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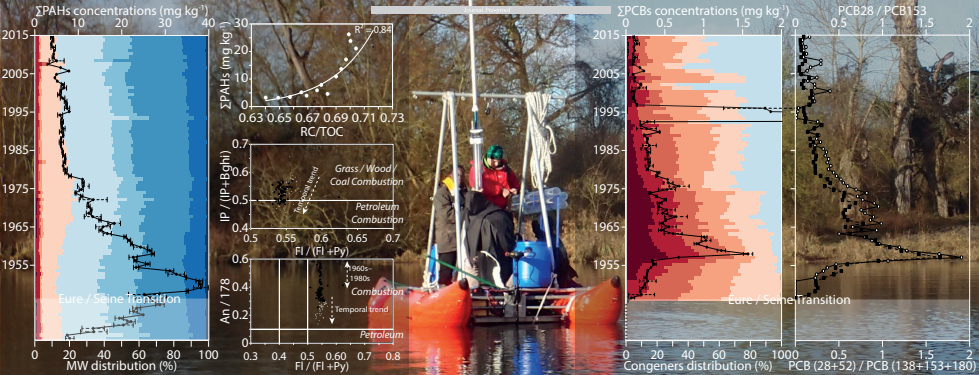
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1 **Temporal trends, sources, and relationships between sediment**
2 **characteristics and polycyclic aromatic hydrocarbons (PAHs) and**
3 **polychlorinated biphenyls (PCBs) in sediment cores from the**
4 **major Seine estuary tributary, France**

5

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12

13 **Abstract**

14 Temporal trends in polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls
15 (PCBs) were reconstructed from sediment cores collected from two ponds downstream of the
16 Eure River watershed. PAHs exhibited a positive correlation with fine fractions, but mainly
17 with the refractory organic carbon measured in the sediments, which suggests PAH inputs
18 from materials largely composed of refractory carbon (e.g. soot). Since the 1940s, PAH
19 concentrations have ranged between 2.93–38.20 and 2.27–28.20 mg kg⁻¹. Based on the
20 temporal distribution of isomers and diagnostic ratios, the PAHs in the sediments were found
21 to be predominantly of pyrogenic origin, particularly in the 1940s–1960s, when PAH levels
22 were particularly high. PCBs also showed an affinity with the fine fraction and with refractory
23 organic carbon, albeit less so than PAHs. Since the 1940s, PCB concentrations ranged
24 between 0.02–1.57 and 0.09–1.60 mg kg⁻¹. The recorded PCB temporal trends were mainly

25 associated with the production, consumption, and banning of these chemicals in France.
26 According to the temporal distribution of PCB congeners, high levels in the 1950s–1970s
27 were linked to "technical mixture" discharges into waterways, which were mainly composed
28 of "low chlorinated congeners", whereas PCB levels after the 1970s were of atmospheric
29 origin.

30

31 **Keywords**

32 Temporal trends; PAHs; PCBs; sediment cores; refractory organic carbon

33

34 **1. Introduction**

35

36 Persistent organic pollutants (POPs) are ubiquitous environmental contaminants that began
37 to be widely produced and consumed after the Second World War (Bigus et al., 2014). These
38 organic compounds are not only very stable and therefore difficult to degrade or biodegrade,
39 but are also often very toxic (Bigus et al., 2014). Additionally, these compounds are generally
40 highly hydrophobic (Wan et al., 2011; Tobiszewski and Namieśnik, 2012) and therefore tend
41 to bind to suspended particulate matter (SPM) transported by rivers, thereby accumulating in
42 aquatic systems (Zennegg et al., 2007).

43 Polycyclic aromatic hydrocarbons (PAHs) are POPs that are released into the environment
44 both from natural (e.g. fires, volcanoes) and anthropogenic sources (e.g. incomplete
45 combustion processes, petroleum product leakage), the latter becoming predominant in the
46 twentieth century (Bigus et al., 2014). PAHs enter aquatic environments via atmospheric
47 deposition, wastewater discharge from industrial sites, or surface runoff from urban or
48 industrial areas (Heemken et al., 2000). Petrogenic PAHs (i.e. those derived from petroleum
49 products or kerogen maturation) are generally emitted directly into aquatic environments,

50 whereas pyrogenic PAHs (i.e. those derived from combustion processes) can be emitted
51 directly into aquatic environments (e.g. from use or release of coal tar, creosote, manufactured
52 gas plant wastes and leaking or improperly disposed of used motor oil) or first emitted into
53 the atmosphere and subsequently enter aquatic environments (Tobiszewski and Namieśnik,
54 2012). Atmospheric PAH emissions may be associated with particles; alternatively, these
55 compounds may occur in the gaseous phase when emitted at high temperatures, after which
56 they may condense onto particles upon cooling (Tobiszewski and Namieśnik, 2012). PAHs
57 are generally adsorbed onto fine particles but can be transferred from fine to coarser particles
58 through aggregation over time (Oliveira et al., 2011). PAHs preferentially accumulate in
59 sediments after entering streams due to their hydrophobicity and generally undergo few or no
60 changes over many years (Hatzinger and Alexander, 1995; Douglas et al., 1996; Page et al.,
61 1999). Unlike light PAHs (2–3-ring PAHs), which are more volatile and metabolisable by
62 microorganisms, heavy PAHs (4–6-ring PAHs) are considered to be relatively stable within
63 sediment matrices. This accumulation in the sediment can be modulated by the sediment's
64 composition and characteristics (e.g. particle size, organic carbon (C_{org}) content) (Means et
65 al., 1980; Tobiszewski and Namieśnik, 2012). Notably, PAHs in streams are preferentially
66 adsorbed onto fine particles (Karickhoff et al., 1979), and thus fine particle sedimentation
67 leads to the concurrent sedimentation of associated PAHs. PAHs are preferentially adsorbed
68 onto C_{org} -rich matrices, and therefore the C_{org} content in the sediment matrix controls PAHs
69 behaviour in sediments (Karickhoff et al., 1979; Zhang et al., 2004; Shi et al., 2007).
70 Moreover, a significant correlation between PAHs and C_{org} (and soot) levels tends to occur
71 when PAHs are derived mainly from atmospheric inputs (Tsapakis et al., 2003).

72 Polychlorinated biphenyls (PCBs) are synthetic compounds that were used in various
73 industrial activities due to their high thermal stability and dielectric properties. Their wide-
74 spread use, especially after the Second World War, has therefore led to a significant

75 accumulation of these compounds in the environment (Piérard et al., 1996; Breivik et al.,
76 2002). In France, the use of PCBs was banned in 1987 due to their proven toxicity (Decree
77 87-59, 1987). The transport of PCBs from terrestrial sources to aquatic environments may
78 result from direct inputs, following leakage from systems containing them (Abarnou et al.,
79 1987; Duursma et al., 1989), or from atmospheric deposition following volatilization
80 (Chevreuil et al., 1989; Quémerais et al., 1994; Granier and Chevreuil, 1997). In the
81 atmosphere, PCBs are predominantly present in their gaseous phase, after which they bind to
82 particles through atmospheric deposition (Granier and Chevreuil, 1997). Similar to PAHs,
83 PCBs are very chemically stable and are only minimally transformed during the
84 sedimentation process. Due to their lipophilic nature, PCBs accumulate in soils and sediments
85 by binding to fine particles that are rich in organic matter (OM) and have a high surface-to-
86 volume ratio (Karickhoff et al., 1979; Gschwend and Wu, 1985). Nevertheless, Piérard et al.
87 (1996) observed that the affinity of PCBs to OM cannot fully explain the distribution of
88 sediment PCB concentrations, and that particle size is the major factor explaining their
89 distribution. Specifically, PCBs generally accumulate in fine particles, especially highly
90 chlorinated PCBs, which have a particular affinity for fine fractions ($< 63 \mu\text{m}$), whereas low
91 chlorinated PCBs have more affinity for coarse fractions ($> 63 \mu\text{m}$) (Piérard et al., 1996;
92 Salvadó et al., 2013).

93 Based on sediment cores collected in accumulation areas (e.g. dams, floodplains, ponds), the
94 temporal trends of PAHs and PCBs can be reconstructed (Sanders et al., 1992; Van Metre et
95 al., 1997; Budzinski et al., 1997; Bertrand et al., 2015; Cai et al., 2016). Thus, it is possible to
96 reconstruct the contamination trends of a watershed, generally in relation to the intensification
97 of significant anthropogenic activities since the industrial revolution (i.e. over the past ~150
98 years). Sediment deposits typically provide insights into multiple contaminant sources and
99 therefore it is necessary to discriminate sources by analysing the distribution of PAH isomers

100 and PCB congeners over time via measured-concentration diagnostic ratios (Budzinski et al.,
101 1997; Yunker et al., 2002; Francú et al., 2010; Cai et al., 2016).

102 The Seine River watershed is among the most heavily impacted watersheds in Europe
103 (Meybeck, 2002) and therefore the Seine River has been afflicted with substantial heavy
104 metal (Le Cloarec et al., 2011) and organic contaminant (Lorgeoux et al., 2016) burdens.
105 Although many studies have examined POP contaminations in water, SPM, and sediments in
106 the Seine River (Chevreuil et al., 1990; Chevreuil and Granier, 1991; Chevreuil et al., 1998;
107 Blanchard et al., 2007; Lorgeoux et al., 2016), few studies have focused on its tributaries (e.g.
108 the Marne River) (Chevreuil and Granier, 1991; Ollivon et al., 2002) or the Seine estuary
109 (Abarnou et al., 1987; Marchand, 1989; Van Metre et al., 2008). Regarding the latter, only the
110 works of Van Metre et al. (2008) have focused on sedimentary archives downstream of the
111 estuary; however, contamination sources in this area appear to be intra-estuarine.

112 The main Seine estuary tributary is the Eure River. Moreover, the Eure River watershed was
113 recently found to carry significant heavy metal burdens since the 1940s, which may have
114 impacted the sediment quality of the Seine estuary (Gardes et al., 2020a, 2020b). Therefore,
115 this study aimed to establish a link between sediment deposit characteristics and POPs, as
116 well as to reconstruct the temporal trends in PAHs and PCBs accumulation based on sediment
117 cores collected downstream of the Eure River watershed. The distribution of some PAH
118 isomers and PCB congeners was also studied to determine contaminant sources and the
119 evolution of these sources over time.

120

121 **2. Materials and Methods**

122

123 2.1. Description of core sites

124

125 The Eure River (watershed: 6017 km²; mean annual flow: $22.13 \pm 6.69 \text{ m}^3 \text{ s}^{-1}$) is one of the
126 largest tributaries of the Seine River (i.e. only surpassed by the Yonne, Marne, and Oise
127 rivers) and the main contributing river in its estuarine section (Fig. 1A). Les Damps Pond
128 (average depth: 50 cm; area: < 1 ha) and Martot Pond (area: ~7 ha) are located approximately
129 10 km and less than 1 km upstream of the Eure River outlet, respectively (Fig. 1B). Unlike
130 Les Damps Pond, Martot Pond is affected by the Seine estuary during tidal flows through the
131 Eure River outlet. Moreover, Martot Dam, located 200 m downstream of the Martot Pond,
132 prevented tidal flows (for tidal coefficients lower than 70) until its removal in October 2017.
133 Sediment cores were collected using a UWITEC® gravity core and 90 mm diameter PVC
134 tubes. The water-sediment interface was preserved for each coring. For Les Damps Pond,
135 sediment cores DAM15-02 and DAM17-02 were collected in January 2015 and January 2017,
136 respectively (Fig. 1C; Table 1). For Martot Pond, sediment cores MAR15-01 and MAR16-02
137 were collected in January 2015 and February 2016, respectively (Fig. 1D; Table 1). This study
138 was conducted on sediment cores from two accumulation zones to (i) ensure that the recorded
139 temporal trends were representative of a global signal and (ii) determine whether
140 sedimentation in Martot pond was impacted by inputs from the Seine estuary.

141

142 2.2. Grain size and total organic carbon analysis

143

144 Grain size distribution was measured by laser diffraction (LS 13320 Particle Size Analyser
145 Beckman Coulter™). The measurements were conducted every cm by integrating 1 cm on the
146 MAR15-01 and DAM15-02 cores.

147 Sediment cores were analysed using Rock-Eval 6 (RE6) pyrolysis ("Turbo" model RE6
148 pyrolyzer; ISTO laboratory, University of Orléans; see details in Copard et al. (2006)). Total
149 organic carbon content (TOC; %) was measured and OM quality was determined by

150 measuring the hydrogen index (HI; i.e. indicator of the hydrogen richness; $\text{mg HC g}^{-1} \text{ TOC}$)
151 and oxygen (OI; indicator of the degree of oxidation of the OM; $\text{mg O}_2 \text{ g}^{-1} \text{ TOC}$) (Lafargue et
152 al., 1998; Carrie et al., 2012). Additionally, the residual carbon content (RC; %), which
153 corresponds to the refractory C_{org} (obtained during the oxidation phase), was also measured
154 (Lafargue et al., 1998). The measurements were conducted on the MAR15-01 and DAM17-02
155 cores at 1- and 2-cm intervals, respectively.

156

157 2.3. Particulate PAHs/PCBs extraction, analysis and quality control and assurance

158

159 Each sediment core segment was freeze-dried, crushed, and stored at $-25\text{ }^{\circ}\text{C}$. Afterwards,
160 PAHs and PCBs extractions were performed using microwave-assisted extraction (MAE)
161 (MarsX, CEM Corporation). Approximately 2–3 g of sub-samples were taken from each dried
162 portion of the sediment cores and spiked with 15 μL of surrogate standards (perdeuterated
163 fluoranthene and benzo[*a*]pyrene, and PCB156 at 100 mg L^{-1}). Each sub-sample was
164 extracted in duplicate with 40 mL of a toluene:acetone 1:1 (v:v) mixture at $130\text{ }^{\circ}\text{C}$ for 30 min
165 (1,200 W). The extracts were filtered through 0.2- μm PTFE filters, evaporated, and
166 reconstituted in 1.5 mL toluene. Each extract (990 μL) was mixed with 10 μL of two internal
167 standards (perdeuterated phenanthrene and perylene at 100 mg L^{-1}), after which 1 μL of the
168 resulting mixture was injected (splitless mode, $285\text{ }^{\circ}\text{C}$) into a gas chromatographer (6850
169 series, Agilent), coupled with a mass spectrometer (5975C series). The separation was
170 performed using a $60\text{ m} \times 0.25\text{ mm}$ i.d. DB-5MS capillary column (0.25 μm film thickness;
171 J&W Scientific), with helium as the carrier gas (1.4 mL min^{-1}). The oven temperature was
172 programmed at $60\text{ }^{\circ}\text{C}$ for 1.2 min, increased to $190\text{ }^{\circ}\text{C}$ ($40\text{ }^{\circ}\text{C min}^{-1}$) and then to $305\text{ }^{\circ}\text{C}$ ($6\text{ }^{\circ}\text{C}$
173 min^{-1}). The MS detector operated at 70 eV. Quantification was based on selected ion
174 monitoring to improve sensitivity. The extraction method was validated using a certified

175 reference sediment (CNS391, Sigma-Aldrich). Mean recoveries (n=5) were in the 86.3–
176 125.8% range for the 16 priority PAHs (US EPA, 2015) and in the 81.9–113.6% range for the
177 6 studied PCBs. Table 2 summarizes all PAHs and PCBs studied herein.

178

179 3. Results and discussion

180

181 3.1. Sedimentology characteristics of the sediment cores

182

183 The sediment deposits in Martot Pond are characterised by two sedimentary facies, as
184 previously described by Gardes et al. (2020b). The “Seine Unit” facies corresponds to
185 sediment deposits from the Seine River watershed until the early 1940s, when Martot Pond
186 was connected to the Seine channel. The grain size distribution exhibited a low D_{50} ($D_{50} =$
187 $13.8 \pm 7.0 \mu\text{m}$), the TOC content ($\text{TOC}_{\text{mean}} = 1.75 \pm 0.33\%$) was low, HI ($\text{HI}_{\text{mean}} = 147 \pm 24$
188 $\text{mg HC g}^{-1} \text{TOC}$) was constant, OI ($\text{OI}_{\text{mean}} = 260 \pm 35 \text{ mg O}_2 \text{ g}^{-1} \text{TOC}$) increased to 103.5 cm
189 followed by a decrease, and the average RC/TOC was 0.76 ± 0.01 . The “Eure Unit” facies, for
190 which an age model has been established, corresponds to the Eure River inputs since the
191 1940s, with a sedimentation rate of $12.73 \pm 2.2 \text{ mm y}^{-1}$ (Gardes et al., 2020b). For this facies,
192 the grain size distribution was centred around a D_{50} of $33.9 \pm 7.8 \mu\text{m}$ and the TOC content
193 ($\text{TOC}_{\text{mean}} = 3.88 \pm 1.49\%$) increased towards the surface, with high contents ($\text{TOC} = 8.26 \pm$
194 0.19%) in the 9–12 cm range. Unlike OI ($\text{OI}_{\text{mean}} = 150 \pm 17 \text{ mg O}_2 \text{ g}^{-1} \text{TOC}$), HI ($\text{HI}_{\text{mean}} =$
195 $279 \pm 23 \text{ mg HC g}^{-1} \text{TOC}$) increased from the transition between the two facies. RC/TOC
196 ($\text{RC/TOC}_{\text{mean}} = 0.70 \pm 0.02$) decreased from the interface between the two facies and
197 continued to decrease towards the surface (Fig. 2).

198 The sediment deposits in Les Damps Pond are also referred to as the “Eure Unit” facies, and
199 correspond to the Eure River inputs since the 1940s, with a sedimentation rate of 12.2 mm y^{-1}

200 (Gardes et al., 2020b). These sediment deposits are characterised by a grain size distribution
201 centred around a D_{50} of $29.5 \pm 6.7 \mu\text{m}$, comparable to that measured for the "Eure Unit" facies
202 in Martot Pond, with a constant TOC content ($\text{TOC}_{\text{mean}} = 5.36 \pm 0.47\%$) that is slightly higher
203 than that of Martot Pond. HI ($\text{HI}_{\text{mean}} = 302 \pm 23 \text{ mg HC g}^{-1} \text{ TOC}$) and OI ($\text{OI}_{\text{mean}} = 145 \pm 10$
204 $\text{ mg O}_2 \text{ g}^{-1} \text{ TOC}$) showed a slight increase towards the surface. RC/TOC ($\text{RC/TOC}_{\text{mean}} = 0.68$
205 ± 0.02) decreased towards the surface, similar to our observations in Martot Pond (Fig. 2).

206 In Martot and Les Damps ponds, HI and OI for the "Eure Unit" facies suggested a mix
207 aquatic/terrestrial origin (Gardes et al., 2020b) and the mean RC/TOC values were similar and
208 comparable to those measured in the surface sediments of other European rivers (e.g. the
209 Danube, Elbe, Ebro, and Meuse rivers; Poot et al. (2014)). For both ponds, the sedimentation
210 rates were found to be high (e.g. $\geq 10 \text{ mm y}^{-1}$), and therefore it is unlikely that the sediments
211 are affected by early diagenesis processes (Van Metre et al., 1997; Callender, 2000).

212

213 3.2. Relationships between PAHs, PCBs, and sediment characteristics

214

215 In Martot Pond, PAH and PCB concentrations were determined on the MAR16-02 core
216 (Sections 3.3 and 3.4), whereas the grain size distribution and TOC contents (and associated
217 OM parameters) were determined on the MAR15-01 core (Section 3.1). In Les Damps Pond,
218 PAH and PCB concentrations were determined on the DAM17-02 core (Sections 3.3 and 3.4),
219 as well as TOC contents, whereas grain size distribution was determined on the DAM15-02
220 core. Therefore, the measurements were averaged over decades for each core to determine the
221 correlations between PAH and PCB contents and grain size or OM in both ponds.

222 In both ponds, total PAH concentrations ($\sum\text{PAHs}$) and light (2-3-ring) or heavy (4-6-ring)
223 PAHs exhibited weak positive correlations with the clay fraction ($< 2 \mu\text{m}$) ($0.28 < R < 0.39$
224 and $0.23 < R < 0.33$ for Martot and Les Damps ponds, respectively) (Fig. 3A). In Les Damps

225 Pond, PAHs showed strong positive correlations with the fine fraction ($< 63 \mu\text{m}$), particularly
226 with the silt fraction ($2\text{--}63 \mu\text{m}$) ($0.74 < R < 0.8$). Finally, PAHs showed negative correlations
227 with the coarse fraction ($> 63 \mu\text{m}$) in Les Damps Pond ($-0.69 < R < -0.75$). Therefore, PAHs
228 tend to bind more strongly to the fine fraction (Karickhoff et al., 1979; Fernandes et al., 1997;
229 Shi et al., 2007), and more specifically to the silt fraction in Les Damps Pond, as previously
230 demonstrated elsewhere by Ab Razak et al. (1996) with sediment cores from the Kinnickinnic
231 River (US) and Burgess et al. (2001) with surface sediments collected in the Narragansett Bay
232 estuary (US), or to the clay fraction in the Martot Pond, as also reported by Zhang et al.
233 (2004) with surficial sediments of Deep Bay (China).

234 PAHs were negatively correlated with (i) the TOC in Martot Pond ($-0.63 < R < -0.80$), (ii)
235 HI ($-0.48 < R < -0.77$ and $-0.89 < R < -0.93$ for Martot and Les Damps ponds, respectively)
236 and OI ($-0.27 < R < -0.76$ and $-0.55 < R < -0.6$ for Martot and Les Damps ponds,
237 respectively). However, ΣPAHs showed strong positive correlations with the RC/TOC ratio
238 ($R = 0.86$ and $R = 0.95$ for Martot and Les Damps ponds, respectively) (Fig. 3A).

239 The distribution of PAHs in the sediment is thus partly controlled by the presence of fine
240 particles, but more predominantly controlled by the presence of refractory C_{org} . Moreover, in
241 Martot Pond, the correlation between PAHs and RC/TOC tended to increase with the molar
242 mass of the PAHs (from $R = 0.53$ for 2-ring PAHs to $R = 0.91$ for 6-ring PAHs). However,
243 this trend was not observed in Les Damps Pond, where the correlation between PAHs and
244 RC/TOC was very strong regardless of molar mass ($0.91 < R < 0.95$). A correlation between
245 the PAHs and the proportion of refractory C_{org} (i.e. RC/TOC) would thus demonstrate that
246 part of the PAHs was bound to refractory carbonaceous compounds. Such an affinity has been
247 previously identified, albeit from the RC (%) (Poot et al., 2014) and not from the RC/TOC
248 ratio. Additionally, PAHs showed a correlation with the RC/TOC ratio regardless of ring
249 number, but only in Les Damps Pond (Fig. 3B). However, this trend remains to be confirmed,

250 especially to determine whether the proportion of refractory C_{org} is indeed the limiting factor,
251 as suggested by the observed correlations.

252 PCBs showed positive correlations with the fine fraction (clay + silt) ($0.20 < R < 0.56$ and
253 $0.16 < R < 0.71$ for Martot and Les Damps ponds, respectively) and negative correlations with
254 the coarse fraction ($-0.20 < R < -0.56$ and $-0.16 < R < -0.71$ for Martot and Les Damps ponds,
255 respectively) (Fig. 3A). A positive correlation of PCBs with the fine fraction suggests an
256 affinity of PCBs for fine particles, but no clear trends (e.g. as a function of PCB chlorination
257 degree) were evident. Moreover, Piérard et al. (1996) demonstrated that low-chlorinated
258 PCBs showed an affinity for the coarse fraction, which was not observed in our study.

259 PCBs also showed negative correlations with TOC in Martot Pond ($-0.69 < R < -0.79$), as
260 well as with HI ($-0.35 < R < -0.79$ and $-0.27 < R < -0.92$ for Martot and Les Damps ponds,
261 respectively) and OI ($-0.37 < R < -0.72$ and $-0.15 < R < -0.79$ for Martot and Les Damps
262 ponds, respectively) (Fig. 3A). However, the Σ PCBs showed positive correlations with the
263 RC/TOC ratio ($R = 0.68$ and $R = 0.79$ for Martot and Les Damps ponds, respectively). The
264 distribution of PCBs in sediments is thus partly controlled by fine particles and refractory
265 C_{org} , but the affinity between PCBs and refractory C_{org} is generally less marked than for
266 PAHs.

267

268 3.3. PAHs in sediment cores

269

270 3.3.1. General PAH trends in sediment cores

271 Total PAH concentrations were measured for the MAR16-02 and DAM17-02 cores (Fig. 4)
272 For the MAR16-02 core Seine Unit (78–90 cm), PAH concentrations ranged from 7.43 to
273 28.8 mg kg^{-1} ($\text{PAH}_{\text{mean}} = 19.9 \pm 1.47 \text{ mg kg}^{-1}$) and showed a constant increase towards the
274 Eure Unit. For the Eure Unit of the MAR16-02 and DAM17-02 cores, concentrations ranged

275 between 2.93–38.20 mg kg⁻¹ (PAH_{mean} = 12.70 ± 0.51 mg kg⁻¹) and 2.27–28.20 mg kg⁻¹
276 (PAH_{mean} = 11.10 ± 0.89 mg kg⁻¹), respectively. For the MAR16-02 core, the upward trend
277 measured in the Seine Unit continued after the transition to the Eure Unit, reaching a peak of
278 38.20 ± 1.70 mg kg⁻¹ in the late 1940s. For the DAM17-02 core, high concentrations were
279 measured during the 1940s–1950s and two peaks were observed at 28.20 ± 2.44 and 26.10 ±
280 0.58 mg kg⁻¹. PAH concentrations began to decrease from the 1960s to the early 1980s. For
281 the most recent deposition (post-1980s), concentrations were largely constant, ranging
282 between 4 and 6 mg kg⁻¹ (MAR16-02: 5.87 ± 0.26 mg kg⁻¹; DAM17-02: 4.00 ± 0.33 mg kg⁻¹).

283 The two sediment records showed high concentrations during the 1940s–1960s, following
284 the trends determined for the Seine River (Lorgeoux et al., 2016). Notably, although the
285 maximum levels measured by these authors were more than twice those measured for the
286 lower reaches of the Eure River, the maximum values obtained in the Eure River were within
287 the same order of magnitude as the concentrations measured in sediments collected
288 downstream of the Marne River watershed (Ollivon et al., 2002). Moreover, the observed
289 maxima were higher than those measured in other French watersheds, such as the Loire River
290 watershed (Bertrand et al., 2015). Nonetheless, the Eure River watershed and the Eure River
291 flow were ~13 and 30 times lower than those of the Seine River and ~20 and 50 times lower
292 than those of the Loire River, showing the severity of PAH contamination in the Eure River
293 watershed, particularly during the 1940s–1960s. Moreover, the obtained maxima were also
294 higher than those measured in surface sediments of several large European lakes (Fernández
295 et al., 1999), SPM from several large French and European rivers (Rhône, Tamar, Scheldt and
296 Rhine rivers; Fernandes et al. (1999)), or in sediments from Canadian lakes located near an oil
297 sands mining site (Ahad et al., 2015). Concentrations for the most recent deposits are
298 comparable to those determined for recent sediment deposits in the Seine Basin (Lorgeoux et
299 al., 2016), SPM collected in the Seine River (Gasperi et al., 2009), or concentrations

300 measured in the Loire River watershed since the late 1980s (Bertrand et al., 2015). In
301 addition, some PAH concentrations recorded during the 1940s–1960s exceeded the probable
302 effect concentrations (PECs; equal to 22.8 mg kg^{-1} for total PAHs) defined by MacDonald et
303 al. (2000), as the level above which effects on benthic biota are likely to be observed,
304 demonstrating the potential toxicity of the accumulated sediments, especially in case of
305 remobilization.

306 The reconstruction of PAH temporal trends therefore demonstrated significant PAH
307 contamination but did not provide information on the sources responsible for these
308 contaminations. To achieve this, it was necessary to study the distribution of isomers over
309 time (Yunker et al., 2002).

310

311 *3.3.2. Distribution of PAH molar weights and isomers throughout the cores*

312 The abundances of 2-ring PAHs (mass 128; Na) were <1% and those of 3-ring PAHs
313 (masses 152, 154, 166, and 178) were between 11–23% and 10–18% of the total PAHs for
314 MAR16-02 and DAM17-02, respectively. Pn and An (mass 178) were the main components
315 of this fraction, representing on average between 11.1% and 12.4% of the total PAHs. 4-ring
316 PAHs (masses 202 and 228) were mostly represented with abundances between 34–51%
317 (MAR16-02) and 36–46% (DAM17-02). The abundances of the 5-ring PAHs (masses 252
318 and 278) were between 24–42% (MAR16-02) and 25–30% (DAM17-02). The abundances of
319 6-ring PAHs (mass 276; IP and Bghi isomers) were between 7–15% (MAR16-02) and 11–
320 25% (DAM17-02).

321 This important contribution of 4-, 5-, and 6-ring PAHs has been observed in other French
322 watersheds (e.g. Seine River watershed (Lorgeoux et al., 2016); Loire River watershed
323 (Bertrand et al., 2015)) and is frequently observed in sediments downstream or adjacent to
324 industrialized and/or urbanized areas (Yunker et al., 2002). Isomers with masses of 202, 228,

325 252, and 276 are the major components of gasoline and diesel soot, as well as coal
326 combustion emissions, of which the 202- and 252-mass isomers are predominant (Wang et al.,
327 1999; Yunker et al., 2002). Low molecular weight (LMW) PAHs (2-3-rings) are more
328 abundant in petrogenic products and low- to moderate-temperature combustion processes (e.g.
329 biomass and coal burning in homes), whereas high molecular weight (HMW) PAHs (5-6-
330 rings) are products of high-temperature combustion of coal or petroleum from large power
331 plants and factories or vehicular emissions (Ding et al., 2014). Thus, sediments of the lower
332 reaches of the Eure River exhibited an anthropogenic pyrogenic PAH signature (Yunker et al.,
333 2002), which can partly explain the strong correlation between PAHs and refractory C_{org} in
334 the sediments. Indeed, soot is mainly composed of refractory C_{org} (Poot et al., 2014) and the
335 strong link between PAHs and RC/TOC could confirm a predominant atmospheric input of
336 PAHs (especially heavy PAHs) through soot from combustion processes. Nevertheless, this
337 hypothesis must be further confirmed, as the link between PAHs and refractory C_{org} could
338 occur during transport or deposition of the latter on the watershed soils.

339 In addition to discriminating between pyrogenic and petrogenic sources, diagnostic PAH
340 ratios can be used to distinguish combustion sources (e.g. petroleum, coal, or wood
341 combustion) (Yunker et al., 2002). Therefore, different diagnostic ratios based on the ratios of
342 light and heavy PAHs were calculated (Fig. 5). The Fl and Py isomers were the first and third
343 most abundant isomers for MAR16-02 (Fl: 14.5%; Py: 12.1%) and DAM17-02 (Fl: 16.6%;
344 Py: 13.6%), respectively. All Fl/(Fl+Py) ratios exceeded 0.5 ($Fl/(Fl+Py)_{mean} = 0.54 \pm 0.01$ for
345 MAR16-02 and $Fl/(Fl+Py)_{mean} = 0.55 \pm 0.01$ for DAM17-02), which is suggestive of a strong
346 preponderance of coal and/or wood combustion as the main sources of PAH contamination
347 (Budzinski et al., 1997; Yunker et al., 2002), as in the Seine River watershed (Lorgeoux et al.,
348 2016). Moreover, the BaA and Ch isomers were among the most abundant for MAR16-02
349 (BaA: 8.8%; Ch: 8.4%) and DAM17-02 (BaA: 6.4%; Ch: 6.5%). The calculated BaA/228

350 (BaA / (BaA + Ch) vs Fl/(Fl+Py)) ratios were all greater than 0.45 ($BaA/228_{\text{mean}} = 0.51 \pm 0.02$
351 for MAR16-02; $BaA/228_{\text{mean}} = 0.50 \pm 0.05$ for DAM17-02), which also suggests that the
352 PAHs stored in the ponds of the lower reaches of the Eure River had pyrogenic rather than
353 petrogenic source signatures (Fig. 5A) (Yunker et al., 2002). However, no logic was
354 established in terms of temporality because the set of calculated ratios was limited to a
355 restricted domain with little variability.

356 The average ratios obtained from the isomers of mass 276 ($IP/(IP+Bghi)$ vs $Fl/(Fl+Py)$) were
357 greater than 0.5 ($IP/(IP+Bghi)_{\text{mean}} = 0.53 \pm 0.02$ for MAR16-02; $IP/(IP+Bghi)_{\text{mean}} = 0.53 \pm$
358 0.04 for DAM17-02) but some values were below 0.5 (Fig. 5B). Fig. 5B shows that a
359 temporal trend could be identified: the $IP/(IP+Bghi)$ ratio was below 0.5 the mid-1980s for
360 MAR16-02 and DAM17-02, due to an increase in the contribution of isomers with a mass of
361 276. This indicates that sources linked to petroleum combustion intensified from the late
362 1980s onwards; however, the BaA/228 ratio (Fig. 5A) was not descriptive of this temporal
363 evolution. BaA (MW = 228) and BaP (MW = 278) have been shown to be more sensitive to
364 photodegradation than most other PAHs (except An) when emitted to the atmosphere (Yunker
365 et al., 2002). Therefore, given that isomers with masses of 276 and 202 are more stable than
366 those with masses of 278 and 228, their use in diagnostic ratios allows for a better
367 differentiation between combustion sources without significant artefacts related to their
368 subsequent transformations.

369 The An/178 ($An/(An+Pn)$ vs $Fl/(Fl+Py)$) ratios obtained for the two sediment records were
370 greater than 0.1 (Fig. 5C). A ratio of 0.1 indicates a very small proportion of An relative to
371 Pn. This is likely associated with substantial An photodegradation (i.e. given that An is much
372 less stable than Pn) from the combustion source to its final deposition via atmospheric
373 transport. On the other hand, the greater the distance from the combustion source to the
374 deposition zone, the more the ratio tends towards 0.1 (Yunker et al., 2002). However, in

375 contrast to previously studied ratios, the An/178 ratio averages are significantly different
376 within the two sediment records ($An/178_{\text{mean}} = 0.41 \pm 0.09$ for MAR16-02; $An/178_{\text{mean}} = 0.25$
377 ± 0.04 for DAM17-02) and their temporal trends were also distinct. In the case of the
378 DAM17-02 core, the ratio generally tended towards 0.10 from the 1940s to the present day,
379 i.e. towards a source corresponding mainly to combustion. This was also true for the MAR16-
380 02 core after the 1990s. However, the An/178 ratio for the MAR16-02 core exhibited high
381 values (> 0.4) over the mid-1960s–1990s due to an increase in An concentrations throughout
382 this period. Within the Seine River watershed, an enrichment in An in sediments was also
383 recorded from 1971 onwards, without its origin being determined (Lorgeoux et al., 2016). It
384 would appear that for the sediments of the Martot Pond, this increase started a few years
385 earlier and stopped around the 1990s. Nonetheless, these inputs may share the same origin,
386 which could be attributed to oil discharges in an aquatic system that did not undergo
387 combustion. As the transport of PAHs was not carried out through the atmosphere, An was
388 not affected by photodegradation and its concentration thus remained close to that of Pn
389 (Tobiszewski and Namieśnik, 2012). As mentioned previously, Martot Pond was likely
390 impacted by the contributions of the Seine estuary during tidal flows, which is not the case for
391 Les Damps Pond, located upstream. However, Martot Pond is close to the industrial areas of
392 Rouen, which were marked by strong petrochemical activity and significant river transport of
393 oil between the 1960s and 1990s. It appears that after the 1990s, oil leaks during transport
394 greatly decreased, leaving combustion processes as the only sources of sediment
395 contamination.

396

397 3.4. PCBs in sediments cores

398

399 3.4.1. General PCB trends in sediment cores

400 Total PCB concentrations were recorded for the MAR16-02 and DAM17-02 cores (Fig. 6).
401 PCBs were not detected in the Seine Unit (78–90 cm) of MAR16-02 core. In contrast, the
402 Eure Unit of MAR16-02 and DAM17-02 exhibited concentrations ranging between 0.02–1.57
403 mg kg^{-1} ($\text{PCB}_{\text{mean}} = 0.72 \pm 0.05 \text{ mg kg}^{-1}$) and 0.09–1.60 mg kg^{-1} ($\text{PCB}_{\text{mean}} = 0.50 \pm 0.06 \text{ mg}$
404 kg^{-1}). For MAR16-02, PCBs levels increased at the transition between the two sedimentary
405 facies and reached a peak of $1.57 \pm 0.06 \text{ mg kg}^{-1}$ in the late 1950s, whereas a $1.60 \pm 0.12 \text{ mg}$
406 kg^{-1} peak was recorded in DAM17-02 in the late 1960s. A general downward trend in PCB
407 levels was then visible up to the surface of the sediment deposits. For MAR16-02, two
408 concentration peaks were observed despite the downward trend, the first around 1976 (PCB =
409 $0.68 \pm 0.13 \text{ mg kg}^{-1}$) and the second in 1992–1996 with an extremely high concentration that
410 reached 16.8 mg kg^{-1} . For the most recent sediment deposits (from the 2000s onward),
411 concentrations are relatively close or equal to $0.12 \pm 0.01 \text{ mg kg}^{-1}$ and $0.18 \pm 0.05 \text{ mg kg}^{-1}$ for
412 MAR16-02 and DAM17-02, respectively.

413 The general temporal trend of PCB contents was similar to previously reported trends in
414 France (Seine River watershed: Lorgeoux et al., 2016; Rhône River watershed: Desmet et al.,
415 2012), Europe (UK: Sanders et al., 1992; Germany: Bruckmeier et al., 1997; Italy: Combi et
416 al., 2020), and the US (Christensen and Lo, 1986; Van Metre et al., 1997), and were similar to
417 temporal trends in global PCB production and consumption (Breivik et al., 2002). The
418 maxima obtained during the 1950s–1970s ($\sim 1.6 \text{ mg kg}^{-1}$ for the two ponds) were higher than
419 those historically recorded in several French watersheds, such as the Loire (1.2 mg kg^{-1} ,
420 Dendievel et al., 2019), Garonne (0.145 mg kg^{-1} , Dendievel et al., 2019) and Rhône rivers
421 watersheds (0.28 mg kg^{-1} , Desmet et al., 2012; 0.42 mg kg^{-1} , Mourier et al., 2014); European
422 watersheds such as the Brno Reservoir, Czech Republic (0.08 mg kg^{-1} , Franců et al., 2010);
423 the Esthwaite Water, England (0.05 mg kg^{-1} , Sanders et al., 1992); or the Chattahoochee River
424 watershed, US (0.38 mg kg^{-1} , Van Metre et al., 1997). It should be noted that total PCB

425 concentrations were calculated from 7 congeners in the cited studies and up to 22 for Sanders
426 et al. (1992), compared with the 6 congeners studied herein. Nevertheless, the maximum
427 concentrations recorded in the Eure River watershed remain lower than those recorded in
428 recent flood deposits in the Rhône River (Dendievel et al., 2019), the Seine River (2.31 mg
429 kg⁻¹, Lorgeoux et al., 2016), or the Seine estuary, France (5 mg kg⁻¹; Dendievel et al., 2019),
430 the Lippe River, Germany (2.63 mg kg⁻¹, Heim et al., 2004), or Milwaukee Harbour, US (13.4
431 mg kg⁻¹, Christensen and Lo, 1986).

432 The detection of PCBs prior to 1955 (i.e. the year in which PCB production and
433 consumption in France began to increase; Lorgeoux et al., 2016) may be consistent with the
434 fact that PCB production in France began approximately in the 1930s (de Voogt and
435 Brinkman, 1989). However, the maximum consumption recorded in France in 1975 does not
436 correspond to the maximum concentrations in sediments recorded a few years earlier. The
437 year 1975 also corresponds to the first bans on the use of PCBs in open systems (e.g.
438 plasticizers, carbonless copy paper, lubricants, inks, laminating and impregnating agents,
439 paints, adhesives, waxes, cement and plaster additives, casting and dedusting agents, sealing
440 liquids, fire retardants, immersion oils, and pesticides (de Voogt and Brinkman, 1989; Bigus
441 et al., 2014)), which may explain why it was after this date that the levels started to show a
442 substantial decrease, especially in Martot Pond. Additionally, PCB concentrations began to
443 stabilise to low levels in the early 1990s (with the exception of the 1992–1996 period in
444 Martot Pond), which can be linked to the cessation of PCB production in France in 1984 (de
445 Voogt and Brinkman, 1989) coupled with the ban on PCB use in France in 1987, including in
446 closed-system applications (e.g. cooling liquids in transformers, dielectric liquids in large and
447 small capacitors, heat-conducting fluids in heat-exchangers and fire- or heat-resistant
448 corrosion-free hydraulic fluids in mining equipment and vacuum pumps (de Voogt and
449 Brinkman, 1989; Kannan et al., 1992; Bigus et al., 2014)). In addition, some PCB

450 concentrations recorded during the 1950s–1960s exceeded the probable effect concentrations
451 (PECs; equal to 0.676 mg kg⁻¹ for total PCBs) defined by MacDonald et al. (2000), as the
452 level above which effects on benthic biota are likely to be observed, demonstrating the
453 potential toxicity of the accumulated sediments, especially in case of remobilization.

454 Thus, the temporal reconstruction of PCB levels demonstrated a significant PCB
455 contamination within the Eure River watershed, but only an analysis of the distribution of the
456 congeners can allow for the determination of the contaminant sources.

457

458 3.4.2. *Distribution of PCB congeners*

459 Congener distributions were recorded for the MAR16-02 and DAM17-02 cores (Fig. 6). For
460 the Eure Unit of MAR16-02 core, PCB180 was, on average, predominantly represented
461 (23.1%), followed by PCB138 (22.1%), PCB153 (20.2%), PCB101 (15.0%), PCB52 (11.3%),
462 and PCB28 (8.2%). Therefore, 6-chlorine PCBs (PCB138 + PCB153) were predominantly
463 represented (42.3%). For DAM17-02, PCB138 represented on average 42.8% of the \sum PCBs,
464 which combined with PCB153 (8.1%) amounted to a 50.9% representation of 6-Chlorine
465 PCBs, whereas PCB101 represented on average 20.7%, followed by PCB180 (18.8%),
466 PCB52 (5.9%), and PCB28 (3.7%). PCB28, the globally least represented congener, was
467 detected beginning in the early 1950s, and its contribution has generally followed the trends
468 shown by PCB concentrations. However, during the peak of PCB levels in the late 1950s for
469 MAR16-02 and the 1960s for DAM17-02, PCB28 was the most represented congener (25.4%
470 and 26.5% respectively). From the late 1970s onwards, PCB28 represented less than 10% of
471 \sum PCBs for MAR16-02, whereas it was almost no longer detected in DAM17-02. PCB52, the
472 second least represented congener, was detected from the beginning of the sediment records
473 and, similar to PCB28, followed the overall global PCB trends. However, PCB52 was the
474 second most represented congener during the 1950s peak concentration (21.7%) for MAR16-

475 02 and the third (21.9%) during the 1960s peak for DAM17-02. The contribution of this
476 isomer decreased overall afterwards (< 10%). PCB101 and PCB153 followed similar trends
477 for MAR16-02, with a strong representation at the Eure/Seine unit transition (>30%) and then
478 decreased as the PCB concentration increased. Following the peak PCB concentration, the
479 contribution of PCB101 decreased, although its contribution was approximately 20%,
480 whereas the contribution of PCB153 also stabilised at approximately 20%. PCB138 also
481 showed strong contributions from the Eure/Seine unit transition of the MAR16-02 core, which
482 also decreased as the PCB concentration increased. Afterwards, the contribution of PCB138
483 increased overall towards the surface as the PCB concentrations decreased. The distribution of
484 PCB101 was also important at the beginning of the DAM17-02 core (>40%). For the
485 MAR16-02 core, this congener decreased as PCB concentrations increased. In contrast to
486 MAR16-02, the contribution of PCB153 was low for DAM17-02 and showed an increasing
487 trend until the early 1980s (~17%). The contribution of PCB138 showed a broadly similar
488 behaviour to that of PCB153 and reached nearly 70% at the end of the 1980s. Finally,
489 PCB180 was only detected from the mid-1950s for MAR16-02 but its contribution increased
490 over time and was very significant from the late 1990s onwards. Conversely, PCB180 showed
491 a strong contribution at the beginning of the DAM17-02 record, which decreased with
492 increasing PCB concentration.

493 Releases of PCBs to the environment can result from inputs to watercourses through leakage
494 from facilities or discharges from landfills, as well as leaching from industrial or urban
495 surfaces, but also from atmospheric deposition, in which case PCBs are mostly transported in
496 particulate form (Zhou et al., 2001; Yang et al., 2012). More generally, industrial activities
497 and urbanization are the primary causes of sediment PCB pollution (Bigus et al., 2014).
498 France was one of the first countries to produce PCBs and is estimated to have contributed
499 approximately 10% of the global production from 1930 to 1984 (i.e. 134,654 t of the 1.5 Mt

500 produced globally) (de Voogt and Brinkman, 1989; Breivik et al., 2002). PCBs in France
501 were produced under the names "Phenoclor" and "Pyralene". Moreover, it can be assumed
502 that the "PCB technical mixture" used in France prior to 1987 was predominantly produced in
503 France, regardless of its form and use.

504 Comparing PCB isomers (and thus comparing PCBs according to their chlorination degree)
505 can be useful to identify the sources responsible for PCB releases to the environment and to
506 assess changes in their use within a given watershed (Franců et al., 2010; Cai et al., 2016).
507 Ratios of PCB₂₈/PCB₁₅₃ and PCB₍₂₈₊₅₃₎/PCB₍₁₃₈₊₁₅₃₊₁₈₀₎ congeners were found to be
508 below 1 for most of the MAR16-02 (mean = 0.43 and 0.36, respectively) and DAM17-02
509 (mean = 0.61 and 0.17, respectively) cores (Fig. 7), confirming a dominance of "high
510 chlorinated congeners" that are generally present in the composition of hydraulic fluids or
511 thermostable lubricants, whereas "lower chlorinated mixtures" are used for less viscous
512 applications (Franců et al., 2010). However, these ratios were greater than 1 during the high-
513 concentration instances recorded in the late 1950s (Martot Pond) and 1960s (Les Damps
514 Pond), confirming the dominance of "low chlorinated congeners" during these periods (Fig.
515 7). This could be explained by a contribution from at least two distinct sources during certain
516 periods of high PCB use. If the production and use of formulations containing highly
517 chlorinated PCBs were staggered over the period spanning from the 1930s to the late 1980s,
518 the temporary dominance of low chlorinated congeners (tri-Cl and tetra-Cl) may indicate the
519 use and subsequent release of specific technical PCB mixtures, such as DP-3 or DP-4 (i.e. two
520 types of Phenoclor mixtures). These technical mixtures are equivalent to the Aroclor 1016 and
521 1242 mixtures (Kannan et al., 1992; Breivik et al., 2002), which are mainly composed PCBs
522 containing 2–5 chlorines (Frame, 1997; Breivik et al., 2002). These observations are
523 consistent with the reports of Franců et al. (2010) (Brno Reservoir, Czech Republic), whereby
524 the temporary dominance of lower chlorinated congeners corresponded to (accidental) input

525 from a former transformer and capacitor manufacturing plant that used a low chlorinated
526 technical PCB mixture called Delor 103 (equivalent to Aroclor 1242, which is produced in the
527 US). As previously reported by Cai et al. (2016) and Yang et al. (2012), the predominance of
528 heavy congeners could correspond to atmospheric inputs over long distances. However, this
529 occurred in countries that were not direct producers of PCBs at the time of deposition. Other
530 authors indicate that the presence of lighter PCBs is more suggestive of substantial
531 atmospheric contribution, given that these congeners are more susceptible to long-range
532 transport as they are less prone to photodegradation than highly chlorinated PCBs. Therefore,
533 the predominance of heavier PCBs seems to suggest a larger contribution of emissions from
534 local sources (Alegria et al., 2016). Halfadji et al. (2019) noted that sites contaminated with
535 highly chlorinated PCBs were near petrochemical industrial zones, which is also the case for
536 Martot Pond.

537 It should be noted that during the pollution peak recorded in Martot Pond during the 1992–
538 1996 period, the previously calculated ratios remained below 1, demonstrating the occurrence
539 of a pollution source that was distinct from that responsible for the heavy contamination a few
540 decades earlier. Given that the studied area was not impacted by major leaks associated with
541 the degradation of electrical installations, this sudden increase in contamination level could be
542 attributed to a very localised wild discharge. Notably, Les Damps Pond (located upstream) did
543 not show this intense pollution peak and the pollution date occurred very shortly after the ban
544 on the use of PCBs in France. Unfortunately, some industrial discharges continued even after
545 1987, as was the case in the Rhone River watershed, where high PCB concentrations were
546 recorded several years after cessation of their use (Desmet et al., 2012).

547

548 **4. Conclusions**

549

550 This study demonstrated that PAHs, particularly heavy PAHs, had a high affinity for
551 refractory C_{org} , whereas PCBs showed a lower affinity. The Eure River watershed has been
552 subject to significant POP contaminations since the 1940s, corresponding to the same order of
553 magnitude as that recorded in other French or European watersheds. The abundance of
554 different PAH isomers and their diagnostic ratios demonstrated that the high concentrations of
555 PAHs recorded during the 1940s–1960s were of pyrogenic origin (i.e. derived from
556 combustion processes), whereas certain signatures recorded in more recent deposits (up to the
557 1990s) exhibited an evolution towards a petrogenic origin. Furthermore, PCB temporal trends,
558 particularly their high concentrations during the 1950s–1970s, are generally linked to the
559 production, consumption, and bans on the use of PCBs in France. The distribution of PCB
560 congeners and certain congener ratios demonstrated that the high releases during the 1950s–
561 1970s were likely linked to the release of "technical mixtures PCBs" composed of "low
562 chlorinated congeners" into the river, whereas the most recent inputs were mainly attributed to
563 atmospheric inputs of "high chlorinated congeners", with the exception of a local high
564 undefined contamination recorded in Martot Pond.

565

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 575 Archive from French LTER (<http://ccwbvps18.in2p3.fr/maps/visualiseur-coyoxhup#project>)
 576 which is a portal for data associated with marine, lake sediment cores stored in LTER French
 577 laboratories.

578

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580

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Table 1. Sediment cores collected in Les Damps and Martot ponds (WGS 84).

Pond	Core ID	IGSN	Longitude (X)	Latitude (Y)	Core Length (cm)
LES	DAM15-02	IEM2C0016	1°10'9.05" E	49°18'16.13" N	80
DAMPS	DAM17-02	IEM2C000E	1°10'13.26" E	49°18'15.66" N	90
MARTOT	MAR15-01	IEM2C0001	1°03'1.68" E	49°17'49.68" N	138
	MAR16-02	IEM2C0008	1°03'2.60" E	49°17'49.30" N	129

Table 2. List of the analysed POPs.

PAHs			PCBs		
Compounds	Molar weight ($g\ mol^{-1}$)	X-Rings	Compounds	Molar weight ($g\ mol^{-1}$)	X-Chlorines
Naphthalene (Na)	128	2-Rings	PCB 28	258	3-Chlorine
Acenaphthylene (Ayl)	152	3-Rings	PCB 52	292	4-Chlorine
Acenaphthene (Aen)	154		PCB 101	326	5-Chlorine
Fluorene (F)	166		PCB 138	361	6-Chlorine
Phenanthrene (Pn)	178		PCB 153	361	6-Chlorine
Anthracene (An)			PCB 180	395	7-Chlorine
Fluoranthene (Fl)	202	4-Rings			
Pyrene (Py)					
Benz[<i>a</i>]anthracene (BaA)	228				
Chrysene (Ch)					
Benzo[<i>b</i>]fluoranthene (BbF)	252	5-Rings			
Benzo[<i>k</i>]fluoranthene (BkF)					
Benzo[<i>a</i>]pyrene (BaP)					
Dibenz[<i>a,h</i>]anthracene (DhA)	278				
Indeno[1,2,3- <i>cd</i>]pyrene (IP)	276	6-Rings			
Benzo[<i>ghi</i>]perylene (Bghi)					

Table 3. Comparison of maximum PCB concentrations in sediment cores of several watersheds.

Location	Concentration (mg kg ⁻¹)	Time interval	References
<i>France</i>			
Eure River (lower section)	1.57 / 1.60	1950s–1970s	This study
Seine River (lower section)	2.31	1960	Lorgeoux et al., 2016
Seine estuary	5	1970s	Dendievel et al., 2019
Loire River (lower section)	1.2	1973–1989	
	1.4	2003–2008	
Garonne River (upper section)	0.145	1998	
Rhône River (lower section)	2.4 (flood deposits)	1995–1996	
	0.42	1990–1995	Mourier et al., 2014
	0.28	1991	Desmet et al., 2012
<i>Europe</i>			
Brno Reservoir (Czech Republic)	0.08	1970s–1980s	Franců et al., 2010
Lippe River (Germany)	2.63	1980–1985	Heim et al., 2004
Esthwaite Water (England)	0.05	1963	Sanders et al., 1992
<i>United States</i>			
Lake Harding (Chattahoochee River)	0.38	1950–1966	Van Metre et al., 1997
Milwaukee Harbour	13.4	1970–1975	Christensen and Lo, 1986

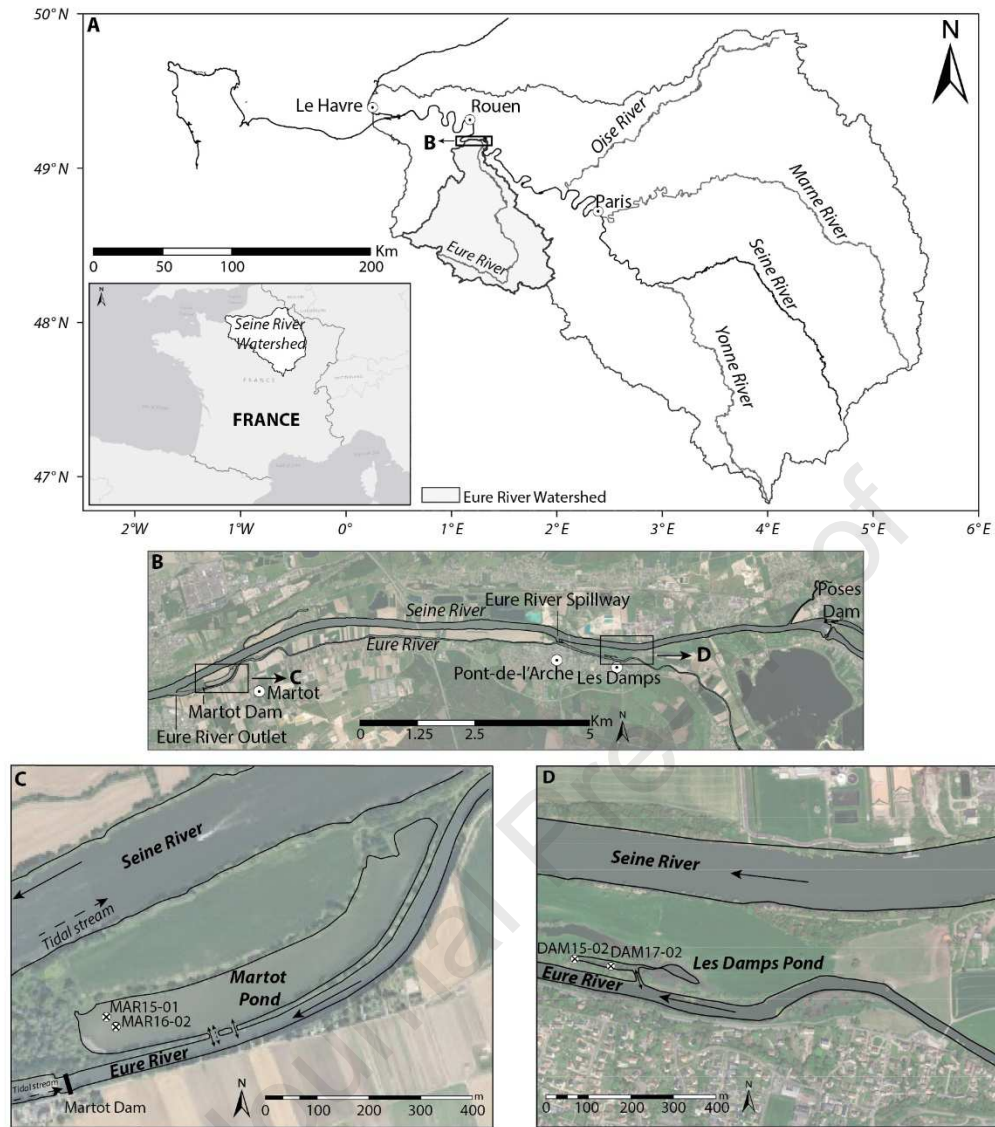


Figure 1. A. Seine River watershed; B. Study Area; C. Sediment core locations in Martot Pond and D. Sediment core locations in Les Damps Pond.

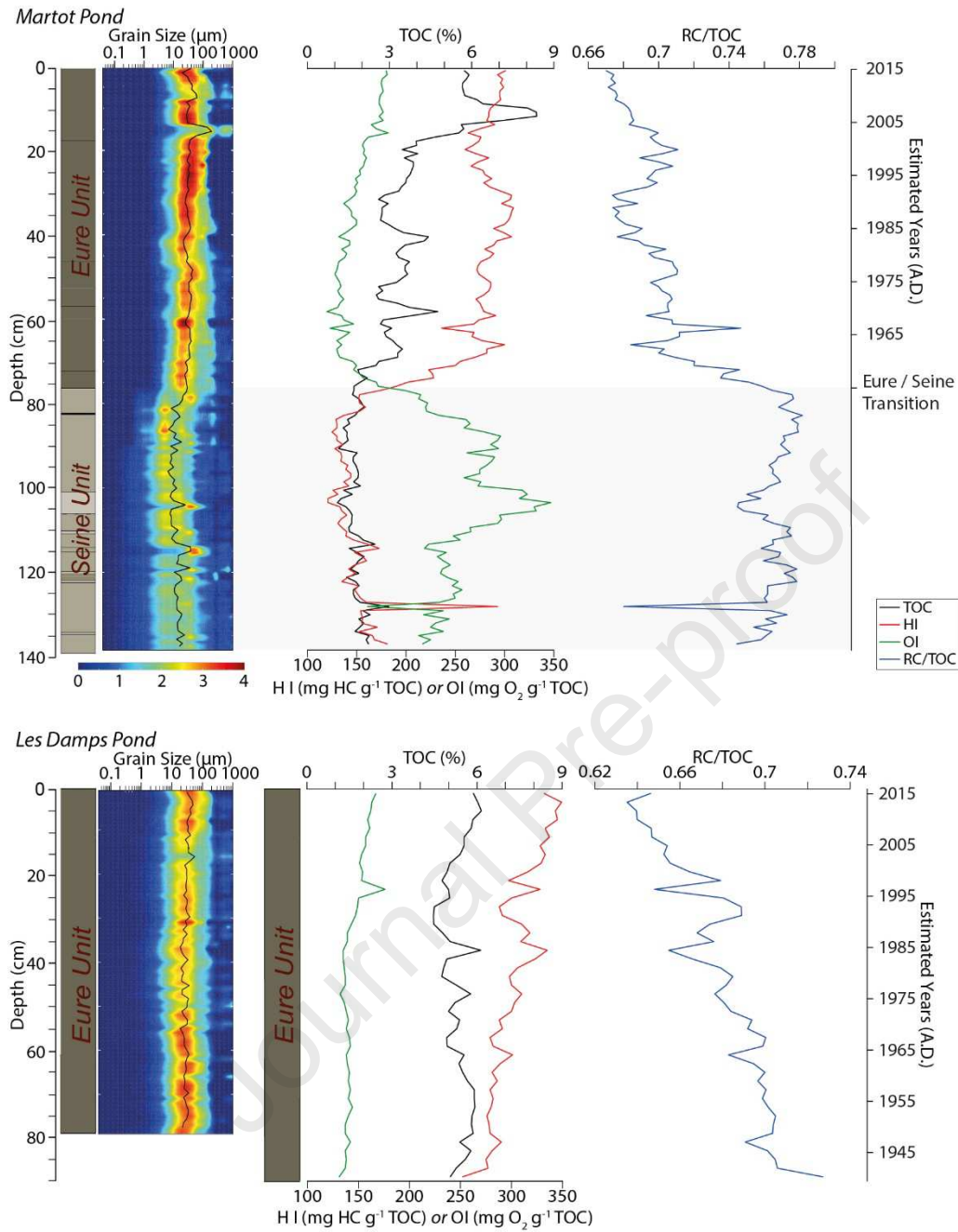


Figure 2. Grain size distribution, D_{50} , TOC, HI, OI, and RC/TOC for the MAR15-01 core (Martot Pond) and for the DAM15-02 and DAM17-02 cores (Les Damps Pond).

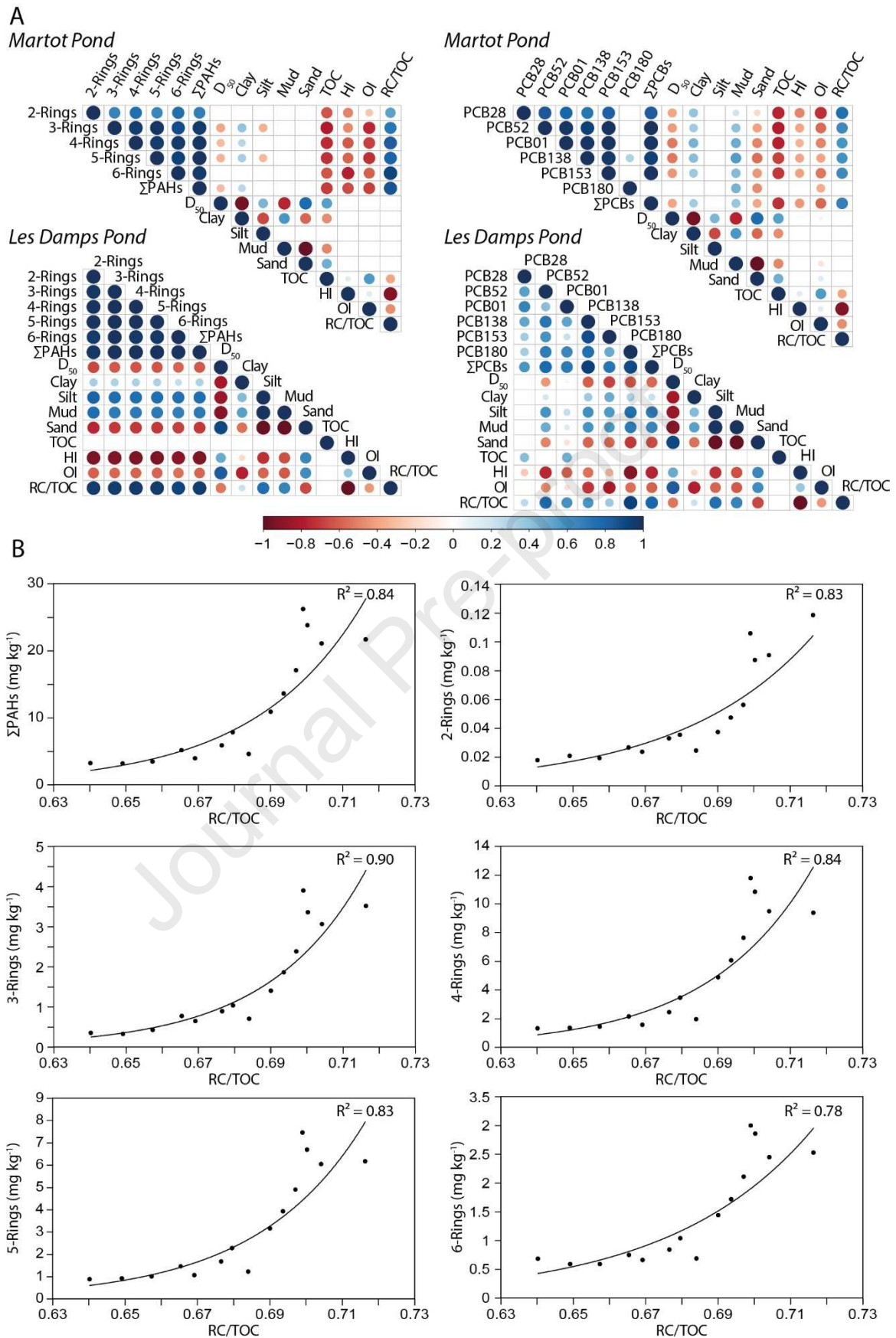


Figure 3. A. Correlation matrix of PAHs/PCBs and sediment characteristics for Martot and Les Damps ponds (Spearman correlation, $p < 0.05$ for all circles presented); B. ΣPAHs, 2-3-Rings, 4-Rings, 5-Rings, and 6-Rings (mg kg⁻¹) versus RC/TOC for Les Damps Pond (from the correlation matrix).

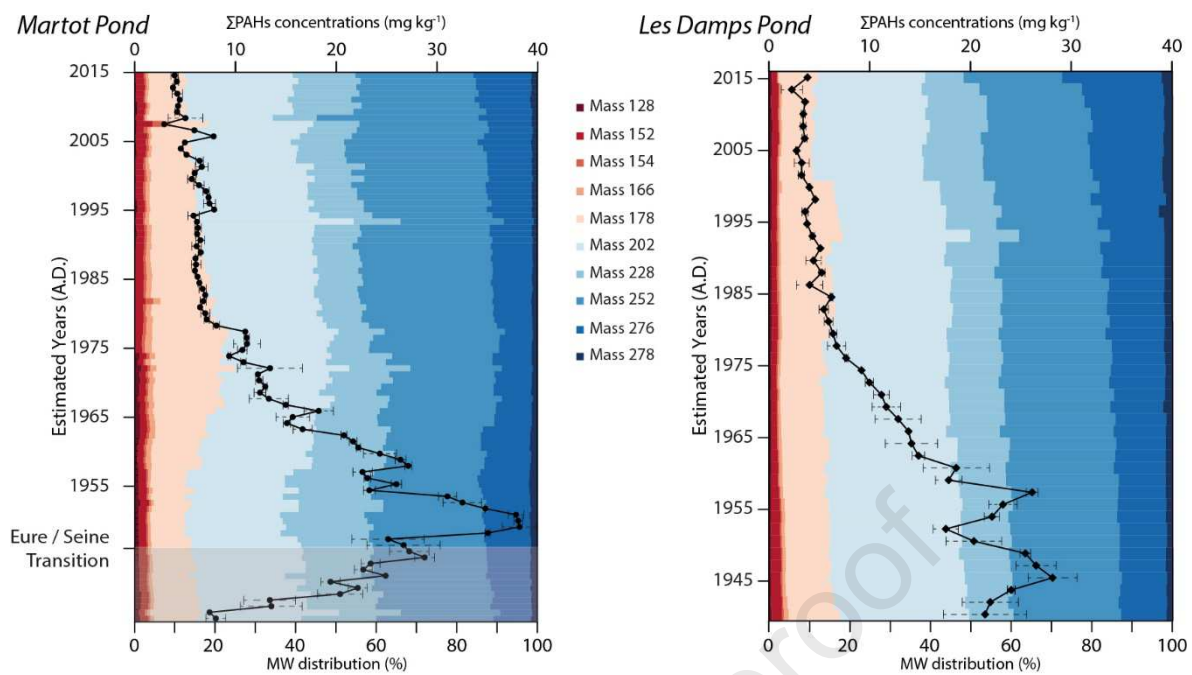


Figure 4. PAH concentrations (mg kg⁻¹) and molar weight (MW) distribution (%) in Martot Pond (MAR16-02 core) and Damps Pond (DAM17-02 core).

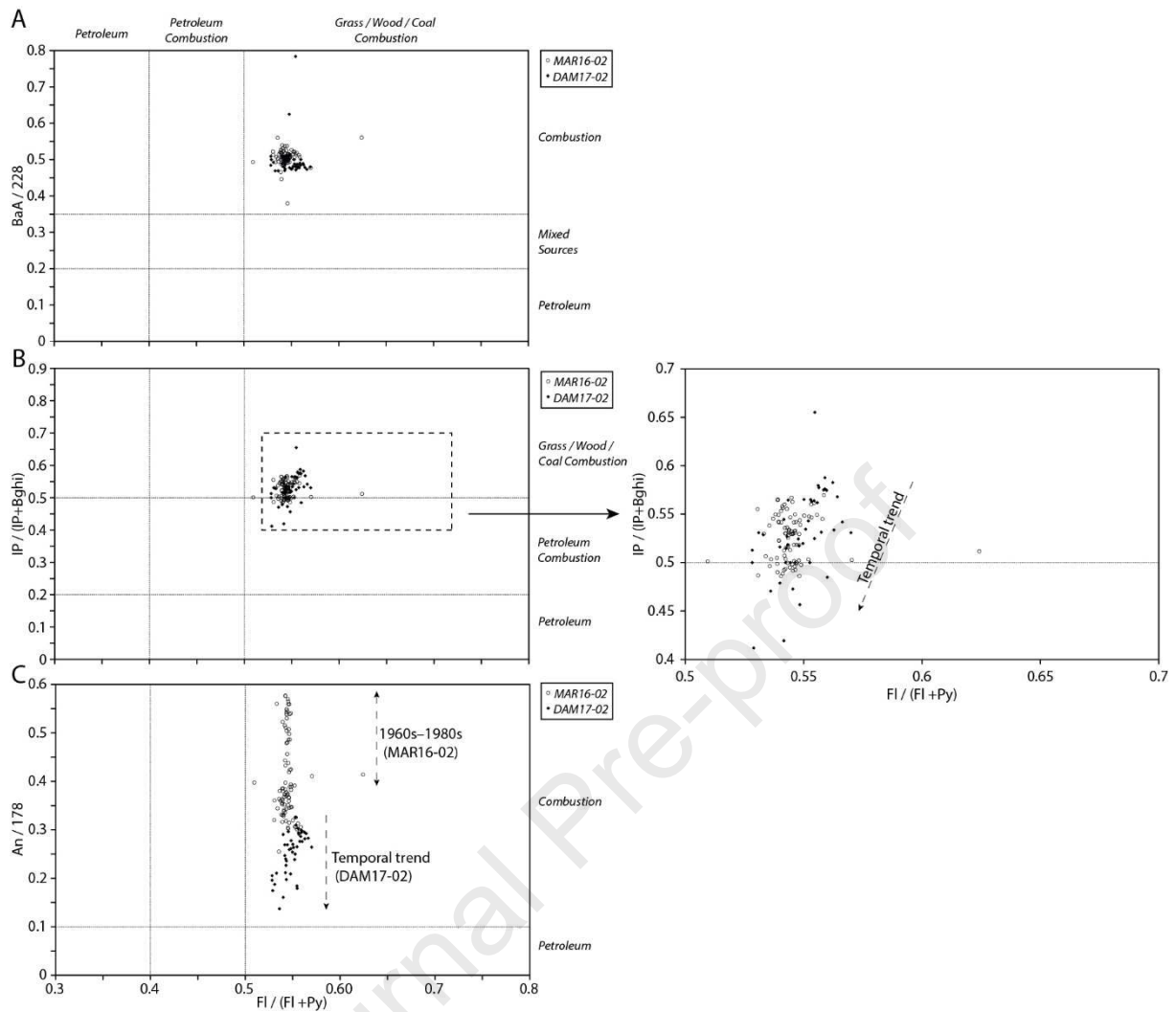


Figure 5. PAH diagnostic ratios A. $BaA/228$ vs $FI/(FI+Py)$; B. $IP/(IP+Bghi)$ vs $FI/(FI+Py)$ and C. $An/178$ vs $FI/(FI+Py)$ for the MAR16-02 (open circle) and DAM17-02 (black diamond) cores.

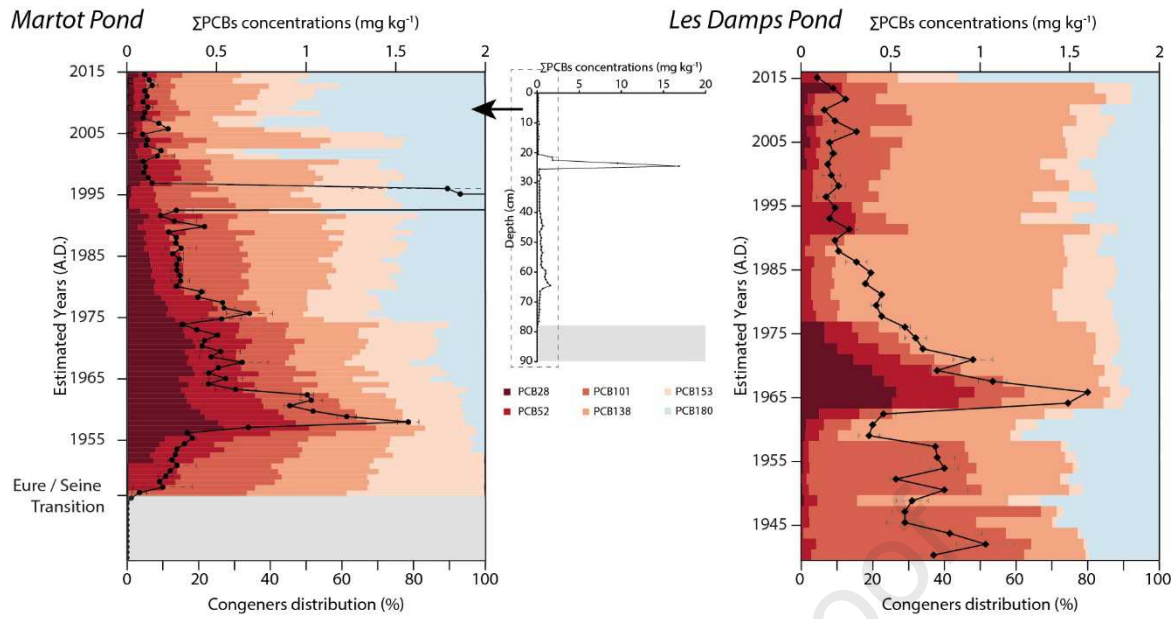


Figure 6. PCB concentrations and homolog distribution in Martot Pond (MAR16-02 core) and Les Damps Pond (DAM17-02 core).

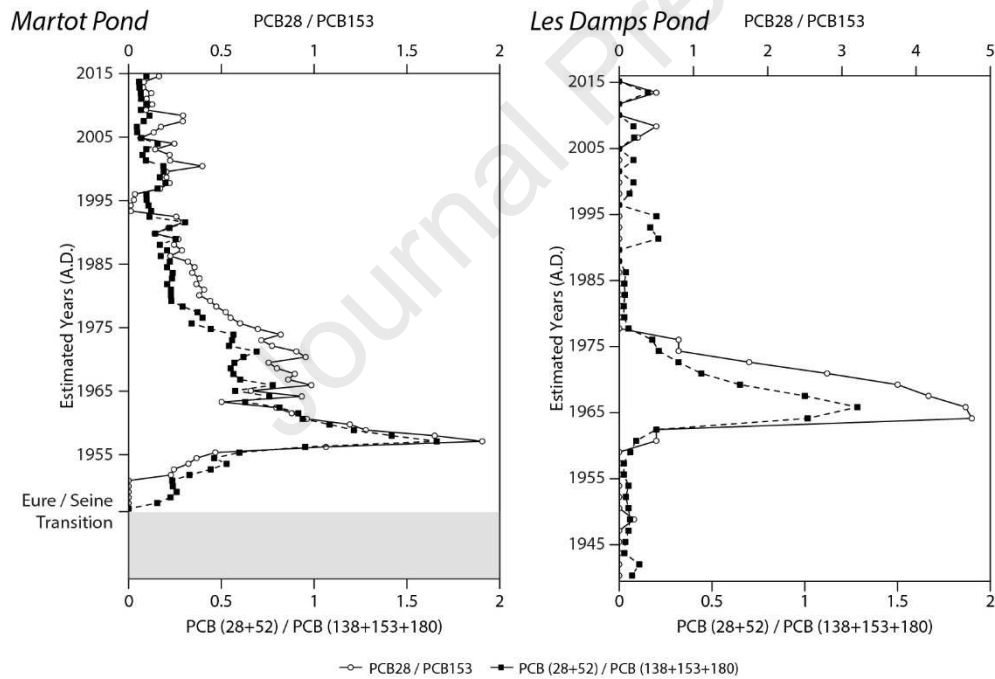


Figure 7. PCBs ratios in Martot Pond (MAR16-02 core) and Les Damps Pond (DAM17-02 core).

- Temporal trends of PAHs and PCBs were reconstructed from sediment cores
- PAHs and PCBs showed a positive correlation with fine fractions
- PAHs showed a positive correlation with the refractory organic carbon
- PAHs were found to be predominantly of pyrogenic origin
- High levels of PCBs were linked to technical mixture discharges into the river

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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