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Thomas Gardes[1*], Florence Portet-Koltalo[2], Maxime Debret[1], Yoann Copard[1]

[1]Normandie Univ, UNIROUEN, UNICAEN, CNRS, M2C, 76000 Rouen, France.

[2]Normandie Univ, UMR CNRS 6014 COBRA, 55 Rue Saint Germain, 27000 Evreux, France.

[*]Corresponding author: thomas.gardes2@univ-rouen.fr

Abstract

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

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

1. Introduction

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

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

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

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

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

2. Materials and Methods

2.1. Core sites in the Eure River watershed

The Eure River has a mean flow of 22.13 ± 6.69 $m^3 s^{-1}$ and is the main tributary of the Seine estuary (the estuarine part of the Seine River is delimited by the Poses Dam). The Eure River watershed (6017 km^2), located in the northern part of the "Beauce Region" is mainly composed of agricultural lands, and cropping systems are diverse including oilseed rape, fibre flax, potatoes, protein peas, cereals (soft and durum wheat, barley, and corn) and sugar beet (Fig. 1A). The Martot Pond is located less than 1 km from the river outlet, has an area of ~ 7 ha, and is affected by the waters of the Seine estuary during tidal flows. Before October 2017, this tidal impact was limited to periods with high tidal coefficients (e.g. > 70) as the Martot Dam located downstream of the pond, removed since October 2017, prevented tidal flows. The sediment cores were collected in January 2015 (MAR15-01) and February 2016 (MAR16-02) using a UWITEC® gravity corer and 90-mm-diameter PVC pipes, and the water-sediment interface was preserved during coring (Fig. 1B). The characteristics of the sediment cores are shown in Table 1.

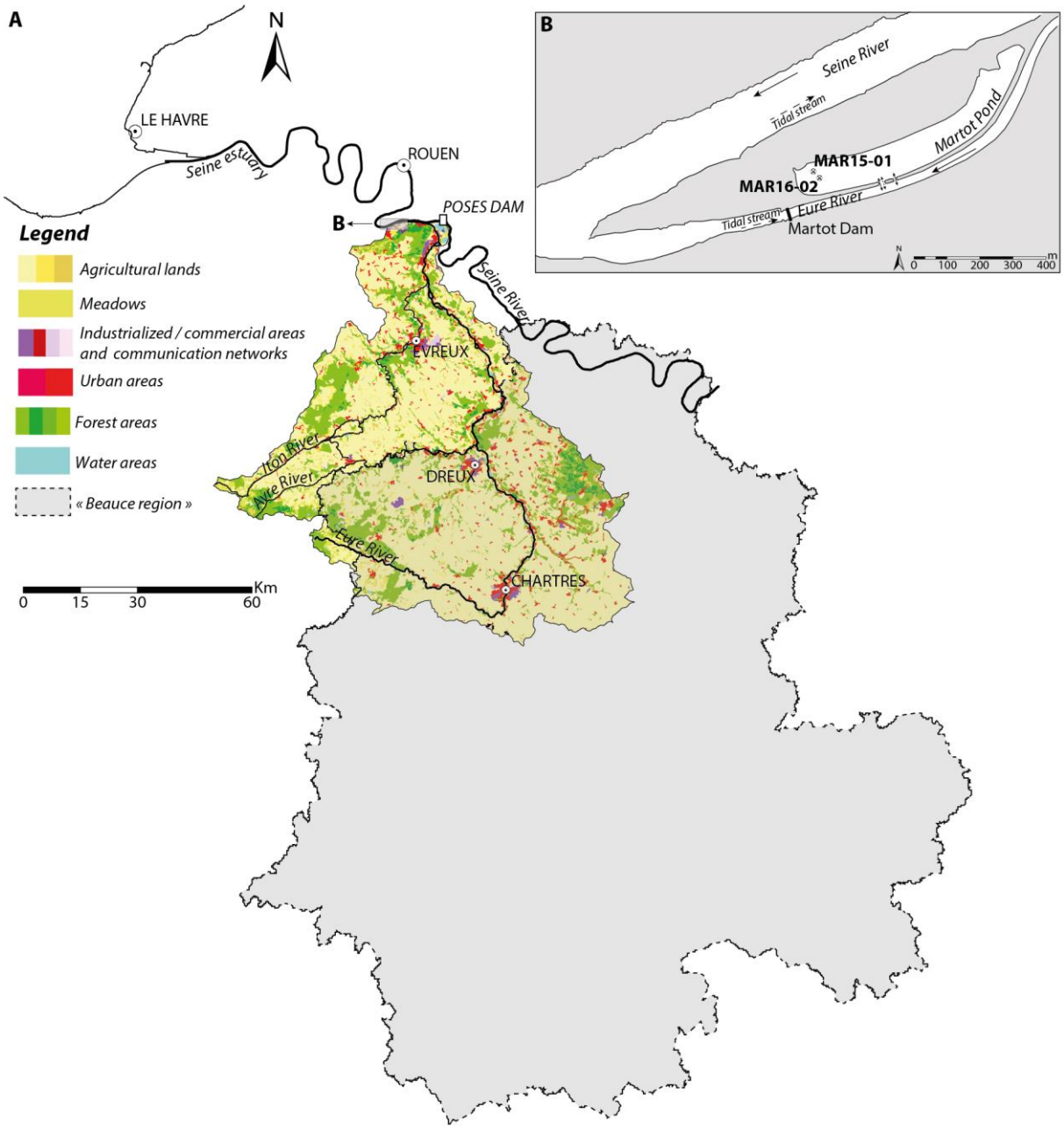

Fig. 1. A. Land use in the Eure River watershed; and B. Sediment core locations in the Martot Pond.

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

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

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

Total organic content (TOC, %) was measured in the MAR15-01 core at 1-cm interval, using Rock-Eval 6 (RE6) pyrolysis ("Turbo" model RE6 pyrolyzer; Institut des Sciences de la Terre d'Orléans (ISTO), University of Orléans). TOC is composed of the pyrolysable organic carbon content (PC = ((S1+S2)×0.083)+(S3×12/440)+(S3CO× 12/280), %), and residual organic carbon content (RC = (S4CO×12/280) + ($S4CO_2$×12/440), %), which corresponds to refractory organic carbon (C_{org}) (Lafargue et al., 1998): S1 (free hydrocarbons (HC), in mg HC g^{-1} sample); S2 (HC released during the pyrolysis step, in mg HC g^{-1} sample); S3 (mg CO_2 g^{-1} sample), and S3CO (mg CO g^{-1} sample), both originating from functional groups bearing oxygen releasing respectively CO2 and CO during the pyrolysis step (Sanei et al., 2005; Duan and Ran, 2015); S4CO (CO released during the oxidation step, in mg CO g^{-1} sample), and $S4CO_2$ (CO_2 released during the oxidation step, mg CO_2 g^{-1} sample). The combination of TOC with these RE6 parameters allowed to calculate some parameters: the hydrogen index (HI = (S2×100)/TOC; mg HC g^{-1} TOC) as an indicator of the hydrogen richness of the sample, and the oxygen index (OI = (S3×100)/TOC; mg CO_2 g^{-1} TOC) as an indicator of the degree of the OM oxidation, were determined to evaluate the quality of the OM.

2.3. XRF core scanning

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

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

2.4. Particulate OCP extraction and analyses

Toluene (HiPerSolv Chromanorm and HPLC Grade) and acetone (AnalaR Normapur® and HPLC Grade) were supplied by VWR and Fischer Scientific. Atrazine-d_5 (internal standard, IS), fluoranthene-d_{10}, benzo[*a*]pyrene-d_{12}, and 7-methylbenzo[*a*]pyrene (surrogate standards, SS) were provided by Sigma-Aldrich. A solution of organochlorine pesticides (EPA CLP Organochlorine Pesticides Mix at 200 µg mL^{-1} in hexane:toluene 1:1 (v:v), provided by Sigma-Aldrich) was prepared in toluene (100 mg L^{-1}).

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

Following MAE, 10 µL of IS (100 mg L^{-1} in toluene) was added to 990 µL of the extracted solutions, and 1 µL was injected (splitless mode, 285 °C) into the gas chromatograph (7890B, 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, hexachlorocychlohexane
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 ^{210}Pb in excess ($^{210}Pb_{ex}$), by subtracting ^{226}Ra from the
176 $^{210}Pb_{total}$ (Goldberg, 1963). Artificial radioelements as ^{137}Cs and ^{241}Am were used to confirm
177 the age model established from the $^{210}Pb_{ex}$ results. Peaks were observed in 1963 and in 1986

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

3. Results

3.1. Chronological framework

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

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

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

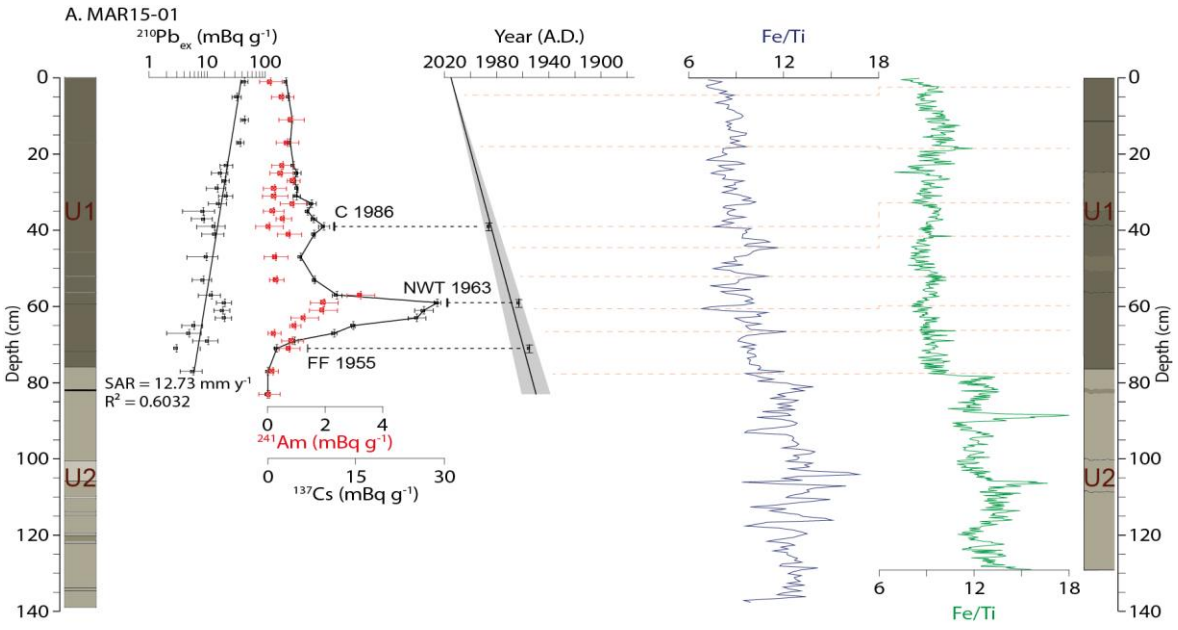

Fig. 2. Chronological correlation established from A. $^{210}Pb_{ex}$ activity (SAR: sediment accumulation rate), ^{137}Cs and ^{241}Am activities (FF 1955: first identification of ^{137}Cs in 1955; NWT 1963: maximum fallout from atmospheric nuclear weapon testing in 1963; C1986: Chernobyl accident in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

3.2. Chronology of organochlorines pesticides releases

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

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

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

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

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

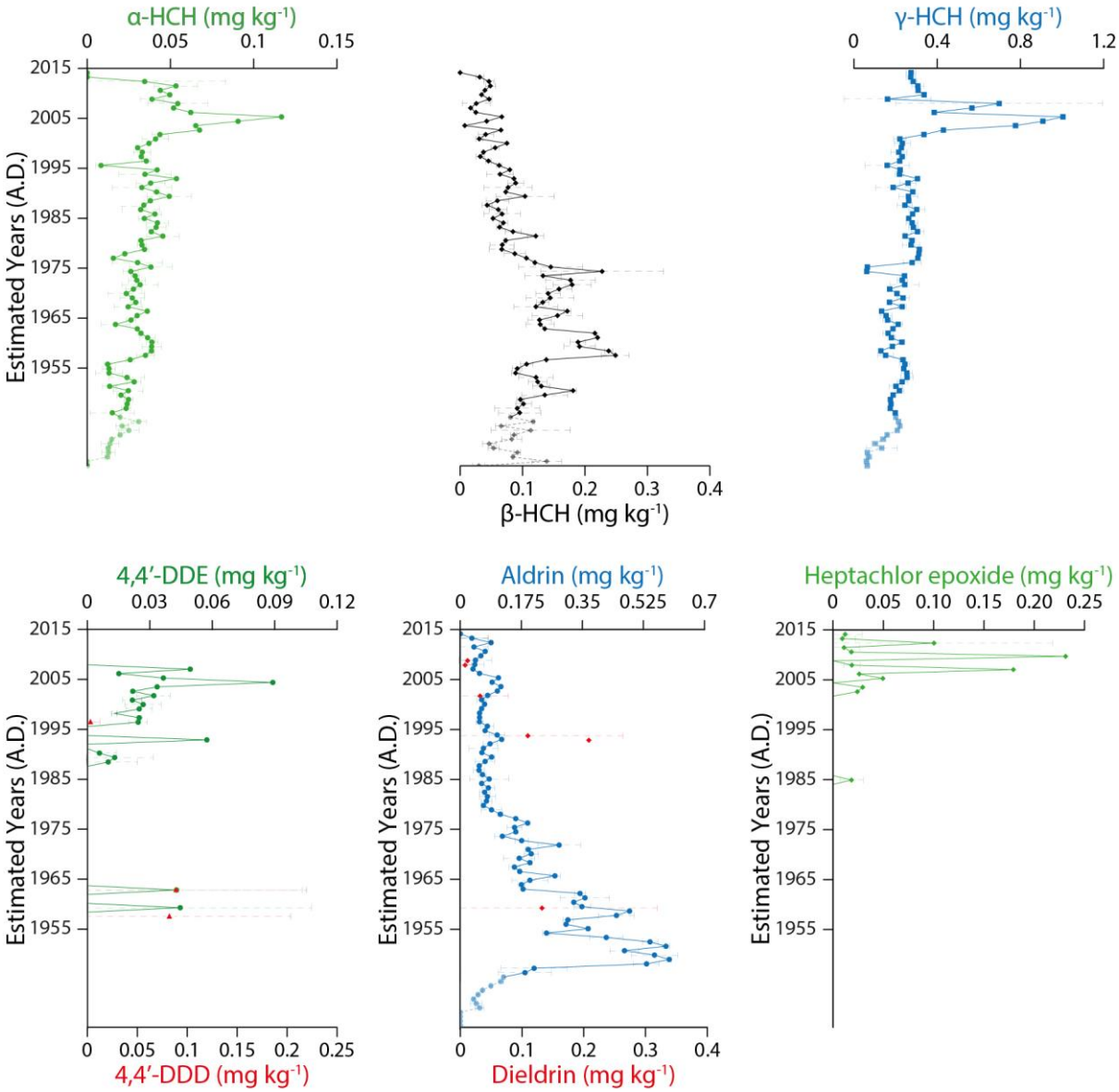

Fig. 3. α-HCH; β-HCH; γ-HCH; 4,4'-DDE (green circles); 4,4'-DDD (red triangles); aldrin (blue circles); dieldrin (red diamonds); heptachlor epoxide (isomer B) in the MAR16-02 core (measurement in the upper part of the Seine Unit are represented by dotted lines and transparent figures).

3.3. Relationships between organochlorines pesticides releases and sediment characteristics

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

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

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

aldrin were related to the $S4CO_2$/TOC ratio (R = 0.75 and R = 0.85, respectively) which was almost constant (23.8 ± 0.8 mg CO_2 g^{-1} TOC) as S4CO/TOC (1.15 ± 0.20 mg CO g^{-1} TOC) in the Eure Unit (Fig. 5).

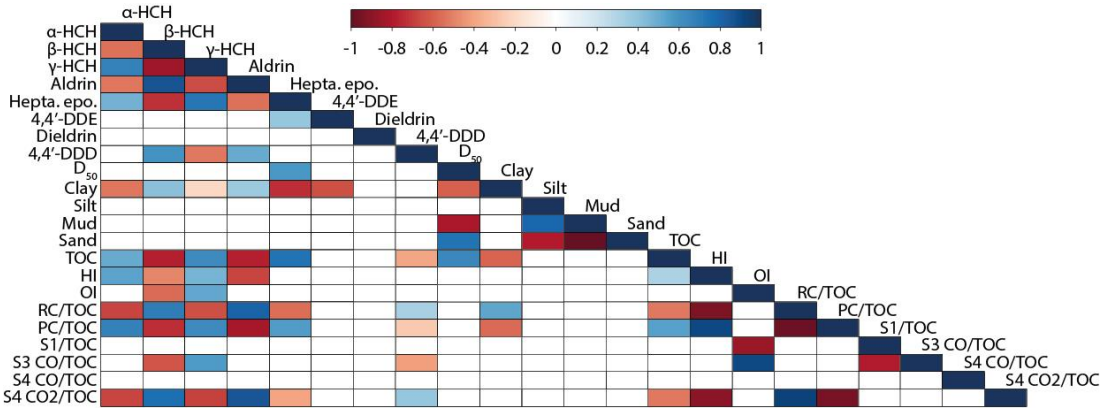

Fig. 4. Correlation matrix for OCP concentrations, grain size parameters, and RE 6 parameters (Spearman's rank correlation, $p < 0.001$ for all circles represented). As OCP concentrations have been determined on the MAR16-02 core and sediment characteristics have been determined on MAR15-01 core, the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

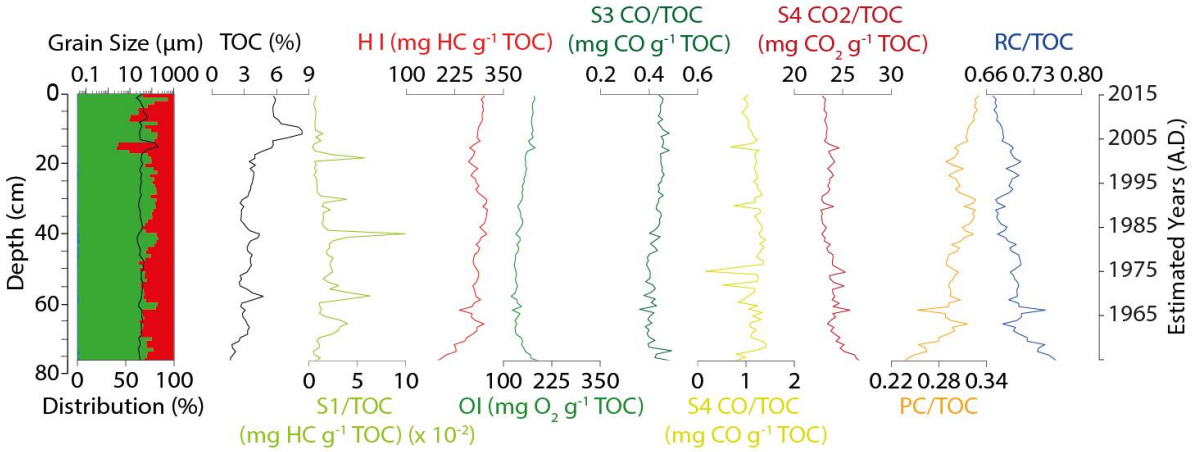

Fig. 5. Grain size distribution (blue: clay; green: silt; red: sand) and D_{50} (solid line); TOC; S1/TOC; HI; OI; S3CO/TOC; S4CO/TOC; S4CO2/TOC; PC/TOC; RC/TOC in the Eure Unit of the MAR15-01 core.

4. Discussion

4.1. Historical applications of aldrin and lindane

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

4.2. Historical and potential post-ban applications of lindane

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

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

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

4.3. Recent releases of historical OCPs

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

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

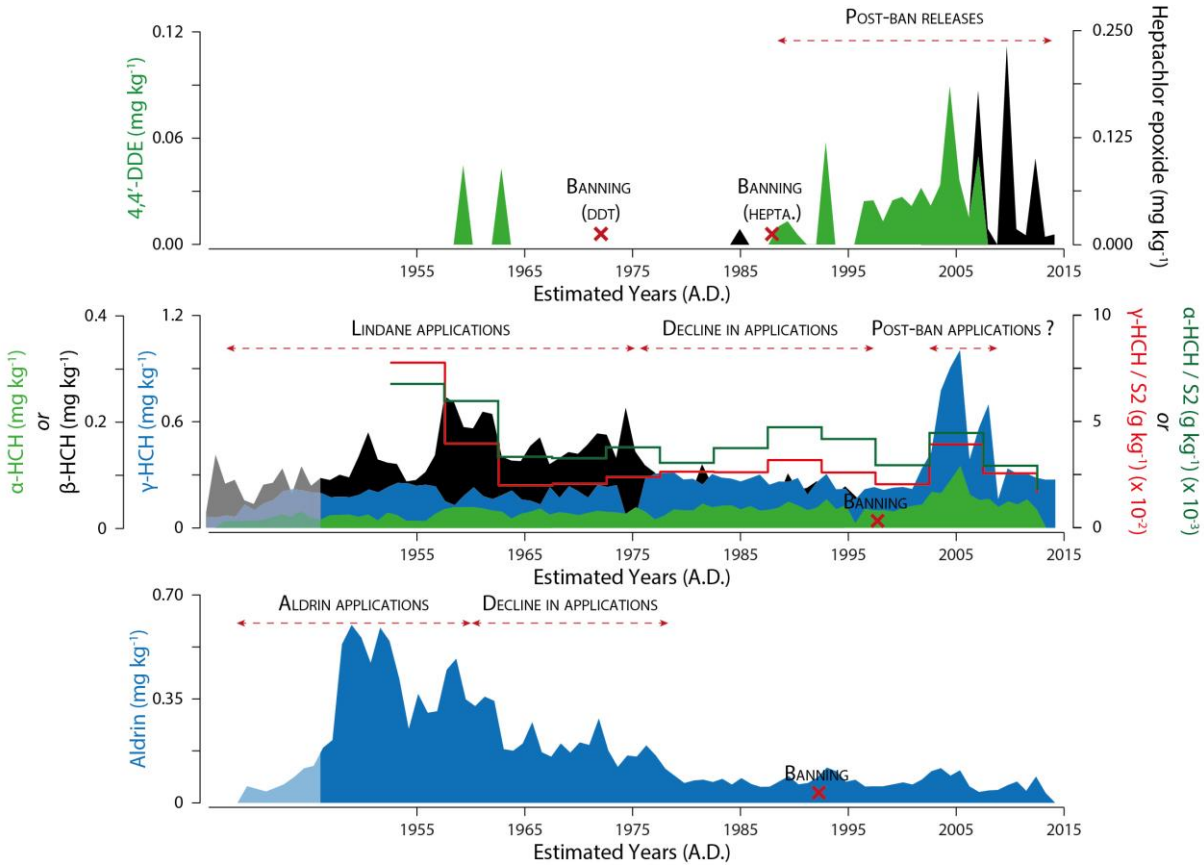

Fig. 6. Chronology of aldrin; α-HCH, β-HCH, γ-HCH, α-HCH / S2; and, γ-HCH / S2; and 4,4'-DDE and heptachlor epoxide historical releases recorded in the Martot Pond.

5. Conclusions

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

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

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

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

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

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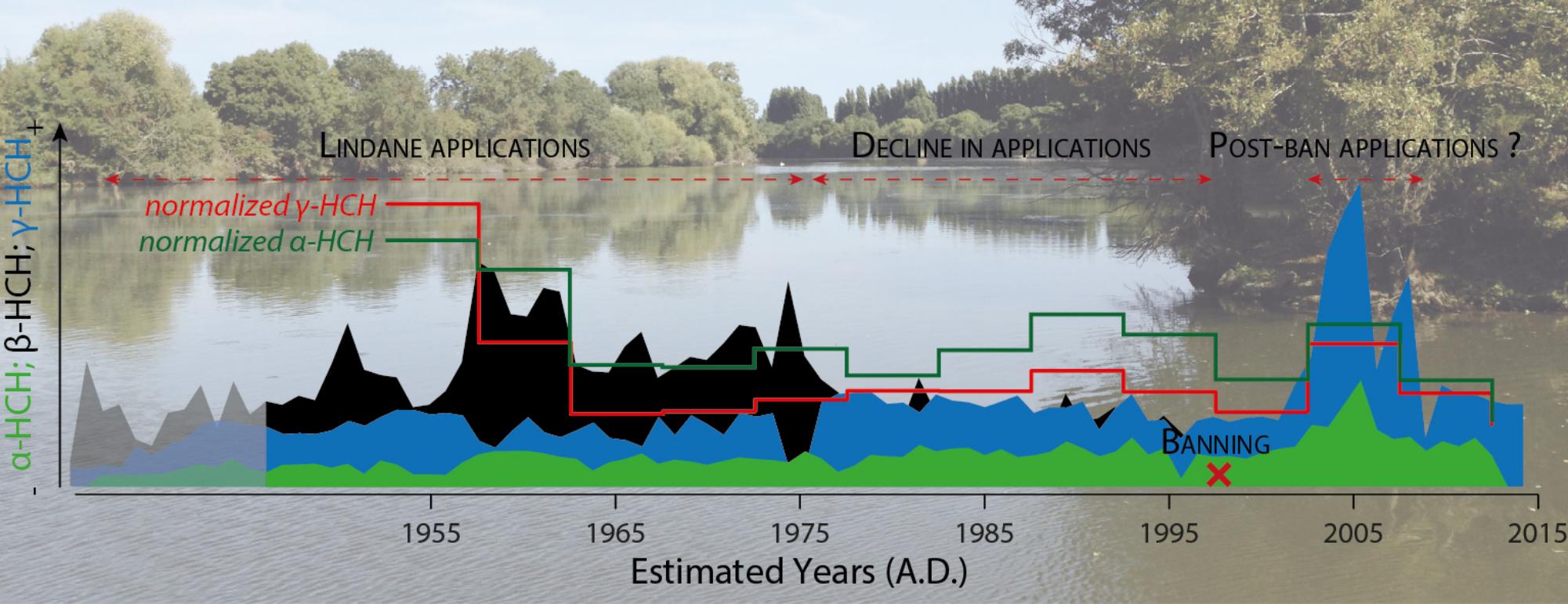
LINDANE APPLICATIONS
DECLINE IN APPLICATIONS
POST-BAN APPLICATIONS ?
normalized γ-HCH
normalized α-HCH
α-HCH; β-HCH; γ-HCH
+
-
BANNING
1955
1965
1975
1985
1995
2005
2015
Estimated Years (A.D.)