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1 **Historical and post-ban releases of organochlorine pesticides**
2 **recorded in sediment deposits in an agricultural watershed,**
3 **France**

4
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10

11 **Abstract**

12 Agricultural use of organochlorine pesticides (OCPs) increased during the twentieth century
13 but many of them have been progressively banned several decades after their introduction.
14 Nevertheless, these lipophilic chemical compounds may persist in soils and sediments. From
15 sediment deposits, it is possible to reconstruct the chronology of OCP releases in relation to
16 former applications through time. Nevertheless, long-term fate of OCPs i.e. source, transfer,
17 and storage through the watershed, is also related to the OCPs-sediment characteristics
18 interactions, and our study showed the significant links between OCPs and labile or refractory
19 organic matter. From sediment cores collected in a mainly agricultural watershed, the Eure
20 River watershed (France), aldrin and lindane widespread applications during the 1950s–1970s
21 have been recorded. While lindane applications declined after that date, according to the
22 temporal trend of the stable isomer of hexachlorocyclohexane (β -HCH), α -, and γ -HCH have
23 been recorded at significant levels in the 2000s, suggesting first local post-ban applications.
24 Nevertheless, the relationships between these OCPs and labile organic matter resulted in an

25 overestimation of the post-ban releases. Also, the detection of stable metabolites of
26 dichlorodiphenyltrichloroethane (DDT) (i.e. 4,4'-DDE) and heptachlor (i.e. heptachlor
27 epoxide) several decades after their ban, revealed the role of old deep soils erosion in the
28 chronology of OCP releases and thus the reemergence of stable transformation products from
29 historical OCPs.

30

31 **1. Introduction**

32

33 Organochlorine pesticides (OCPs) are part of persistent organic pollutants (POPs) and are
34 ubiquitous contaminants in the environment, released by human activities. These synthetic
35 compounds mainly used in agriculture have significant half-lives in air, soils, sediments, and
36 biota, and have a variety of toxic effects on living organisms including humans (Willett et al.,
37 1998; Jones and de Voogt, 1999; Hidayati et al., 2021). OCPs are relatively lipophilic and
38 show an affinity for fine particles and organic matter (OM) in soils, suspended particulate
39 matter (SPM) in rivers, and sediments (Warren et al., 2003; Thevenon et al., 2013; Li et al.,
40 2015; Varnosfaderany et al., 2020). Therefore, it is accepted that fluvial or estuarine
41 sediments can be considered as the main sink for OCPs, and their temporal trends can be
42 reconstructed by their analysis from sediment cores in combination with fine-scale analysis of
43 the sedimentological characteristics of sediment deposits (Van Metre et al., 1997; Li et al.,
44 2015; Liber et al., 2019; Varnosfaderany et al., 2020). Nevertheless, studies of past and
45 current sources, transport and fate of OCPs in watershed using sediment cores have been
46 mainly carried out in Asia or USA, while there is a lack of OCPs-associated sediments studies
47 over time in Europe (Bigus et al., 2014).

48 There are numerous pesticides release points (e.g. production area, industrial, or urban
49 applications) but agricultural practice is known as the main source in the environment (e.g.

50 Désert et al., 2018). France is a historically agricultural country that is currently the leading
51 European country in terms of i. utilised agricultural area (23.98 M ha), with cereals, oilseed,
52 and sugar beet being the main crops, ii. production (18.3% of European production), and is
53 only ranked ninth in Europe in terms of pesticide use; however, their use does not seem to be
54 decreasing, and was estimated to 4.1 t of active component per 1000 ha in 2014 (Hossard et
55 al., 2017). Although many pesticides including some OCPs were banned in France during the
56 twentieth century, their persistence in the environment means that they can still be detected in
57 soils, sometimes many years after they were banned, while soil erosion can lead to the
58 contamination of rivers (Villanneau et al., 2009; Schreiner et al., 2016). The Seine River
59 watershed (95000 km²) contains large urban areas (e.g. Paris Megacity) but also a significant
60 amount of agricultural land that accounts for more than 60% of the total watershed area.
61 Among the Seine River tributaries, the Eure River is the main tributary of the Seine estuary
62 and drains a watershed of which 70 % of the soil area is used for crops. Moreover, the Eure
63 River watershed is partially located in the “Beauce Region” an emblematic national
64 agricultural region (~ 5740 km²) known as the breadbasket of France.

65 Although studies have examined the current transfer of pesticides within the tributaries of
66 the Seine River (Blanchoud et al., 2004, 2007) and the contamination of aquatic species by
67 OCPs in the Seine River and Seine estuary (Blanchard et al., 1997; Lesueur et al., 2015), no
68 studies have examined the temporal trends in OCPs from riverine sediments and in particular
69 those from the Eure River watershed. Therefore, this study aims to reconstruct the chronology
70 of OCP releases in this watershed. Sediment cores were collected in the lower reaches of the
71 watershed in order to be representative of the whole watershed. In addition, we paid attention
72 on the poorly studied interactions between OCPs and sediment characteristics. Yet, this focus
73 is considered to be essential to well interpret the temporal distribution of OCPs since i. the
74 affinity of POPs for particles and particulate OM can exhibit significant differences regarding

75 the considered contaminant (Warren et al., 2003; Poot et al., 2014), and ii. the deposition of
76 POPs in aquatic environment can be affected by OM fractions as the algae-derived OM
77 (Taylor et al., 1991; Berrojalbiz et al., 2011; Duan and Ran, 2015).

78

79 **2. Materials and Methods**

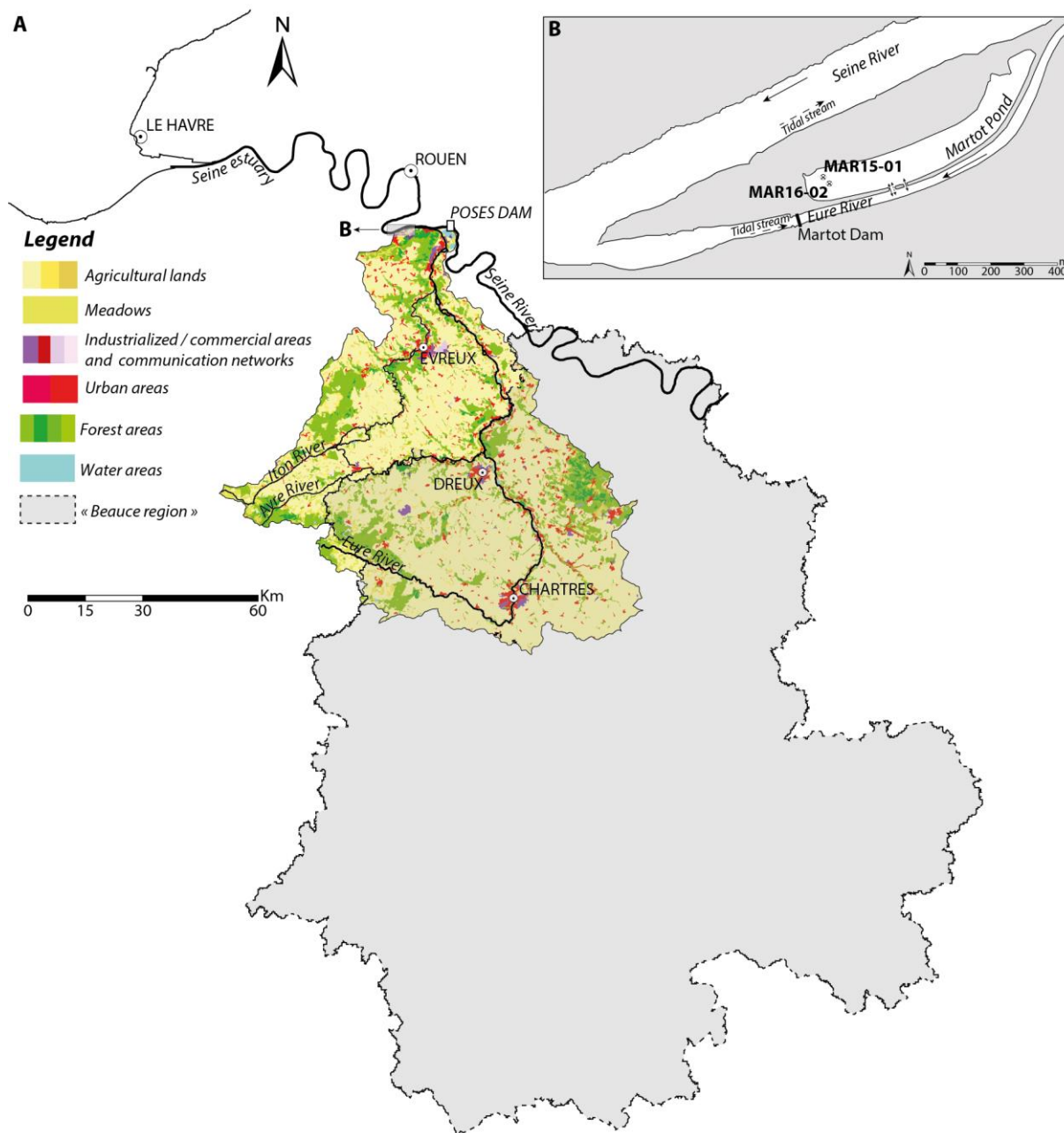
80

81 **2.1. Core sites in the Eure River watershed**

82

83 The Eure River has a mean flow of $22.13 \pm 6.69 \text{ m}^3 \text{ s}^{-1}$ and is the main tributary of the Seine
84 estuary (the estuarine part of the Seine River is delimited by the Poses Dam). The Eure River
85 watershed (6017 km²), located in the northern part of the “Beauce Region” is mainly
86 composed of agricultural lands, and cropping systems are diverse including oilseed rape, fibre
87 flax, potatoes, protein peas, cereals (soft and durum wheat, barley, and corn) and sugar beet
88 (Fig. 1A). The Martot Pond is located less than 1 km from the river outlet, has an area of ~ 7
89 ha, and is affected by the waters of the Seine estuary during tidal flows. Before October 2017,
90 this tidal impact was limited to periods with high tidal coefficients (e.g. > 70) as the Martot
91 Dam located downstream of the pond, removed since October 2017, prevented tidal flows.
92 The sediment cores were collected in January 2015 (MAR15-01) and February 2016
93 (MAR16-02) using a UWITEC® gravity corer and 90-mm-diameter PVC pipes, and the
94 water-sediment interface was preserved during coring (Fig. 1B). The characteristics of the
95 sediment cores are shown in Table 1.

96



97

98 **Fig. 1.** A. Land use in the Eure River watershed; and B. Sediment core locations in the Martot Pond.

99

100 **Table 1.** Sediment cores collected in the Martot Pond (WGS 84).

Core ID	IGSN	Longitude (X)	Latitude (Y)	Core Length (cm)
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

101

102 2.2. Grain size, total organic carbon, and Rock-Eval 6 analysis

103

104 Grain size distribution was measured using laser diffraction (LS 13320 Particle Size
105 Analyser Beckman Coulter™) in the 0.04–2000 μm range, in the MAR15-01 core at a 1-cm
106 resolution.

107 Total organic content (TOC, %) was measured in the MAR15-01 core at 1-cm interval,
108 using Rock-Eval 6 (RE6) pyrolysis ("Turbo" model RE6 pyrolyzer; Institut des Sciences de la
109 Terre d'Orléans (ISTO), University of Orléans). TOC is composed of the pyrolysable organic
110 carbon content ($PC = ((S1+S2) \times 0.083) + (S3 \times 12/440) + (S3CO \times 12/280)$, %), and residual
111 organic carbon content ($RC = (S4CO \times 12/280) + (S4CO_2 \times 12/440)$, %), which corresponds to
112 refractory organic carbon (C_{org}) (Lafargue et al., 1998): S1 (free hydrocarbons (HC), in mg
113 HC g⁻¹ sample); S2 (HC released during the pyrolysis step, in mg HC g⁻¹ sample); S3 (mg
114 CO₂ g⁻¹ sample), and S3CO (mg CO g⁻¹ sample), both originating from functional groups
115 bearing oxygen releasing respectively CO₂ and CO during the pyrolysis step (Sanei et al.,
116 2005; Duan and Ran, 2015); S4CO (CO released during the oxidation step, in mg CO g⁻¹
117 sample), and S4CO₂ (CO₂ released during the oxidation step, mg CO₂ g⁻¹ sample). The
118 combination of TOC with these RE6 parameters allowed to calculate some parameters: the
119 hydrogen index ($HI = (S2 \times 100)/TOC$; mg HC g⁻¹ TOC) as an indicator of the hydrogen
120 richness of the sample, and the oxygen index ($OI = (S3 \times 100)/TOC$; mg CO₂ g⁻¹ TOC) as an
121 indicator of the degree of the OM oxidation, were determined to evaluate the quality of the
122 OM.

123

124 2.3. XRF core scanning

125

126 X-Ray fluorescence spectrometry (XRF) was used to semi-quantitatively determine major
127 and trace elements in sediment deposits (Richter et al., 2006). They were measured using an

128 Avaatech XRF core scanner (EDYTEM, University of Savoie Mont Blanc). Measurements
129 were realised every 5 mm for the MAR15-01 cores and every 2 mm for the MAR16-02 cores.

130

131 2.4. Particulate OCP extraction and analyses

132

133 Toluene (HiPerSolv Chromanorm and HPLC Grade) and acetone (AnalaR Normapur® and
134 HPLC Grade) were supplied by VWR and Fischer Scientific. Atrazine-d₅ (internal standard,
135 IS), fluoranthene-d₁₀, benzo[*a*]pyrene-d₁₂, and 7-methylbenzo[*a*]pyrene (surrogate standards,
136 SS) were provided by Sigma-Aldrich. A solution of organochlorine pesticides (EPA CLP
137 Organochlorine Pesticides Mix at 200 µg mL⁻¹ in hexane:toluene 1:1 (v:v), provided by
138 Sigma-Aldrich) was prepared in toluene (100 mg L⁻¹).

139 The analysis of particulate OCPs from the sediment core was performed using microwave-
140 assisted extraction (MAE) (MarsX, CEM Corporation, US). For this, subsampling of the
141 MAR16-02 core was performed (sampling interval = 1 cm) without the sediment in contact
142 with the PVC pipe, and approximately 2 g (in duplicate) of freeze-dried, crushed, and
143 homogenised sediment from the cut fractions of the sediment core (was spiked with 15 µL of
144 the solution containing the SS (100 mg L⁻¹). Samples were then introduced into Teflon
145 reactors with 20 mL of a 1:1 (v:v) toluene:acetone mixture for extraction at 130 °C for 30 min
146 (1,200 W). The extracts were then filtered through a 0.2-µm (Phenomenex) PTFE filter.
147 Following the addition of 60 µL of solvent keeper (octanol), evaporation was carried out
148 using a vacuum centrifugal pre-concentrator (MiVac, Genevac, UK) after which 1,440 µL of
149 toluene was added.

150 Following MAE, 10 µL of IS (100 mg L⁻¹ in toluene) was added to 990 µL of the extracted
151 solutions, and 1 µL was injected (splitless mode, 285 °C) into the gas chromatograph (7890B,
152 Agilent, US) coupled to a mass spectrometer (MS; 7000C). Separation was performed in a

153 capillary column (HP-5MS, Agilent, size = 60 m × 0.25 mm; film thickness = 0.25 μm) with a
154 helium flow rate of 1.4 mL min⁻¹. The oven temperature was programmed at 60 °C (1.3 min)
155 rising to 190 °C (40 °C min⁻¹), 240 °C (4 °C min⁻¹), and 305 °C (6 °C min⁻¹) for 12 min. The
156 MS detector was operated at 70 eV and quantification was performed in selected ion
157 monitoring (SIM) mode.

158 The following OCPs were analysed: desethylatrazine and atrazine, hexachlorocyclohexane
159 (HCHs; α, β, γ, and δ), dichlorodiphenyltrichloroethane (DDTs; 4,4'-DDT, 4,4'-DDE, and
160 4,4'-DDD), chlordanes (CHLs; α and γ), heptachlors (heptachlor, heptachlor epoxide B-
161 isomer), drins (aldrin, dieldrin, endrin, endrin aldehyde, and endrin ketone), endosulfans
162 (endosulfan I α, endosulfan II β, and endosulfan sulfate), and methoxychlor. The detection
163 limits for these compounds were 0.0472; 0.0223; 0.0376; 0.0365; 0.0423; 0.057; 0.1375;
164 0.0226; 0.0258; 0.0497; 0.0237; 0.0757; 0.0274; 0.0358; 0.0343; 0.0496; 0.0486; 0.0442;
165 0.0497; 0.0293; 0.1039; and 0.1397 mg kg⁻¹, respectively. The extraction method was
166 validated using a certificate reference material (CRM; CNS391, Sigma-Aldrich). The OCPs
167 presented in this study – i.e. HCHs (α, β, γ), DDTs (4,4'-DDE, and 4,4'-DDD), heptachlor
168 epoxide B-isomer, and drins (aldrin, dieldrin) – are the compounds for which the analysis of
169 the CRM are included in the prediction intervals for each compounds.

170

171 2.5. Core dating

172

173 Activities of radioelements with short periods were analysed to date recent sediment
174 deposits within sediment cores and estimate a sedimentation rate. The sedimentation rate was
175 determined from the activity of ²¹⁰Pb in excess (²¹⁰Pb_{ex}), by subtracting ²²⁶Ra from the
176 ²¹⁰Pb_{total} (Goldberg, 1963). Artificial radioelements as ¹³⁷Cs and ²⁴¹Am were used to confirm
177 the age model established from the ²¹⁰Pb_{ex} results. Peaks were observed in 1963 and in 1986

178 corresponding to the maximum fallout from atmospheric nuclear weapon testing, and the
179 Chernobyl nuclear power plant accident respectively (Robbins and Edgington, 1975; Appleby
180 et al., 1991). The activities of radioelements were determined using gamma spectrometry with
181 a germanium spectrometer in ultra-low background noise settings at the Laboratoire
182 Souterrain de Modane. The age model was computed with serac R package
183 (<https://github.com/rosalieb/serac>; Bruel and Sabatier, (2020)). The MAR15-01 core was
184 sampled at intervals of 2, 4, and 6 cm from 0 to 80 cm.

185

186 **3. Results**

187

188 3.1. Chronological framework

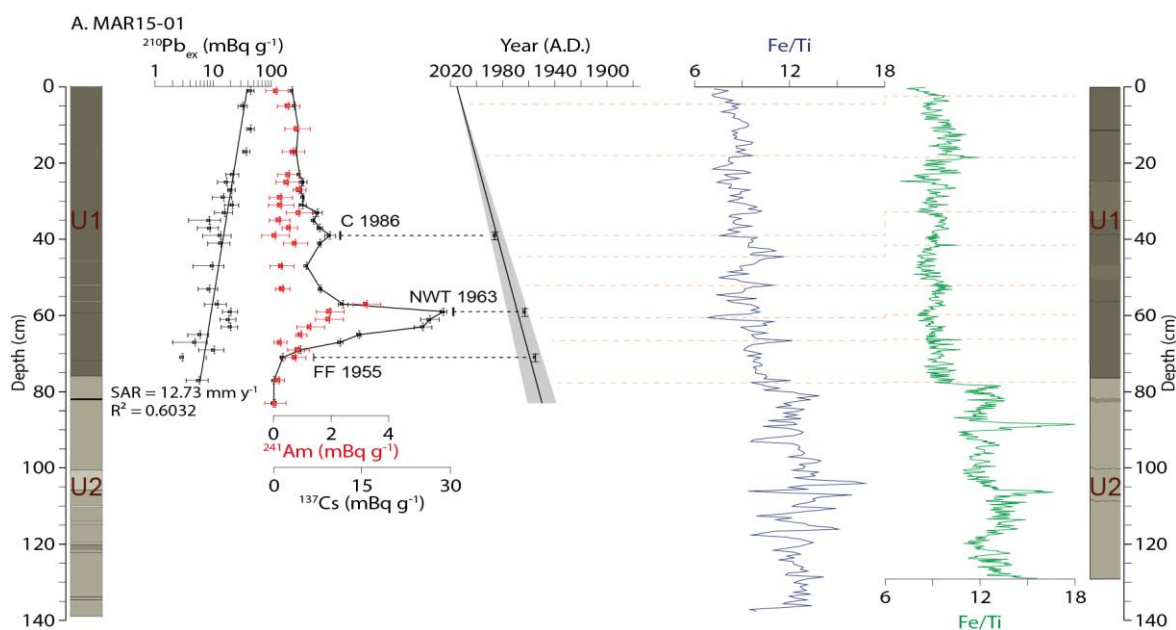
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190 Measurement of short-lived radionuclides in sediment cores is required to estimate a
191 sediment accumulation rate and build an age model (Appleby and Oldfield, 1978).
192 Concerning the MAR15-01 core, the activity of $^{210}\text{Pb}_{\text{ex}}$ has decreased almost constantly with
193 depth in the sedimentary unit 1 (U1) (Fig. 2A), and the use of the Constant Flux, Constant
194 Sedimentation Rate (CFCS) model (Goldberg, 1963; Krishnaswamy et al., 1971) indicated a
195 sediment accumulation rate of $12.73 \pm 2.20 \text{ mm y}^{-1}$. ^{137}Cs activity has been identified for the
196 first time at 71 cm depth, corresponding to 1955 (Pennington et al., 1973), and showed a peak
197 at 60 cm depth which, associated with the peak of ^{241}Am activity at 58 cm depth, corresponds
198 to the maximum fallout from atmospheric nuclear weapon testing in 1963 (Robbins and
199 Edgington, 1975; Appleby et al., 1991). At 40 cm depth, another peak of ^{137}Cs activity is
200 recorded and is linked to the Chernobyl accident in 1986 (Fig. 2A). The mean sediment
201 accumulation rate and the artificial radionuclides trends were consistent with each other and
202 provided a robust depth-associated age relationship within the sediment deposit. According to

203 previous works carried out on these sediment deposits, U1 was i. the result of constant inputs
 204 from the Eure River watershed since the 1940s (and called Eure Unit hereinafter) and ii. not
 205 disturb by changes in hydrological conditions (e.g. floods) and erosion processes through
 206 time, while U2 came from inputs of the Seine River but could not be dated (Gardes et al.,
 207 2020a), and will not be discussed hereinafter.

208 This age model was applied to the MAR16-02 core used for OCPs analyses. The plot of the
 209 Fe/Ti ratio from both cores displayed several concordances (Fig. 2) which confirmed the
 210 correlation between these two cores and the mean sediment accumulation rate of 11.3 mm y^{-1}
 211 previously established with other ratios (Gardes et al., 2020b).

212



213

214 **Fig. 2.** Chronological correlation established from A. $^{210}\text{Pb}_{\text{ex}}$ activity (SAR: sediment accumulation rate), ^{137}Cs and ^{241}Am
 215 activities (FF 1955: first identification of ^{137}Cs in 1955; NWT 1963: maximum fallout from atmospheric nuclear weapon
 216 testing in 1963; C1986: Chernobyl accident in 1986), age model built, and Fe/Ca from the MAR15-01 core; and B. Fe/Ca
 217 from the MAR16-02 core.

218

219 3.2. Chronology of organochlorines pesticides releases

220

221 HCHs (i.e. the total concentrations of α -, β -, and γ -HCH) ranged from 0.09 mg kg^{-1} to 1.19
 222 mg kg^{-1} (mean value: $0.38 \pm 0.15 \text{ mg kg}^{-1}$). α -HCH was the less represented isomer (range:

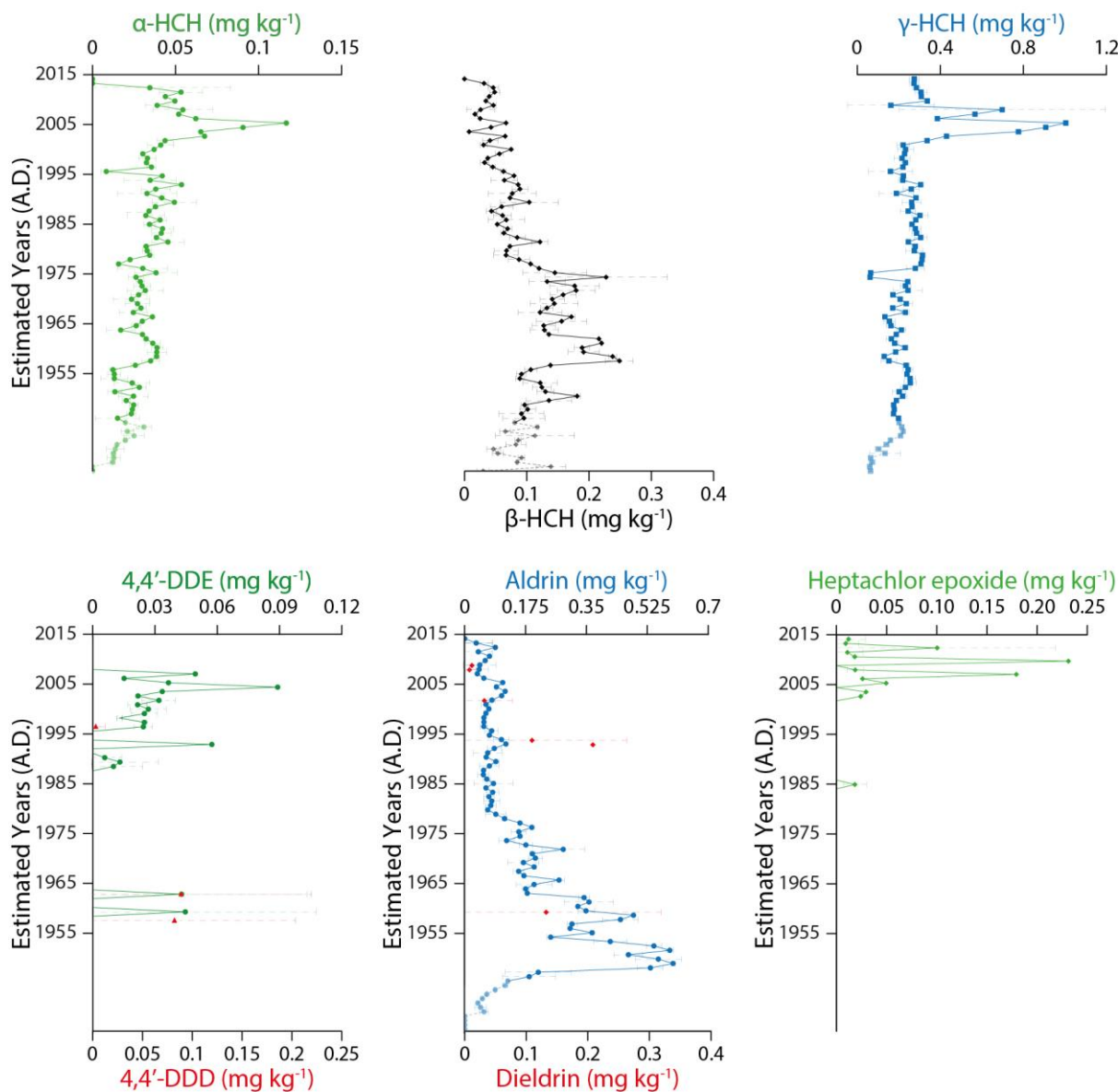
223 <LOD–0.12 mg kg⁻¹; mean value = 0.03 ± 0.01 mg kg⁻¹), while γ -HCH was the most
224 represented isomer (range: 0.06–1.00 mg kg⁻¹; mean value = 0.25 ± 0.02 mg kg⁻¹). They both
225 showed a small increase towards the surface of the sediment deposits with a significant peak
226 around 2005 (Fig. 3). β -HCH was recorded (range: <LOD–0.25 mg kg⁻¹; mean value = 0.10 ±
227 0.01 mg kg⁻¹) at significant concentrations during the period 1955–1975, and showed a
228 downward trend in the recent sediment deposits (Fig. 3). The concentrations measured are
229 higher than the maximum recorded between 1985–1995 in sediment cores from the Rhône
230 River, France (Liber et al., 2019), but comparable with those recorded in 1950s in sediment
231 cores from salt marshes of the Mersey estuary, UK except for γ -HCH (Fox et al., 2001), or in
232 sediment cores from floodplains of the Elbe River, Germany and dating from ~ 1964 (Götz et
233 al., 2007).

234 In the MAR16-02 core, DDT could not be detected but its stable metabolite 4,4'-DDE was
235 only seen in the early 1960s (~ 0.04 mg kg⁻¹), and during the period 1990–2007 (<LOD–0.09
236 mg kg⁻¹). 4,4'-DDD was also detected in only two fractions in the early 1960s (~ 0.08 mg kg⁻¹)
237 ¹), and in ~ 1996 (0.003 mg kg⁻¹) (Fig. 3). These concentrations are higher than the maximum
238 measured in 1964 in a sediment core collected in Lake Brêt, Switzerland (Thevenon et al.,
239 2013), but are in the same order of magnitude or lower than those obtained in 1985–1995 in
240 sediment cores from the Rhône River, France (Liber et al., 2019), in ~ 1964 in sediment cores
241 from the Elbe River, Germany (Götz et al., 2007), in the mid-1960s in sediment cores from
242 salt marshes of the Mersey estuary, UK (Fox et al., 2001).

243 Aldrin (<LOD–0.60 mg kg⁻¹, mean value = 0.07 ± 0.01 mg kg⁻¹) was recorded at significant
244 concentrations during the period 1950s–1970s (Fig. 3). Dieldrin was only detected in the late
245 1950s (dieldrin = 0.13 ± 0.19 mg kg⁻¹), during the period 1992–1994 (dieldrin = 0.21 and 0.11
246 ± 0.15 mg kg⁻¹), in the early and late 2000s (dieldrin = 0.03 ± 0.05; 0.01 ± 0.01 and 0.01 ±
247 0.02 mg kg⁻¹). Heptachlor could not be detected but its stable metabolite heptachlor epoxide

248 ($<LOD=0.23 \text{ mg kg}^{-1}$, mean value = $0.008 \pm 0.002 \text{ mg kg}^{-1}$) was seen in ~ 1985 ; but mainly
249 since the early 2000s (Fig. 3).

250



251

252 **Fig. 3.** α -HCH; β -HCH; γ -HCH; 4,4'-DDE (green circles); 4,4'-DDD (red triangles); aldrin (blue circles); dieldrin (red
253 diamonds); heptachlor epoxide (isomer B) in the MAR16-02 core (measurement in the upper part of the Seine Unit are
254 represented by dotted lines and transparent figures).

255

256 3.3. Relationships between organochlorines pesticides releases and sediment characteristics

257

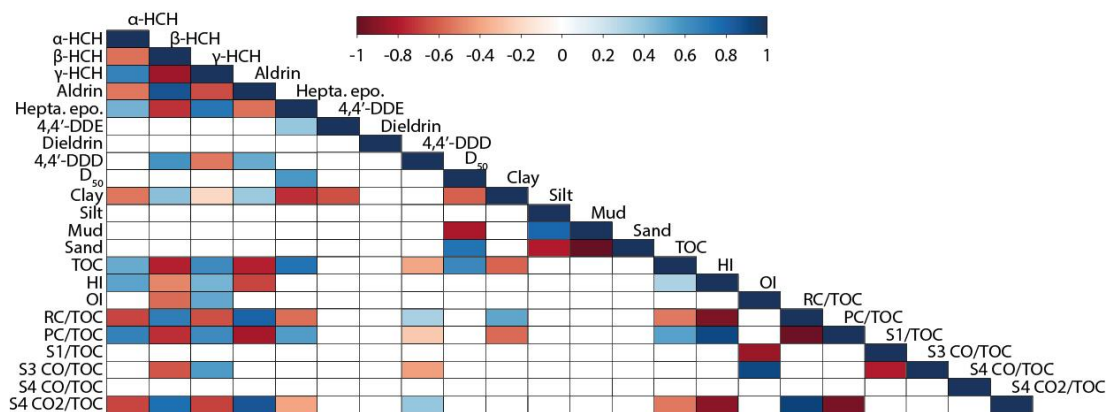
258 The lack of significant correlation between the temporal trends of OCPs and grain size
259 parameters (D_{50} , clay, silt, and sand fractions; Fig. 4) suggests that the grain size distribution
260 may not control the parent OCPs distribution in the sediment deposits. Only negative
261 correlations between the clay fraction and some OCP metabolites such as 4,4'-DDE ($R = -$
262 0.62), and heptachlor epoxide ($R = -0.74$) were observed, and also a positive correlation
263 between 4,4'-DDE and D_{50} ($R = 0.40$; $p < 0.005$). The affinity of OCPs to fine particles is
264 complex, and literature showed that this organic compounds were preferentially adsorbed on
265 fine fractions (Warren et al., 2003; Opel et al., 2011; Oliveira et al., 2016). Nevertheless, grain
266 size distribution did not always control the OCPs distribution in sediment deposits as
267 evidenced by previous studies (Salvadó et al., 2013; Qu et al., 2018). In the present case, this
268 could be explained by the composition of the sediment deposit – i.e. mainly composed of the
269 silt fraction ($72 \pm 9\%$) – and the grain size distribution which did not show any significant
270 variation, and was centred around a low median ($D_{50} = 33.9 \pm 7.8 \mu\text{m}$) (Fig. 5). Nevertheless,
271 the temporal trends of parent OCPs (and some metabolites) could be controlled by TOC
272 content as shown by the significant positive correlations with α -HCH ($R = 0.51$), γ -HCH ($R =$
273 0.63), heptachlor epoxide ($R = 0.74$), while β -HCH and Aldrin were negatively correlated
274 with TOC ($R = -0.77$ for both of them) (Fig. 4). Thus, the temporal trends of OCPs may be
275 impacted by sediment characteristics. In some studies, the clay content seemed to be the main
276 parameter controlling the concentration of OCPs in sediment cores (Wang et al., 2013), but
277 other studies presented OM as a key parameter (Opel et al., 2011; Li et al., 2015), especially if
278 the TOC content is high – e.g. if it exceeds 0.2% – in the sediment deposits (Oliveira et al.,
279 2016). In the Martot Pond, the TOC content ($3.88 \pm 1.49\%$) which slightly increased towards
280 the surface, and reached a maximum in the 2000s ($\text{TOC} = 8.26 \pm 0.19\%$) (Fig. 5), impacted
281 the temporal trends of OCPs.

282 α -, γ -HCH, and heptachlor epoxide showed a positive relationship with the PC/TOC ratio (R
283 = 0.67, R = 0.63, R = 0.55, respectively), demonstrating that their distribution is linked to the
284 proportion of labile C_{org} (Fig. 4). OCPs did not exhibit any affinity with the S1 fraction
285 representing the most labile and volatile fraction of PC and may originate from algal-derived
286 OM (Sanei et al., 2005; Sanei and Goodarzi, 2006; Duan and Ran, 2015). α -HCH, showed
287 positive correlation with HI (Fig. 4) which was almost constant in the Eure Unit (279 ± 23 mg
288 $HC\ g^{-1}\ TOC$) (Fig. 5). Thus, α -HCH presented an affinity for the S2 fraction (representing HI)
289 and its temporal trend could be controlled by algal production as the S2 fraction could contain
290 hydrogen-rich aliphatic biomacromolecules mainly derived from the cell walls of algal-
291 derived OM (Carrie et al., 2012; Duan and Ran, 2015). γ -HCH also showed positive
292 correlation with HI but also with OI, and the S3CO/TOC ratio (Fig. 4) which both slightly
293 increased towards the top of the Eure Unit ($OI = 150 \pm 17$ mg $O_2\ g^{-1}\ TOC$; $S3CO/TOC = 0.43$
294 ± 0.03 mg $CO\ g^{-1}\ TOC$) (Fig. 5). As the S3 fraction (representing OI) is mainly composed by
295 carbohydrates, lignins, and plant matters (as S3CO) (Carrie et al., 2012), γ -HCH showed
296 affinities for both labile algal-derived OM and labile terrestrial OM.

297 Conversely, β -HCH and aldrin showed a strong affinity for the RC/TOC ($R = 0.70$ and $R =$
298 0.80 , respectively) representing the proportion of refractory C_{org} (Fig. 4). The recorded
299 RC/TOC ratio was constant (0.70 ± 0.02) and greater than the PC/TOC ratio, showing that the
300 TOC was mainly composed by refractory C_{org} (Fig. 5). Thus, the temporal trends of β -HCH
301 and aldrin are related to the inputs of refractory C_{org} which is the most stable fraction of OM
302 (Sanei et al., 2005; Hetényi and Nyilas, 2014). As the proportion of labile C_{org} , the proportion
303 of refractory C_{org} remained constant along the Eure Unit. It indicated that the TOC content
304 increase in the recent sediment deposits did not originate from a change in the source of OM
305 (Fig. 5), which was only weakly altered along U1 and had both an aquatic and terrestrial
306 origin according to the HI/OI ratio indicator (Gardes et al., 2020a). Moreover, β -HCH and

307 aldrin were related to the S4CO₂/TOC ratio (R = 0.75 and R = 0.85, respectively) which was
 308 almost constant (23.8 ± 0.8 mg CO₂ g⁻¹ TOC) as S4CO/TOC (1.15 ± 0.20 mg CO g⁻¹ TOC) in
 309 the Eure Unit (Fig. 5).

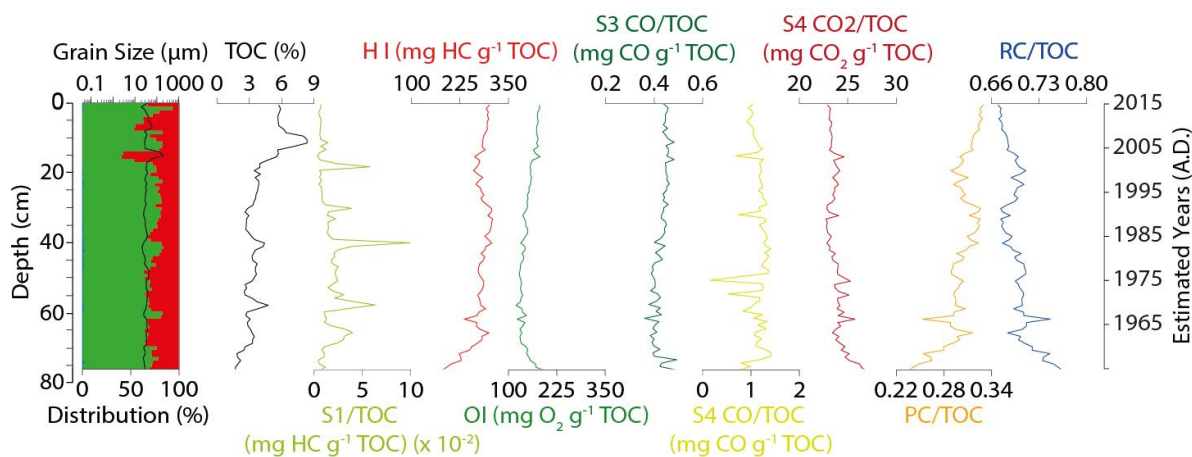
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311

312 **Fig. 4.** Correlation matrix for OCP concentrations, grain size parameters, and RE 6 parameters (Spearman's rank correlation,
 313 $p < 0.001$ for all circles represented). As OCP concentrations have been determined on the MAR16-02 core and sediment
 314 characteristics have been determined on MAR15-01 core, the measurements were averaged by half-decades to investigate the
 315 correlation between them.

316



317

318 **Fig. 5.** Grain size distribution (blue: clay; green: silt; red: sand) and D₅₀ (solid line); TOC; S1/TOC; HI; OI; S3CO/TOC;
 319 S4CO/TOC; S4CO₂/TOC; PC/TOC; RC/TOC in the Eure Unit of the MAR15-01 core.

320

321 4. Discussion

322

323 4.1. Historical applications of aldrin and lindane

324

325 Aldrin and dieldrin are synthetic OCPs used to control soil-dwelling insects (Hendy and
326 Peake, 1996), and dieldrin is also the main persistent degradation product of aldrin. Their
327 presence in the aquatic system is due to surface runoff from treated land surfaces, or from
328 surfaces they were deposited after volatilization and aerial transport (Sakan et al., 2017).
329 Although aldrin is poorly soluble in water, it is rarely detected in soils or sediments because
330 of its rapid degradation (by oxidation) into dieldrin (Hendy and Peake, 1996; Qu et al., 2018).
331 Dieldrin tends to bond to SPM and to accumulate in sediments because of its hydrophobicity
332 and its affinity for organic materials (Sakan et al., 2017). Thus, the prevalence of aldrin
333 combined with the low detection of dieldrin in the lower reaches of the Eure River watershed
334 could indicate its rapid adsorption onto fine fraction with refractory C_{org} in soils after its
335 application, its transfer through erosion of agricultural areas, then sedimentation and storage
336 under anaerobic conditions, limiting its degradation (Hendy and Peake, 1996; Qu et al., 2018).
337 Hence, the temporal trend of aldrin could be explained by the widespread use of this OCP
338 during the 1950s–1960s, followed by a decline in applications since 1960s because of its
339 toxicity and persistence in the environment (INERIS, 2011). The temporal trend of aldrin
340 could indicate that the decline in applications was gradual until the 1980s. Moreover, the
341 recorded concentrations of aldrin are stable since the 1980s, i.e. approximatively a decade
342 before the ban of use declared in France in 1992 (Decree 92-1074, 1992). Post-ban releases
343 are also recorded in recent sediment deposits at low and stable contents probably due to
344 erosion of agricultural soils and/or remobilization of sediments-associated contaminants
345 trapped in the river (Fig. 6).

346

347 4.2. Historical and potential post-ban applications of lindane

348

349 Lindane is an organochlorine insecticide (Walker et al., 1999) used for a wide range of crops
350 (e.g. corn, beet, cereals, colza, flax) and also vegetables, wood preservative, or seed treatment
351 (Villanneau et al., 2009; Orton et al., 2013). France has been one of the main lindane users
352 and emitters in Europe since the 1940s (Prevedouros et al., 2004). Lindane is 99% composed
353 of γ -HCH (Willett et al., 1998; Wang et al., 2013; Cai et al., 2016), but the detection of β -
354 HCH could reflect lindane applications since i. it can be derived from the slow conversion of
355 α -, and γ -HCH in soils and sediments (Buser and Mueller, 1995; Willett et al., 1998; Walker
356 et al., 1999; Zhao et al., 2010), and ii. it is the most stable isomer, less soluble in water, and
357 more resistant to microbial degradation (Walker et al., 1999; Lee et al., 2001; Götz et al.,
358 2007). As aldrin, β -HCH presented an affinity for the refractory C_{org} , and the recorded
359 concentrations were detected as early as the 1940s, when lindane was introduced to the
360 French market. The temporal trend of β -HCH revealed the widespread use of lindane during
361 the period 1955–1975, followed by a decline in its applications until the ban on the use in
362 France in 1998 (Fig. 6) (decree 92-1074, October 2nd, 1992 and the Aarhus Protocol, June
363 25th, 1998). Despite this ban on the use, lindane and its conformers are still detectable,
364 particularly in agricultural soils (e.g. north regions of France) (Villanneau et al., 2009; Orton
365 et al., 2013), and erosion of these soils could be the main factor explaining the post-ban
366 detection in sediment deposits.

367 Unlike β -HCH, α -, γ -HCH presented an affinity to labile C_{org} and the algal-derived OM.
368 Thus, the bonding between α -, and γ -HCH and OM may have occurred during aquatic
369 primary OM production under very low flow conditions, i.e. in the Martot Pond, as algal OM
370 can accumulate hydrophobic organic contaminants in the water column (Taylor et al., 1991;
371 Berrojalbiz et al., 2011; Duan and Ran, 2015). Moreover, as β -HCH comes from the
372 conversion of α - or γ -HCH, their surprising post-ban peaks during the 2000s may indicate
373 local post-ban applications of lindane and can likely reflect short transport time (i.e. short

374 distance) before sedimentation, without the conversion of these isomers. Nevertheless, in
375 order to go correct the process of algal scavenging on the temporal trends of α -, and γ -HCH,
376 they have been normalized by the S2 fractions. The normalized temporal trends showed
377 significant levels during the 1950s–1960s and low levels afterwards, which is more in
378 agreement with lindane applications (Fig. 6A). In addition, the amplitude of post-ban peaks of
379 concentrations was significantly decreased, and therefore could be mainly explained by
380 sedimentary matrix effects. This overestimation of the post-ban peaks demonstrated the
381 importance of taking account the process of algal scavenging in the investigation of historical
382 trends of organic contaminants releases (Duan and Ran, 2015), and the importance of the
383 normalization process.

384

385 4.3. Recent releases of historical OCPs

386

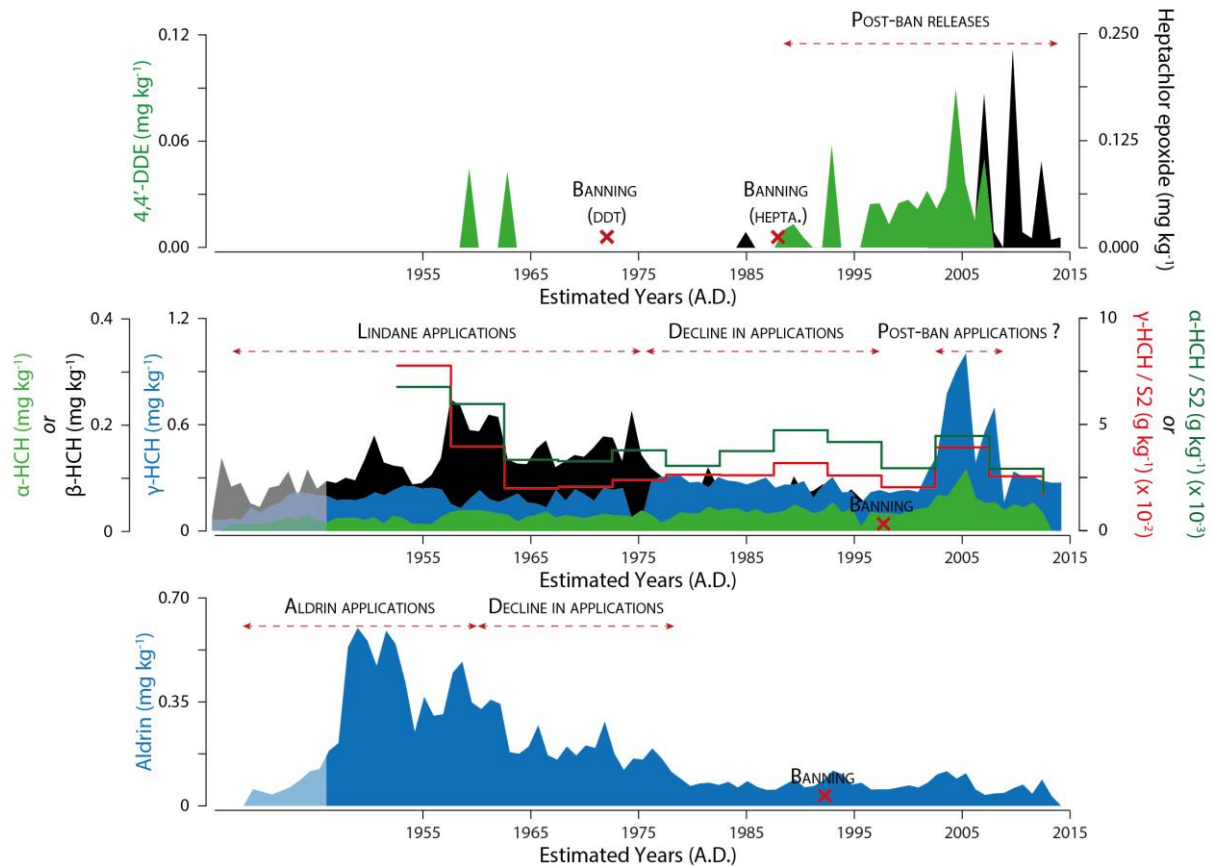
387 4,4'-DDT is the active component and represents ~80% of the composition of DDT
388 formulation (Bopp et al., 1982; Hendy and Peake, 1996), used to control pests since the mid-
389 1940s. Its use declined steadily from 1972 after it was banned in the US and France, but 4,4'-
390 DDT can persist in the environment for decades along with the primary metabolites 4,4'-DDE
391 and 4,4'-DDD. DDE results from the degradation of DDT by dehydrochlorination under
392 aerobic conditions while DDD results from the degradation of DDT by dechlorination under
393 anaerobic conditions (Hitch and Day, 1992; Hendy and Peake, 1996; Aislabie et al., 1997;
394 Gong et al., 2007; Anderson et al., 2013; Li et al., 2015). Heptachlor is an insecticide (also
395 present in technical chlordane) used for insect control, seed treatment, wood protection, and
396 agricultural uses since the mid-1940s (Berntssen et al., 2017). Its use has been banned in UE
397 since 1984 but the ban for agricultural use could be pushed back to 1988 (Convention de
398 Rotterdam, 1991). Heptachlor can persist in soils and sediments, but heptachlor epoxide, its

399 photo-oxidation transformation product, is more persistent (Barakat et al., 2013; Qu et al.,
400 2018).

401 Thus, 4,4'-DDE and heptachlor epoxide have been detected several decades after the ban of
402 use of their parent compounds (Fig. 6). While post-ban applications of lindane may have been
403 previously suggested because of the short-time interval between its ban of use and the
404 potential post-ban applications, this hypothesis is not applicable for 4,4'-DDE and heptachlor
405 epoxide because of the long-time intervals between ban of uses of DDT and heptachlor and
406 the detection of their stable transformation products. Moreover, the affinity between these
407 metabolites and the main sediment characteristics were less pronounced than for the other
408 studied OCPs (Fig. 4). As a matter of fact, these increases could be related to that of soil
409 erosion since previous studies have shown that the reemergence of historical OCPs (e.g.
410 DDTs, chlordane) in the recent years can be induced by land transformation and changes in
411 agricultural practices and land uses, (Santschi et al., 2001; Zhang et al., 2002; Sabatier et al.,
412 2014, 2021). In Zhang et al. (2002); and Sabatier et al. (2014, 2021), post-ban releases
413 (expressed as fluxes) which were higher than those recorded during the authorised
414 applications of the studied OCPs, were associated to an increase in terrigenous flux and
415 sediment accumulation rate due to a greater soil erosion. As in Santschi et al. (2001), post-ban
416 releases in the Eure River watershed were also higher than those recorded during the
417 authorised applications, but might be not related to an increase in soil erosion as the sediment
418 accumulation rate is constant in the accumulation area (Fig. 2). Thus, the detection of 4,4'-
419 DDE since the early 1990s and of heptachlor epoxide since the 2000s, while they were almost
420 undetected when their parent compounds were used, could be the result of recent inputs from
421 erosion of deeper and older soils where parent OCPs were still present. The emergence of
422 deep soils to the surface could explain the prevalence of 4,4'-DDE over 4,4'-DDD, DDE
423 being the DDT transformation product under aerobic conditions (Hendy and Peake, 1996; Cai

424 et al., 2016), and could explain the transformation of heptachlor into heptachlor epoxide under
 425 sun irradiation (Fig. 6).

426



427

428 **Fig. 6.** Chronology of aldrin; α -HCH, β -HCH, γ -HCH, α -HCH / S2; and, γ -HCH / S2; and 4,4'-DDE and heptachlor epoxide
 429 historical releases recorded in the Martot Pond.

430

431 5. Conclusions

432

433 The chronology of OCP releases in the Eure River have been reconstructed from dated
 434 sediment cores collected in homogeneous riverine sediment deposits, and this study
 435 demonstrated the necessity to examine the relationships between OCPs and sediment
 436 characteristics to discriminate the influence of former applications, soil erosion, and also
 437 potential post-ban applications in these temporal trends.

438 The affinity of aldrin and β -HCH for the refractory C_{org} indicated that these OCPs have been
439 bound to OM in agricultural soils after their deposit, and their inputs into the river system was
440 a result of the erosion of these soils. Thus, the temporal trends of aldrin and lindane have been
441 reconstructed and showed former widespread applications during the 1950s–1960s and
442 1955s–1975s respectively, followed by declines in applications before their ban of uses
443 because of the highlighting of their toxicity. Thereafter, low and stable contents in recent
444 sediment deposits were measured, due to the continuous erosion of agricultural soils and/or
445 remobilization of contaminants associated to trapped sediments in the river.

446 α - and γ -HCHs have the same origin as β -HCH, i.e. lindane applications; but α - and γ -
447 isomers, unlike β - isomer, were preferentially bound to labile C_{org} . Their sorption process
448 occurred in the river system, during aquatic primary OM production under very low flow
449 conditions. Moreover, a potential local post-ban application might have been recorded in the
450 Martot Pond, but its amplitude was overestimated. Indeed, it appeared that the process of algal
451 scavenging must not be neglected when lindane chronology is studied.

452 The detection in recent sediment deposits of 4,4'-DDE and heptachlor epoxide, i.e. several
453 decades after the ban of use of their parent compounds, showed the influence of soil erosion
454 in the chronology of OCP releases. Indeed, remobilization and erosion of old deep soils led to
455 the reemergence of stable transformation products from historical OCPs, undetected during
456 their period of application.

457 This study highlighted that i. the chronology of OCP releases recorded in sediment deposits
458 is not always an indicator of active applications and of direct releases in the environment (i.e.
459 in agricultural soils), ii. investigations of OCP temporal trends require an interest in sediment
460 characteristics, and the role of the different fractions of OM on the sorption and transport of
461 organic pollutants deserves to be further investigated.

462

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476

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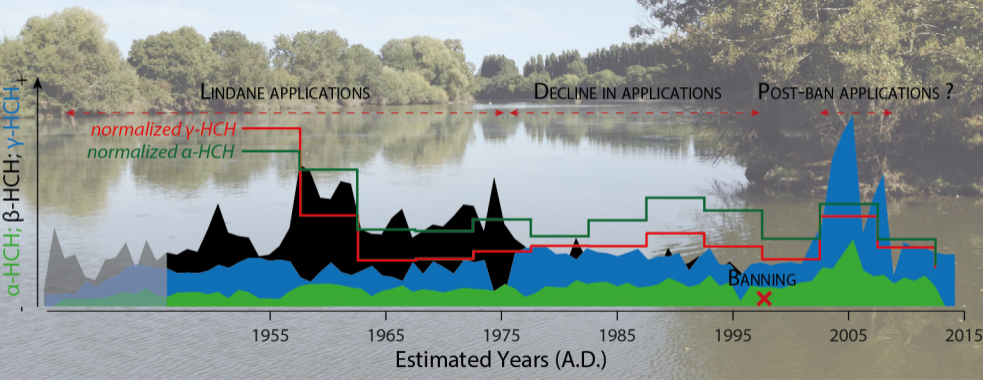
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726



α -HCH; β -HCH; γ -HCH; δ -HCH

LINDANE APPLICATIONS

DECLINE IN APPLICATIONS

POST-BAN APPLICATIONS ?

normalized γ -HCH

normalized α -HCH

BANNING

1955

1965

1975

1985

1995

2005

2015

Estimated Years (A.D.)