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Record of trace organic contaminants in a river sediment core: from historical wastewater management to historical use

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Abstract

Some trace organic contaminants (TrOCs) can be considered as ubiquitous contaminants since the 1950s, and the study of their historical distribution within river sediments allows us to better understand the temporal variation of the chemical quality of sediments, and make assumptions about the most insightful forcings impacting these distributions. In this study, the occurrence of 41 TrOCs of various classes (i.e. pharmaceutical products and pesticides) was studied in a sedimentary core sampled in a disused dock along the Seine River, France. This core covers a 60 year-long period between 1944 and 2003, and 23 TrOCs were detected at least once. Their concentrations mainly ranged between 1 and 10 ng g⁻¹ within the core, except for tetracycline that exhibited higher concentrations (~hundreds of ng.g⁻¹). The dating of the core, based on previous studies, enabled the characterization of the changes since 1945, potentially impacted by (i) the sewer connectivity, (ii) the upgrading of wastewater treatment technologies, (iii) historical modifications in the use of each TrOC, and (iv) the sedimentary composition. In every case the deepest occurrence of each TrOC in the core matched its market authorization date, indicating the potential of TrOC to be used as chronomarkers. This study also reveals that the recent upgrading of wastewater treatment technologies within the

26 watershed decreased the concentrations of each TrOC, despite an increase in TrOC diversity
27 in the most recent years.

28 **Keywords**

29 Sediments, Wastewater treatment, Trace Organic Contaminants, Pharmaceuticals,
30 Pesticides

31

32 **1. Introduction**

33 Since WWII, a large number of trace organic contaminants (TrOCs) have been regularly
34 launched on the market for different uses (Bernhardt et al., 2017), e.g. pharmaceutical products,
35 crop protection products, and personal care products. These contaminants are generally
36 classified as contaminants of emerging concern, meaning that their detection in environmental
37 compartments is “recent” and raises serious issues about their ecotoxicological impact
38 (Daughton, 2004; Väitalo et al., 2017).

39 Moreover, as no environmental impact evaluation was performed prior to market launch (until
40 a pesticide directive by the European Commission (1991a)), a significant and growing number
41 of TrOCs (as main products or metabolites) have been detected in numerous environmental
42 compartments, for example since the 1960s and 1970s for some pesticides (Robeck et al., 1965)
43 and pharmaceutical products (Garrison et al., 1976; Hignite and Azarnoff, 1977), and still at
44 the present time, despite strict legislations.

45 In the European Union, two political decisions had a major effect in raising awareness about
46 the quality of water bodies: firstly, the urban wastewater treatment directive in 1991 (European
47 Commission, 1991b), and then, in 2000, the water framework directive (European Commission,
48 2000). These two texts aimed at improving the quality of water environments in Europe by
49 targeting the collection and treatment of wastewater, and ensuring a good ecological status of

50 water bodies in the future, respectively. These political decisions were accompanied by
51 technical evolutions allowing the detection and quantification of numerous TrOCs in natural
52 environments (Altenburger et al., 2015; Loos et al., 2009; McCance et al., 2018). However,
53 depending on the TrOC targeted, the contamination of environmental compartments can be
54 much older than the first detection, hindering the proper understanding of the historical
55 contamination of water bodies.

56 In order to reconstruct the historical contamination of water bodies, sedimentary archives are
57 considered as particularly relevant, especially concerning PAHs or PCBs (Ayrault et al., 2020;
58 Dendievel et al., 2020; Santschi et al., 2001), which are hydrophobic and persistent organic
59 contaminants. However, recent studies have demonstrated that more hydrophilic contaminants,
60 such as pesticides (excluding organo-chlorine pesticides such as DDT) and pharmaceutical
61 products, may also be recorded in sedimentary archives (Lahti and Oikari, 2012; Lara-Martín
62 et al., 2015), showing the relevance of sedimentary archives to study the temporal record of
63 TrOC deposition associated with particulate matter.

64 Yet, once the vertical distribution of contaminants has been obtained, interpreting the patterns
65 may be challenging. Generally, most authors concur that the oldest detection of a specific
66 contaminant is concurrent with or posterior to the market launch date of the investigated
67 contaminant (Kerrigan et al., 2018; Klaminder et al., 2015), in view of their weak mobility
68 within the sedimentary column and limited degradation due to adsorption onto solids (Keil et
69 al., 1994). Another strong assumption is that the sedimentary occurrence of contaminants is
70 related to their dissolved concentration and solid/water partition coefficient (Lara-Martín et al.,
71 2015; Thiebault et al., 2017). However, unlike hydrophobic contaminants, for which the
72 sedimentary occurrences are considered to be proportional to the historical environmental
73 contamination through the organic content of sediment (Castro and Vale, 1995), for hydrophilic
74 contaminants, variations in both watercourse conditions (da Silva et al., 2011; Zhou and

75 Broodbank, 2014) or sedimentary compositions (Al-Khazrajy and Boxall, 2016; Kodešová et
76 al., 2015; Stein et al., 2008) may impact the solid/water partition non-linearly. It is therefore
77 important to assess the vertical variation of the sediment composition (granulometry, organic
78 content) in order to avoid misunderstanding the observed pattern. Moreover, it is also
79 mandatory to develop an appropriate age model to date such sedimentary archives in order to
80 assess the temporal continuity of sediment deposition, and the potential presence of major
81 disturbances or hiatuses along the core (Fuller et al., 1999; Vrel et al., 2013).

82 The vertical variation in the concentration of rather hydrophilic contaminants therefore depends
83 on several factors, as already mentioned, (i) the adsorption potential of the sediment; (ii) the
84 amount of contaminant used in the watershed; and finally, (iii) the impact of potential filters
85 between the place of use and the watercourse. On the latter point, it is very important to have a
86 proper evaluation of the main sources of the contaminants investigated. For example, it has
87 been known for some time that most pharmaceutical products (except livestock production
88 sources) are discharged into the environment through wastewater treatment plants (WWTP), in
89 which their removal are incomplete (Verlicchi et al., 2012). However, both sewer networks and
90 wastewater treatment technologies have considerably evolved in the last 60 years (De Feo et
91 al., 2014; Hara et al., 2016). Pesticides discharged into the environment are more difficult to
92 trace, as even though most pesticides are used in the field for crop protection, generating a
93 diffuse source toward water bodies, a significant amount of pesticides is also rejected by point
94 sources, such as wastewater and stormwater discharge points (Blanchoud et al., 2004; Botta et
95 al., 2009; Zgheib et al., 2012).

96 Moreover, the vertical distribution of TrOCs such as pharmaceutical products and pesticides
97 within sedimentary archives is the result of multiple factors and a careful investigation into the
98 historical evolution of the watershed is needed. In this study, therefore, we investigated the
99 occurrence of 41 TrOCs in a sedimentary archive located in a highly anthropized estuary (Seine

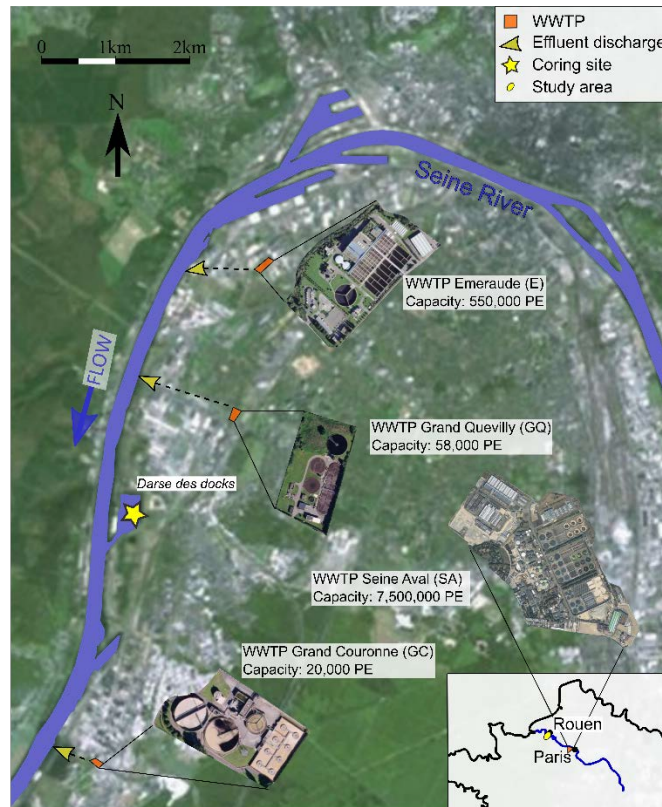
100 estuary, downstream the cities of Rouen and Paris, France). The targeted TrOCs are
101 pharmaceutical products and pesticides, both parent compounds and some major metabolites.
102 From an analysis of their vertical distribution, the aim was (i) to investigate the use of TrOCs
103 as chronomarkers; (ii) to access a long term chronology of TrOC contamination; and (iii) to
104 evaluate the respective impact of the sedimentary composition, the WWTP evolution and the
105 change in use in the watershed on TrOC sedimentary occurrences.

106 **2. Material and Methods**

107 **2.1. Site Settings**

108 The coring site is located in the upper estuary of the Seine River (Figure 1), in a disused dock
109 at Rouen called “Darse des Docks”. Historical bathymetric charts and data provided by the
110 Grand Port Maritime de Rouen (GPMR; Rouen harbor authority) allowed us to assume that the
111 site chosen for the coring had remained undisturbed since 1960 (Kaci et al., 2014; Vrel et al.,
112 2013). Sediments from the harbor basin were lying on semi-confined gravel and chalk aquifers
113 that were connected to groundwater. The coring site is located in the Rouen agglomeration
114 (110 000 inh. for the city and 660 000 inh. for the entire urban area) and is situated downstream
115 the discharge points of two major WWTPs, E and GQ, and upstream the discharge of GC
116 effluents (Figure 1). The Seine river is also impacted upstream (i.e. > 100 km) by the discharge
117 of the effluent of SA, the largest WWTP in France.

118 This site was also selected as the Seine estuary is the outlet of contamination of the Seine
119 watershed, where nearly 40% of the French population is concentrated, including the Paris
120 megacity, 30% of French industrial activity until recent decades and nearly 40% of national
121 agricultural activity. It therefore appeared that this site should be particularly relevant for the
122 analysis of the historical contamination by TrOCs of various classes.



123

124 Figure 1: Aerial photograph (www.geoportail.gouv.fr) showing the coring site “Darse des docks” (yellow star)
 125 within the urban area of Rouen. Local wastewater effluent inputs into the Seine River and their current treatment
 126 capacities and technologies are highlighted (E, GQ, GC), and the upstream SA WWTP is also indicated. PE for
 127 Population-Equivalent.

128

129 2.2. Sediment coring and sampling

130 The core sampling was performed in 2010, using a percussion corer adapted for use on a barge,
 131 allowing the collection of a 580-cm core of consolidated mud. Then, a long box-corer (gravity
 132 corer) was also used to collect the superficial unconsolidated mud, thus making it possible to
 133 retrieve a 105-cm-long core which included the soft surface mud (not analyzed in this study,
 134 but useful for the age-modeling). Subsequently, the two cores were combined together into a
 135 single profile. The loss of sediment at the interface and the compaction induced by the
 136 percussion corer were corrected by assuming that no such sampling artefacts occurred using the
 137 gravity corer, and combining water content profiles (Vrel et al., 2013). Compaction was not
 138 estimated for deeper sediments.

139 Immediately after the coring, the cores were aseptically cut in half lengthwise in a confined
140 chamber. One half of each core was used for geochemical analyses and sediment dating, while
141 the other half was subsampled into 5cm-thick sub-fractions using a sterile sub-corer and further
142 placed in storage at -80°C in less than an hour as previously described (Kaci et al., 2014).

143 **2.3. Sediment analysis and dating**

144 The particle size was determined by an enhanced laser diffraction particle size analyzer
145 (Beckman Coulter, LS230). The total organic carbon (TOC) content of sediment samples was
146 determined by elementary analysis after decarbonation of the bulk sediment with HCl (3M).
147 Fourier transform infrared (FTIR) measurements in the range 400-4000 cm⁻¹, were recorded
148 using a Bruker 55 FT-IR spectrometer equipped with an Nd:YAG laser operating at 1064 nm
149 and a Ge detector. The analyses were performed in transmission mode and each spectrum was
150 the average of 256 scans collected at 2 cm⁻¹ resolution. About 0.01 g of material was mixed
151 with 0.99 g of potassium bromide (KBr) and pelletized with a hydraulic press at 10 kPa during
152 5 minutes.

153 The analyses of artificial radionuclides (¹³⁷Cs and plutonium isotopes) coupled with
154 hydrological and bathymetric data made it possible to constrain a precise age-model, previously
155 published (Vrel et al., 2013). This age-model allows the characterization of two sedimentary
156 hiatuses along the profile, the first one between 1949 and 1960, and the second one between
157 1962 and 1965, explaining the lack of samples for these dates.

158 Hereafter, samples are labelled according to the date of the layer.

159 **2.4. Chemical reagents**

160 LC-MS grade acetonitrile (AcN) and methanol (MeOH) were purchased from VWR and ultra-
161 pure water (H₂O) was prepared with a Pure Lab Chorus water purification system (Veolia
162 Water). Formic acid (99% purity) was purchased from Sigma-Aldrich. Isotopically labeled

163 internal standards (ILIS) and reference standards were purchased from LGC Standards,
 164 assuming a purity $\geq 97\%$. TrOCs were selected following the most frequently detected organic
 165 contaminants in European river waters (Loos et al., 2013).

166 2.5. Enrichment and clean-up of sediment extracts

167 Sediments were collected on cores following a regular sampling step (5 cm). After freezing at
 168 -80°C , they were then freeze-dried during 24 h before being crushed in a mortar, and 1 ± 0.1 g
 169 was subsampled. Samples were then spiked with 100 ng of each ILIS at 4°C overnight. Spiked
 170 samples were then extracted by pressurized liquid extraction, using ASE-350 (Thermo). The
 171 extraction mixture was MeOH/H₂O (1:1 v/v) and the operating temperature and pressure were
 172 100°C and 1000 psi respectively. Extracts were then reduced to 1 mL using an EZ-2 evaporator
 173 (Biopharma Technologies), prior to refilling at 100 mL of H₂O before purification by solid-
 174 phase extraction (SPE) on Oasis-HLB columns (6 mL x 150 mg, Waters). Cartridges were
 175 conditioned with 5 mL of MeOH followed by 5 mL of ultra-pure water. Then, the cartridges
 176 were filled with the sample (100 mL) prior to flushing with 2 x 5 mL of ultra-pure water before
 177 drying for 30 minutes under vacuum. Finally, elution of TrOCs was performed with 2 x 5 mL
 178 of MeOH before drying under nitrogen flow and filtration at $0.22 \mu\text{m}$. Extracts were finally
 179 recovered in MeOH before injection. The analytical and quantification procedure is further
 180 detailed in the supplementary data (Tables S1-S2).

181 Table 1: General properties of the targeted TrOCs, with Ab. the abbreviation, M_w the molecular weight in g.mol⁻¹,
 182 Sol_w the water solubility at 25°C and pH=7 in mg.L⁻¹, Charge the charge state at pH=7 and MAD the market
 183 authorization date, deriv. for derivatives, * indicates by-products. Data extracted from Chemspider Database

Type	Chemical Group	Name	Ab.	Formula	CAS-Number	M _w	pK _a	log K _{ow}	log K _{oc}	Sol _w	Charge	MAD ^{a,b}
Pharmaceutical Products												
Antibiotics	β-Lactam	Amoxicillin	AMO	C ₁₆ H ₁₉ N ₃ O ₅ S	26787-78-0	365.40	3.2-7.4	0.97	2.94	2,702	+/-	1972
	Cycline	Tetracycline	TET	C ₂₂ H ₂₄ N ₂ O ₈	60-54-8	444.43	8.2	-1.33	1.76	231	+	1948
	Diaminopyrimidine	Trimethoprim	TMP	C ₁₄ H ₁₈ N ₄ O ₃	738-70-5	290.32	7.2	0.73	2.96	400	0/+	1968
	Fluoroquinolone	Ciprofloxacin	CIP	C ₁₇ H ₁₈ FN ₃ O ₃	85721-33-1	331.34	5.8-8.7	0.28	1.55	1,350	+/-	1987
		Enrofloxacin	ENR	C ₁₉ H ₂₂ FN ₃ O ₃	93106-60-6	359.39	5.7-6.7	0.70	1.92	612	-	1970s
		Norfloxacin	NOR	C ₁₆ H ₁₈ FN ₃ O ₃	70458-96-7	319.33	5.8-8.7	-0.31	1.96	280	+/-	1985
		Ofloxacin	OFL	C ₁₈ H ₂₀ FN ₃ O ₄	82419-36-1	361.37	5.5-6.2	-2.00	1.65	4,000	-	1986
	Macrolide	Erythromycin	ERY	C ₃₇ H ₆₇ NO ₁₃	114-07-8	733.93	8.4-12.4	3.06	1.00	4.2	+	1952
	Quinolone	Flumequine	FLQ	C ₁₄ H ₁₂ FNO ₃	42835-25-6	261.25	6.0	2.60	1.85	308	-	1976
		Oxolinic Acid	OXO	C ₁₃ H ₁₁ NO ₅	14698-29-4	261.23	5.6	1.70	1.00	3.2	-	1974
Sulfonamide	Sulfamethoxazole	SMX	C ₁₀ H ₁₁ N ₃ O ₃ S	723-46-6	253.28	2.0-6.2	0.89	3.19	610	-	1968	
Analgesics	Acetylaniline	Acetaminophen	ACM	C ₈ H ₉ NO ₂	103-90-2	151.16	9.6	0.46	1.79	14,000	0	1957
	Opioids	Codeine	COD	C ₁₈ H ₂₁ NO ₃	76-57-3	299.36	8.2	1.28	3.12	577	+	1840s
		Tramadol	TRA	C ₁₆ H ₂₅ NO ₂	27203-92-5	263.37	9.4	3.01	2.91	1,151	+	1997
Anticonvulsants	Dibenzazepine	Carbamazepine	CBZ	C ₁₅ H ₁₂ N ₂ O	298-46-4	236.27	13.9	2.45	3.56	18	0	1974
β-blockers	Ethanolamine	Atenolol	ATE	C ₁₄ H ₂₃ N ₂ O ₃	29122-68-7	266.34	9.6	0.16	2.17	13,300	+	1978

		Propranolol	PRP	C ₁₆ H ₂₁ NO ₂	525-66-6	259.34	9.7	2.60	3.09	61.7	+	1965
Hypolipidemic	Fibrate	Bezafibrate	BZB	C ₁₆ H ₂₃ ClNO ₄	41859-67-0	361.82	3.87	4.25	3.17	1.55	-	1982
Non-Steroidal Anti-Inflamm.	Acetic acid deriv.	Diclofenac	DCF	C ₁₄ H ₁₁ Cl ₂ NO ₂	15307-79-6	296.15	4.2	4.02	2.92	2.37	-	1950's
	Propionic acid deriv.	Ketoprofen	KET	C ₁₆ H ₁₄ O ₃	22071-15-4	254.28	4.5	3.00	2.46	51	-	1970's
Psychotropic drugs	Benzodiazepine	Diazepam	DIA	C ₁₆ H ₁₂ ClN ₂ O	439-14-5	284.74	3.4	2.70	4.05	50	0	1963
		Oxazepam	OXA	C ₁₅ H ₁₁ ClN ₂ O ₂	604-75-1	286.71	1.7-11.6	3.34	3.08	150	0	1965
	Diphenylamine deriv.	Fluoxetine	FLX	C ₁₇ H ₁₈ F ₂ NO	54910-89-3	309.33	9.8	4.65	5.32	1.7	+	1989
	Phenethylamine deriv.	Venlafaxine	VEN	C ₁₇ H ₂₇ NO ₂	93413-69-5	277.40	8.9	3.28	3.17	267	+	1993
Pesticides												
Fungicide	Benzimidazole	Carbendazim	CBD	C ₉ H ₉ N ₃ O ₂	10605-21-7	191.19	4.5	1.55	2.24	8	0	1967
	Triazole	Tebuconazole	TEB	C ₁₆ H ₂₂ ClN ₅ O	107534-96-3	307.82	5.0	3.89	4.32	36	0	1986
Biocide	Triazine	Irgarol	IRG	C ₁₁ H ₁₉ N ₃ S	28159-98-0	253.37	4.1	4.07	2.38	7.52	0	-
Herbicide	Organochlorine	Metazachlor	MTZ	C ₁₄ H ₁₆ ClN ₃ O	67129-08-2	277.75	-	2.38	2.80	430	0	1983
		Metolachlor	MTC	C ₁₅ H ₂₂ ClNO ₂	51218-45-2	283.79	-	3.24	2.47	530	0	1975
	Oxadiazole	Oxadiazon	OXD	C ₁₅ H ₁₈ Cl ₂ N ₂ O ₃	19666-30-9	345.22	2.7	4.81	3.54	0.7	-	1969
	Phenoxyacetic acid deriv.	Diffenican	DFD	C ₁₉ H ₁₇ F ₃ N ₂ O ₂	83164-33-4	394.30	-	3.53	5.04	0.05	0	1988
	Phenylurea	3,4 Dichloroaniline*	DCA	C ₆ H ₃ Cl ₂ N	95-76-1	162.02	3.0	2.37	2.08	92	0	-
		Chlortoluron	CHT	C ₁₀ H ₁₃ ClN ₂ O	15545-48-9	212.67	14.0	2.58	2.13	70	0	1970
		Isoproturon	ISO	C ₁₂ H ₁₈ N ₂ O	34123-59-6	206.28	0.1	2.84	2.40	70	0	1974
	Sulfonyleurea	Nicosulfuron	NIC	C ₁₅ H ₁₈ N ₆ O ₆ S	111991-09-4	410.41	4.3	-1.15	1.33	1,200	-	1993
		Prosulfuron	PRS	C ₁₅ H ₁₆ F ₂ N ₂ O ₄ S	94125-34-5	419.38	3.8	3.56	3.54	4,000	-	1999
	Triazine & deriv.	Atrazine	ATZ	C ₈ H ₁₄ ClN ₅	1912-24-9	215.68	1.7	2.82	2.36	33	0	1959
		Desethylatrazine*	DEA	C ₈ H ₁₀ ClN ₅	6190-65-4	187.63	1.4	1.78	1.94	3,200	0	-
		Deisopropylatrazine*	DIA	C ₅ H ₈ ClN ₅	1007-28-9	173.60	1.5	1.36	1.75	670	0	-
		Hydroxyatrazine*	HTZ	C ₈ H ₁₅ N ₅ O	2163-68-0	197.24	4.6	2.09	2.25	5.9	0	-
		Simazine	SIM	C ₇ H ₁₂ ClN ₅	122-34-9	201.66	1.6	2.40	2.17	6.2	0	1957

184 References: ^aChast, (2012); ^bChauvel et al., 2012)

185 2.6. Quantification procedure

186 TrOC separation was achieved at 40°C with a Zorbax Eclipse Plus C18 chromatographic
187 column (2.1 mm x 150 mm x 3.5µm; Agilent) using a 1200 SL HPLC system (Agilent). The
188 injection volume was 10 µL and the flow rate 0.3 mL.min⁻¹. Two solvents were used as mobile
189 phase; AcN (solvent A) and Milli-Q water (solvent B) both acidified with 0.1% of formic acid.
190 The elution gradient was a transition from 95% to 0% of B in 9.5 min followed by 4 min of
191 100% of A and then a return to the initial conditions (95% of B) during 3.5 min for a total
192 analysis time of 18.5 min. The chromatography system was coupled to a 6410B triple
193 quadrupole mass spectrometer (Agilent) equipped with a heated electrospray ionization (H-
194 ESI) interface operating in positive mode and at a flow rate of 0.3 mL.min⁻¹. The multiple
195 reaction monitoring (MRM) transitions and further details on the detection and quantification
196 procedures are given in the supplementary data (Tables S1-S2). During each analytical run,
197 blanks and quantification controls were regularly used in order to crosscheck the quantification
198 quality.

199 2.7. Validation

200 The limits of quantification (LOQ) and limits of detection (LOD) of the method were calculated
201 using the signal-to-noise (S/N) ratios (Table S3). LOD and LOQ were determined by extracting

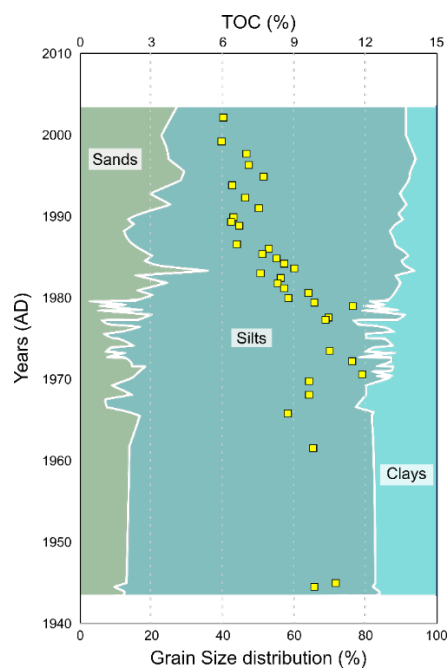
202 spiked (100 ng.g^{-1}) matrix-matched ($n = 5$) sediment samples. Then, LOD and LOQ were
203 respectively calculated based on a ratio between spiked amount and S/N ratios multiplied by 3
204 and 10 for LOD and LOQ respectively. The recovery ratios were also evaluated in these
205 experiments (spiking concentration = 100 ng.g^{-1} , $n = 5$), using the same extraction and
206 quantification protocol as for the samples.

207 **3. Results**

208 **3.1. Sedimentary composition**

209 The qualitative composition of the samples according to their deposition date was evaluated
210 using FTIR analyses (Figure S1). The main bands are associated with the main components of
211 the sediments; i.e. carbonates, silicates and organic matter (Tinti et al., 2015). The relative
212 proportion of each is not the point here, although it is worth noting that no significant variations
213 in the spectra were visible for the samples selected. This means that no sudden variations
214 occurred in the whole sedimentary composition, at least using this qualitative analysis,
215 confirming a relatively homogeneous organo-mineral composition along the sedimentary
216 profile.

217 The grainsize distributions of the sampled sediments are presented in Figure 2. All along the
218 vertical profile, the grainsize is dominated by silts which are almost steady around 70%.
219 Conversely, the relative proportion of sands overall increased from a mean value of 12%
220 between 1945 and 1980 to a mean value of 21 % in the most recent layers. The opposite pattern
221 is visible for clay grainsize, for which the relative proportion decreased from 17% between
222 1945 and 1980 to a mean value of 9% since 1980.



223

224 Figure 2: Total organic carbon (yellow squares, in %) and grain size distribution in three major fractions
 225 in % (clays in light green, silts in green and sands in light brown) of the sampled sediments

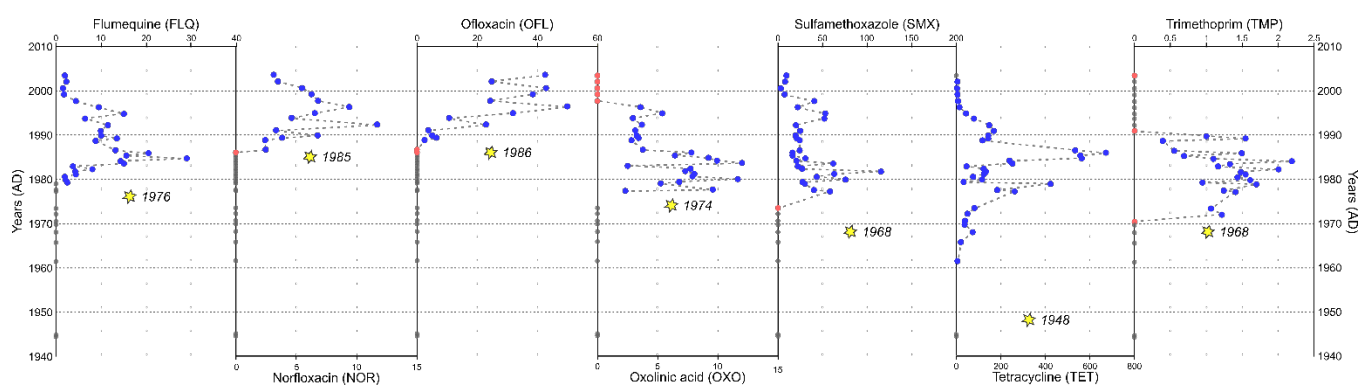
226 The change in TOC values along the core seems to be closely connected with the grainsize
 227 variations, as TOC is almost steady between 1945 and 1980 with a mean value of 10%, followed
 228 by a decrease in the TOC value between 1980 and 1990, and since then, an almost constant
 229 TOC value around 6.5%.

230 These similar temporal fluctuations of clay grainsize and TOC are significantly correlated ($p <$
 231 0.001), and even if the TOC content does not exclusively depend on the clay proportion (i.e. R^2
 232 $= 0.41$), the higher surface area of the finest grainsize fractions plays an important role in the
 233 organic carbon storage.

234 3.2. Occurrences of TrOCs in sediments

235 Among the 41 targeted TrOCs, 23 were quantified at least once. Most of the concentrations
 236 ranged between 1 and 10 ng.g^{-1} except for COD and several antibiotics. The maximum
 237 concentrations were 256 and 550 ng.g^{-1} for COD and TET, respectively. Whatever the TrOC,
 238 the vertical distribution was characterized by a first occurrence, at different depths depending
 239 on the molecule, followed by an almost continuous detection until the most recent sedimentary

240 layers. Two main patterns were displayed: (i) an increase in the concentrations followed by a
 241 decrease in the most recent sediments (e.g. FLQ and TET, Figure 3); and (ii) a continuous
 242 increase in the concentrations since the first detection (e.g. TRA, Figure 4 and CBD, Figure 5).
 243 It is noteworthy that for the TrOCs investigated, the market authorization date was
 244 systematically older than their first detection. In this archive, other authors have indicated the
 245 possible connection with groundwaters (Kaci et al., 2016), which is not confirmed here as the
 246 oldest sampled layers (respectively dating from 1944.5 and 1945) were deprived of any TrOC
 247 contamination (Figures 3, 4 and 5). For clarity, the vertical distribution of TrOC will be
 248 hereafter discussed within three main groups, antibiotics, pharmaceutical products and
 249 pesticides.



250
 251 Figure 3: Distribution of antibiotics along the sedimentary profile by year. Concentrations are expressed in ng g^{-1}
 252 of dried sediment. Grey squares indicate concentrations below LOD, whereas red squares indicate concentrations
 253 below LOQ. The yellow star refers to the market authorization date (MAD, Table 1).

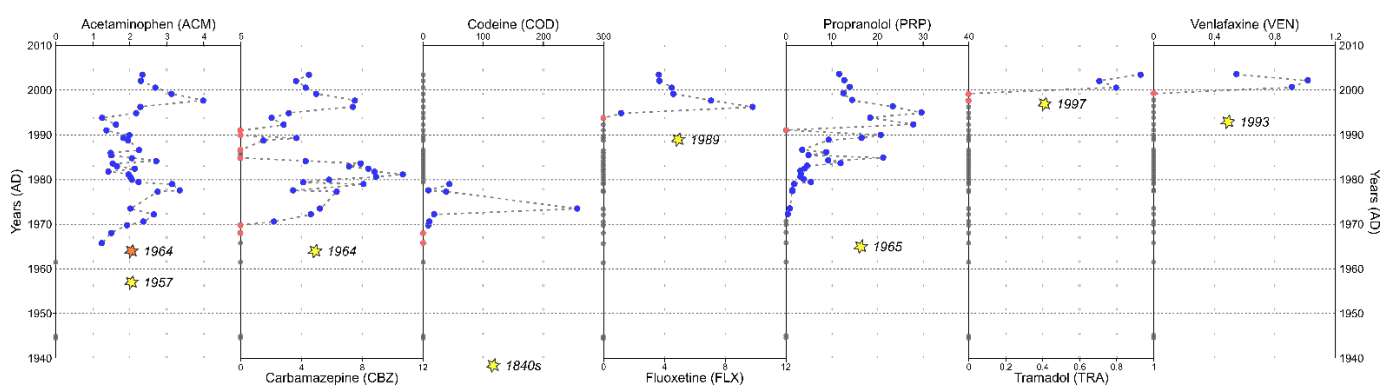
254 3.2.1. Antibiotics

255 Among 11 targeted antibiotics, 7 were quantified and displayed in general an increase in
 256 concentration followed by a decrease in the most recent sedimentary layers (Figure 3). The
 257 maximum concentrations were reached between 1980 and 1985 for FLQ, OXO, SUL, TET and
 258 TMP, whereas the maximum concentrations of NOR and OFL were more recent, i.e. between
 259 1991 and 1997 due to their later market authorization date. A significant decrease in the
 260 concentrations of all the compounds can be observed in the latest layers, especially since 1990
 261 for TMP, since 1992 for TET and since 1997 for the other antibiotics. This decrease is

262 particularly noticeable on OXO which has been <LOQ since 1998 and TMP, which has been
263 mostly <LOD since 1990.

264 3.2.2. Other Pharmaceuticals

265 Within this group, 7 compounds were detected amongst 13 (Figure 4). The MADs of these
266 TrOCs range from ~1842 for COD, to 1997 for TRA. COD displays an atypical pattern with
267 several occurrences between 1968 and 1980 with a very high concentration (i.e. 256 ng.g⁻¹) in
268 1973 whereas this molecule was not detected in the other samples.



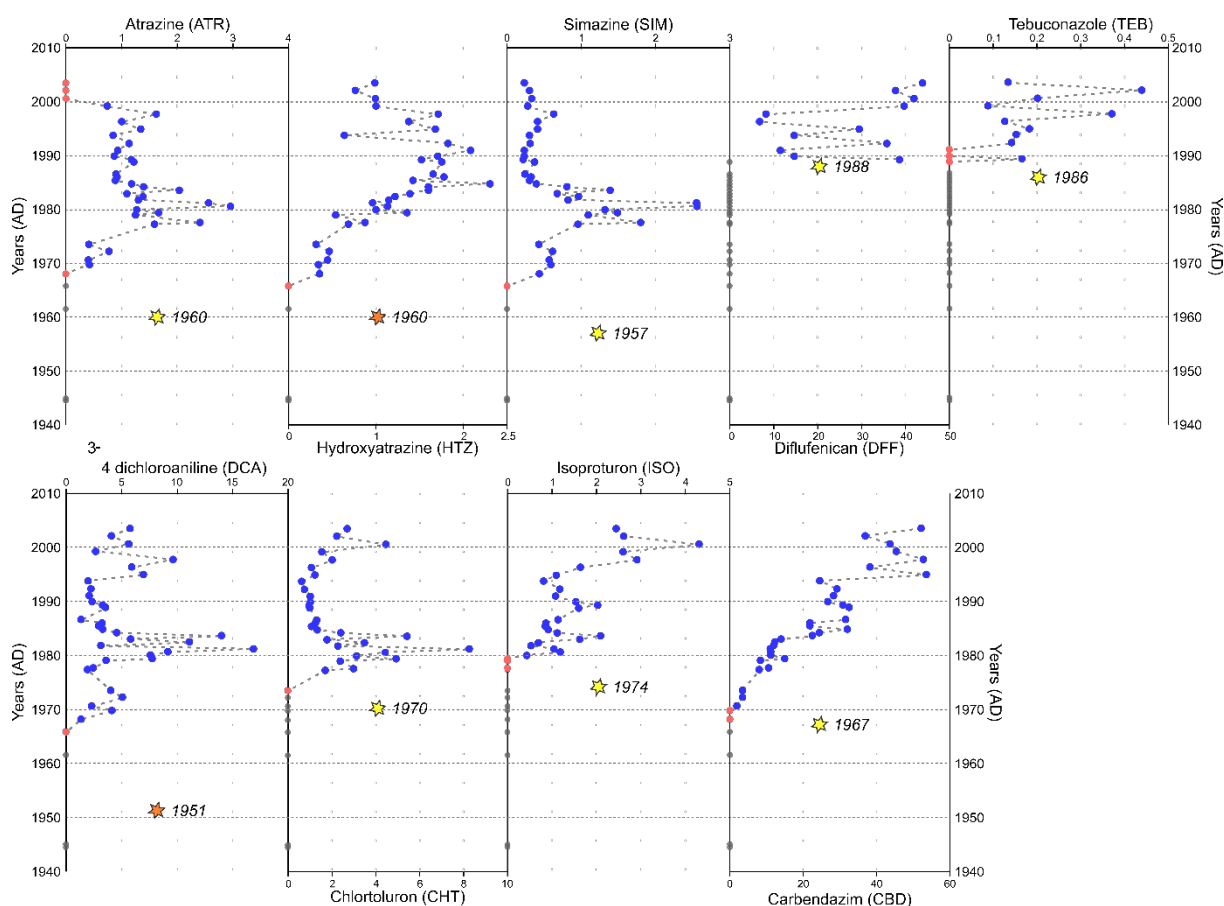
269
270 Figure 4: Distribution of PPs (other than ATBs) along the sedimentary profile by year. Concentrations are
271 expressed in ng g⁻¹ of dried sediment. Grey squares indicate concentrations below LOD, whereas red squares
272 indicate concentrations below LOQ. The yellow star refers to the market authorization date (MAD, Table 1),
273 whereas the orange star refers to another MAD event.

274 FLX, VEN and TRA were the most recently marketed pharmaceuticals, respectively in 1989,
275 1993 and 1997. Whereas for VEN and TRA only 3 quantifications were made, in the three latest
276 sedimentary layers, FLX displayed an increase in concentration until 1997, followed by a
277 regular decrease in concentration. The same pattern (i.e. global increase until the late 1990s) is
278 visible for PRP, despite an older MAD. ACM was initially launched for pediatric use only,
279 before an extension to the entire population in 1964. Its pattern displays a first increase in
280 concentration between 1965 and 1979, followed by a steady profile between 1980 and 1992, a
281 second increase between 1993 and 1998, and a final decrease.

282 3.2.3. Pesticides

283 Among the 16 pesticides and derivatives investigated, 9 were detected (Figure 5). The highest
 284 concentrations were observed for CBD, DCA and DFF with several tens of $\text{ng}\cdot\text{g}^{-1}$. DCA and
 285 DFF displayed limited recovery ratios respectively due to a significant volatility (Crossland,
 286 1990; Gatidou et al., 2004) and a high affinity with solids (Table 1).

287 The MAD of the detected pesticides ranged between 1951 for diuron (which with propanil and
 288 linuron launched in 1960 and 1965, and other biocides or industrial products, are the potential
 289 parent compounds of DCA) and 1988 for DFF. As observed for other TrOCs, no detection
 290 occurred before the MAD. The historical distribution of pesticides followed two types of
 291 patterns: (i) an almost constant increase in concentration, as for ISO and CBD, and (ii) an
 292 increase since the MAD until the beginning of the 1980s followed by a decrease which became
 293 more pronounced in the most recent layers.



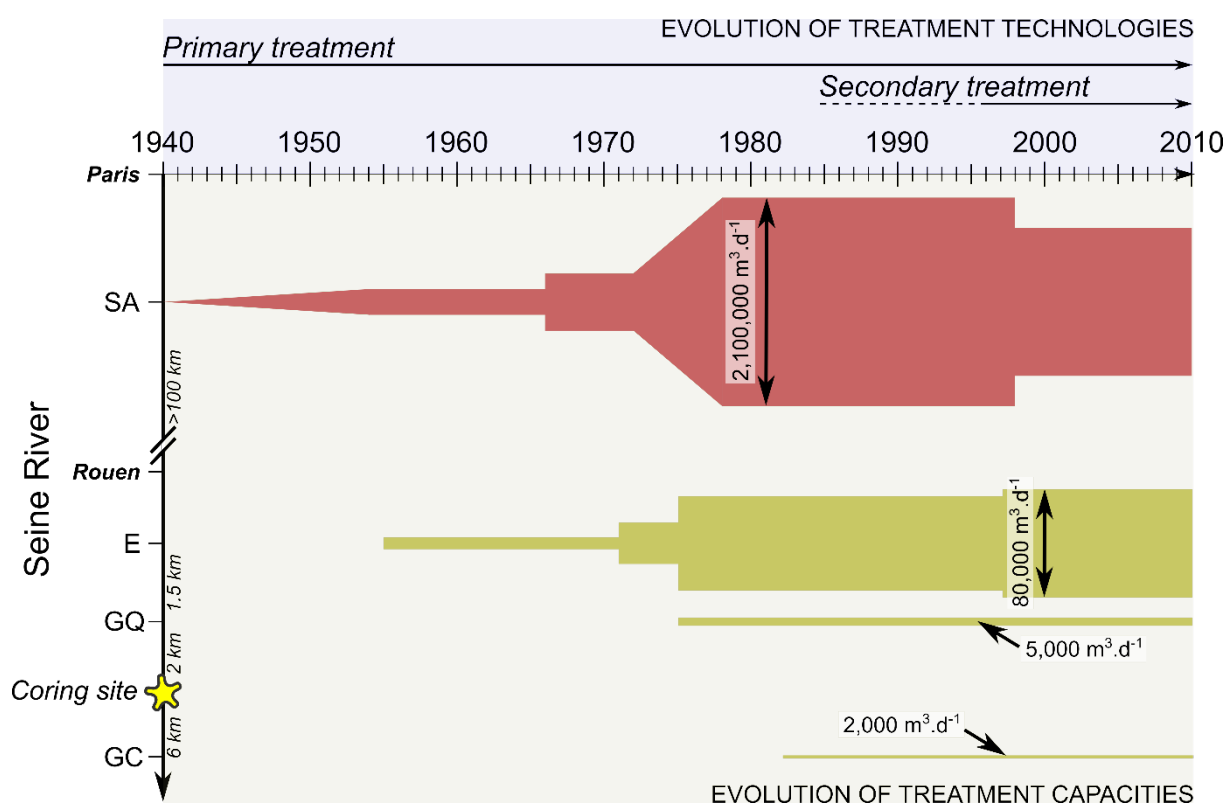
294
 295 Figure 5: Distribution of pesticides along sedimentary profile by year. Concentrations are expressed in $\text{ng}\cdot\text{g}^{-1}$ of
 296 dried sediment. Grey squares indicate concentrations below LOD, whereas red squares indicate concentrations

297 below LOQ. The yellow star refers to the market authorization date (MAD, Table 1), whereas the orange star refers
298 to other MAD events (e.g. by-products).

299

300 3.3. WWTP technology evolution

301 WWTP effluents can be considered as the main environmental source of pharmaceuticals (Tran
302 et al., 2019), and depending on the sewage network (i.e. separative or unitary), a significant
303 amount of pesticides may also be present (Paijens et al., 2021). Located in an urban area, the
304 coring site is impacted by the effluent discharge of the main WWTP of the Rouen conurbation,
305 3.5 km upstream, with a treatment capacity of 550,000 PE. Two minor effluent discharges, 2
306 km upstream and 6 km downstream (indicated here due to the tide effect), QG and GC
307 respectively, also impacted the coring site. Finally, the effluents of the largest French WWTP,
308 SA, located downstream Paris with a maximum treatment capacity of almost 7,500,000 PE in
309 normal conditions are discharged into the Seine River more than 100 km upstream.



310

311 Figure 6: Temporal evolution of the main WWTPs (both treatment capacities and technologies)
312 impacting the coring site (yellow star) along the Seine River. Data from Rocher et al. (2017) for SA and
313 from Rouen sanitation service (personal communication) for E, GC and GQ.

314 The evolution of the treatment technology used in these WWTPs primarily focused on
315 improving the removal of classical parameters such as BOD₅, N (mostly organic) or suspended
316 solids. As shown in Figure 6, for SA and E, there was a progressive increase in the treatment
317 capacity following the increase in urbanization and the decline in agricultural spreading of
318 wastewaters. This increase in the treatment capacity was accompanied by an evolution of the
319 treatment technology, especially since the mid-1990s. For example, between 1954 and 1997 the
320 E treatment chain was only a physico-chemical treatment with a focus on suspended solids and
321 carbonaceous load, whereas since then a biological treatment, allowing a correct removal of N
322 and P loads, was implemented.

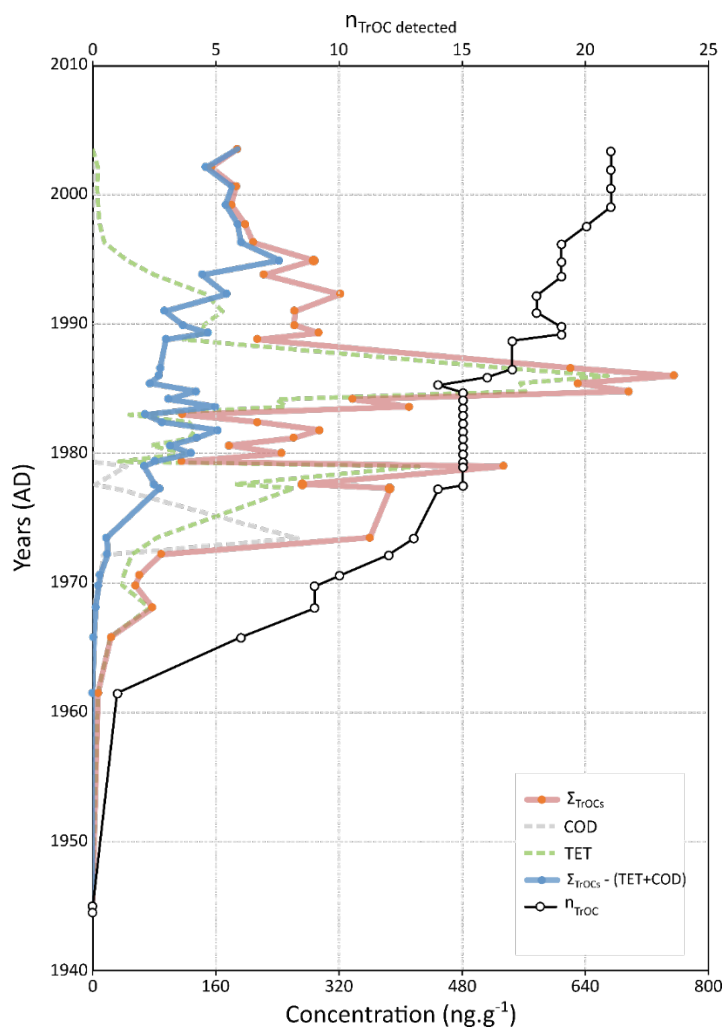
323 It is difficult to gain precise historical knowledge of the feeding water in a sewage network.
324 From the oldest available information (i.e. 2017) almost one third of the sewage network of the
325 Rouen agglomeration is unitary, whereas two thirds are separative. However, it is most likely
326 that these relative proportions have varied since 1945. Specifically, the unitary network might
327 have been predominant during a long, but unknown, period of time.

328 **4. Discussion**

329 **4.1. A 50 years overview?**

330 Several authors have assumed that the vertical distribution of TrOCs within sedimentary
331 archives may be connected with their historical occurrences in the dissolved phase, and thus
332 their use in the watershed (Chiaia-Hernández et al., 2020). Considering this assumption, an
333 increasing impact of two factors are expected since 1945: (i) the number of TrOCs detected
334 should increase, in view of the exponential increase in the number of TrOCs marketed since
335 this date, and (ii) the global concentration of TrOCs should also increase extensively as a result
336 of the increase in the use of TrOCs. Of these two assumptions, the first one is verified in the
337 sampled archive (Figure 7), with only one TrOC (i.e. TET) detected in the level 1961.5 and 21

338 since the level 1999.2. This increase is consistent with the market authorization dates of the
 339 targeted TrOCs, which are distributed all along the last 50 years. Consequently, it can be
 340 assumed that sediments reflect the diversity of TrOC contamination well, at least for the most
 341 persistent or the most concentrated of them. However, the comparison between the sedimentary
 342 occurrences of TrOCs and their historical use in the watershed is not so obvious. First of all,
 343 the historical use of pharmaceuticals and pesticides is not available at such a time scale (e.g.
 344 records of the amounts of antibiotics sold in France began in 1999, Fig S3), and while it can be
 345 considered that there has been an overall increase in the use of TrOCs in general since 1945,
 346 this does not take into account the historical variation for one product, which can be more
 347 complex (i.e. banning, substitution, competition).

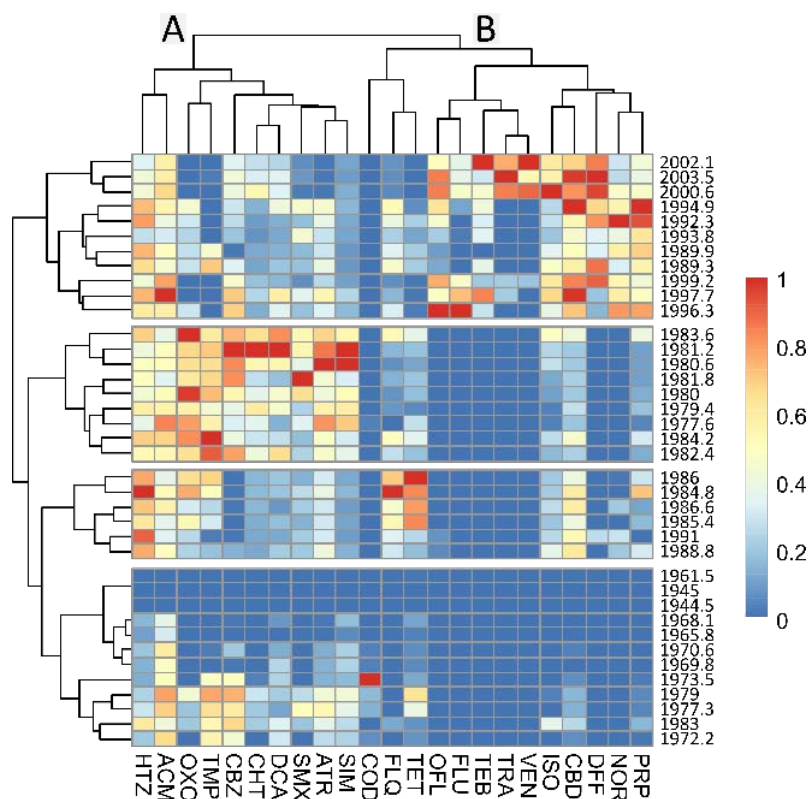


348

349 Figure 7: Total TrOC concentration (red line, Σ_{TrOCs}), Total TrOC concentration without COD and TET
350 (blue line $\Sigma_{\text{TrOCs}} - (\text{TET} + \text{COD})$) and number of detected individual TrOCs (black line, n_{TrOC}) along the
351 core. COD (grey dotted line) and TET (green dotted line) distribution.

352 Looking at the sum of all TrOC occurrences, the layers with the highest concentrations dated
353 from the late 1970s and middle 1980s (Figure 7). Yet, this pattern is heavily influenced by two
354 TrOCs, TET and COD respectively (Figure S2), which can represent up to 88% of the total
355 TrOC concentration for specific layers. Removing the concentrations of these two TrOCs, the
356 total concentration reveals a progressive increase since the first occurrences in the middle
357 1960s. The concentrations of TET and COD are so much higher than the concentrations of other
358 TrOCs that it directly affects the hierarchical cluster distribution of each sample when using
359 raw concentration data (Figure S2). Indeed, each cluster only reflects the relative occurrence of
360 TET or COD, and to a minor extent, SMX.

361 As a result, a second hierarchical cluster analysis was carried out on normalized concentrations
362 between 0 and 1 for each TrOC (0 for <LOD and 1 for the highest concentration, Figure 8).
363 Two main TrOC clusters emerged from this analysis, mostly impacted by the market
364 authorization dates on the one hand and by the historical increase in the sedimentary
365 occurrences on the other hand. From this point of view, cluster A mostly accounts for TrOCs
366 that exhibited their highest concentrations in the 1970s and the 1980s whereas cluster B mostly
367 accounts for TrOCs that have exhibited their highest concentrations since 1990s. The sediment
368 samples are also grouped in four distinct clusters that appear to be affected by TrOC diversity
369 in sediments. There is a cluster for the oldest samples, containing the lowest diversity of TrOCs
370 (< 1979), another for the most recent samples (since 1989) and two other clusters in the 1980s
371 impacted by the relative contribution of each TrOC cluster. This approach confirms that the
372 1980s were a period of significant modifications in the diversity and relative occurrence of
373 TrOCs in this core that need to be addressed.



374
 375 Figure 8: Heatmap analysis between the normalized occurrence of TrOCs and each analyzed layer by
 376 using R software (pheatmap package). The distance matrix was based on the Euclidian distance.

377

378 4.2. Atypical patterns

379 Several TrOCs displayed an atypical vertical distribution, considering that a typical pattern is
 380 an expected one and comparable between TrOCs. While in general we can observe an overall
 381 increase between the MAD and the late 1990s, this pattern is not visible for several TrOCs. For
 382 example, TMP has mostly been consumed in association with SMX since their common MAD
 383 in 1968 (Salter, 1982; Thiebault, 2020). However, although SMX, a persistent molecule often
 384 detected in the environment, was continuously detected since its first detection in 1973, TMP
 385 concentrations have been below LOQ or LOD since 1990. Yet, TMP was briefly sold alone on
 386 the French market between 1983 and 1990, the date at which TMP alone was withdrawn (Caron
 387 et al., 2017), unlike in other European countries such as the UK and Sweden where TMP alone
 388 remains available for medication purposes. Even if this factor alone is probably not sufficient
 389 to explain the non-detection of TMP in the most recent layers, this withdrawal may play a

390 significant role. Moreover, the impact of wastewater treatment technologies may impact the
391 removal of TMP and SMX differently as a monitoring study of the antibiotics' occurrence in
392 the Seine River (Tamtam et al., 2008) revealed high concentrations of SMX ($\sim 100 \text{ ng.L}^{-1}$) and
393 very limited concentrations of TMP ($< 10 \text{ ng.L}^{-1}$), consistent with their sedimentary occurrences
394 in the recent layers.

395 Regarding antibiotics, the maximum concentration of FLQ and OXO occurred in the middle
396 1980s, which is older than for most TrOCs. Both these antibiotics belong to the quinolone
397 group, it is worth noting that the latter was progressively substituted by fluoroquinolones
398 especially in human medicine (Figure S2), such as OFL, NOR and CIP (non-detected in this
399 work) launched in 1985, 1986 and 1987, respectively (Zhanel et al., 2002).

400 Lastly, the distribution of TET is original and exhibited very significant concentrations. This
401 molecule is heavily used in veterinary medicine, where its use represents more than 98% of the
402 total use in France (Figure S2), and also displays a high affinity with solid matrices (Zhou et
403 al., 2016). In several studies, tremendous amounts of TET were observed in livestock feces (e.g.
404 $\sim 10 \mu\text{g.g}^{-1}$ in pig feces in Zhou et al. (Zhou et al., 2013)) at concentrations a hundred times
405 higher than other antibiotics such as fluoroquinolones and sulfonamides. Also, in France, the
406 use of tetracyclines largely exceeds the use of the other antibiotics detected in this work,
407 especially for veterinary purposes (Figure S2). Therefore, this high use associated with high
408 excretion and affinity with solid particles may be key factors in explaining these very significant
409 concentrations of TET (Kuang et al., 2020). Moreover, livestock effluent management may
410 directly impact the water quality in the absence of any treatment (Chiffre et al., 2016). The
411 antibiotic loads of the effluents may be very high and contribute significantly to the total
412 environmental loads of some veterinary antibiotics, such as TET (Jaffrézic et al., 2017).

413 Among pharmaceutical products, the most atypical pattern is displayed by COD, with very
414 significant concentrations in the middle 1970s and no detection until this date. These erratic

415 occurrences are largely impossible to explain, but were also observed in other sedimentary cores
416 (Thiebault et al., 2017).

417 Finally, another atypical pattern is displayed by herbicides in general, and specifically ATR.
418 This is one of the most frequently detected TrOCs in French water bodies due to its high
419 mobility and persistency. It was widely used on maize and vineyard but also in urban areas with
420 maximal application reported in the 80's in France. Then, uses slowly decreased due to lower
421 maize areas and limited application rates from 3 to successively 1.5 kg.ha⁻¹ in 1992 and 1 kg.ha⁻¹
422 in 1997 before its ban in 2003 (Blanchoud et al., 2019). Furthermore, urban uses of ATR and
423 SIM were restricted in 1998 due to high contamination of surface waters by direct runoff
424 (Blanchoud et al., 2004). Yet, in the sampled cores, ATR occurrences were below the
425 quantification limit between 2000 and 2003, and in addition, were the highest in the early 1980s,
426 as for some other herbicides. This may reflect mostly an agricultural origin in the 1980s, and
427 then, a mostly urban source until 1997. A precise knowledge of the sewer connectivity may
428 confirm such assumption, but is unreachable. Some other pesticides were more recently banned
429 to limit pesticide contamination like diuron (2003), CBD (2009) and ISO (2017), and new
430 products are now in use like DFF and TEB, which were detected in the most recent layers.

431 **4.3. What can we learn from the historical distribution of TrOCs?**

432 The sedimentary occurrence of TrOCs is the result of several driving factors: (i) the use of the
433 molecule in the watershed, (ii) the sewer connectivity (depending on the main source of the
434 product), (iii) the wastewater treatment technology, (iv) the distance from the sources, (v) the
435 physico-chemical properties of the targeted molecule and (vi) the sediment composition. As a
436 result, a direct interpretation of a sedimentary occurrence into a historical use is somewhat
437 speculative and requires a correct understanding of the contribution of each driving factor.

438 In this work, the sedimentary composition varied weakly in the analyzed samples, as only a
439 slight decrease in the organic content, associated with an increase in the clay content was
440 observed between 1980 and 1990 (Figure 2). Such a small variation may not significantly
441 impact the sorption of TrOCs. As the targeted molecules were in general intermediately
442 hydrophilic/hydrophobic, a K_{OC} normalization appeared unnecessary for a correct
443 understanding of the vertical variations, unlike studies working on hydrophobic contaminants
444 (Alegria et al., 2016; Peters et al., 2020).

445 Another important driving factor may be the TrOC discharge in environmental compartments.
446 Some of them are directly discharged in water bodies, without any treatment (e.g. pesticides,
447 and some veterinary antibiotics), while for others, such as pharmaceuticals, the almost exclusive
448 source is human consumption/excretion and discharge through wastewater effluents. For the
449 latter TrOCs, the historical wastewater management and treatment technology is of great
450 importance.

451 Lastly, the location of the core sampling is of prime importance as some contaminants are
452 sparsely persistent in aquatic environments, especially amongst pharmaceutical products (Zhi
453 et al., 2020). A previous study analyzed the occurrences of antibiotics in sediments of the same
454 watershed, but 50 km upstream (Tamtam et al., 2011). In their study, the authors found a global
455 increase in antibiotic concentrations until the late 1980s, since when a global decrease was
456 observed. The same pattern was found in the present work for the three common molecules
457 (SMX, FLQ, OXO). Yet, we have detected several antibiotics that were not detected in
458 upstream sediments, such as NOR and TMP. It can therefore be assumed that the main drivers
459 of the human-excreted TrOCs vertical distribution are the WWTP effluents nearby (E, GQ)
460 rather than WWTP effluents farther upstream (i.e. SA) even if the former represent a much
461 lower volume.

462 This assumption is also validated by the decreasing concentrations of almost all TrOCs since
463 1996, the date at which the water treatment technology of WWTP E was significantly upgraded
464 by the addition of a biological treatment (Figure 6). It can be considered that this supplementary
465 treatment is more efficient than physico-chemical treatment alone for the removal of TrOCs
466 (Joss et al., 2005; Petrie et al., 2014). Yet, no precise knowledge of the sewer connectivity prior
467 to this date was available. Consequently, it is possible to discriminate the main sources of
468 TrOCs only with this date, 1997. What is particularly interesting considering this key date is
469 that beyond pharmaceuticals and most antibiotics, for which the main source is well-known to
470 be wastewater effluents, several pesticides (e.g. ATR) also display decreasing concentrations
471 since 1997. This can be attributed to the fact that pesticide occurrences in river waters result
472 from a mix between agricultural and urban uses (i.e. between diffuse and point sources). Yet,
473 several studies revealed that some pesticides (e.g. ATR, ISO) were more concentrated in the
474 combined sewer systems of urban areas than in agricultural catchments (Paijens et al., 2021),
475 even during the application period of these products (Wittmer et al., 2010). The urban
476 contribution to the total pesticide contamination must therefore not be neglected, especially in
477 an urban context where sediments were sampled close to the discharge of urban effluents.
478 Therefore, counter to the claim made in a recent study dealing with lacustrine sediments in a
479 less anthropized catchment (Chiaia-Hernández et al., 2020), in a more anthropized context, a
480 proper understanding of the vertical variations of pesticides is challenging, because the
481 distribution patterns were not expected. The only regular pattern was for CBD, whose
482 concentrations have increased regularly since the 1970s. It is therefore possible that this
483 molecule presents a more regular source than other pesticides, as agricultural use only for
484 example.

485 **5. Conclusion**

486 This study assessed the sedimentary occurrences of TrOCs between 1944 and 2003 with an
487 almost yearly resolution. Various classes of contaminants, such as pesticides and
488 pharmaceutical products were evaluated. Their oldest occurrence was closely related to their
489 historical use, as the first occurrence of each TrOC was systematically later than the market
490 authorization of the product, highlighting the contaminants' preservation and their non-mobility
491 within sedimentary layers and confirming their possible use as chronomarkers in sedimentary
492 archives.

493 The picture is less straightforward, however, when looking at the vertical distribution of each
494 molecule. In general, the highest occurrences were found during the 1980s, even if it is well-
495 known that the use of pharmaceutical products has dramatically increased since this date, which
496 is validated by the increase in TrOC diversity in the most recent sediments. There is therefore
497 an offset between the sedimentary occurrences of some TrOCs, and their use in the watershed.
498 As the cores were sampled close to the discharge of one major WWTP, it can be considered
499 that the evolution of sewage collection, and sewage treatment technology has dramatically
500 modified the concentrations of TrOCs in surface waters, and in turn, their sedimentary
501 occurrences. This is especially highlighted by the overall decrease in TrOC occurrences since
502 the implementation of a biological treatment (i.e. for N and P removal) since 1997. Yet, other
503 modifications (such as sewage collection improvement) were not recorded by the local
504 authorities, making further assumptions about the occurrences of TrOCs in the older layers
505 speculative.

506 Hence, this work provides some clues to the meaning of the vertical distribution of TrOCs from
507 various classes in sedimentary environments. Further analyses remain necessary, however, in
508 order to fully understand how historical sedimentary concentrations can be used beyond the use
509 of the market authorization date. The possibility to sample new cores at the same site for the
510 most recent period (i.e. since 2003) therefore represents a great potential for improving our

511 understanding of the historical distribution as the information about the national use of TrOCs
512 in tonnage and a precise record of the sewage collection and treatment have been recorded since
513 this date.

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