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## Sediments accumulated in sewer settling basins as recorders of historical use of drugs: Potential and limitations

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### ABSTRACT

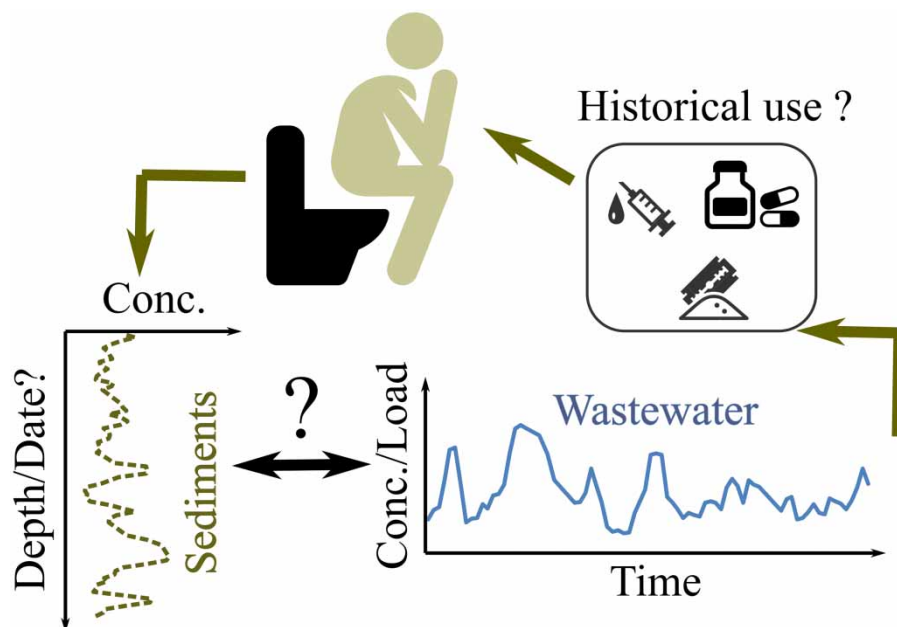
This study assesses the occurrence of various types of drugs in a sedimentary archive cored in a sewer settling basin with a depth of 14 m. The coring operations were conducted before the basin was drained. A 2.2-m long sedimentary core was recovered. The sediments consisted of successions of coarse minerals and coarse or fine organic layers. One of the main challenges is to be able to date such a very recent archive. This was realized by using an event-based approach with 19 <sup>14</sup>C Carbon dating out of the rising and decay phase of atmospheric <sup>14</sup>C content linked to the aerial explosion of thermonuclear bombs (bomb peak). The first results revealed the potential of these sediments to record diverse contaminants. Eighteen of the 20 molecules targeted were quantified at least once. The potential of such archives to record the first use of each drug in the city is questioned, as well as the potential of back-calculated drug consumption on the basis of sedimentary occurrences. The estimated wastewater concentrations fit quite well for some molecules, whereas further work remains necessary for other drug values, especially concerning the back-calculation parameters.

**Key words:** archive, illicit drugs, pharmaceuticals, sediments, wastewater-based epidemiology

### HIGHLIGHTS

- The dynamics of sedimentation was performed using postbomb <sup>14</sup>C dating.
- Sediments accumulated in the sewer settling basin record a wide diversity of drug target residues.
- The vertical distribution of drug target residues is consistent with market knowledge and opens up new perspectives in estimating historical consumption for some drugs.
- Sediment-based epidemiology necessitates further work but seems promising.

## GRAPHICAL ABSTRACT



## INTRODUCTION

The occurrence of drugs (i.e. pharmaceutically active compounds and illicit drugs) in numerous environmental compartments raises serious concerns about their potential hazard for living beings (Richmond *et al.* 2018). A significant part of the current literature focuses on both assessing the removal of organic contaminants in classical wastewater treatment plants (Wilkinson *et al.* 2017) and optimizing their removal via tertiary treatments (Altmann *et al.* 2015).

However, wastewater treatment plant influents (WWIs) could also represent a tremendous source of information because of the link between their chemical composition and the excretion of various chemical compounds by the population in the catchment (Castiglioni *et al.* 2014; Choi *et al.* 2018). Several studies have demonstrated the consistency of such analyses on illicit drugs and pharmaceutically active compounds to back-calculate the consumption of the population (Baker *et al.* 2014). This new scientific discipline has been called wastewater-based epidemiology and currently investigates not only the chemicals consumed as pharmaceuticals but also passive exposure to other markers, such as industrial chemicals and pyrethroid pesticides (Rousis *et al.* 2017; Lopardo *et al.* 2019), among many examples. Such studies provide near real-time dynamics of practices, whereas the assessment of past uses is not accessible.

However, several studies have highlighted the potential of sedimentary archives to record such historical use or historical environmental contamination through analyses of the vertical distributions of drugs and other contaminants (Klaminder *et al.* 2015; Thiebault *et al.* 2021a). Among these latter studies, few described the distribution of contaminants within silt traps (Flanagan *et al.* 2021; Wei *et al.* 2023), directly in the sewer system, as sampled sediments are generally coarse and therefore considered unfavourable for the trapping of organic molecules owing to limited reactivity (Crabtree 1989). One of the major advantages of settling basins, considering consumption/excretion amount assessment, is their position upstream in the sewer network and wastewater treatment plant and close to excretion areas (Karlsson *et al.* 2010; Spahr *et al.* 2020). As a result, settling basin sediments are potentially able to record a wider variety of contaminants than are riverine sediments because of the significant degradation or removal of some contaminants during wastewater treatment (Castiglioni *et al.* 2006; Behera *et al.* 2011).

A common prerequisite to assess the historical distribution of organic molecules within sedimentary cores is also to be able to build a robust age-depth model that establishes a relationship between depth and age. Whereas  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  are classically used to date the sediments of the 20th century (Kirchner & Ehlers 1998), very recent sediments retrieved in settling basins necessitate new dating processes (Kaizer *et al.* 2020).

In this study, we analysed the occurrence of drugs in a core sampled from a settling basin with the following objectives: (i) investigate the occurrence and vertical distribution of drugs in this record; (ii) date such archives for which curation operations were not recorded and propose an age-depth model highlighting the first detection of drugs; and (iii) evaluate the potential of such archives to perform sediment-based epidemiology, considering that settling basins are close to excretion sources, before the wastewater treatment plant removal effect, and therefore potentially record a wide diversity of drugs.

## METHODS

### General settings and sample collection

The 'Chambre à Sable' (CSA, [Figure 1](#)) settling basin is a 17-m deep 8-m diameter cylindrical and then conical underground building, with an estimated volume of 440 m<sup>3</sup>, situated on the Loire River dockside in Orléans, France. The CSA annually collects 7.10<sup>6</sup> m<sup>3</sup> of water (i.e. flow ranges from 1 to 4 m<sup>3</sup> s<sup>-1</sup>) from the combined (i.e. wastewater and stormwater) sewer network that drains the northern part of the Orléans conurbation, 100 km south of Paris. The construction of this building in 1942 initially aimed at removing coarse fractions from water discharged directly into the Loire River ([Jacob et al. 2020](#)). In the early 1970s, the exit flow was redirected to two wastewater treatment plants.

In 2014, a renovation of the CSA was performed by local authorities to facilitate cleaning operations and modify flow management to limit the direct discharge of wastewater into the Loire River during intense precipitation events. This represented a unique opportunity to perform the coring of this settling basin that has presumably never been cleaned since its building. The coring occurred in February 2015, prior to the major cleaning that removed ~7 m of sediment in May 2015 ([Figure 1](#)).

Among the several cores sampled in this settling basin ([Thiebault et al. 2021b](#)), core CSA-02-2015-A is 2.54 m long and was collected with a UWITEC gravity corer, whereas the coring potential was expected to be 14 m. The top sediment was recorded 33.5 cm from the top of the coring tube, which corresponds to an altitude of -2.9425 m from the technical platform ([Figure 1](#)). The depths given below are homogeneously relative to the top of the tube.

The core was cut into two sections; A1, 1.5 m long, and A2, 1.08 m long. Both sections were split into two halves ('work' and 'archive') and the macroscopic facies description was performed (Supplementary material, Table S1). A total of 72 samples were then taken following the lithology of the 'Work' half core. One sub-sample was taken from each observed facies (Supplementary material, Table S1), ranging from 0.5 to 20 cm in thickness ([Figure 2](#)).

### Granulometry and bulk organic geochemistry

After drying, granulometry analysis of all the samples ( $n = 72$ ) was conducted by sieving 20 g of sediment through four screens of different square mesh sizes (>1 mm; >200 μm; >50 μm and <50 μm). The rejects were collected and weighted.

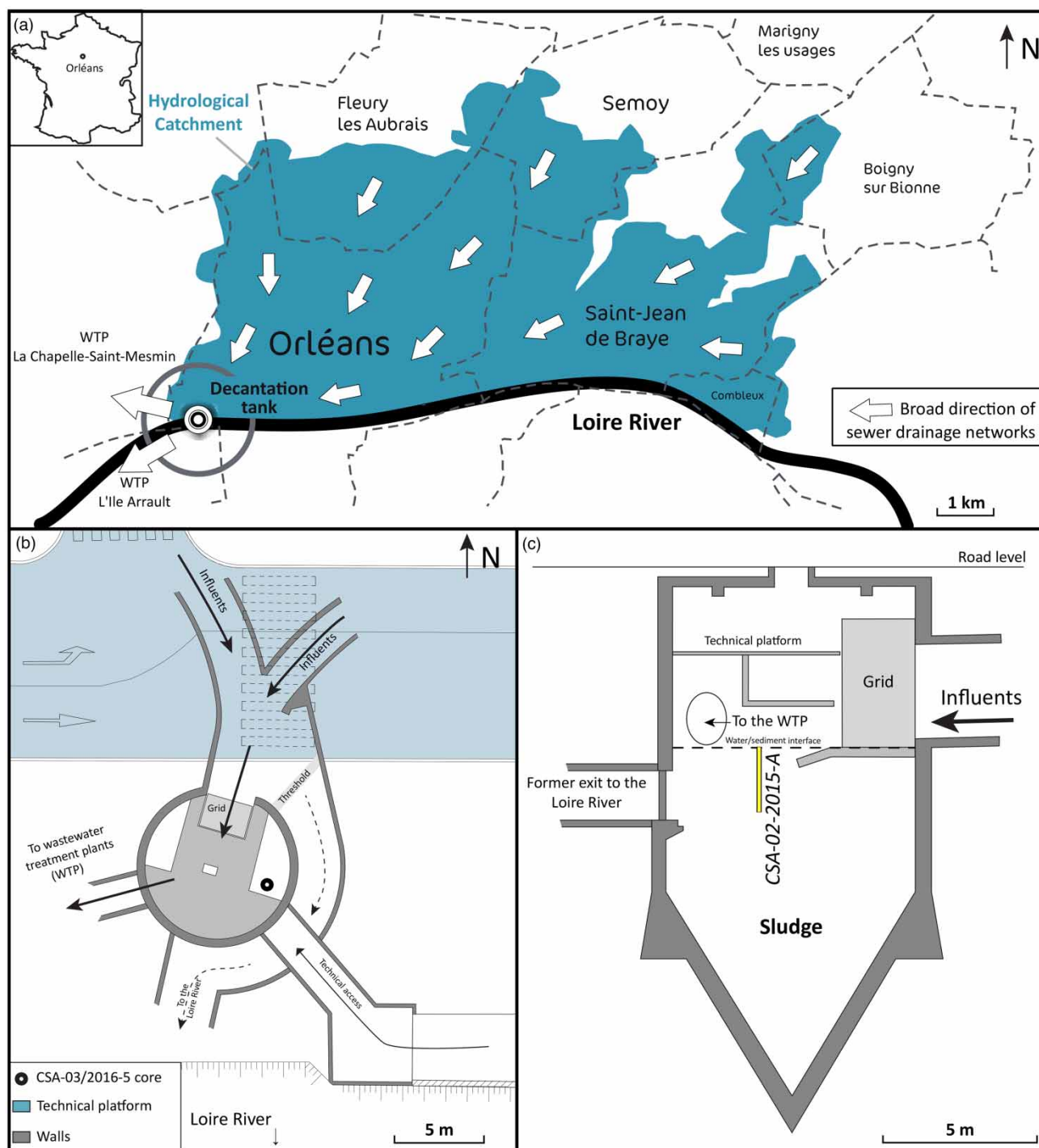
The 50–200 μm of fraction was used to determine the total organic carbon (TOC) (in %) via Rock-Eval6 (Vinci Technologies, Rueil-Malmaison, France) pyrolysis ([Behar et al. 2001](#)).

### Chemical reagents

Standards for acetaminophen (ACM), atenolol (ATE), bezafibrate (BZB), carbamazepine (CBZ), codeine (COD), diazepam (DIA), diclofenac (DCF), ibuprofen (IBP), ketoprofen (KET), metoprolol (MET), oxazepam (OXA), salicylic acid (SCA), sulfamethoxazole (SMX), tramadol (TRA), and trimethoprim (TMP) were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France) with purities >98%. The standards for benzoylecgonine (BZE), cocaine (COC), 3,4-methylene-dioxy-N-methylamphetamine (MDA), methadone (MED) and morphine (MOR) were purchased from LGC Standards (Wesel, Germany). Further information about the selected contaminants and their physicochemical properties is given in [Table 1](#). The extraction and separation solvents dichloromethane (DCM), methanol (MeOH) and acetonitrile (AcN) were purchased from Thermo Fisher-Scientific (Illkirch-Graffenstaden, France) and were of analytical grade (purity up to 99.95%).

### Sample extraction

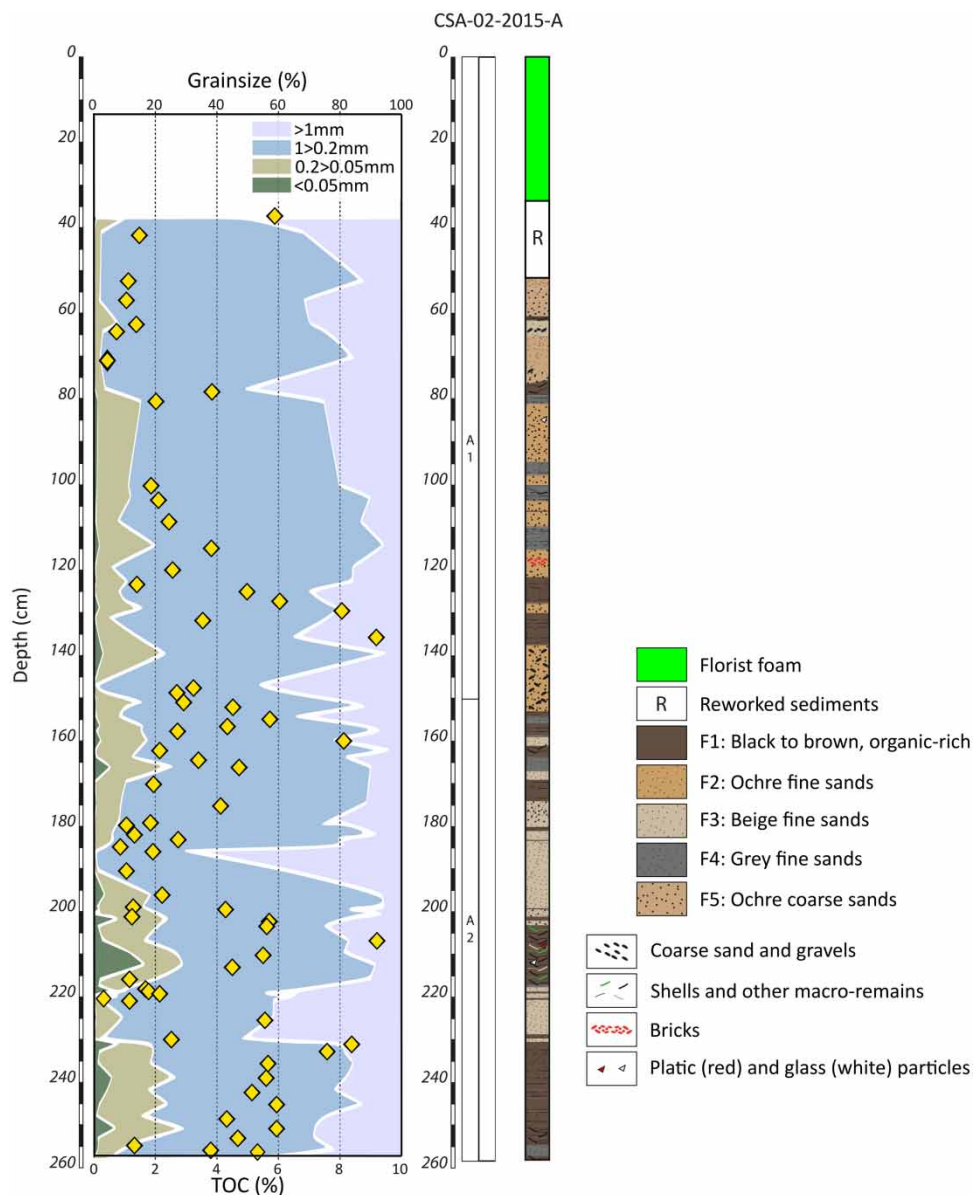
One gram of the 50–200 μm of granulometric fraction was extracted via pressurized liquid extraction via an accelerated solvent extractor (ASE-200, Dionex, Sunnyvale, CA, USA). The extraction mixture was MeOH/H<sub>2</sub>O (1:1 v/v); the operating temperature and pressure were 100 °C and 6,895 kPa, respectively. The extracts were then fully dried at 60 °C under nitrogen flow and stored at -18 °C. The extracts were recovered in ultrapure water acidified with 0.1% formic acid before liquid chromatography analysis. Standards and controls were prepared with surface waters sampled from the Loiret River (filtered at 0.22 μm), which, after analysis, were found to be deprived of drugs.



**Figure 1** | (a) Location of the 'Chambre à Sable' settling basin collecting both wastewater and stormwater from the combined sewer network that drains the northern hydrological catchment area of Orléans conurbation; (b) aerial map of the 'Chambre à Sable'. View from above at the Quai Madeleine with influents and flow directed towards wastewater treatment plants; (c) Cross section of the basin, illustrating the technical platform and water/sediment interface before the 2015 cleaning operations. The sampled core CSA-02-2015-A is shown in yellow.

### Quantification and validation

Drug separation was achieved at 30 °C and a flow rate of 0.4 mL min<sup>-1</sup> with a Nucleodur C<sub>18</sub> Gravity column (150 mm × 2 mm × 1.8 μm, Macherey-Nagel, Hoerd, France) supplemented by a guard column using an Ultimate 3,000 RSLC



**Figure 2** | Total organic carbon (TOC, yellow diamonds, in %), grain size distribution in four major fractions in % of the sampled sediments, calibrated years of  $^{14}\text{C}$  dating and sediment description with depth from the top tube (cm), each facies corresponds to one sub-sample.

(Thermo Fisher-Scientific, San Jose, CA, USA) ultrahigh-performance liquid chromatography system equipped with a binary pump. The injection volume was  $3\ \mu\text{L}$ . Ultrapure water (A) and AcN (B), acidified with 0.1% formic acid, were used as the mobile phase. The elution gradient was a transition from 95 to 5% A in 16.2 min followed by 0.3 min of 100% B and then a return to the initial conditions (95% A) for 3.35 min for a total analysis time of 19.85 min. The chromatography system was coupled to a TSQ Endura triple quadrupole mass spectrometer equipped with a heated electrospray ionization (H-ESI) interface (Thermo Fisher-Scientific, San Jose, CA, USA) at a flow rate of  $0.3\ \text{mL}\ \text{min}^{-1}$ .

An electrospray ionization source was used for quantification, operating in positive mode (except for SCA), with a vapourizer temperature of  $425\ ^\circ\text{C}$ , an ion transfer temperature of  $325\ ^\circ\text{C}$ , an electrospray voltage of 3,600 V, an auxiliary gas of 20 Arb, a sheath gas of 50 Arb, and a sweep gas of 1 Arb. Xcalibur 2.2 software was used to evaluate the qualitative and quantitative analysis of the selected drugs.

**Table 1** | Physicochemical properties of the targeted drugs

Class/Drug	Abb.	Formula	CAS-Number	$M_w$	$pK_a^a$	$\log K_{oc}^b$	Charge	MAD
<i>Antibiotics</i>								
Norfloracin	NOR	$C_{16}H_{18}FN_3O_3$	70458-96-7	319.33	5.77–8.68	1.96	+ / –	1985
Sulfamethoxazole	SMX	$C_{10}H_{11}N_5O_3S$	723-46-6	253.28	6.16–1.97	3.36	–	1968
Trimethoprim	TMP	$C_{14}H_{18}N_4O_3$	738-70-5	290.32	7.2	2.96	0	1968
<i>Benzodiazepines</i>								
Diazepam	DIA	$C_{16}H_{13}ClN_2O$	439-14-5	284.74	3.40	4.05	0	1963
Oxazepam	OXA	$C_{15}H_{11}ClN_2O_2$	604-75-1	286.97	1.7–11.6	3.08	0	1965
<i><math>\beta</math>-blockers</i>								
Atenolol	ATE	$C_{14}H_{22}N_2O_3$	29122-68-7	266.34	9.6	2.17	+	1978
Metoprolol	MET	$C_{15}H_{25}NO_3$	56392-17-7	267.36	9.6	1.79	+	1974
Acetaminophen	ACM	$C_8H_9NO_2$	103-90-2	151.16	9.4	1.59	0	1964
Diclofenac	DCF	$C_{14}H_{11}Cl_2NO_2$	15307-79-6	296.15	4.15	3.52	–	1950
Ketoprofen	KET	$C_{16}H_{14}O_3$	22071-15-4	254.28	4.45	2.46	–	1970
Salicylic acid	SCA	$C_7H_6O_3$	69-72-7	138.12	2.79	2.60	–	1899
Codeine	COD	$C_{18}H_{21}NO_3$	76-57-3	299.36	8.21	3.12	+	1840
Morphine	MOR	$C_{17}H_{19}NO_3$	57-27-2	285.34	8.21	3.47	+	1833
Methadone	MED	$C_{21}H_{27}NO$	76-99-3	309.45	9.12	4.86	+	1995
Tramadol	TRA	$C_{16}H_{25}NO_2$	27203-92-5	263.37	9.41	2.91	+	1997
<i>Other pharmaceuticals</i>								
Bezafibrate	BZB	$C_{19}H_{20}ClNO_4$	41859-67-0	361.82	3.87	3.17	–	1982
Carbamazepine	CBZ	$C_{15}H_{12}N_2O$	298-46-4	236.27	13.9	3.59	0	1964
Benzoylcegonine	BZE	$C_{16}H_{19}NO_4$	519-09-5	289.33	3.15-9.54	2.55	+	n.d.
Cocaine	COC	$C_{17}H_{21}NO_4$	50-36-2	303.35	8.61	3.28	+	n.d.
MDMA	MDA	$C_{11}H_{15}NO_2$	42542-10-9	193.24	10.14	2.70	+	n.d.

Here,  $M_w$  is the molecular weight in  $g\ mol^{-1}$ ,  $pK_a$  is the acid dissociation constant,  $\log K_{ow}$  is the octanol/water partition coefficient,  $\log K_{oc}$  is the organic carbon partition coefficient, Charge is the dominant form at  $pH = 7.5$ , MAD the market authorization date.

<sup>a</sup>drugbank.ca.

<sup>b</sup>chemspider.com (predicted, PCKOCWIN v1.66 estimate).

The following procedure was systematically used for the analysis validation: a calibration curve (six standards from 0.5 to 100  $ng\ L^{-1}$ ), followed three times by four samples, one quantification control (a standard at 5  $ng\ g^{-1}$ ) and one blank (pure water), and finally, another calibration curve. This procedure allowed the assessment of the drift of the analysis between each calibration curve, as described in other studies (Thiebault *et al.* 2017b). According to classical organic analysis, the limits of quantification (LOQ) and limits of detection (LOD) were calculated with signal-to-noise ratios of 3 and 10, respectively. The linearity considers the three calibration curves that frame the sample analysis and was determined by the linear correlation coefficient  $r^2$ . Recovery values were calculated by first extracting three randomly selected sampled sediments with a DCM/MeOH (9:1, v/v) mixture to avoid all the drugs (Thiebault *et al.* 2021b). Then, a concentration of 100  $ng\ g^{-1}$  for each drug was spiked onto these sediments prior to extraction, which was carried out following the same procedure (MeOH/H<sub>2</sub>O, 1:1, v/v) and compared to the standard injection value.

### Sediment and drug first occurrence dating

Nineteen <sup>14</sup>C datings (Table 2) were obtained from the LSCE (Laboratoire des Sciences du Climat et de l'Environnement; GifA/ECHO lab identification) and Poznań Radiocarbon Laboratory (Poz lab identification). The organic materials visible in the core were sampled, identified and selected for <sup>14</sup>C dating according to their nature. Short-lived materials were selected, giving preference to seeds. The idea is to integrate the shortest possible period of time and thus achieve a fine dating in time. They have been

**Table 2** | Identification, depth and error, material, laboratory code pMC (percent modern carbon) and F<sup>14</sup>C results of samples of core CSA-02-2015 selected for <sup>14</sup>C dating

Section	Depth (m)	Depth error (m)	Material	Laboratory code	pMC	± (error)	F <sup>14</sup> C	± (error)
A1	0.528	0.018	Rubus sp. seed	GifA21217 – ECHo 4257	105.02	0.29	1.050	0.003
	0.573	0.033	Rubus sp. seed	GifA21218 – ECHo 4258	103.83	0.28	1.038	0.003
	0.608	0.008	Grape seed	GifA21219 – ECHo 4259	104.98	0.29	1.050	0.003
	0.621	0.000	Grape seed + twig	Poz-80772	104.27	0.34	1.043	0.003
	0.626	0.010	Rubus sp. seed	GifA21220 – ECHo 4260	104.19	0.28	1.042	0.003
	0.706	0.055	Rubus sp. seed	GifA21221 – ECHo 4261	103.22	0.28	1.032	0.003
	0.776	0.000	Grape seed + twig	Poz-80769	115.19	0.36	1.152	0.004
	0.801	0.010	Rubus sp. seed	GifA21222 ECHo - 4262	115.90	0.31	1.159	0.003
	0.988	0.013	Rubus sp. seed	GifA21223 ECHo - 4263	120.35	0.32	1.204	0.003
	1.011	0.000	Grape seed	Poz-80770	118.68	0.35	1.187	0.004
	1.241	0.000	Grape seed	Poz-80771	122.76	0.34	1.228	0.003
	1.328	0.014	Twig	GifA17461 – ECHo - 2055	122.15	0.31	1.222	0.003
	1.331	0.000	Nut	Poz-80774	121.21	0.36	1.212	0.004
A2	1.576	0.000	Grape seed	Poz-80768	122.27	0.37	1.223	0.004
	1.746	0.000	Grape seed	Poz-80764	127.00	0.36	1.270	0.004
	1.806	0.003	Seed	Poz-80767	125.91	0.36	1.259	0.004
	2.156	0.000	Seed	Poz-80762	127.51	0.38	1.275	0.004
	2.171	0.000	Seed	Poz-80766	126.65	0.36	1.267	0.004
	2.511	0.000	Grape seed	Poz-80765	126.61	0.38	1.266	0.004

sent for dating either to the LSCE for the smaller ones, or to Poznan for the larger ones. The LSCE operates a MICADAS that can run samples down to a few tens of µg of carbon (Thil *et al.* 2024). In the laboratory, samples are chemically treated to remove potential contaminants from the sand chambers (e.g. Hatté *et al.* 2023). Those for which several hundred µg of carbon were accessible were transformed into CO<sub>2</sub> and reduced in the form of C graphite. At LSCE, these operations are combined and carried out using an automatic system, AGE3; at Poznan, the two operations are carried out separately. Measurements are carried out using the ECHoMICADAS solid source or the Poznan AMS. The smallest samples (after chemistry) were introduced as CO<sub>2</sub> into the ECHo gas source via a gas interface system connected to an elemental analyzer (EA-GIS).

In both laboratories, normalization standards, blanks and reference materials of equivalent matrix and surrounding age are measured at the same time as the samples. These are used to standardize results and check the reliability of all sample processing steps. In line with community recommendations, results are reported as F<sup>14</sup>C (fraction of modern carbon). Throughout the manuscript, the core depths correspond to the sediment-depth from the core top (see Figure 2), with the top sediment being ~2.943 m below the platform (Figure 1(c)). The depth error corresponds to the thickness of the layer in which the material was found. If zero, it corresponds to the exact depth of the sample.

F<sup>14</sup>C data were computed via Bayesian chronological modelling with ChronoModel (Lanos & Dufresne 2024) 3.2.7 software. Since the CSA was built after 1945, F<sup>14</sup>C data have been calibrated by restricting the range of possible ages to the period post 1945. The bomb13 calibration curve for the Northern Hemisphere zone 1 was used (Hua *et al.* 2013), considering that the grape whose seeds were dated came from this geographical area. This curve was extended for 2010–2015 with data from Graven *et al.* (2017). The 19 F<sup>14</sup>C data and their depths were considered stratigraphic successions of events incorporated into a single phase that terminated on top of the sedimentary sequence (Supplementary material, Table S2), dated from February 2015 (coring date). The study period was considered to be from 1947 to 2016. The Markov chain Monte-Carlo settings were as follows: three chains, 1,000 iterations during the burn-in phase, 200 iterations during the adaptation phase, and 1,000,000 iterations during the acquisition phase.

The age-depth model was then used in the ChronoModel ('ChronoCurve' tool) as a calibration curve for determining the date of deposition of the 72 samples, taking into account their mean depth and thickness for depth and depth error (Supplementary material, Table S3). The same approach and calibration curve were applied to evaluate the date of appearance of specific molecules (TRA, MED, MOR, paracetamol, and ATE). The depth at which the first occurrence of a molecule occurred was considered the mean depth between the deepest sample with > LOQ concentration followed by quantification and the sample below. The depth error was half the difference between the two sample depths.

## RESULTS

### Sediment description

As expected in view of the role of the settling basin, the sediments were very coarse with very limited fine particle contents (i.e.  $<50\ \mu\text{m}$ ), which were mostly approximately 1% (with minimum and maximum values of 0.05 and 16.1%, respectively) all along the profile, with a main contribution of  $0.2 < 1\ \text{mm}$  fractions with a median of 74.8% (Figure 2).

Five distinct facies (F1, F3, F5, and less frequent F2 and F4) can be distinguished and are repeated across the core into 39 distinct and successive units (Figure 2, full description in Supplementary material, Table S1). F1 corresponds to brownish/black organic layers, F2 to ochre fine sands, F3 to beige fine sands, F4 corresponds to grey fine sands, and F5 corresponds to ochre coarse sands.

Glass and plastic particles, shells, brick pieces, and numerous seeds were found over the core.

The TOC content varied widely, with values ranging from 0.4 to 9.2%. Higher TOC contents were generally observed in specific layers (Figure 2), particularly the F1 facies.

### Sediment dating

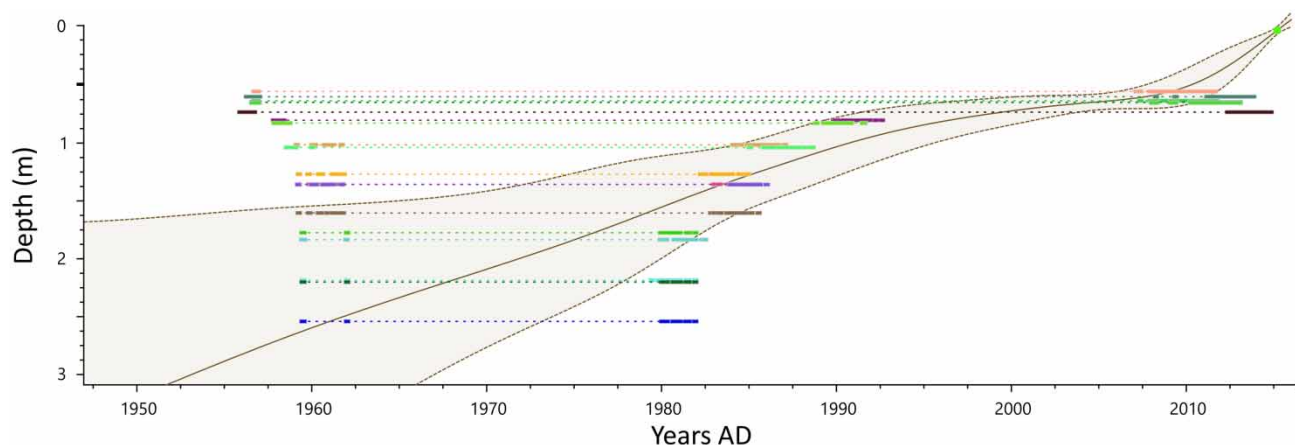
The age-depth model is illustrated in Figure 3, and the calibrated dates are provided in Supplementary material, Table S3.

According to this age-depth model, the oldest sediments in the core were deposited in approximately the 1950s, and the youngest were deposited in approximately 2009. More recent sediments (from 2009 to 2015) correspond to the rework interval (Figure 2). The age-depth model is consistent with the fact that this structure has not been cleaned since it was installed.

### Drug occurrence and vertical distribution

Among the 20 targeted drugs, 18 were quantified at least once within the CSA-02-2015-A core, with the highest concentrations of CBZ, ATE, and SCA. Stimulants were sparsely quantified in the sediment, with only one quantification and three additional detections for COC, whereas MDMA and BZE were not detected (Table 3). Except for SCA, with a quantification frequency of 70%, the quantification frequencies of the drugs varied from several percent to 37% for CBZ. Drug concentrations range from hundreds of  $\text{pg g}^{-1}$  to hundreds of  $\text{ng g}^{-1}$ .

Regardless of the molecule, a consistent pattern emerges with  $<\text{LOD}$  concentrations for the bottom part of the core, the occurrence of some detections followed by quantification in the upper part of the core (Figure 4). The first detection and quantification occurred at various sediment depths; for example, the first occurrences of ACM were quantified at 136 cm, whereas those for TRA were quantified at 77.5 cm (Figure 4). In general, the vertical distribution expressed sharp variations in drug content, sometimes fluctuating from one sample to another, such as for the surface sample and some others in which the diversity of quantified molecules is very limited.



**Figure 3** | Age-depth model of core CSA-02-2015-A obtained after the computation of  $^{19}\text{F}^{14}\text{C}$  results with ChronoModel in postbomb mode. Details about high profile density (HPD) intervals are provided in Supplementary material, Table S2.

**Table 3** | Occurrences of drugs in the investigated core with quantification (FQ, i.e. concentration > LOQ) and detection (FD, i.e. concentration > LOD) frequencies (in %,  $n = 72$ ), maximum concentration (Max), limit of quantification (LOQ) and detection (LOD) in  $\text{ng g}^{-1}$ 

		FQ (%)	FD (%)	Max $\text{ng g}^{-1}$	LOD $\text{ng g}^{-1}$	LOQ $\text{ng g}^{-1}$
Antibiotics	Norfloxacin	4.1	23.3	1.76	0.33	0.95
	Sulfamethoxazole	16.4	20.5	7.04	0.11	0.35
	Trimethoprim	26.0	53.4	1.91	0.23	0.67
Benzodiazepines	Diazepam	2.7	24.7	0.44	0.12	0.38
	Oxazepam	15.1	34.2	14.93	0.11	0.36
B-blockers	Atenolol	34.2	46.6	94.98	0.22	0.52
	Metoprolol	31.5	67.1	2.96	0.12	0.48
NSAIDs/Analgesics	Acetaminophen	21.9	45.2	7.69	0.16	0.44
	Diclofenac	15.1	47.9	1.67	0.22	0.78
	Ketoprofen	5.4	23.3	0.95	0.22	0.64
	Salicylic acid	69.9	74.0	88.23	0.79	2.45
Opioids and derivatives	Codeine	17.8	39.7	8.57	0.17	0.42
	Methadone	5.5	11.0	0.14	0.06	0.17
	Morphine	1.4	1.4	0.22	0.07	0.2
	Tramadol	11.0	12.3	29.66	0.44	1.31
Others drugs	Bezafibrate	12.3	28.8	0.74	0.13	0.35
	Carbamazepine	37.0	38.4	318.54	0.97	2.69
Stimulants	Benzoylcegonine	0.0	0.0	0.0	0.06	0.18
	Cocaine	1.4	6.8	0.32	0.03	0.09
	MDMA	0.0	0.0	0.0	0.03	0.08

### Dates of first-molecule occurrence

The calibration process and resulting date of appearance in sediments of MED is provided in [Figure 5](#).

The calibrated dates of the first occurrence of the targeted drugs are given in Supplementary material, Table S4 by using the same process.

Depending on the drug, the first occurrence depth is very different, from 40.5 cm for MED and TRA to 2.575 m for SCA (Supplementary material, Table S4). Based on the above-mentioned age-depth model, this corresponds to first sedimentary occurrences between 1952 and 1998 with most first detections in the 1970s ([Figure 5](#)). It is worth mentioning that age-depth model precision decreases with depth, with 10 years of interval for the top core and 25 years interval in the bottom part of the core.

## DISCUSSION

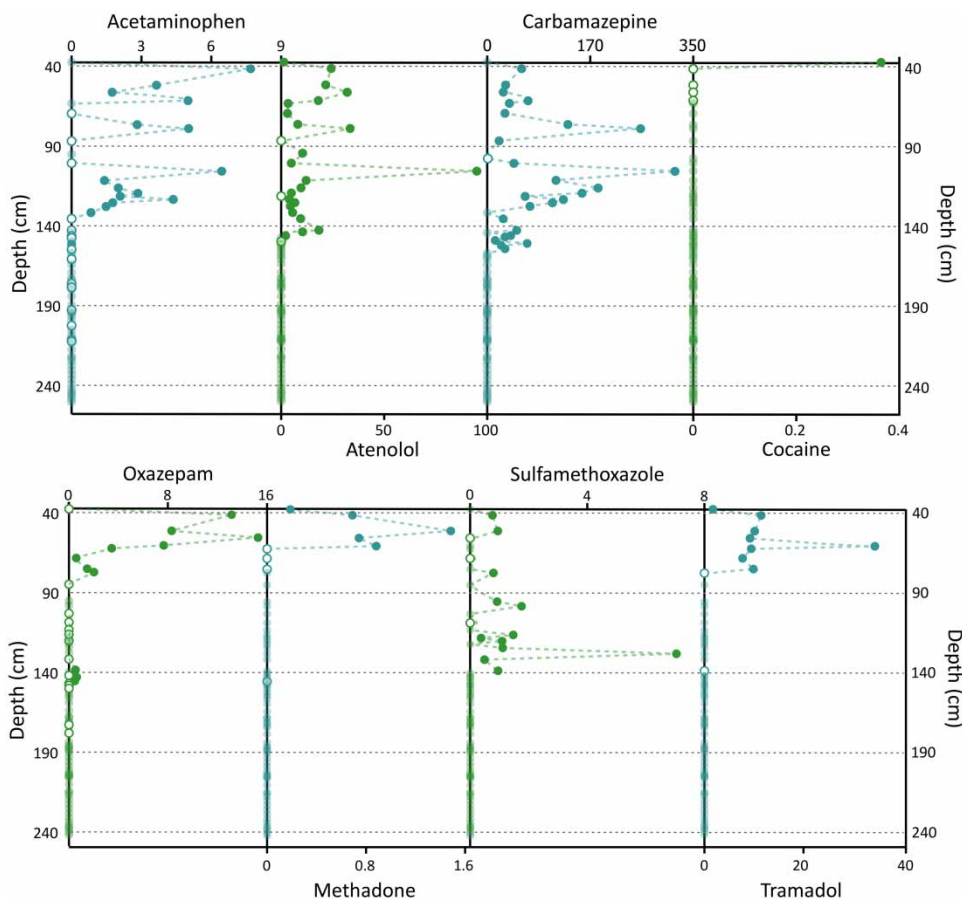
### Potential of the sewer sediment archive to record the first use of the drug

The first detections for all molecules are compared with their marketing dates in [Figure 6](#). It can be seen that for the oldest molecules, i.e. those marketed before 1900, the first detections are made at very different ages. Conversely, for molecules marketed since the 1950s, there is very good consistency between the first detection and the systematically earlier or simultaneous MAD ([Table 1](#)), or within the margin of error of the calibrated age of the sedimentary layer.

The 10-year time lag observed for certain molecules (e.g. DIA, ACM, SMX) can be due to their unfavourable physicochemical properties. Such molecules are besides rarely observed in sediments, whereas for less hydrophilic molecules (e.g. CBZ, TRA), first quantification is almost simultaneous with MAD as already observed in riverine sediments ([Thiebault et al. 2017a](#); [Kerrigan et al. 2018](#)).

This shows that the detection of drugs in this type of sediment allows them to be dated at a minimum, and therefore reinforces the robustness of the age-depth model.

In line with studies that have investigated fluvial or lacustrine sedimentary archives, the molecules appear to be trapped on particles, settled in the sedimentary column, and therefore not mobile. In addition, no in-situ degradation in the changes in



**Figure 4** | Concentrations of eight drugs in  $\text{ng g}^{-1}$  (d.w.) within the CSA2015 core against the sediment-depth in cm. White symbols for values  $<\text{LOQ}$  and clear symbols for values  $<\text{LOD}$ .

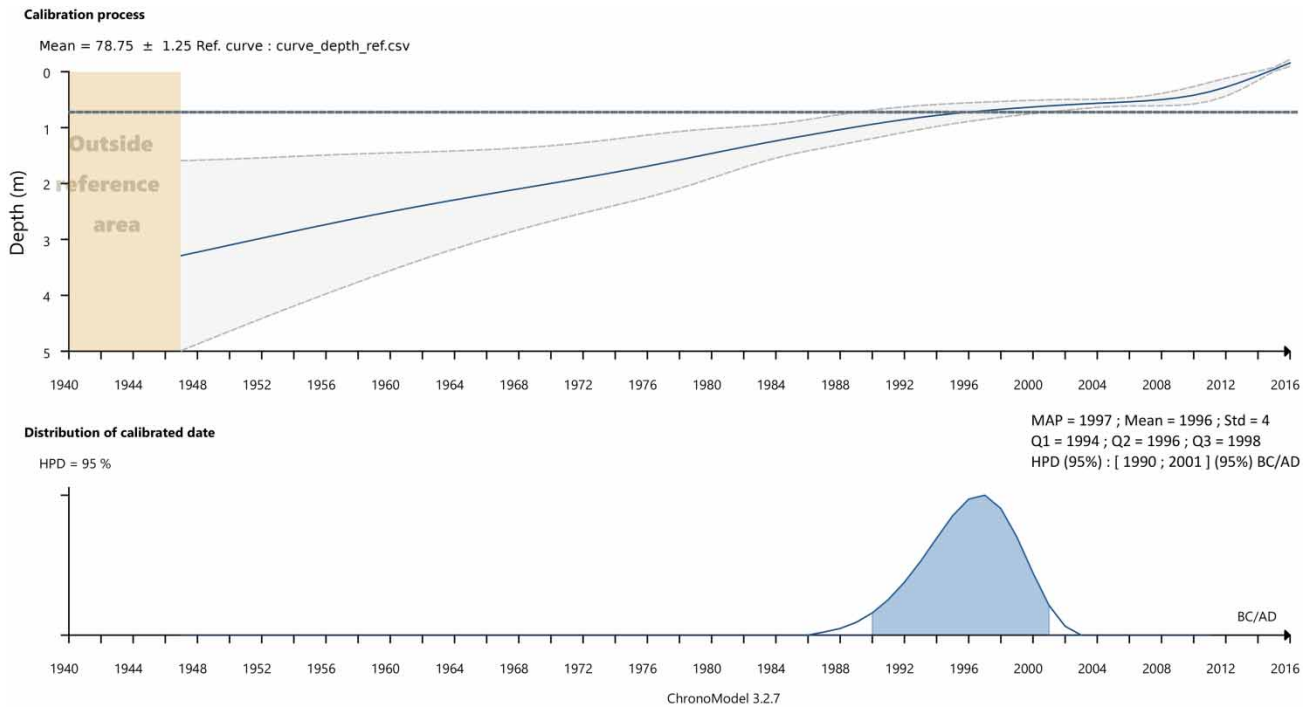
concentrations was observed, attesting to good preservation of the recorded signal. However, in contrast to environmental archives, the highly heterogeneous nature of sediment geochemistry makes it difficult to assess general trends in contamination.

#### Estimation of historical concentrations in WWI based on sedimentary contamination?

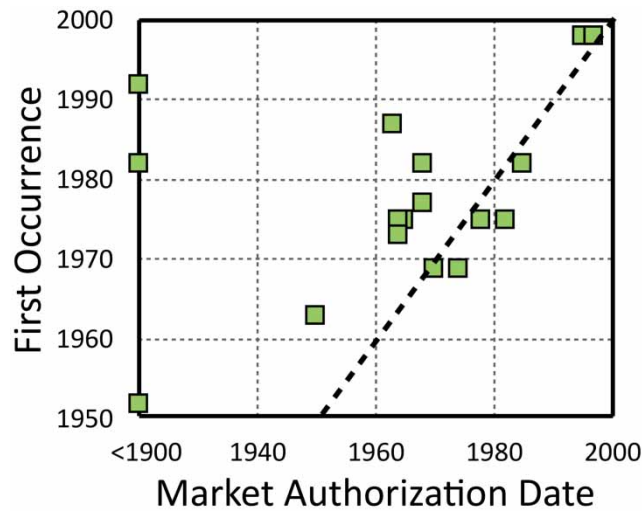
Beyond the knowledge of the first uses detected in the study area, the potential of these archives for estimating historical consumption arises. Indeed, one of the prerequisites for carrying out sediment-based epidemiology is to be able to estimate a dissolved concentration (which is used in wastewater-based epidemiology) from the sediment content. As demonstrated in a previous study from the same site (Thiebault *et al.* 2021b), the main factor that controls the adsorption of dissolved molecules onto particles (which can then settle in sediments) is organic carbon (Al-Khazrajy & Boxall 2016), particularly for noncationic molecules. It is therefore possible to estimate historical dissolved concentrations from  $K_{oc}$  (organic carbon partition coefficient) values (Table 1). To compare these estimated concentrations with the actual dissolved concentrations, it is possible to use 85 consecutive days of monitoring of the same drugs in the WWI in the same area (Thiebault *et al.* 2017b).

The sediment-based estimations (Figure 7) are in good agreement (i.e. on the same order of magnitude) for five drugs out of the 11 displayed drugs, carbamazepine (CBZ), OXA, SCA, TMP, and TRA. For the other molecules, the historical dissolved concentration is underestimated by approximately one order of magnitude, except for MET, for which the value is overestimated by one order of magnitude. In contrast to previous results, speciation does not seem to play a key role in archiving information on past consumption, as the different ionization states are distributed within each group.

A first parameter that can specifically impact the calculated concentration for each drug is the value of  $K_{oc}$ . Most published values are estimated or experimental data, but the conditions behind each result are not systematically relevant for the

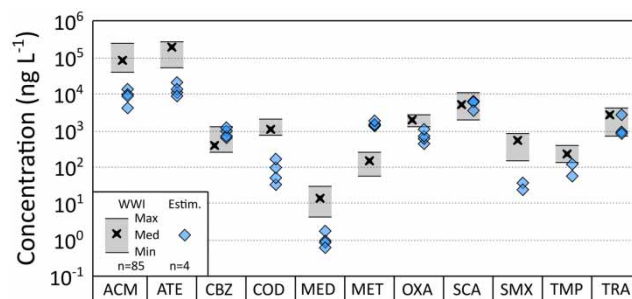


**Figure 5** | Example of the calibration of methadone first occurring in core CSA-02-2015-A using the Chronocurve function in ChronoModel, with the age-depth model used as a calibration curve.



**Figure 6** | Comparison of the first sedimentary occurrences of drugs and their market authorization date (black dotted line corresponds to 1:1 curve).

sampled system. It would therefore be preferable to adapt the  $K_{oc}$  value to current conditions in the settling basin to increase this potential. The second parameter, which will impact all the content homogeneously, is the characterization of the TOC. Such analyses were conducted on  $50 < 200 \mu\text{m}$  fractions because  $< 50 \mu\text{m}$  was very limited and coarser fractions were not adapted for such analyses. The hypothesis of a weak contribution of coarser fractions to the sorption of drugs was also made, resulting in this choice. If it is difficult to conclude here on the automatic use of sediment for the estimation of



**Figure 7** | Comparison of measured dissolved concentrations during 85 consecutive days in 2016 and dissolved concentrations estimated from sediments near this year.

historical concentrations and consumption, one can reasonably be optimistic as the breakdowns of the concentration ranges are close between the estimated and measured values.

Once these estimates have been made, two key points still need to be resolved to be able to calculate historical usage: (i) To know more about the sources and dynamics of sediment deposition in this settling basin (e.g. event-driven or long-term?), and (ii) to determine the historical or approximate cumulative annual discharge.

## CONCLUSIONS

This study reveals for the first time that coarse sediments from settling basins contain a wide diversity of drugs generated by excretion, although some of them were never detected in river sediments. This diversity of drugs makes it possible to estimate the consumption/excretion history once the sediments have been dated. In contrast to those from environmental archives, sediment cores from settling basins show contrasting accumulation patterns, with highly heterogeneous organic and mineral contents due to distinct sediment sources (i.e. stormwater and wastewater). This heterogeneity makes it difficult to use conventional age modelling, whereas an event-based model has been used here for the first time for this type of sediment. The good agreement between the first detection of each drug, what is known about their historical use, and the age model was a further clue to confirm the potential of these sediments to record the history of the city. Beyond this chronological assessment, a second objective of this study was to attempt to quantitatively estimate the historical amount of drug excreted. Using the solid/water partition coefficient equation, the back-calculated wastewater concentrations were found to be mostly lower than the actual concentrations, indicating that further work remains necessary to fully understand the solid-water partitioning of the drug and the parameters impacting the achievement of a quantitative assessment.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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