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# **Trace organic contaminants within solid matrices along an anthropized watercourse: Organo-mineral controls on their spatial distribution**

Maëlla Le Gaudu<sup>a</sup>, Thomas Thiebault<sup>a\*</sup>, Katell Quééné<sup>a</sup>, Fabrice Alliot<sup>a</sup>, Elodie Guigon<sup>a</sup> and Laurence Le Callonnec<sup>b</sup>

<sup>a</sup> METIS, Sorbonne Université, CNRS, EPHE, PSL University, UMR 7619, F-75005, Paris, France

<sup>b</sup> IStEP, Sorbonne Université, CNRS, UMR 7193, F-75005, Paris, France

\*To whom correspondence should be addressed. E-mail: thomas.thiebault@ephe.psl.eu Phone: +33

(0) 1 44 27 59 97

## **Abstract**

Although numerous studies have determined significant contamination in terms of trace organic contaminant (TrOC) diversity and concentration, the occurrence of TrOCs within solid matrices as suspended solids and sediments flies under the radar. In this study, the occurrence of 35 TrOCs of various classes (i.e. pharmaceutical products and pesticides) was investigated in three compartments, namely dissolved phase, suspended particulate matter (SPM) and sediments, within an anthropized river in France. The sampling was performed to assess the spatial contamination dynamics and the impact of a major wastewater treatment plant (WWTP), under two contrasted hydrological conditions, i.e. base level and flood conditions. Solid samples were finely characterized (XRD, grainsize, TOC) in order to assess the impact of organic and mineral composition on the sorption extent of TrOCs. The study reveals that the clear spatial pattern of contamination in water samples, mostly generated by the effluent discharge of WWTPs, is less clear in solid matrices as the variability of the organo-mineral composition of such samples strongly impacts their favourability for sorption. Moreover, the flood event strongly impacted the sedimentary compartment, remobilizing fine and TrOC contaminated particles that were further found in suspended particulate matter. Lastly, the representativeness of contaminant

diversity and concentration within the solid matrices displayed more favourable insights for SPM.

## **Keywords**

Pharmaceuticals; Pesticides; Sediments; Partition; Sorption

## **1. Introduction**

In recent decades, trace organic contaminants (TrOCs) have been detected in numerous aquatic environments (Birch et al., 2015; Gogoi et al., 2018; Golovko et al., 2020). Many xenobiotic contaminants can be considered as TrOCs, among which pharmaceutical products and pesticides are particularly monitored, as they are considered as contaminants of emerging concern (Daughton, 2004). Several TrOCs, such as pharmaceutical products, are excreted via urine and faeces and reach aquatic environments after their incomplete removal within wastewater treatment plants (WWTP, Tran et al., 2018). Other possible sources are overflow from the urban water network (Kay et al., 2017; Paijens et al., 2021) or the leaching of sewage sludge from fields (Verlicchi and Zambello, 2015).

For pesticides, the main sources are agricultural or individual use with the runoff, leaching of field soil and/or atmospheric deposits (Botta et al., 2009; Carter, 2000), although urban point sources may account for a significant proportion of the flow (Blanchoud et al., 2004). Due to their global use in large quantities, TrOCs are continuously discharged into environmental compartments and especially water bodies. They are mostly considered as pseudo-persistent (Warner et al., 2019), as this continuous environmental discharge maintains the contamination despite significant mitigation through various processes such as photolysis, biodegradation and/or sorption (Yamamoto et al., 2009; Zhou and Broodbank, 2014). TrOCs may have some effects on aquatic organisms, for example the feminization of fishes (Brodin et

al., 2013), gill deformity (Golovko et al., 2020) or even death in the event of very high concentrations (Li and Lin, 2015; Nunes et al., 2005). TrOCs may also have effects on human health, since contaminated surface waters or ground waters are used for drinking purposes and water treatment quality can be highly variable (Bexfield et al., 2019; Bruce et al., 2010). TrOCs can be carcinogenic, reprotoxic and may impact humans (Farré et al., 2008; Gwenzi and Chaukura, 2018). Because of these effects, these contaminants have become an important issue in aquatic pollution and it is therefore important to improve our knowledge about their fate.

TrOCs, which are rather hydrophilic, are mostly studied in the dissolved phase, even if their occurrences in solid matrices as sediments (Kerrigan et al., 2018; Thiebault et al., 2021a) and suspended particulate matter (SPM) are increasingly investigated (Ledieu et al., 2021; Niu et al., 2021). The distribution of contaminants between solid and dissolved phases differs according to the properties of both the solid phase and the TrOC (Kodešová et al., 2015; Nunes et al., 2019). The physico-chemical properties of the TrOC, such as the charge,  $K_{ow}$  and  $K_{oc}$ , may have an impact (Vazquez-Roig et al., 2012; Zhou and Broodbank, 2014). The total organic carbon (TOC) content of the solid phase as well as the hydrodynamic phase may also impact the TrOC partition in sediments or SPM (Boulard et al., 2019; Quesada et al., 2014). In previous studies, it was assumed that rather hydrophobic TrOCs (e.g. amitryptiline, oxazepam) exhibited more pronounced sorption onto sediments presenting higher TOC values (Al-Khazrajy and Boxall, 2016; Stein et al., 2008; Svahn and Björklund, 2015). But beyond this significant impact of TOC content, the role of other factors is often overlooked. Yet, contrary to hydrophobic contaminants, for which it is considered that the role of mineral surfaces in their adsorption can be neglected (Mader et al., 1997), it is possible that for more hydrophilic compounds, such as those investigated below, mineral surfaces, which are also hydrophilic, may play a more important role (Schaffer et al., 2012; Scheytt et al., 2005), in particular clay minerals (Droge and Goss, 2013a; Thiebault, 2020). Due to their cation exchange capacity (which is the same

as that of organic matter, Droge and Goss, 2013b) and high specific surface area, clay minerals are considered as favourable for the sorption of TrOCs, and especially cationic ones (Dordio et al., 2017; Thiebault et al., 2021b). Therefore, the objective of this paper is to try to go beyond TOC alone to understand the factors controlling the spatial dynamic of TrOC sedimentary occurrences within an anthropized catchment. To achieve this objective, TrOC levels in different finely characterised matrices were analysed spatially and temporally in an anthropized river.

## **2. Material and Methods**

### **2.1. Site settings and sampling**

The study area is situated in the Orge River catchment (956 km<sup>2</sup>) in the North of France (Figure 1). The catchment is situated 30 km south of Paris and the Orge River is a tributary of the Seine River. The Orge basin presents a population density of 3000 inh. km<sup>-2</sup> in the downstream area. This catchment shows an urbanization gradient from prevalently agricultural and partially forested areas upstream to more densely urbanized areas downstream and nearer the junction with the Seine River, as exhibited in Figure 1. A major WWTP with a capacity of 66,667 PE (population-equivalent) is located in the centre of the study area and discharges 60% of its effluent into the Orge river and 40% into the Rémarde river (which is a tributary of the Orge river). Upstream, about 10 small WWTPs discharge their effluents into the Rémarde river with a cumulative PE of 8,000. The upstream Rémarde contamination by TrOCs, especially by antibiotics, was already characterized in previous studies (Dinh et al., 2017a, 2017b)

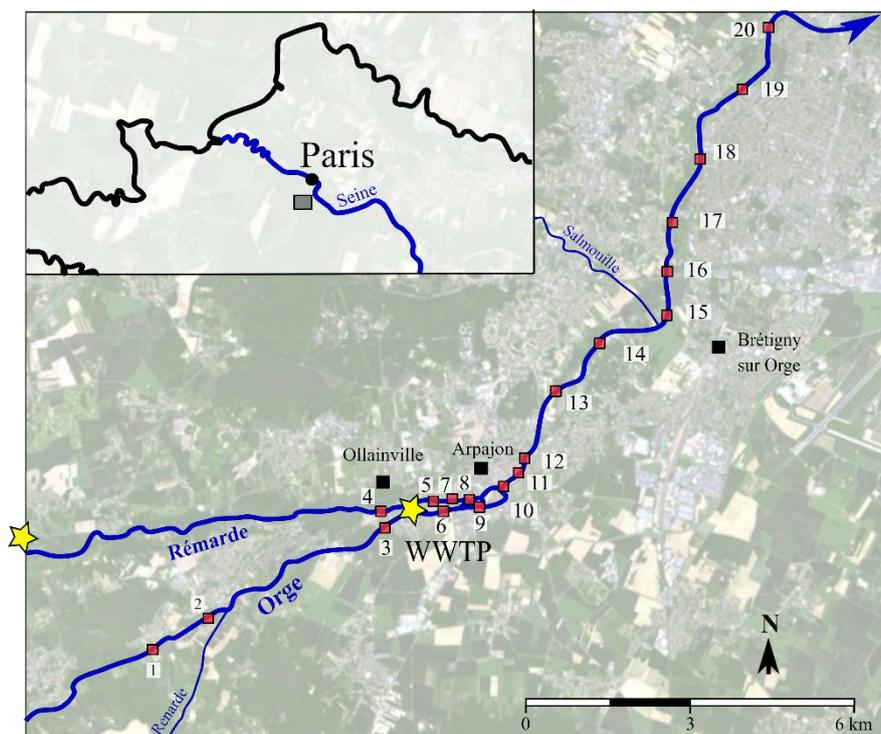


Figure 1. Aerial photograph ([www.geoportail.gouv.fr](http://www.geoportail.gouv.fr)) showing the sampling stations within the Orge catchment. Yellow stars indicate the significant WWTP effluent discharges, with a major WWTP in Ollainville and effluents from rural WWTPs in the Rémarde catchment

The major WWTP operates on the principle of activated sludge followed by ultrafiltration.

Two sampling campaigns were carried out, respectively in October 2020 (I) and in February 2021 (II) in the Orge and Rémarde rivers. 20 stations (i.e. 16 in the Orge river, 4 in the Rémarde river) were targeted during each campaign with sediment sampling in all stations, and water sampling (10 L) in only 10 stations per campaign. Some basic water parameters (pH, Temperature and Conductivity) were systematically measured in the field, and Dissolved Organic Carbon (DOC) was also evaluated on 0.45  $\mu\text{m}$  filtered and 1M  $\text{HNO}_3$  acidified samples using a DOC analyser (Shimadzu). These data are available in Table S1.

Sediments were sampled using an Eckman grab, and SPM were recovered after GF/F filtration of the 10 L water sample.

The main difference between the two campaigns is the hydrological conditions, with baseline water levels in October 2020 (mean flow value of  $1.5 \text{ m}^3 \text{ s}^{-1}$ ) and flood conditions in February

2021 with a mean flow value of  $4.5 \text{ m}^3 \text{ s}^{-1}$  (and a maximum flow rate of  $12.3 \text{ m}^3 \text{ s}^{-1}$  few days earlier).

## 2.2. Chemical reagents

LC-MS grade acetonitrile (AcN) and methanol (MeOH) were purchased from VWR and ultra-pure water ( $\text{H}_2\text{O}$ ) was prepared with a Pure Lab Chorus water purification system (Veolia Water). Formic acid (99% purity) was purchased from Sigma-Aldrich. Isotopically labeled internal standards (ILIS) (Table S2) and reference standards (Table 1) were purchased from LGC Standards, assuming a purity  $\geq 97\%$ . TrOCs were selected following the most frequently detected organic contaminants in European river waters (Loos et al., 2013).

Table 1: General properties of the targeted TrOCs, with Ab. the abbreviation,  $M_w$  the molecular weight in  $\text{g mol}^{-1}$ ,  $\text{Sol}_w$  the water solubility at  $25^\circ\text{C}$  and  $\text{pH}=7$  in  $\text{mg L}^{-1}$ , Charge the charge state at  $\text{pH}=7$  and \* indicates by-products. <sup>‡</sup>Data extracted from Chemspider Database

Type	Name	Ab.	Formula	CAS-Number	$M_w^{\ddagger}$	$\text{pK}_a^{\ddagger}$	$\log K_{ow}^{\ddagger}$	$\log K_{oc}^{\ddagger}$	$\text{Sol}_w^{\ddagger}$	Charge
Pharmaceuticals										
Antibiotics	Flumequine	FLQ	$\text{C}_{14}\text{H}_{12}\text{FNO}_3$	42,835-25-6	261.25	6.0	2.60	1.85	308	-
	Ofloxacin	OFL	$\text{C}_{18}\text{H}_{20}\text{FN}_3\text{O}_4$	82,419-36-1	361.37	5.5-6.2	-2.00	1.65	4000	-
	Oxolinic Acid	OXO	$\text{C}_{13}\text{H}_{11}\text{NO}_5$	14,698-29-4	261.23	5.6	1.70	1.00	3.2	-
	Sulfamethoxazole	SMX	$\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_5\text{S}$	723-46-6	253.28	2.0-6.2	0.89	3.19	610	-
	Trimethoprim	TMP	$\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3$	738-70-5	290.32	7.2	0.91	2.96	400	0/+
Analgesics	Acetaminophen	ACM	$\text{C}_8\text{H}_9\text{NO}_2$	103-90-2	151.16	9.6	0.46	1.79	14,000	0
	Codeine	COD	$\text{C}_{18}\text{H}_{21}\text{NO}_3$	76-57-3	299.36	8.2	1.28	3.12	577	+
	Tramadol	TRA	$\text{C}_{16}\text{H}_{25}\text{NO}_2$	27,203-92-5	263.37	9.4	3.01	2.91	1,151	+
Anticonvulsants	Carbamazepine	CBZ	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$	298-46-4	236.27	13.9	2.45	3.56	18	0
$\beta$ -blockers	Atenolol	ATE	$\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$	29,122-68-7	266.34	9.6	0.16	2.17	13,300	+
	Metoprolol	MET	$\text{C}_{15}\text{H}_{25}\text{NO}_3$	51,384-51-1	267.36	9.7	1.79	1.79	4,700	+
	Propranolol	PRP	$\text{C}_{16}\text{H}_{21}\text{NO}_2$	525-66-6	259.34	9.7	2.60	3.09	61.7	+
Non-Steroidal Anti-Inflammatory Drugs	Diclofenac	DCF	$\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{NO}_2$	15,307-79-6	296.15	4.2	4.02	2.92	2.37	-
	Ibuprofen	IBU	$\text{C}_{13}\text{H}_{18}\text{O}_2$	15,687-27-1	206.28	4.9	3.79	2.60	21	-
	Ketoprofen	KET	$\text{C}_{16}\text{H}_{14}\text{O}_3$	22,071-15-4	254.28	4.5	3.00	2.46	51	-
Psychotropic drugs	Oxazepam	OXA	$\text{C}_{15}\text{H}_{11}\text{ClN}_2\text{O}_2$	604-75-1	286.71	1.7-11.6	3.34	3.08	150	0
	Venlafaxine	VEN	$\text{C}_{17}\text{H}_{27}\text{NO}_2$	93,413-69-5	277.40	8.9	3.28	3.17	267	+
Pesticides										
Fungicide	Tebuconazole	TEB	$\text{C}_{16}\text{H}_{22}\text{ClN}_3\text{O}$	107,534-96-3	307.82	5.0	3.89	4.32	36	0
Herbicides	3,4 Dichloroaniline*	DCA	$\text{C}_6\text{H}_5\text{Cl}_2\text{N}$	95-76-1	162.02	3.0	2.37	2.08	92	0
	Atrazine	ATZ	$\text{C}_8\text{H}_{14}\text{ClN}_5$	1912-24-9	215.68	1.7	2.82	2.36	33	0
	Desethylatrazine*	DEA	$\text{C}_6\text{H}_{10}\text{ClN}_5$	6190-65-4	187.63	1.4	1.51	1.94	3200	0
	Deisopropylatrazine*	DIA	$\text{C}_5\text{H}_8\text{ClN}_5$	1007-28-9	173.60	1.5	1.15	1.75	670	0
	Hydroxyatrazine*	HTZ	$\text{C}_8\text{H}_{15}\text{N}_5\text{O}$	2163-68-0	197.24	4.6	2.09	2.25	5.9	0
	Chlortoluron	CHT	$\text{C}_{10}\text{H}_{13}\text{ClN}_2\text{O}$	15,545-48-9	212.67	-	2.58	2.13	70	0
	Diflufenican	DFF	$\text{C}_{19}\text{H}_{11}\text{F}_3\text{N}_3\text{O}_2$	83,164-33-4	394.30	-	4.90	5.04	0.05	0
	Isoproturon	ISO	$\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$	34,123-59-6	206.28	0.1	2.84	2.40	70	0
	Metolachlor	MTC	$\text{C}_{15}\text{H}_{22}\text{ClNO}_2$	51,218-45-2	283.79	-	3.24	2.47	530	0
	Nicosulfuron	NIS	$\text{C}_{15}\text{H}_{18}\text{N}_6\text{O}_6\text{S}$	111,991-09-4	410.41	4.8-7.6	0.60	1.33	7500	-
	Oxadiazon	OXD	$\text{C}_5\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_3$	19,666-30-9	345.22	-	5.33	3.54	0.7	0
	Prosulfuron	PRS	$\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}_5\text{O}_4\text{S}$	94,125-34-5	419.38	3.8	1.50	1.20	4000	-
	Pendimethalin	PEN	$\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_4$	40,487-42-1	281.31	11	3.95	4.05	2.6	0
	Simazine	SIM	$\text{C}_7\text{H}_{12}\text{ClN}_5$	122-34-9	201.66	1.6	2.40	2.17	6.2	0
	Terbutylazine	TER	$\text{C}_9\text{H}_{16}\text{ClN}_5$	5915-41-3	229.71	2.0	3.21	2.52	9	0
Insecticides	Imidacloprid	IMI	$\text{C}_9\text{H}_{10}\text{ClN}_5\text{O}_2$	138261-41-3	255.66	14	-0.41	3.83	50,000	0
	Tebufenozide	TEF	$\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$	112410-23-8	352.47	10.8	4.25	4.54	0.83	0

## 2.3. Enrichment and clean-up of samples

Sampled sediments and suspended solids were frozen and then freeze-dried during 48h. For sediments,  $1 \pm 0.1$  g was subsampled and crushed in a mortar, while for suspended solids, loaded filters were directly used for extraction. Samples were then spiked with 50 ng of each ILIS at 4°C overnight. Spiked samples were then extracted by pressurized liquid extraction, using ASE-350 (Thermo). The extraction mixture was MeOH and the operating temperature and pressure were 70°C and 1000 psi respectively. Extracts were then reduced to 1 mL using an EZ-2 evaporator (Biopharma Technologies), prior to refilling at 100 mL of milli-Q H<sub>2</sub>O. For water samples, 200 mL were aliquoted and spiked with 50 ng of each ILIS.

The next step was common to the three matrices investigated, the only difference being the sample volume for water samples (i.e. 200 mL) contrary to the 100 mL of solid samples. Solid-phase extraction (SPE) was performed on CHROMABOND-HLB columns (6 mL x 150 mg x 30 µm, Macherey-Nagel). Cartridges were conditioned with 5 mL of MeOH followed by 5 mL of ultra-pure water. Then, the cartridges were filled with the sample (100 or 200 mL) prior to flushing with 2 x 5 mL of ultra-pure water before drying for 30 minutes under vacuum. Finally, elution of TrOCs was performed with 2 x 5 mL of MeOH before drying under nitrogen flow and filtration at 0.22 µm (Nylon filter, VWR). Extracts were finally recovered in MeOH before injection. The analytical and quantification procedure is further detailed in the supplementary data (Tables S1-S2).

## **2.4. Instrumentation**

TrOC separation was achieved at 40°C with a Nucleoshell Biphenyl chromatographic column (2 mm x 100 mm x 2.7µm; Macherey-Nagel ) with a fritted disc (0.2 µm) used as pre-column, using a 1200 SL HPLC system (Agilent). The injection volume was 5 µL and the flow rate 0.65 mL.min<sup>-1</sup>. Two solvents were used as mobile phase, AcN (solvent A) and Milli-Q water (solvent B), both acidified with 0.1% of formic acid. The elution gradient was a transition from 98% to 0% of B in 9.5 min followed by 2 min of 100% of A and then a return to the initial conditions

(98% of B) during 2 min for a total analysis time of 15 min. The chromatography system was coupled to a 6410B triple quadrupole mass spectrometer (Agilent) equipped with a heated electrospray ionization (H-ESI) interface operating in positive mode ( $T^\circ$ : 350°C; Gas flow: 3 L.min<sup>-1</sup>; Nebulizer: 15 psi). The dynamic multiple reaction monitoring (dMRM) transitions and further details on the detection and quantification procedures are given in the supplementary data (Tables S2-S3).

## 2.5. Validation

The limits of quantification (LOQ) and limits of detection (LOD) of the method were calculated using the signal-to-noise (S/N) ratios (Table S4). LOD and LOQ were determined by extracting spiked (100 ng g<sup>-1</sup>) matrix-matched (n = 5) sediment samples. Then, LOD and LOQ were respectively calculated based on a ratio between spiked amount and S/N ratios multiplied by 3 and 10 for LOD and LOQ respectively. The recovery ratios were also evaluated in these experiments (spiking concentration = 100 ng g<sup>-1</sup>, n = 5), using the same extraction and quantification protocol as for the samples. Finally, during each analytical run, blanks and quantification controls were regularly used in order to crosscheck the quantification quality.

## 2.6. Geochemical analyses

The particle size of solid samples (i.e. sediments and SPM) was determined by an enhanced laser diffraction particle size analyzer (Beckman Coulter, LS 13 320 XR). The granulometer operates with sample cells designed for particles suspended in liquids (Universal Liquid Module). The total organic carbon (TOC) content of sediment and SPM samples was determined by elementary analysis after decarbonation of the bulk sediment with HCl (3M).

X-ray powder diffraction (XRD) patterns of the different samples were recorded on a Bruker - D2 Phaser with a Lynxeye detector diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ; 30kV, 10mA) and  $\Theta$ -2 $\Theta$  mounting (Bragg-Brentano geometry). Measurements were achieved for 2 $\Theta$

angles values between 2 and 70°, step 0.02° 2 $\Theta$ , on powdered samples (granulometry: 40 $\mu$ m). Relative quantification of the mineralogical phases was performed using Rietveld refinements (from Malvern Panalytical's HighScore Plus software) and assuming an error margin of 5%.

### 3. Results

#### 3.1. TrOC occurrences

The occurrences of TrOCs in the three matrices investigated (i.e. water, SPM and sediments) are presented in Table 2. Among the 35 TrOCs screened, all were detected at least once in one matrix.

In water, three molecules were not quantified: FLQ, PRS and TEF (Table S5). The quantification frequencies (QF) of the other TrOCs ranged from 10% (for DCA and OXD) to higher than 80%, for almost all the molecules. The maximum pesticide concentrations were tens of ng L<sup>-1</sup>, whereas for pharmaceuticals, hundreds of ng L<sup>-1</sup> were reached by 5 TrOCs, namely ACM, TRA, DCF, OXA and VEN.

In SPM, 6 TrOCs were not quantified (Table 2), and a limited amount of TrOCs exhibited very significant quantification frequencies with 9 molecules displaying QF values higher than 80%, including 7 pesticides. The concentrations ranged from around 1 ng g<sup>-1</sup> to several tens of ng g<sup>-1</sup> with an equivalent order of magnitude between pharmaceuticals and pesticides.

Finally, in sediments, one TrOC (i.e. DFF) was systematically quantified and on the other hand, 4 molecules (i.e. SMX, NIS, SIM and IMI) were not (Table S7). The median concentrations were around a few ng g<sup>-1</sup> and the quantification frequencies were very variable. The maximum concentrations of 9 molecules exceeded tens of ng g<sup>-1</sup> among which 8 pharmaceuticals.

Table 2: Minimum (min), median (med) and maximum (max) concentrations, in ng L<sup>-1</sup> for Water samples and ng g<sup>-1</sup> for Suspended Particulate Matter (SPM) and Sediments, of TrOCs for the whole collected dataset with n<sub>Q</sub> the quantification number, n.d. for not detected molecule.

		Water (n=20)				SPM (n=20)				Sediments (n=40)			
		min	med	max	n <sub>Q</sub>	min	med	max	n <sub>Q</sub>	min	med	max	n <sub>Q</sub>
<b>Pharmaceuticals</b>													
Antibiotics	FLQ	n.d.	n.d.	n.d.	0/20	n.d.	n.d.	n.d.	0/20	2.8	3.5	38.6	5/40
	OFL	2.1	9.7	25.1	19/20	n.d.	n.d.	n.d.	0/20	0.6	1.2	32.7	17/40
	OZO	1.0	2.9	5.3	20/20	1.9	1.9	1.9	1/20	1.9	4.4	6.3	6/40
	SMX	1.4	28.0	63.2	19/20	1.2	1.5	4.0	5/20	n.d.	n.d.	n.d.	0/40

	TMP	2.3	5.4	15.7	18/20	0.3	1.8	2.9	16/20	1.1	4.6	159.7	17/40
Analgesics	ACM	17.0	69.3	1171.5	20/20	1.2	7.7	83.3	15/20	0.6	1.0	2.5	10/40
	COD	0.5	12.7	57.5	18/20	n.d.	n.d.	n.d.	0/20	0.7	1.6	5.5	6/40
	TRA	4.0	61.8	335.2	19/20	2.7	14.0	95.0	20/20	0.8	6.4	212.9	26/40
Anti-epileptics	CBZ	1.2	33.7	81.9	20/20	2.0	3.2	16.7	12/20	0.8	2.1	4.6	11/40
$\beta$ -blockers	ATE	4.3	15.0	47.6	18/20	0.7	0.9	5.8	4/20	1.4	3.4	6.6	7/40
	MET	1.3	2.8	9.1	17/20	0.9	0.9	0.9	3/20	0.6	1.4	5.3	9/40
	PRP	1.4	15.0	57.0	20/20	0.8	1.5	20.2	13/20	0.4	4.6	43.7	30/40
NSAIDs	DCF	7.0	74.1	159.8	20/20	2.6	4.6	10.0	8/20	0.6	1.1	2.2	11/40
	IBU	9.8	14.3	29.9	6/20	7.7	11.8	15.8	2/20	1.9	2.8	11.5	10/40
	KET	3.5	6.9	60.1	19/20	1.5	2.6	5.5	8/20	5.1	8.3	67.1	3/40
Psychotropic drugs	OXA	6.4	36.9	112.5	16/20	2.1	18.4	38.0	6/20	1.8	5.5	11.6	8/40
	VEN	0.5	38.7	113.6	20/20	5.3	7.6	27.4	12/20	0.5	1.5	5.0	21/40
Pesticides													
Fungicides	TEB	1.3	2.9	4.4	20/20	0.9	2.5	8.2	19/20	0.4	0.6	1.3	21/40
Herbicides	DCA	2.8	3.8	4.9	2/20	1.2	3.4	4.3	4/20	2.0	3.3	9.7	17/40
	ATZ	7.6	11.4	18.6	20/20	0.2	0.6	2.6	15/20	0.3	0.4	0.4	4/40
	DEA	19.3	29.0	38.4	20/20	0.5	1.1	6.6	14/20	0.3	0.5	0.7	4/40
	DIA	4.3	6.5	12.4	20/20	n.d.	n.d.	n.d.	0/20	0.8	0.8	0.8	1/40
	HTZ	2.0	2.9	4.5	18/20	0.3	1.0	3.6	19/20	0.6	1.3	5.8	9/40
	CHT	1.9	18.3	29.0	20/20	0.9	2.7	29.3	17/20	0.5	1.3	4.5	24/40
	DFP	5.1	8.2	13.8	20/20	2.7	20.1	41.1	20/20	0.5	3.1	23.9	40/40
	ISO	0.9	1.4	3.1	7/20	0.5	0.8	12.0	6/20	0.3	0.4	0.5	2/40
	MTC	6.3	11.7	21.8	17/20	0.2	0.4	1.0	16/20	0.2	0.3	0.4	14/40
	NIS	1.8	9.3	20.3	7/20	n.d.	n.d.	n.d.	0/20	n.d.	n.d.	n.d.	0/40
	OXD	1.4	1.4	1.4	2/20	0.8	3.0	31.3	19/20	1.3	2.3	5.9	15/40
	PEN	2.7	6.2	8.5	20/20	2.2	5.3	22.8	20/20	1.0	2.3	9.6	33/40
	PRS	n.d.	n.d.	n.d.	0/20	2.6	2.7	2.8	2/20	0.2	0.3	1.1	8/40
SIM	0.6	2.9	26.5	20/20	1.1	1.7	3.2	5/20	n.d.	n.d.	n.d.	0/40	
TER	0.9	1.1	5.4	11/20	n.d.	n.d.	n.d.	0/20	0.6	0.7	1.8	3/40	
Insecticides	IMI	2.9	10.9	17.1	14/20	3.7	6.2	11.6	4/20	n.d.	n.d.	n.d.	0/40
	TEF	n.d.	n.d.	n.d.	0/20	1.8	2.2	11.7	7/20	1.3	1.8	2.9	11/40

## 3.2. Geochemical analyses

### 3.2.1. Dissolved samples

Beyond TrOC occurrence, some other parameters (Table S1) were measured on water samples in order to identify possible atypical samples. Whatever the station or the campaign, the pH value remained stable from station 5 onwards despite a slight decrease upstream from 8.2 to 8.0 during the first campaign, and from 8.3 to 8.2 during the second. Conversely, the conductivity increased steadily upstream to downstream, with higher values during the second campaign. During the second campaign, DOC concentrations increased up to station 10, then were stable downstream with values around 4.5 ppm, except for the stations located in the Rémarde river, which had higher concentrations (i.e. 5-5.5 ppm). During the first campaign, the same pattern occurred upstream, whereas downstream, much more variable values were measured (Table S1).

### 3.2.2. Solid samples

The TOC of both SPM and sediment samples was analysed, whereas the grainsize and mineralogical content of sediments only were assessed due to limited SPM availability. The mean TOC value of SPM samples was 6.8% with a minimum value of 3.1% and a maximum value of 11.9%, whereas the mean TOC value of sediment samples was 2.6% with a minimum value of 0.1 and a maximum value of 7.8%. For SPM samples, the TOC values were higher during the second campaign with an average value of 8.2% compared to the first campaign with an average value of 5.3%. The opposite pattern was observed for sediment samples, with a mean TOC value of 1.7% during the second campaign and of 3.5% during the first.

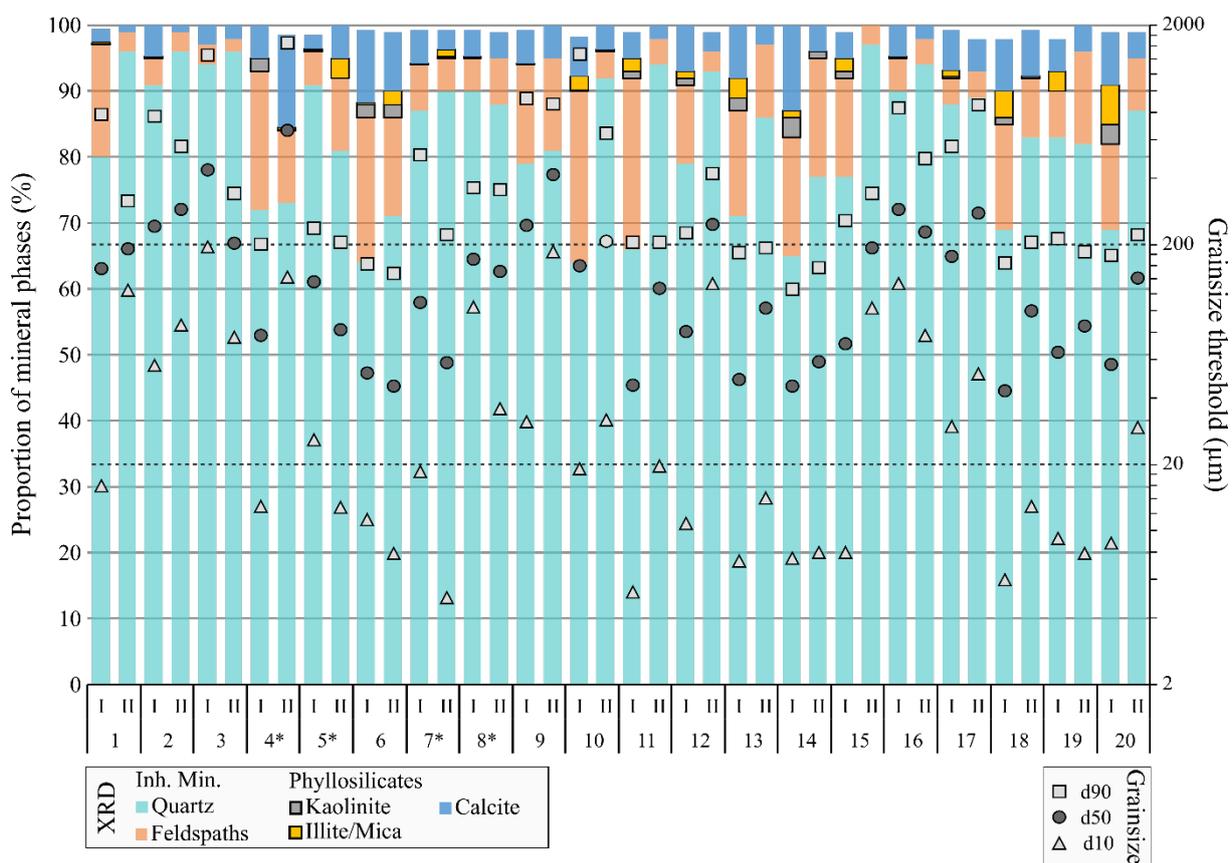


Figure 2: Mineralogical composition of each sediment sample, and grainsize threshold, with I for the October 2020 campaign, II for the February 2021 campaign and \* for stations sampled in the Rémarde river.

Quantification of the mineralogical phases approximated through Rietveld refinement revealed 5 major phases. Quartz was the major mineral, accounting for at least 60% (Figure 2). The

second most abundant phase was feldspaths with relative proportions between 2% and 26% and a mean value around 10%. The third most abundant phase were calcium carbonates, which were dominated by calcite despite some occurrences of aragonite and dolomite. For clarity, these minerals were grouped under the label Calcite; they represented between 0.5 and 14% of the mineralogical composition of the samples, with a mean value of 5%. The remaining phases were phyllosilicates which were separated into Kaolinite (for 1:1 clay minerals) and Illite/Mica (for 2:1 clay minerals). These minerals were not systematically present in the samples, and the maximum proportion of kaolinite was estimated at 3%, and 6% for illite/mica. It is worth noting that the proportion of quartz systematically increased for the same station during the second campaign. The only exception was station 5. This systematic increase in quartz content was accompanied by an almost general decrease in other mineralogical phases, mainly phyllosilicates and feldspaths (Figure 2). Hereafter, quartz and feldspaths will be grouped as inherited minerals, kaolinite and illite/mica as clay minerals, and all the carbonates are considered as calcite for clarity.

The particle size thresholds d10, d50 (i.e. median) and d90 are presented in Figure 2. D50 values ranged from 43 to 656  $\mu\text{m}$  with a mean value of 163. No clear spatial pattern related to these threshold values was found, highlighting the high variability of hydrodynamic conditions (i.e. accumulation or transport areas), however, what is worth pointing out between the two campaigns is the better particle size sorting during the second campaign, except for two stations, 4 and 16. This better sorting is emphasized by the decrease in d90, the increase in d10, or both (Figure 2).

## **4. Discussion**

### **4.1. Spatial distribution of TrOCs**

As often described in the literature, the main sources of pharmaceuticals are WWTP effluents. This is confirmed by the aqueous concentrations of pharmaceuticals (Figure 3), as the highest concentrations for each campaign were measured at station 7 (campaign I) or station 6 (campaign II), just downstream the major WWTP discharge. Station 4, on the Rémarde river, was also significantly contaminated due to upstream effluent discharge. Station 3, in contrast, was almost free of pharmaceutical contamination, except for antibiotics and ACM. From station 9 onwards, the overall pharmaceutical concentrations decreased slightly (Figure 3).

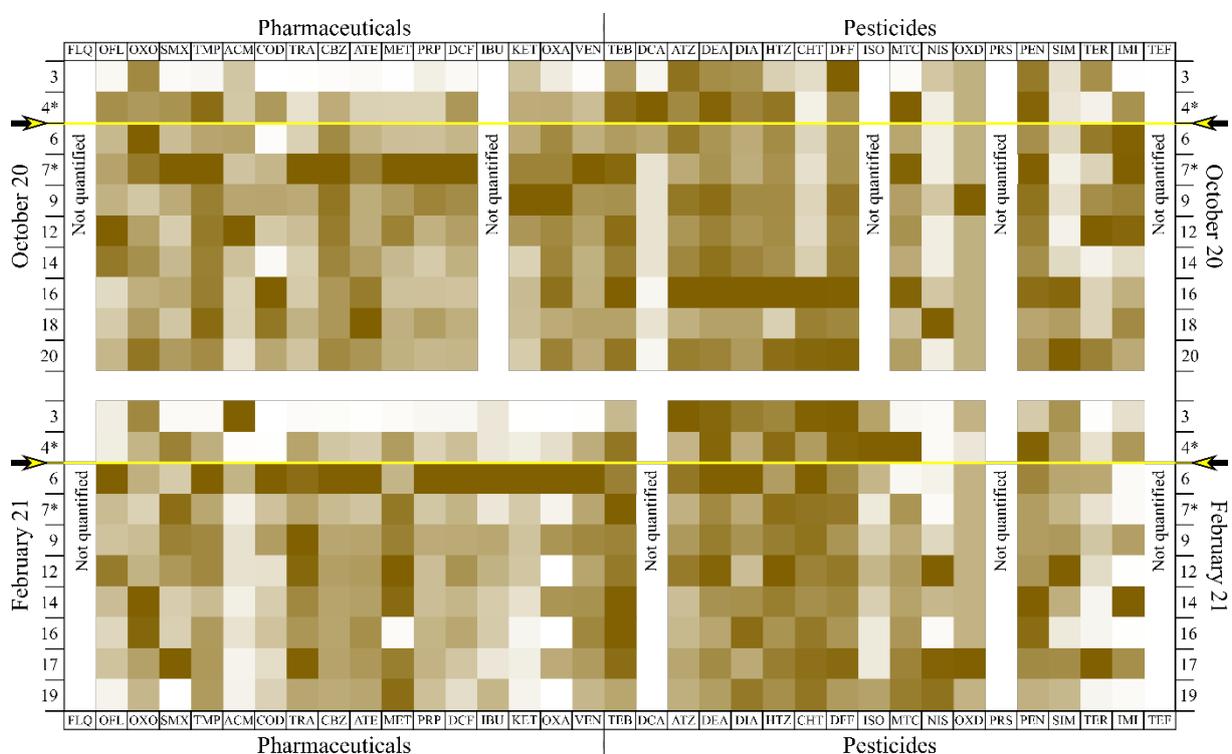


Figure 3: Spatial distribution of normalized (between 0 and 1) concentrations of TrOCs in aqueous samples for each sampling campaign. Full data are available in Table S5. Yellow arrows mark the WWTP effluent discharge locations.

The spatial distribution of pesticides in aqueous samples was less clear, which is unsurprising in view of their more diversified sources (i.e. diffuse and/or punctual). During campaign I, the most contaminated station was station 16, just downstream the confluence between the Orge and Salmouille rivers (Figure 1), whereas during the second campaign, pesticide concentrations

were predominantly higher at the most upstream stations, despite some exceptions (e.g. IMI, TEF) illustrating the potential diversity of sources.

Turning to the spatial distribution in sedimentary concentrations (Figure 4), with a focus on pharmaceuticals for which the source is better identified, some common points with the aqueous distribution were observed. Among the 14 pharmaceuticals investigated, only 2 (i.e. OXO and ACM) were quantified (and only 1 during the second campaign) within the Orge catchment and before WWTP effluent discharge (stations 1-3). The diversity of quantified pharmaceuticals strongly increased in Rémarde samples, and after the discharge of WWTP effluents in the Orge river stations. Sediments may therefore be considered as a good compartment in order to assess contamination diversity. However, whereas the aqueous distribution exhibited an increasing concentration followed by a decreasing plateau, the sedimentary occurrences are far more irregular with variations over several orders of magnitude as for example for PRP or DFF (Figure 4).

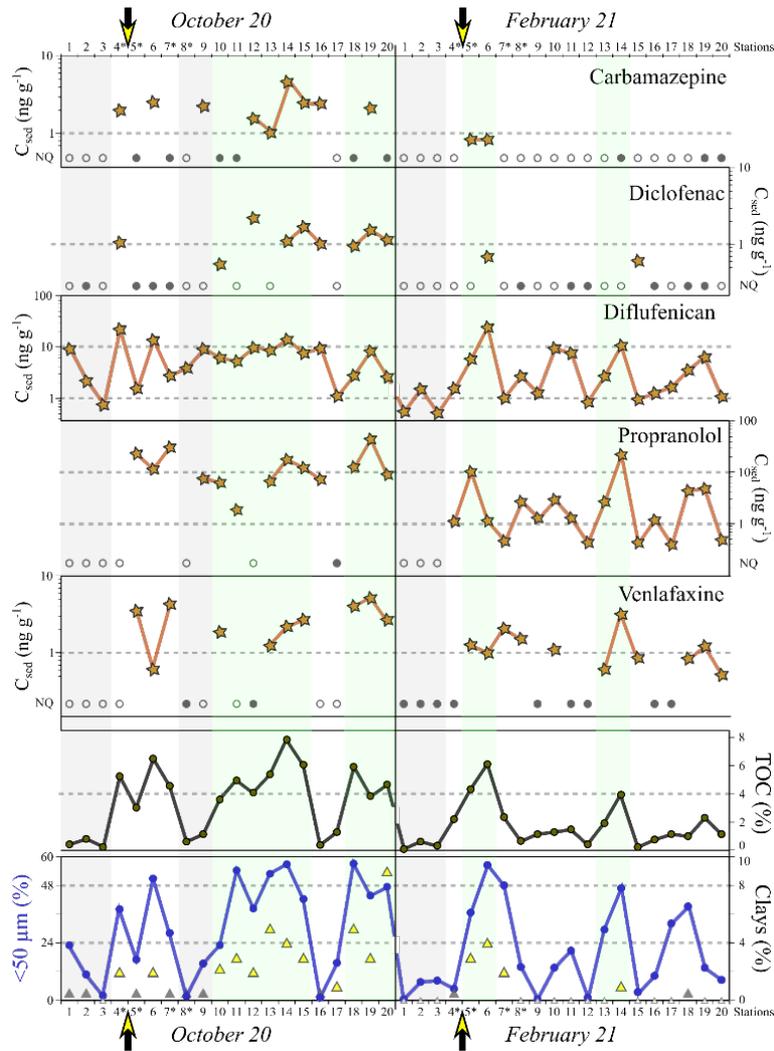


Figure 4: Spatial distribution of 5 TrOC sedimentary concentrations (Carbamazepine, Diclofenac, Diflufenican, Propranolol and Venlafaxine) in  $\text{ng g}^{-1}$ , the TOC in %, the mineralogical clay proportion (triangles) in % and grainsize  $<50\mu\text{m}$  percentage (blue squares) in %. White symbols mean  $<LOD$ , grey symbols mean  $<LOQ$ . Yellow arrows mark the WWTP effluent discharge locations and \* for stations sampled in the Rémarde river.

This erratic spatial distribution can be explained by the variation in sediment composition itself. From one station to another, the organo-mineral composition of sediments can change radically, from fine, organic and clay-rich composition, to coarse and mineral ones. It is obvious that these variations impact the sorption/partition extent of TrOCs onto sediments. For example, sample 14-II, which was organic-rich and fine, is heavily contaminated in comparison with 12-II which is coarse and mineral (Figure 4). It is therefore impossible to delineate a spatial distribution of TrOCs within riverine sediments without any normalization.

Conversely, SPM samples were devoid of coarse particles (even if grain size analyses were not performed on these samples) and more organic than sediment samples, and were therefore less heterogeneous along the water course. Some authors assume that the level of SPM contamination may be, in certain conditions, in equilibrium with that of the dissolved phase (Niu et al., 2021), which means that the solid/water partition coefficient (i.e.  $K_d$ ) can be used in order to link aqueous and solid contamination. Judging from our results, such an equilibrium is not clearly evidenced (Figure S1). Even if the TrOC diversity (i.e. especially for pharmaceuticals), and the cumulative TrOC concentration increased after the discharge of WWTP effluents during the two campaigns, the trend is less clear than in dissolved samples as the upstream station (i.e. 3) is contaminated by pharmaceuticals, and the impact of WWTP effluent discharge on the cumulative concentration is not clearly evidenced, particularly during the second campaign (Figure S1).

#### **4.2. Impact of hydrological conditions on TrOC occurrences**

The two sampling periods covered very different hydrological conditions. Whereas the first campaign, in October 2020, was performed during baseline water level conditions, the second one was performed in a flooding context. By comparing the geochemical analyses of the sediment samples between the two campaigns, the mean TOC value was 1.7%, the mean percentage of <50 $\mu$ m grain size was 20%, and clay minerals were quantified in 6 samples during the second campaign, whereas these values were respectively 3.5%, 31% and 19 samples during the first campaign (Figure 4). The impact of the resuspension of fine materials between the two campaigns strongly controls the whole sorption capacity of sediments (Stachel et al., 2005), which is particularly supported by TOC and fine grain size. The detection frequencies of TrOCs during the second campaign in sediments were therefore significantly lower than during the first campaign (Table S7), with median quantification frequencies of 30% during the first campaign and 10% during the second. The impact of the flood event on SPM contamination

was different, as SPM samples were more organic during the second campaign, highlighting either the resuspension of fine particles or erosion on the watershed (Lepage et al., 2020), and the hydrological continuity was also more pronounced, as underlined by the particularly stable DOC values during the second campaign, except for the Rémarde samples (Table S1). However, the TrOC occurrence was not significantly affected, as the same mean detection frequency of 44% was found for the two campaigns. During the flood event, both water flow and SPM flow increased, and in this study the SPM concentration was in the same order of magnitude. Considering that the solid/water partition is primarily controlled by the respective concentrations in the two matrices, and the fact that the geochemical properties of SPM did not dramatically change, it is logical to find similar concentrations during the two campaigns. It would obviously be very different if the reasoning were based on flow values (Poulier et al., 2019).

#### **4.3. What is the most representative solid matrix?**

As mentioned above, the monitoring of particulate concentrations of TrOCs is often neglected for some good reasons, such as their mostly hydrophilic character, and for some not so good reasons, such as the lack of representativeness of the sample (i.e. both spatial and temporal). However, these matrices are contaminated and it is important to assess their role in contaminant transfer within watersheds (Boulard et al., 2019), and what they have to tell us about the state of contamination of the environment. Our results show that the diversity of contaminants between the two matrices was almost the same (Figure 5), whereas the concentrations were systematically higher in SPM samples, even often within the same order of magnitude. It can be assumed that SPM are more favourable for the sorption of TrOC due to their higher TOC content and lower grainsize. This pattern is however not true for three molecules (TMP, PRP and ATE), all protonated at the occurring pH value. Therefore,  $\log K_{ow}$  (or  $K_{oc}$ ) was not the only parameter controlling the adsorption extent onto solid matrices (Hörsing et al., 2011; Li et

al., 2020), as the mean TrOC concentrations remained almost within the same order of magnitude whatever the hydrophobicity. However, what is worth noting is the overall higher quantification frequencies for hydrophobic contaminants (Figure 5).

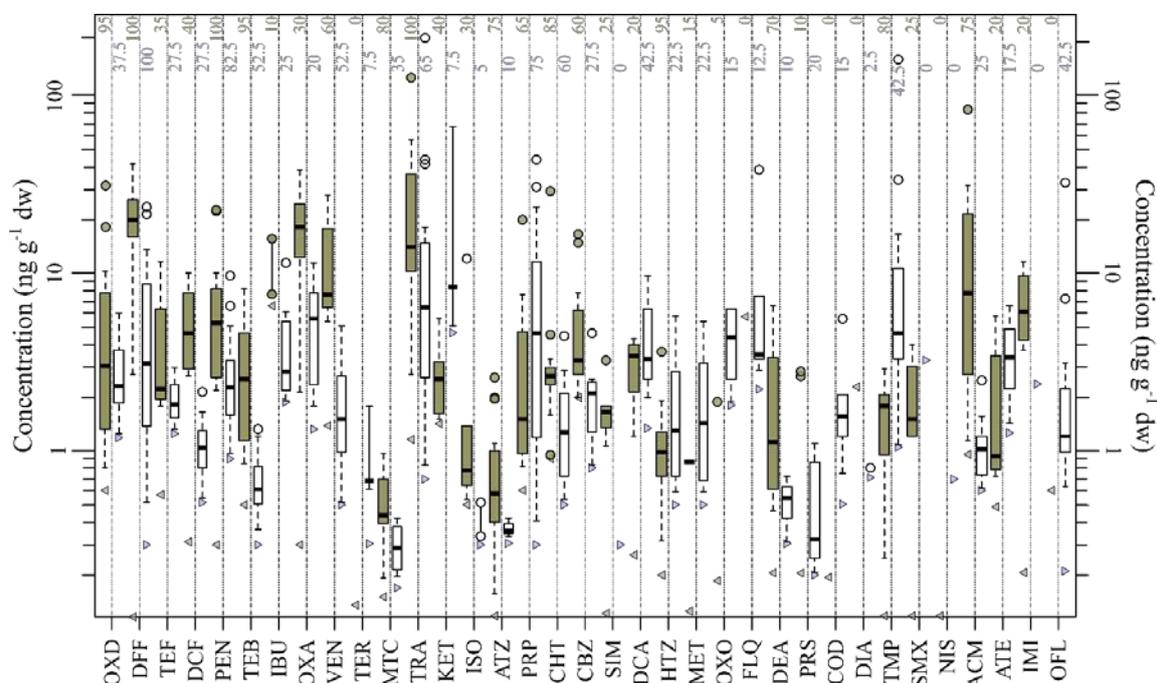


Figure 5: Boxplot of the TrOC concentrations in SPM (green box) and sediments (white box) sorted from the most hydrophobic (left) to the most hydrophilic (right) based on  $\log K_{ow}$  values. Triangles mark the LOQ for each matrix. The line within the box marks the median, boundaries indicate the 25<sup>th</sup> and 75<sup>th</sup> percentiles, error bars indicate the maximum and minimal value in  $\pm 1.5 \sigma$  variations and circles indicate individual values outside this range. Quantification frequencies are indicated in the upper part.

Therefore, SPM and sediment contamination appear to provide almost the same information about the contamination state of a water body, in terms of TrOC diversity. However, the more favourable organo-mineral properties of SPM imply higher levels of contamination, as previously observed for other contaminants (Dendievel et al., 2022), that may be easier to analyse and involve more consistent values for the evaluation of the chemical status.

#### 4.4. Relevant organo-mineral control of TrOC concentration

In this study, sediment samples were characterized in detail. Specifically, beyond the TOC content and grainsize measurement, XRD analysis was also performed. This dataset also benefits from a statistical analysis in order to understand the potential correlation between the

sediment properties and the TrOC occurrences (Figure 6). Indeed, organic carbon content is often considered as the main control of sedimentary occurrences of contaminants (Golovko et al., 2020), especially for hydrophobic contaminants (Castro and Vale, 1995). However, beyond organic carbon, some authors highlighted the impact of grainsize or even clay minerals (Kodešová et al., 2015; Sadutto et al., 2021). What reinforces the hypothesis of the impact of mineralogy is the frequent detection of very hydrophilic TrOCs in sediments (e.g. ACM, ATE), despite their high water solubility and theoretical low susceptibility to sorption (López-García et al., 2021; Thiebault et al., 2021b).

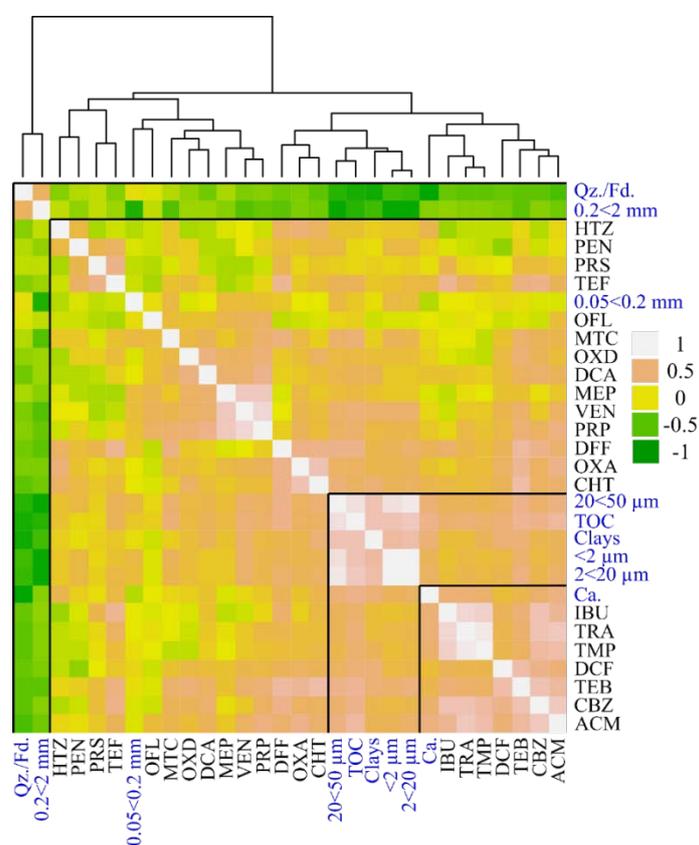


Figure 6: Heatmap analysis of the correlation coefficients between TrOC sedimentary concentrations and geochemical sediment analyses (full data Table S8)

According to the results of the statistical analysis, two parameters were anti-correlated with the others in a first cluster (Figure 6), namely inherited minerals (i.e. quartz and feldspaths) and coarse granulometry. This is unsurprising, as these two parameters are significantly correlated (Table S8) and are not favourable for the sorption of TrOCs due to their limited specific surface

and reactivity. The other organo-mineral parameters of sediment (fine grainsize, clays and TOC) are all strongly intercorrelated. It is unfortunately impossible to clearly distinguish the respective impact of each of them, as 15 out of the 21 TrOCs are significantly correlated with both TOC and fine grainsize (Table S8). An attempt at correlation assessment using the sediment/water partition coefficient did not provide more precise results (Figure S2), and resulted in an almost identical clusterization.

Yet, what is worthy of note is the lack of TrOCs sorted by physico-chemical properties, reinforcing the assumption that in this context with significant spatial variations in TrOC aqueous concentrations, the source effect strongly impacts the solid/water partition of TrOC as well. Further work is required to clearly distinguish the impact of each organo-mineral parameter on TrOC occurrence, especially in highly urbanized areas carrying very diverse materials (Rivett et al., 2019).

## **5. Conclusion**

The sediments of the Orge river catchment displayed a varied organo-mineral composition, with a low organic carbon content (i.e. between 0.5 and 8%) and clay mineral content (i.e. between 0 and 9%). This is consistent with conventional knowledge of river sediments, as is the fact that SPM were more organic and fine than sediments. This impacted the diversity and the concentration level of TrOCs within these two matrices as SPM displayed more diverse and concentrated contamination with higher detection frequencies than sediments among the 35 TrOCs investigated.

While it was not possible from a statistical point of view to clearly discriminate the respective impact of mineralogical composition, grainsize and TOC on the TrOC occurrences, it was clear that fine grainsize, high clay and TOC content are significantly correlated and can be considered as favourable for TrOC sorption. The impact of a flood particularly, generating the

resuspension of fine particles from sediments, strongly contributes to validating this assumption.

From a spatial point of view, whereas the TrOC pattern in water samples was clearly impacted by WWTP effluent discharge, this was less clear concerning the two solid matrices. Environmental solids (i.e. SPM and sediments) have the potential to point out TrOC diversity along a watercourse to a certain extent, but the question of representativeness and standardisation of TrOC content still requires research.

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