, and supplemented by bed sediment sampling using an Eckman  
117 grab. Immediately after sampling, the samples were packaged and transported to the laboratory in an ice-

118 cooled box. In the laboratory, the samples were stored at -20°C, freeze-dried, sieved to 2 mm with a stainless  
119 steel mesh, packaged in amber glass vials and stored at room temperature until further analysis.

120

### 121 2.3 Sediment core collection and characterization

122 The coring site is located in a backwater area adjacent to the Rhône River, 38 km downstream from the Saône-  
123 Rhône confluence (Fig. 1). Before 1977, the side channel was not connected to the Rhône River due to river  
124 infrastructures that were implemented for navigation. After 1977, the construction of the Vaugris dam located  
125 a few kilometers downstream raised the water level and, in 1984, removal of the debris dam allowed the  
126 connection of this channel with the Rhône at its upstream end. Thus, depending on the period, the water body  
127 was connected to the main channel via its upstream and downstream ends, or solely at its downstream end.

128

129 A sediment core was sampled in June 2013 using a Uwitec gravity corer using a 2-m liner with a diameter of  
130 63 mm operated from a specially adapted river boat (e.g. quadiraft). By means of an extension rod and  
131 weights, the corer is first gently pushed into the sediment, and then hammered until it meets resistance. Once  
132 extracted, the core is immediately conditioned in the dark and in an ice-cool box, and brought back to the  
133 laboratory the same day. The core was first visually described and then cut up at 3-cm intervals using a clean  
134 stainless steel slicer. The identified sandy layers were sampled in their entirety, and then attributed to flood-  
135 events or reconnection works on the backwater area. The separated samples were homogenized and then  
136 stored in polypropylene (PP) tubes. All samples were stored at -20°C, freeze-dried, subsequently sieved to 2  
137 mm with a stainless steel mesh, packaged in amber glass vials and stored at room temperature until further  
138 analysis.

139 The grain-size distribution of the sediment core was determined with a Mastersizer 3000® laser particle size  
140 analyzer fitted with a Hydro SM small-volume dispersion unit. Percentage of particle size classes and  
141 parameters of grain size distribution were determined for each depth interval according to (Blott and Pye,  
142 2001). Rock-Eval 6 pyrolysis was used to determine the Total Organic Content (TOC). This thermal  
143 degradation method consists of pyrolysis of a previously crushed sample, in an oven within a temperature  
144 range from 200 to 650°C, following by oxidation at 400-750°C of the pyrolysed carbonaceous residue. Each  
145 step provides an amount of OC which contributes to the cumulative TOC content of the sample (expressed in  
146 wt.%), see (Lafargue et al., 1998).

147 Sediment core samples were analysed for radionuclides at USGS, Menlo Park (CA, USA). Except for the three

148 largest sandy layers (bottom of the core), each sample was analysed for  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ , and  $^{137}\text{Cs}$  using gamma  
149 spectrometry by counting for at least 24 h. Abrupt changes in grain-size identified in the cores were matched  
150 to flood discharges measured at the nearest streamflow-gauging station (Ternay, Fig. S1) or to changes  
151 following river-management operations to restore connection with the Rhône.

152

## 153 2.4 Chemicals

154 Certified standard solutions of analytes and internal standards (ISs) were purchased from Wellington  
155 Laboratories (via BCP Instruments, Irigny, France). Full details on the respective standard compositions are  
156 provided in the SI (section 3). Table S2 presents the list of analysed compounds, and their respective acronyms  
157 and ISs. Note that, unless otherwise stated, the PFOS concentrations presented below correspond to the sum  
158 of linear and branched isomers.

159

## 160 2.5 Extraction and Analysis of PFASs

161 Sediment samples (1 g dry weight, dw) were spiked with ISs and extracted by microwave-assisted extraction  
162 with methanol (5 min at 70°C) using a Start E Milestone system (Munoz et al., 2017a). Extracts were filtered  
163 through a polyethylene frit (20  $\mu\text{m}$ ) and concentrated to 1 mL under a nitrogen stream. Extracts were  
164 subsequently cleaned up using SuperClean Envi-Carb cartridges (250 mg, 6cc, Supelco, St Quentin Fallavier,  
165 France), the aliquots being taken down to 300  $\mu\text{L}$  and then stored at -20 °C until further analysis.

166 The analysis of PFASs was performed by high-performance liquid chromatography coupled with tandem mass  
167 spectrometry (LC-MS/MS) using an electrospray ionization source (for full details, see Munoz et al., 2015).

168

## 169 2.6 Quality control

170 PFAS recovery rates were determined using sediment sample aliquots fortified at 2 ng g<sup>-1</sup>. Actual recovery  
171 rates were determined by subtracting the analyte levels found in unspiked samples from the levels  
172 experimentally determined in the corresponding spiked samples, and were in the range 65–115 %. Procedural  
173 blanks (i.e. 10 mL of MeOH) were analysed for each samples batch (n=5). The most recurring analytes are  
174 PFHxA and PFOA, which are systematically detected in procedural blanks (0.15  $\pm$  0.25 and 0.18  $\pm$  0.04 ng,  
175 respectively). For these two compounds, the reporting limits are calculated as the standard deviation of blanks  
176 multiplied by the  $t_{n-1,95}$  student coefficient, where n is the number of blanks (Muir and Sverko, 2006). For

177 analytes undetected in blanks, the detection limit is defined as the concentration yielding a signal-to-noise ratio  
178 of 3 (Table 1). Limits of detection (LDs) are generally around 0.02 – 0.03 ng g<sup>-1</sup> (dw, dry weight).

179

## 180 2.7 Statistics

181 We used Pro-UCL 5.0 software (U.S. Environmental Protection Agency) to determine compound distributions  
182 accounting for left-censored results. A Mann-Whitney test was applied to compare contamination levels  
183 between groups. The significance threshold was set at 0.05 in all analyses.

184

## 185 3. Results

### 186 3.1 Spatial trends of bed sediment contamination

187 The detection rates of the 22 PFASs in bed sediment samples range from 0% for PFHxS and PFHpS, to 84%  
188 for MeFOSAA and 96 % for PFOS. Among the PFCAs, the most frequently detected compounds are PFOA  
189 (44%), PFNA (64%), PFUnDA and PFDoDA (60% each), and PFTTrDA and PFTTeDA (36% each). Short-chain  
190 PFCAs (i.e. PFBA, PFPeA and PFHxA) were only detected at site R4, just downstream from the fluoropolymer  
191 manufacturing plant. Table 1 reports the respective concentration ranges of the most frequently detected  
192 compounds. The full dataset of compound concentrations are provided in the SI table.

193

	6:2 FTSA	PFOA	PFNA	MeFOSAA	PFOS (Linear + Branched)	EtFOSAA	PFUnDA	PFDoDA	PFTTrDA	PFTTeDA	ΣPFAS
LD	0.02	0.03	0.03	0.01	0.03	0.01	0.06	0.03	0.49	0.076	-
Detection rate	40%	44%	64%	84%	96%	56%	60%	60%	36%	36%	-
1 <sup>st</sup> quartile	0.02	0.03	0.03	0.02	0.51	0.01	0.06	0.03	0.49	0.076	0.75
median	0.02	0.03	0.18	0.03	0.65	0.01	0.32	0.10	0.49	0.076	1.77
3 <sup>rd</sup> quartile	0.13	0.15	0.40	0.05	0.80	0.03	0.86	0.24	3.72	0.468	5.73
maximum	1.09	1.05	2.70	1.20	2.10	2.86	5.32	2.30	20.9	4.35	49.3

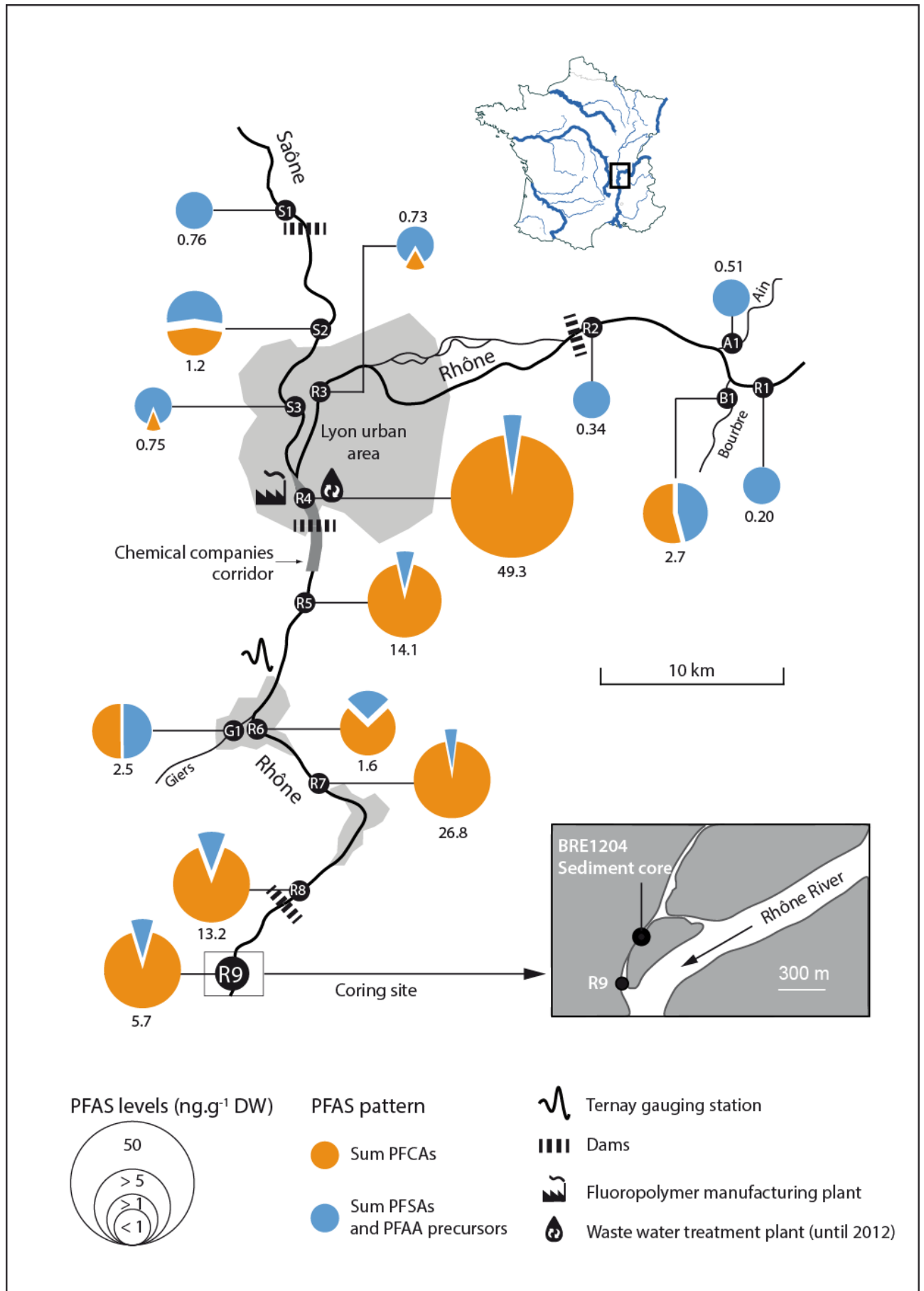
194 **Table 1 – Distributions of PFASs (n=25) most frequently detected in bed sediments and flood**  
195 **deposits (ng g<sup>-1</sup> dw)**

196

197 The molecular profiles in bed sediment sharply changes from upstream to downstream of site R4: for instance,  
198 detection rates of 6:2 FTSA, PFNA and PFTTrDA increase from 0% to 69 %, from 18 % to 100%, and from 0%  
199 to 61%, respectively. PFOS detection rates are not affected, while MeFOSAA and EtFOSAA show a moderate



200 variation, with detection rates of 72.7% to 92.3% and 45.5% to 61.5%, respectively. The respective proportions  
201 of compounds are quite different between river stretches (Fig. S2). PFOS is predominant in the Saône River  
202 sediments (Fig. S2-A), as well as in other tributaries (Fig. S2-B in SI). Some PFCAs, i.e. PFNA, PFUnDA and  
203 PFDoDA, are present in moderate proportions in some samples from the tributaries (S2, B1, G1), but not in  
204 samples from the Rhône River upstream of site R4, except in one case where the PFCAs, in particular long-  
205 chain PFCAs (N perfluorinated C atoms  $\geq 8$ ), as well as PFDoDA, are predominant downstream from site R4  
206 (Fig. S2-D in SI). These compounds represent 99 to 100% of  $\Sigma$ PFCAs at all sites, except at R4, which is the  
207 only site where short-chain carboxylates were detected as mentioned above. Meanwhile, as shown on Fig. 1,  
208 PFCA concentrations increase significantly from up- to downstream of R4, even when this site is ignored as  
209 an outlier. Conversely, the concentrations of PFOS and its precursors remain similar (Mann-Whitney,  $p$ -value  
210 = 0.95), despite locally higher concentrations at sites R4 and R5 (Fig. S3 in SI). PFCA concentrations tend to  
211 decrease gradually downstream from site R4 to site R9, although not linearly. This is probably a consequence  
212 of complex hydro-sedimentary processes along the investigated river stretches (Fig. 1, Fig. S4 in SI). In  
213 addition, 6:2 FTSA is undetected upstream from site R4 (Fig. S2-C), while it is generally detected in Rhône  
214 River bed sediments downstream from this site (concentrations ranging between 0.02 and 1.09 ng g<sup>-1</sup> dw), but  
215 not in samples from the Gier river: this strongly suggests the existence of a local source close to site R4.  
216



217  
218

219  
220 **Figure 1 – PFAS contamination of sedimentary deposits (ng g<sup>-1</sup> dw) collected in the drainage network**  
221 **of the Lyon area (France). To simplify the data presentation, PFOS precursors and 6:2 FTSA are**  
222 **grouped into perfluoroalkyl acid (PFAA) precursors. Blue segments represent the sum of PFASs and**  
223 **PFAA precursors; orange segments correspond to the sum of PFCAs. When several samples are**  
224 **available for a given site, we use the arithmetic mean of the respective measurements.**

225  
226 In a few cases, several kinds of sediment sample (i.e. dry deposits, wet deposits or bed sediments) are  
227 available from the same location. These samples provide similar records of  $\Sigma$ PFASs contamination, except at  
228 site R5.2, where there is a discrepancy of 5 ng g<sup>-1</sup> in  $\Sigma$ PFASs concentrations on a dry weight basis between  
229 wet and dry deposits (Fig. S5 in SI).

230 In summary, this survey shows (i) multiple sources of PFASs and PFOS precursors along the investigated  
231 river stretches, (ii) a local discharge of both short-chain (PFHxA) and long-chain (PFNA, PFUnDA, PFTrDA)  
232 PFCAs related to a fluoropolymer production platform, as well as (iii) another local discharge of 6:2 FTSA, Me-  
233 FOSAA and Et-FOSAA, probably from a WWTP.

234

## 235 3.2 Sediment core

### 236 3.2.1 Core description and characterization

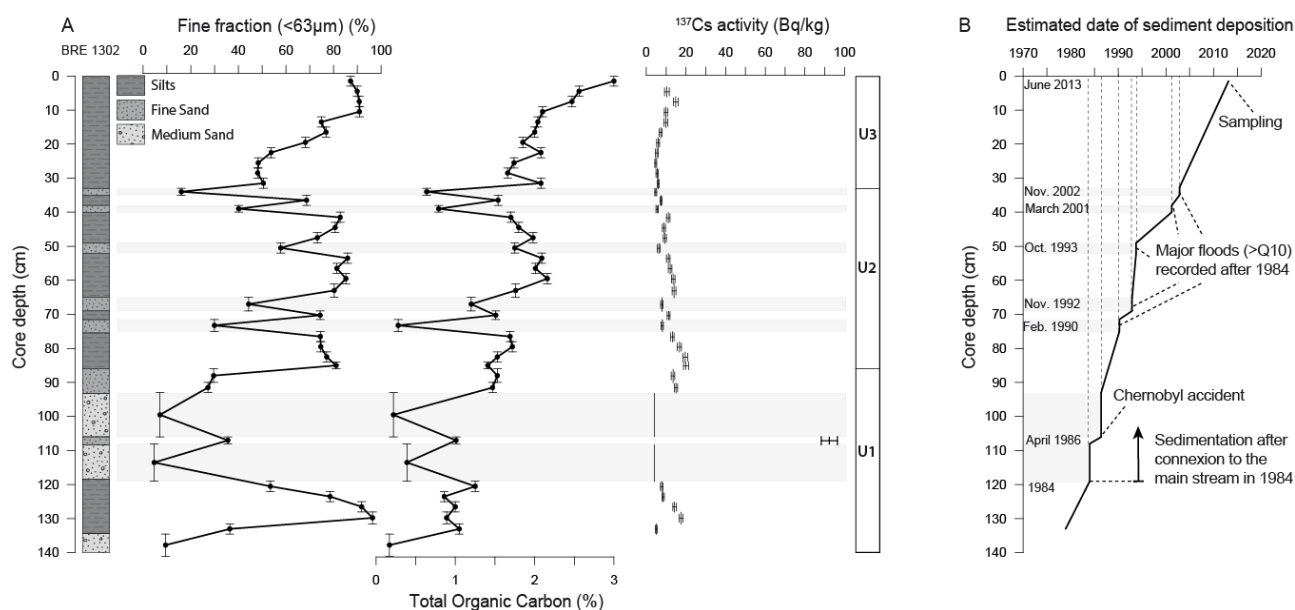
237 The 140-cm sediment core is characterized in terms of its visual description, grain-size distribution and TOC  
238 content. The sediment consists of light-grey sand in the lower part of the core and homogenous brown silt  
239 interrupted by event-layers in the upper part. Three sedimentary units are distinguished (Fig. 2). The bottom  
240 unit (Unit I) includes three thick sandy intervals at 93-106 cm, 108-119 cm and 134.5-141 cm (D50 of 337, 366  
241 and 444  $\mu$ m, respectively). These deposits have a low TOC content (<0.5%). Between 119 and 134.5 cm, the  
242 sediments are uniformly fine-grained with TOC contents close to 1%. An increase of fine particles and TOC  
243 content is observed between 86 and 93 cm. Unit II includes silty deposits (D50 of  $18.8 \pm 4.0 \mu$ m) interrupted  
244 by 5 layers characterized by their coarser grain size (D50 of  $151.5 \pm 87.2 \mu$ m). The TOC content is  $1.8 \pm 0.2\%$   
245 in the silty deposits, whereas it drops to  $0.9 \pm 0.8\%$  in coarser layers. The uppermost unit (Unit III) includes  
246 silty deposits with grain size decreasing upward. Finally, the TOC content ranges between 1.6 and 2% at the  
247 bottom of Unit III and is marked by an increase to almost 3% at the top of the core.

248

### 249 3.2.2 Dating

250 The date of deposition of the sediments is estimated on the basis of the  $^{137}\text{Cs}$  profile and by correlating changes  
251 in grain-size distribution in the sediment cores to the timing of flood events as well as major changes at the  
252 site (Fig. 2). The radionuclide profile of the core yields a calibrated date at 107 cm (Fig. 2), corresponding to  
253 the  $^{137}\text{Cs}$  fallout resulting from the Chernobyl accident in 1986 (Anspaugh et al., 1988). The sudden change in  
254 grain-size distribution in U1, associated with the occurrence of two thick sandy layers, is interpreted as  
255 corresponding to debris removal works carried out in 1984 which re-established the connection to the Rhône  
256 as already shown by Desmet et al. (2012). This event is consistent with the radionuclide profile. Flood-event  
257 deposits are matched to flood discharges measured at the nearest streamflow-gauging station (Ternay, Fig.  
258 S1-A). Five major flood events (defined as  $Q_{10} > 4200 \text{ m}^3 \text{ s}^{-1}$ ) identified in the core are dated in the early 1990s  
259 and 2000s (Fig. S1-B). Since November 2002, no major flood has been recorded at the Ternay station. By  
260 matching dated flood facies with removal work facies and the  $^{137}\text{Cs}$  peak, an age-depth model can be  
261 calculated, assuming a constant deposition rate between two successive date markers. Prior to 1984, we  
262 assume that this site was not directly connected to the Rhône River.

263



264

265

266 **Fig. 2. A/ Profiles of fine fraction (<63 μm), total organic carbon (TOC, %) and  $^{137}\text{Cs}$  activity (Bq/kg) in**  
267 **BRE1202 sediment core. B/ Date of sediment deposition estimated on the basis of  $^{137}\text{Cs}$  profile and**  
268 **variations in grain size matched with flood events and works for reconnection to the river.**

269

### 270 3.2.3 PFAS concentrations and molecular patterns

271 Figure 3 shows the temporal trends of PFASs in the sediment core and the full dataset of compound  
272 concentrations are provided in the SI. Values are expressed in terms of dry weight as well as on a TOC-  
273 normalized basis since Organic Carbon (OC) is a major factor affecting PFAS sorption onto sediments (Higgins  
274 and Luthy, 2006 ; Munoz et al., 2015).

275 Five compounds are detected among the sulfonates and PFOS precursors: PFOS, FOSA, MeFOSA, EtFOSA  
276 as well as 6:2 FTSA. Their frequency of detection (or detection rate) ranges from 85 to 100 %. The maximum  
277 concentration of PFOS and its precursors was attained between 1988 and 2002 (maximum concentration of  
278  $2.3 \text{ ng g}^{-1} \text{ dw}$  or  $134.3 \text{ ng g}^{-1} \text{ OC}$  at the end of 1993); a similar trend is observed for 6:2 FTSA, with a maximum  
279 concentration of  $0.88 \text{ ng g}^{-1} \text{ dw}$  (or  $43.6 \text{ ng g}^{-1} \text{ OC}$ ) in the sediment layer deposited in 1993. In terms of  
280 compound profiles, the maximum relative contribution of sulfonates and PFOS precursors is observed before  
281 1988, accounting for 10–60% of  $\Sigma\text{PFASs}$ . In the 1988– 2013 sediment interval, the relative contribution of the  
282 same compounds lies in the range 4 –15%.

283 Ten PFCAs can be detected in the sediment core samples. In sediments deposited before 1988, the detection  
284 frequencies range from 0 to 36%, with exceptions for PFPeA (100%), PFDA (82%) and PFDODA (91%).  
285 Nevertheless, the detection rates for all samples are relatively high and range between 75 and 98 %, except  
286 for short-chain PFCAs such as PFHxA (30%), PFHpA (58 %) and PFOA (43. In addition, PFOA and PFHpA  
287 show a maximum frequency of detection between 1988 and 2003, while PFPeA is detected in 98% of samples  
288 in sediment layers deposited over this time interval. The maximum concentration for PFCAs is recorded in  
289 1993 for 6 compounds (PFHpA, PFOA, PFNA, PFDA, PFDODA and PFTeDA), and this sediment interval also  
290 coincides with the maximum concentration of  $\Sigma\text{PFASs}$  ( $51.4 \text{ ng g}^{-1} \text{ dw}$  or  $2459 \text{ ng g}^{-1} \text{ OC}$ ). PFHxA, PFUnDA  
291 and PFTrDA reach their maximum levels in the most recent layers (2010s).

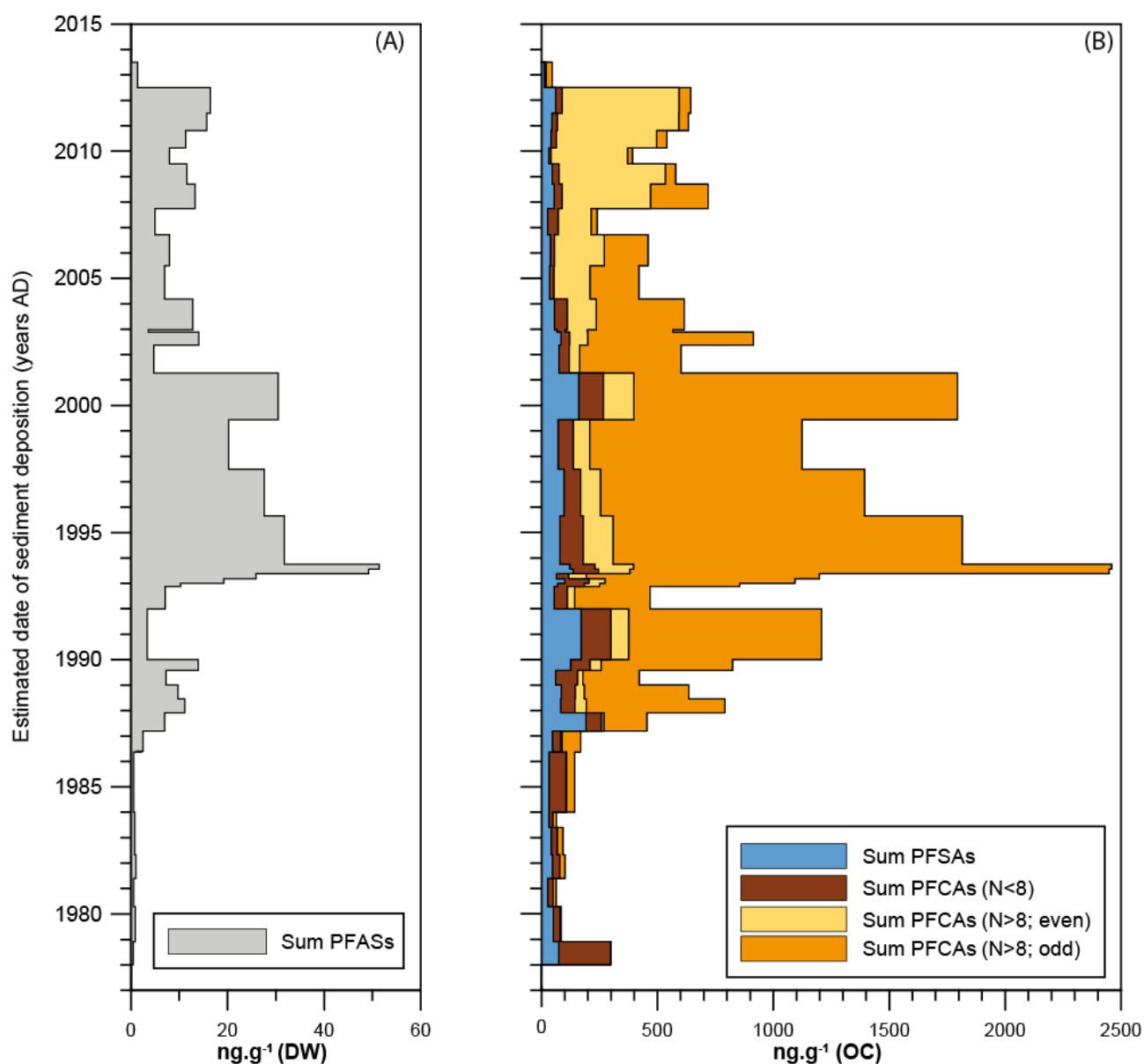
292 When considering the three sedimentary units described above, the following conclusions can be drawn:

293 (i) Unit 1 – (< 1988): the average concentration of  $\Sigma\text{PFASs}$  is  $3.4 \pm 4.0 \text{ ng g}^{-1} \text{ dw}$  and is dominated by  
294 carboxylates (PFPeA, PFOA and PFDA) and 6:2 FTSA, while the contribution of PFOS is lower than 8%;

295 (ii) Unit 2 (1988-2003): the average concentration of  $\Sigma\text{PFASs}$  is  $20.3 \pm 15.1 \text{ ng g}^{-1} \text{ dw}$ . The PFAS molecular  
296 pattern is dominated by long-chain PFCAs, especially compounds with an odd fluorinated carbon number  
297 (PFDA, PFDODA and PFTeDA) which conjointly account for 59 – 85% of  $\Sigma\text{PFASs}$ ;

298 (iii) Unit 3 (2003-2013): the average concentration of  $\Sigma\text{PFASs}$  is  $9.8 \pm 4.7 \text{ ng g}^{-1} \text{ dw}$  and is lower than in unit  
299 2. The PFAS molecular pattern is still dominated by long-chain PFCAs, but a rapid decrease is observed in

300 the relative abundances of long-chain PFCAs with an odd fluorinated carbon number, while long-chain PFCAs  
301 with an even fluorinated carbon number progressively become predominant (e.g. PFUnDA and PFTrDA  
302 account for up to 75 % of  $\Sigma$ PFASs in the most recent sediment layers).



303  
304 **Figure 3** Temporal evolution of the total concentration of PFASs (A) and OC-normalized  
305 concentrations of four PFASs groups (B): sum of PFASs and PFOS precursors (6:2 FTSA included);  
306 sum of short-chain PFCAs; sum of long-chain PFCAs with an even number of perfluorinated carbon  
307 atoms; sum of long-chain PFCAs with an odd number of perfluorinated carbon atoms.

308

## 309 4. Discussion

### 310 4.1 PFAS sources

311 In terms of PFAS levels, there is a clear spatial trend between sediments collected upstream and downstream  
312 of industrial and urban areas of the city of Lyon. PFOA and PFOS distributions appear similar to those observed  
313 in other urban/industrialized regions (e.g. (Bečanová et al., 2016; Myers et al., 2012; Zhao et al., 2014), while  
314 long-chain PFCAs (especially PFUnDA, PFDoDA, PFTrDA and PFTeDA) display unusually high levels and  
315 relative abundances at site R4 and further downstream, as already noted by Dauchy et al. (2012) and Munoz  
316 et al.(2015). 6:2 FTSA is not detected in sediments upstream from site R4, while it is found in most samples  
317 collected downstream. Together with other potential precursor degradation products (e.g. MeFOSAA and  
318 EtFOSAA), this compound has been frequently identified downstream of WWTPs (Ahrens et al., 2009a) or  
319 industrial plant (Dauchy et al., 2017).

320 We therefore conclude that PFASs contamination in the upstream part of the study area results from a complex  
321 combination of multiple point and non-point sources. The molecular patterns observed in this area are similar  
322 to those previously reported in a wide variety of settings across French fluvial systems (Munoz et al. 2015). In  
323 this latter study, PFOS is found to be the prevalent compound, accounting for between 34 and 100% of  
324  $\Sigma$ PFASs. The large increase in concentrations downstream of site R4 indicates substantial inputs of PFASs to  
325 the Rhône River via local point sources such as the fluoropolymer manufacturing plant. Another potential  
326 sources of 6:2 FTSA and PFOS precursors include the St-Fons WWTP ( $\sim 10^6$  population equivalents) and the  
327 Gier River, a well-documented tributary affected by industrial activities (Poulier et al., 2019) where sediments  
328 show one of the highest concentrations reported in this study for bed sediments or deposits (>90<sup>th</sup> percentile  
329 of  $\Sigma$ PFASs). As regards long-chain PFCAs, the increase in PFNA, PFUnDA and PFTrDA is very probably  
330 related to inputs from the fluoropolymer production plant, which is consistent with the results of Dauchy (2012).  
331 PFNA was actually used as a processing aid in fluoropolymer synthesis (e.g. polyvinylidene fluoride, PVDF).  
332 PFUnDA and PFTrDA likely represent impurities of the ammonium perfluorononanoate (APFN) used for  
333 industrial applications (Buck et al., 2011).

334  
335 4.2 Influence of deposition patterns on PFAS concentrations in the sediment core  
336 Floods and river-management operations have affected sediment deposition patterns at the sediment core  
337 site. Sediments deposited just after the debris dam removal in 1984 are assumed not to represent the same  
338 depositional conditions as recorded in more recent intervals. Indeed, sandy and well-sorted intervals in the  
339 deepest part of the core contrast with fine-grained and poorly classified sediments deposited in the upper part  
340 of the core. Such changes in the connectivity conditions that control deposition processes might also explain

341 some short-term variations in the vertical profile of PFASs. Major flood events occurring in the early 1990s and  
342 2000s, result in lower PFAS levels as reflected by increased sand content and a decrease in organic carbon  
343 content in some core layers. The relatively low total PFAS concentration measured in the most recent sample  
344 ( $1.4 \text{ ng g}^{-1} \text{ dw}$ ) indicates a possible dilution effect attributed to upstream sediment flushing that occurred in  
345 2012, just before coring operations.

346  
347  $\Sigma$ PFAS concentrations appear to decrease in each layer corresponding to a flood event. This is consistent with  
348 (Ahrens et al., 2011), who showed a lower sorption capacity for sandy sediment with a low TOC content,  
349 whereas higher sorption capacities are found for muddy sediments with higher TOC content. When normalized  
350 according to OC content, PFAS concentrations in flood layers converge with the values measured in adjacent  
351 layers. Similarly, the apparent increase of PFAS concentrations in the upper part of the core is mainly due to  
352 a change in OC content in these layers. However, considering OC-normalized concentrations, there is no  
353 significant change in concentrations of  $\Sigma$ PFAS from about 2008 to layers from the top of the core dated at  
354 2013 (Kendall's tau test of correlation,  $p=0.45$ ).

355  
356 4.3 Temporal trend in the sediment core and comparison with sediment cores worldwide  
357 Numerous studies have been published during the last decade using sediment cores for assessing the spatial  
358 or temporal trends of PFAS contamination (e.g. (Ahrens et al., 2009b; Bao et al., 2009; Codling et al., 2018a;  
359 Codling et al., 2018b; Codling et al., 2014; Yeung et al., 2013). These studies differ in several ways, such as  
360 objectives, dating methods and range of analysed compounds. Some studies have targeted remote lakes to  
361 elucidate PFCA atmospheric pathways to these areas (Benskin et al., 2011), while others have dealt with large  
362 water bodies in industrialized regions to better understand PFAS fate and observe the effects of production  
363 using changes at a large spatial scale (Myers et al., 2012; Zushi et al., 2010). Several studies have focused  
364 on river stretches or lake sections directly influenced by industrial parks (Zhao et al., 2014; Zhou et al., 2013)  
365 or cities (Bao et al., 2010). Sediment sample dates were either not determined, or estimated using a range of  
366 radionuclides ( $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ,  $^{241}\text{Am}$ ).

367 The range of PFASs analysed in these studies varies from a few PFCAs to large sets of compounds including  
368 PFASs, FTSAAs, FOSAs and FOSAAs; only few studies normalize PFAS concentrations to TOC content (Zhou  
369 et al., 2013; Zushi et al., 2010), making it impossible to directly compare contamination levels. It would be  
370 more reasonable, however, to use indicators such as  $\Sigma$ PFASs,  $\Sigma$ PFCAs or  $\Sigma$ PFASs as trend indicators,



371 provided the range of analysed compounds is large enough, because they would account for changes in  
372 production processes, e.g. from PFOS to shorter chain PFASs, and for degradation of precursors into PFCAs  
373 (Benskin et al., 2011) or PFOS (Zushi et al., 2010).  $\Sigma$ PFASs or  $\Sigma$ PFCAs/PFASs trend patterns as well as the  
374 period of maximum concentration (peak date) could therefore provide information about such changes.  
375 In the Rhône River, the increase of  $\Sigma$ PFASs in the 1990s (up to 51.4 ng g<sup>-1</sup> dw in 1994), was followed by a  
376 decrease in concentrations (to ~10 ng g<sup>-1</sup> dw), which have remained stable since the late 2000s. Overall, the  
377 molecular profile is largely dominated by long-chain PFCAs. Moreover, a shift is observed from odd to even  
378 perfluorinated carbon atom numbers: PFDA and PFDODA were dominant before 2002, (i.e. mean contributions  
379 to  $\Sigma$ PFCAs of 37% and 31%, respectively), while PFUnDA and PFTTrDA represent the highest contributions  
380 (29 and 45% of  $\Sigma$ PFCAs, respectively) in the post-2005 deposits. This shift is very likely related to changes in  
381 the production process at the industrial plant, as already mentioned in similar contexts (Zhou et al., 2013).  
382 Such a trend is similar to that in Tokyo Bay cores, where long-chain PFCA concentrations (e.g. PFUnDA and  
383 PFTTrDA) have been continuing to increase at the top of the cores since 2005 (Ahrens et al., 2009b; Zushi et  
384 al., 2010). A similar increase of long-chain PFCA concentrations was also reported in Lake Ontario (Myers et  
385 al., 2012) as well as in some other Laurentian Great Lakes (Codling et al., 2018a). Nevertheless, published  
386 data on long-chain PFCAs in cores show either increasing trends (Bao et al., 2010; Gao et al., 2014; Yeung  
387 et al., 2013; Zhao et al., 2014) or indeterminate trends (Codling et al., 2018a; Codling et al., 2018b).  
388 The PFOS trend in the Rhône River core is not obvious, as concentrations vary a great deal over the years,  
389 even when normalized to OC. There are nevertheless three distinct periods (Fig. S6): before ca. 1985, PFOS  
390 concentrations remain below 15 ng g<sup>-1</sup> OC. During the next period (1985-2000), PFOS concentrations range  
391 between 20 to 60 ng g<sup>-1</sup> OC, whereas OC-normalized concentrations range between 20 and 40 ng g<sup>-1</sup> OC in  
392 the most recent layers (since the years 2000). After exclusion of the two outliers measured in 1987 and 1999,  
393 PFOS concentrations normalized to OC content are significantly (Mann-Whitney,  $p=0.028$ ) higher during the  
394 1985-2000 period compared to the most recent period (with respective means of 35.9 and 25.4 ng g<sup>-1</sup> OC),  
395 indicating a downwards shift after 2002. Similar shifts are also noted in other parts of the world, e.g. Tokyo  
396 Bay in Japan (Ahrens et al., 2009b) or Lake Michigan (USA) (Codling et al., 2014), as well as Lake Ontario  
397 (Canada) (Myers et al., 2012), owing to the withdrawal of PFOS from industrial applications (Paul et al., 2009),  
398 and thus their reduced levels in consumer products (Boulanger et al., 2005). Interestingly, in the  
399 abovementioned Lake Ontario study, the suspended sediment from its main tributary, the Niagara River,  
400 responded rapidly to the phase-out of PFOS, with a concentration drop in 2000, while PFOS concentrations

401 were still increasing at the top of the sediment cores (middle of the lake) in 2006. Sediment records from  
402 riverine systems, such as the Niagara and Rhône rivers, might accordingly track the consequences of  
403 contaminant phase-out more rapidly compared with large lakes.

## 404 **5. Conclusion**

405 The Rhône River upstream and downstream from Lyon is subject to multiple sources of emission of  
406 perfluoroalkyl substances, generating a complex pattern of sediment contamination. An extended spatial  
407 survey of flood and bed sediments reveals multiple sources of PFASs and PFOS precursors, as well as local  
408 discharges of short-chain (PFHxA) and long-chain (PFNA, PFUnDA and PFTTrDA) PFCAs, 6:2 FTSA and  
409 FOSAs. Based on the analysis of a sediment core collected in a secondary channel 38 km downstream from  
410 the local discharge, we show that industrial emissions of PFAS became quite significant by the late 1980s,  
411 reaching a maximum in the 1990s (maximum recorded  $\Sigma$ PFASs: 51.4 ng g<sup>-1</sup> dw in 1994). During this period,  
412 PFDA, PFDoDA and PFTeDA provided the main contribution (74%) to  $\Sigma$ PFASs. From ca. 2005 onwards,  
413 concentrations decreased to a plateau, but were still influenced by local inputs and activities. The molecular  
414 profile of PFCAs in the sediment column shifted from an odd to even number of fluorinated carbon atoms,  
415 PFTTrDA and PFUnDA representing about 75% of  $\Sigma$ PFASs in sediment core samples after 2005. Such a  
416 compositional shift strongly suggests that changes occurred in the production process of the industrial plant.  
417 PFASs concentrations measured in this sediment core appear to be amongst the highest recorded in sediment  
418 cores worldwide. This spatial and retrospective study provides valuable insights into the long-term  
419 contamination patterns of PFAS chemicals in river basins impacted by both urban and industrial activities.

420

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