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RESEARCH

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Occurrence of drug target residues within decantation tank sediments: a good clue to assess their historical excretion?

Thomas Thiebault^{1*} , Laëticia Fougère², Anaëlle Simonneau³, Emilie Destandau², Claude Le Milbeau³ and Jérémy Jacob⁴

Abstract

This study investigated the potential of sediments accumulated in sewer systems to record human activities through the occurrence of drug target residues (DTR). The installation studied is 17 m deep underground decantation tank that traps the coarse fractions of a unitary sewer system (northern part of Orléans, France), collecting both stormwater and wastewater. The sediments deposited in this tank could constitute a nonesuch opportunity to study the historical evolution of illicit and licit drug consumption in the catchment, however, the deposition processes and the record of DTRs remain largely unknown at present. Five cores were acquired from 2015 to 2017. One hundred fifty-two sediment samples were extracted using a mixture of ultra-pure water: methanol (1:1) prior to analysis of the extracts by high-pressure liquid chromatography coupled to tandem mass spectrometry. Several classical sedimentological analyses such as total organic carbon, facies description and granulometry were also performed on these samples, in order to understand the most important factors (e.g., physico-chemical properties of the DTRs, solid type, assumed load in wastewater) impacting their deposition. The key role of the speciation of DTRs was highlighted by the higher contents in neutral and anionic DTRs in organic layers, whereas only cationic DTRs were found in mineral layers. The considerable modifications in the sediments' properties, generated by distinct origins (i.e., stormwater or wastewater), are therefore the most important drivers that must be taken into account when back-calculating the historical patterns of drug consumption from their DTR concentrations in decantation tank sediments. Further research remains necessary to fully understand the deposition process, but this study provides new clues explaining these temporal evolutions.

Keywords: Pharmaceuticals, Illicit drugs, Sediments, Organic matter, Adsorption, Wastewaters

Introduction

Two distinct types of information can be drawn from the occurrence of drug target residues (DTRs) in sewer networks. The quantification of DTRs such as licit and illicit drugs can provide useful information on the consumption behavior of the population within a catchment [1–3]. Beyond this consumption assessment, the presence of organic contaminants within environmental

compartments raises a serious health issue for living beings [4, 5].

Most studies focus on the occurrence and fate of DTRs within wastewater treatment plants (WWTPs) and their removal during wastewater treatment [6–9]. However, several others have highlighted that the vertical distribution of DTRs and other contaminants within sedimentary archives makes them suitable for the historical reconstruction of drug use [10–12]. Among these works, few studies have described the distribution of contaminants within decantation tanks, directly in the sewer system [13–16], as in this type of installation,

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sediments are generally coarse and considered unfavorable for the trapping of organic molecules due to limited specific surface areas [17, 18]. One of the major advantages of decantation tanks, however, is their position upstream in the sewer network and therefore very close to excretion/production areas. As a result, decantation tank sediments are potentially able to record a wider variety of contaminants than riverine sediments, due to the significant degradation or removal of some contaminants during wastewater treatment [19, 20].

Decantation tanks are classically designed to trap suspended solids that could damage sanitation installations. Moreover, depending on the network (i.e., unitary or separate) the sediments can originate from wastewaters and/or stormwaters resulting in different types of solids: (i) mostly organic from wastewater and (ii) mostly inorganic from stormwater [17, 21]. Hence, the sedimentary composition will differ strongly depending on the main source of solids.

The aim of this work was to analyze the occurrences of 20 DTRs (both licit and illicit drugs) within different cores sampled in a decantation tank, located in a unitary network, and to assess for the first time the vertical distribution of DTRs within such sediments in order to assess their potential to reconstruct historical consumption within the catchment. Highly significant vertical variations in the sedimentary composition (i.e., granulometry, organic content) of the sediments were found. Statistical analysis was therefore applied to distinguish the affinity of DTRs for solids, depending on the origin and chemical properties of both. We focused particularly on the speciation of contaminants, due to the adsorption mechanisms that can be expected from their molecular charge.

Materials and methods

General settings and sample collection

The “Chambre à Sable” (CSA) decantation tank is a 17 m deep 8 m diameter cylindrical and then conical underground building sited on the Loire river dockside. The CSA collects 7.10^6 m^3 of water annually (i.e., flow ranges from 1 to $4 \text{ m}^3 \text{ s}^{-1}$) from the unitary sewer network (i.e., wastewater and stormwater) that drains the northern part of the Orléans conurbation. The construction of this building in 1942 initially aimed at removing coarse fractions from water discharged directly into the Loire River [21]. In the early 1970s the exit flow was redirected to two WWTPs.

In 2014, a renovation of the tank was decided by the local government in order to facilitate cleaning operations and to modify the flow management so as to limit the direct discharge of wastewater into the Loire River during intense precipitation events. Since then, cleaning operations have been undertaken every 6 months-1 yr, depending on the volume of sediments accumulated. We took advantage of this situation to perform a systematic bathymetric survey and several campaigns of sediment coring. The first coring occurred in April 2015, prior to the major cleaning that removed $\sim 7 \text{ m}$ of sediments in May 2015 (Fig. 1). Then, we pursued regular coring operations, with some sedimentary cores drilled prior to cleanings. This constitutes a collection of 21 sedimentary cores of various lengths collected from April 2015 to April 2017.

The present study focuses on 5 cores (CSA-02/2015-A, CSA-03/2016-5, CSA-07/2016, CSA09/2016, CSA-04/2017-5) collected with a UWITEC gravity corer. Cores were labeled according to the core location (i.e.,

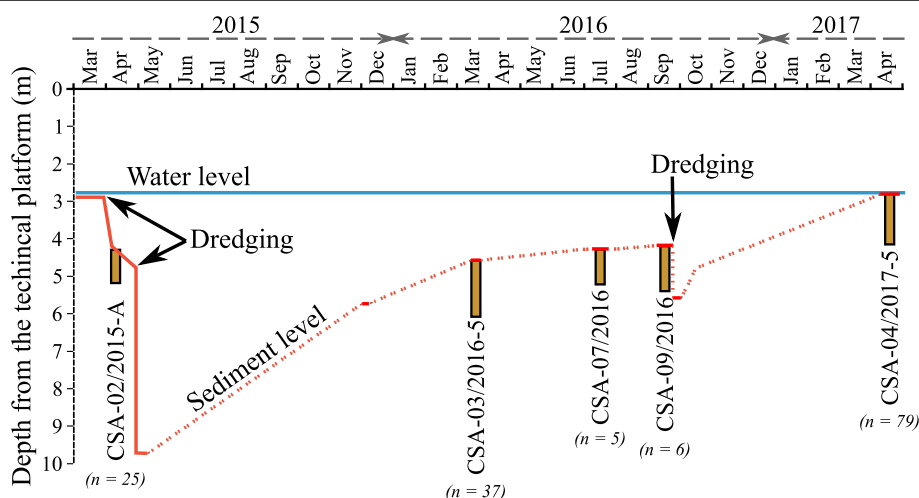


Fig. 1 Evolution of the water level and the sediment level during the sampling, with the label used hereafter for each core. Numbers in brackets correspond to the number of samples analyzed for DTR contents per core

CSA), the coring date with month and year, and the core number in the case of multiple coring on the same date. These cores were selected because of their length and facies diversity. After splitting them into two half cores ("Work" and "Archive"), the facies description of each was performed. Then, samples were taken following the lithology on the "Work" half core. Over the 5 cores, this represents a total of 152 samples. Further description of these samples is given in the Supplementary Materials (Table S1).

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 a purity > 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 physico-chemical properties are given in Table S2, and their chemical structures are given in Fig. S1. Extraction and separation solvents, dichloromethane (DCM), methanol (MeOH) and acetonitrile (AcN) were purchased from Thermo Fisher Scientific (Illkirch-Graffenstaden, France), assuming an analytical grade (purity up to 99.95%).

Sample extraction

Around 20 g (precise weight determined after extraction and after drying the sediments) of still wet sediment were extracted by pressurized liquid extraction, using an accelerated solvent extractor (ASE-200, Dionex, Sunnyvale, CA, USA). The extraction mixture was MeOH/H₂O (1:1 v/v); the operating temperature and pressure were 100 °C and 6895 kPa, respectively. Extracts were then fully dried at 60 °C under nitrogen flow and stored at -18 °C. Extracts were recovered in ultra-pure water acidified with 0.1% of formic acid before liquid chromatography analysis. Standards and controls were prepared with surface waters sampled in the Loiret river (filtered at 0.22 µm), which after analysis were found to be deprived of DTRs.

Quantification and validation

DTR separation was achieved at 30 °C and a flow rate of 0.4 mL min⁻¹ with a Nucleodur C₁₈ Gravity column (150 mm × 2 mm × 1.8 µm, Macherey-Nagel, Hoerd, France) supplemented by a guard column using an Ultimate 3000 RSLC (Thermo Fisher Scientific, San Jose,

CA, USA) ultra-high performance liquid chromatography system equipped with a binary pump. The injection volume was 3 µL. Ultra-pure water (A) and AcN (B), acidified with 0.1% of formic acid, were used as mobile phase. The elution gradient was a transition from 95 to 5% of A in 16.2 min followed by 0.3 min of 100% of B and then a return to the initial conditions (95% of A) during 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 mL min⁻¹.

An electrospray ionization source was used for quantification, operating in positive mode (except for SCA), with a vaporizer temperature of 425 °C, ion transfer temperature of 325 °C, electrospray voltage of 3600 V, auxiliary gas of 20 Arb, sheath gas of 50 Arb, and sweep gas of 1 Arb. Xcalibur 2.2 software was used to evaluate the qualitative and quantitative analysis of selected DTRs. Quantification performances are given in Table S3.

The following procedure was systematically used for the analysis validation: a calibration curve (6 standards from 0.5 to 100 ng L⁻¹), followed three times by 4 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 [22, 23]. According to classical organic analysis, LOQ and LOD were calculated with a signal-to-noise ratio of 3 and 10, respectively. The linearity takes into account the three calibration curves that framed the sample analysis and was determined by the linear correlation coefficient R². Recovery values were calculated by first extracting three randomly selected sampled sediments with a DCM/MeOH (9:1, v/v) mixture in order to avoid all the DTRs. Then, a concentration of 100 ng g⁻¹ for each DTR was spiked onto these sediments prior to extraction, carried out following the same procedure (MeOH/H₂O, 1:1, v/v) and compared to the standard injection value.

Granulometry and bulk organic geochemistry

After drying, granulometry analysis of all the samples (*n* = 152) was conducted by sieving sediment through four screens of different square mesh sizes (> 1 mm; > 200 µm; > 50 µm and < 50 µm). The rejects were collected and weighed.

The 50–200 µm fractions of 139 samples were used to determine the Total Organic Carbon (in %) using Rock-Eval6 (Vinci Technologies, Rueil-Malmaison, France) analysis [24]. This analysis was

not possible for 13 samples due to limited sediment availability.

Statistical treatment

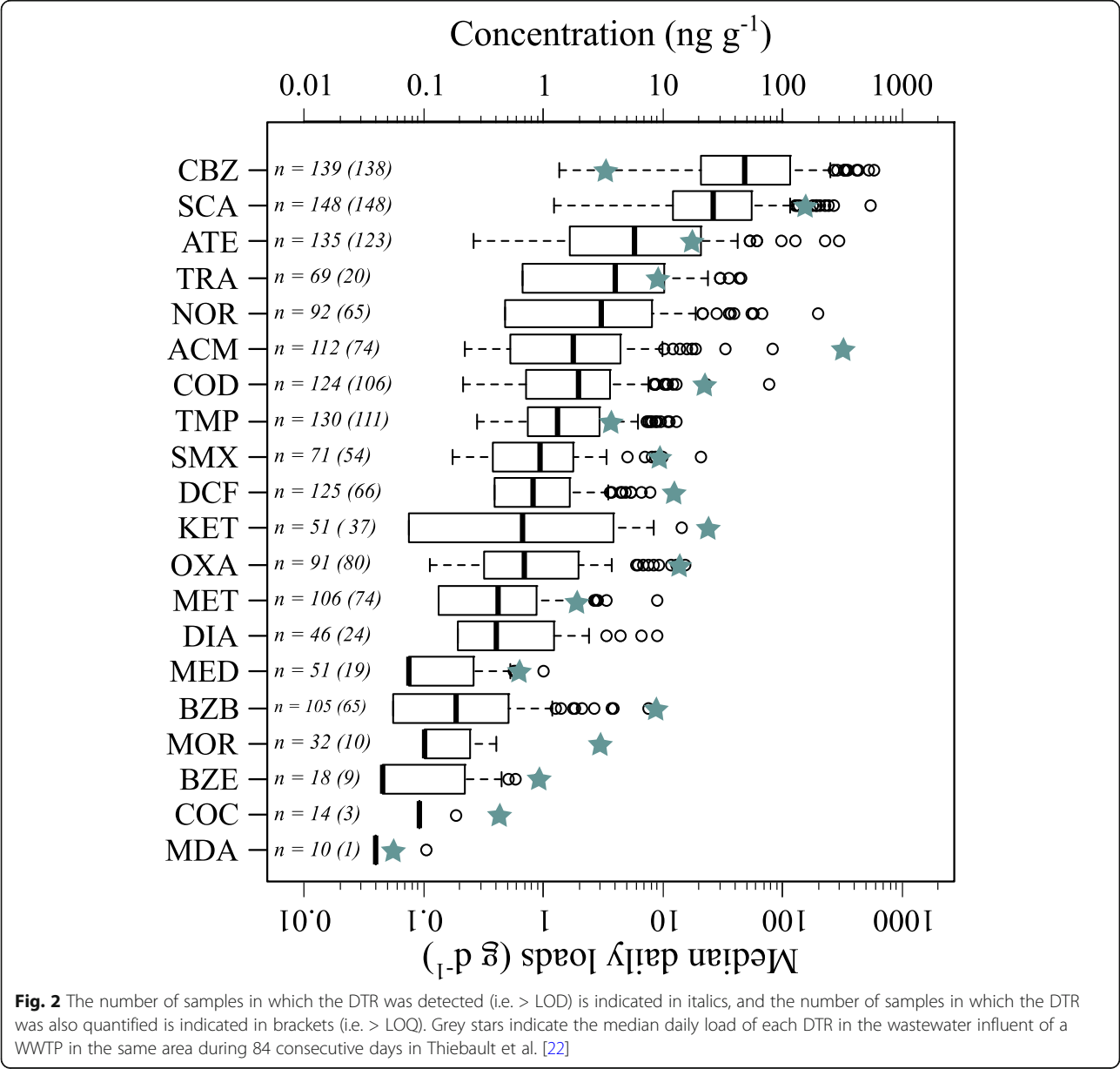
Principal component analysis (PCA), correlation matrix, pairwise *p*-values and heatmap were performed with the R software (packages corplot and FactoMineR, [25]). The Pearson correlation was used to assess both the correlation matrix and *p*-values. Two types of statistical analyses were performed; (i) with DTR occurrence only (*n* = 152) and (ii) with DTR occurrence, granulometry and TOC analyses (*n* = 139 samples). During statistical analysis a concentration of 0 was attributed to DTR concentrations < LOD, and for DTR concentrations between

LOD and LOQ, a concentration of LOQ/2 was attributed [26].

Results and discussion

Occurrences of contaminants within sediments

Among all the samples analyzed, the most abundant DTRs were CBZ and SCA (Fig. 2). Their concentrations ranged from 3.8 to 587 and from 2.6 to 296 ng g⁻¹, respectively. The median dissolved loads determined in a WWTP influent in the same area during a long-term monitoring performed in 2016 are also presented (Fig. 2, [22]) in observe to compare the DTR diversity in the two compartments.



The interest of presenting these results is mostly to assess the significance of recorded concentrations in sediments for back-calculation of drug use, rather than a direct comparison of dissolved loads and recorded concentrations, which would be meaningless.

The high concentrations of SCA in sediments were expected, considering the high loads determined in wastewater in the area [6, 22]. CBZ, however, was not expected to be as highly concentrated in sediments because it was detected at significantly lower levels in wastewaters (Fig. 2). The hydrophobic nature of CBZ (Table S3) and its reputed recalcitrance to any degradation [27] are possible factors explaining the elevated concentration levels observed in the sediments. The median concentrations of most of the other DTRs ranged between 0.1 and 10 ng g⁻¹. The lowest median concentrations and the lowest detection frequencies were found for illicit drugs and derivatives (i.e., BZE, COC and MDA), as well as for MOR that may derive from COD, MOR or even heroin consumption [28]. These low concentrations appear consistent with the weak loads observed in wastewater influents [22]. However, such a detection of these illicit drugs in sediments is the first to be reported in the literature.

In general, the DTRs determined in wastewater influents were also recorded in the sampled sediments. Looking at extreme values, ACM was by far the most abundant DTR in wastewater influent, but displayed concentrations in sediments equivalent to those of COD, a compound found a hundred-fold times less in wastewaters. The fact that ACM is considered as a highly biodegradable contaminant may explain these low occurrences [29]. Finally, these results constitute a significant database (20 DTRs, 152 samples) to analyze the vertical distribution of DTRs and perform statistical analyses in order to better understand the main factors

(physico-chemical properties, sources) driving their record in sediments.

Vertical distribution

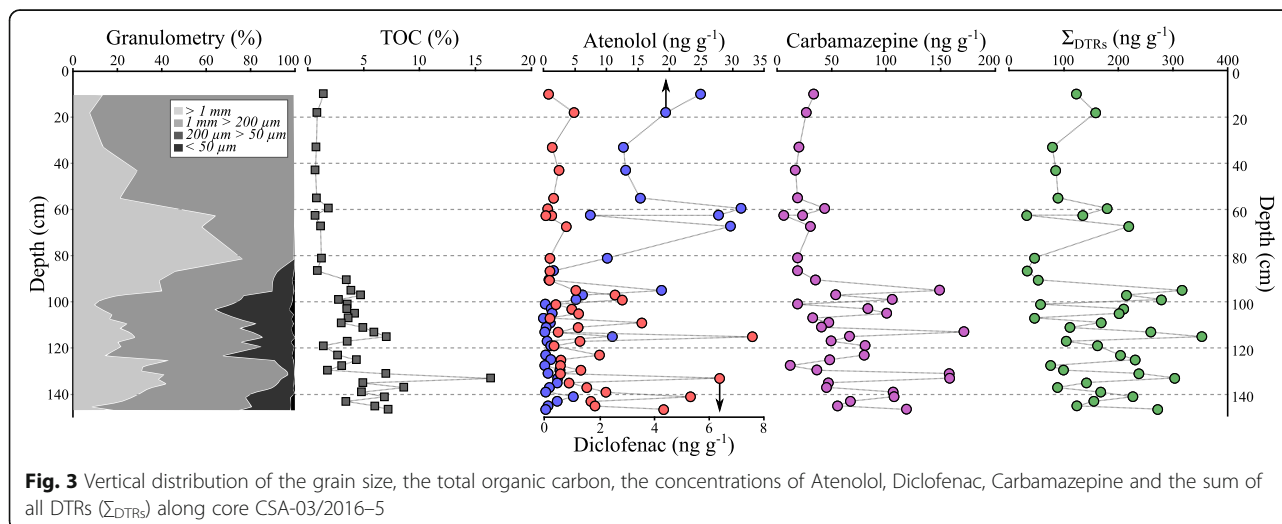
The vertical distribution of DTRs is here discussed in cores CSA-03/2016–5 and CSA-04/2017–5, in which the number of samples (i.e., 37 and 79 respectively) was the greatest, enabling the vertical distribution of selected DTRs to be compared with the composition of sediments (i.e., grainsize and TOC).

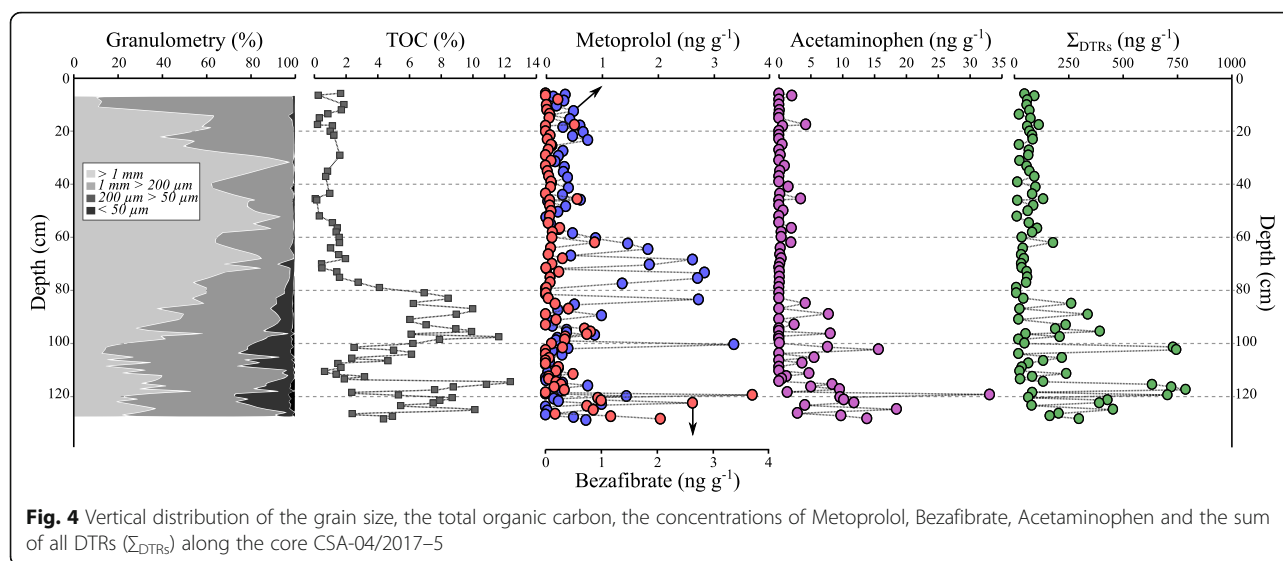
Core CSA-03/2016–5 is characterized by three distinct facies (Fig. 3): (i) In the upper part (10–50 cm) of the core, the sediment is mostly composed of coarse mineral particles (i.e., sands) and shows low TOC values; (ii) in the medium part of the core (50–90 cm), the sediment is mostly composed of sands and gravels, also displaying low TOC values; and (iii) in the lower part of the core (90–150 cm), the sediment is composed of a higher proportion of smaller particles (mineral and organic) with higher TOC values. These three distinct facies were attributed to deposition during strong energy currents for the intermediate unit, whereas the upper and lower units were accumulated under lower energy [21].

The sum of DTR concentrations is impacted by the vertical composition of the sediment. In the upper part of the core, the total concentration ranged between 5 and 200 ng g⁻¹ whereas in the lower part, it ranged between 15 and 350 ng g⁻¹.

The vertical distribution of contaminants is therefore impacted by the variation in the sediment composition. For example, the concentrations of both CBZ and DCF were higher in the lower part of the core (despite very significant fluctuations), whereas the concentrations of ATE were higher in the upper part of the core.

Core CSA-04/2017–5 also displays distinct facies: (i) in the upper part of the core, the sediment is coarse with





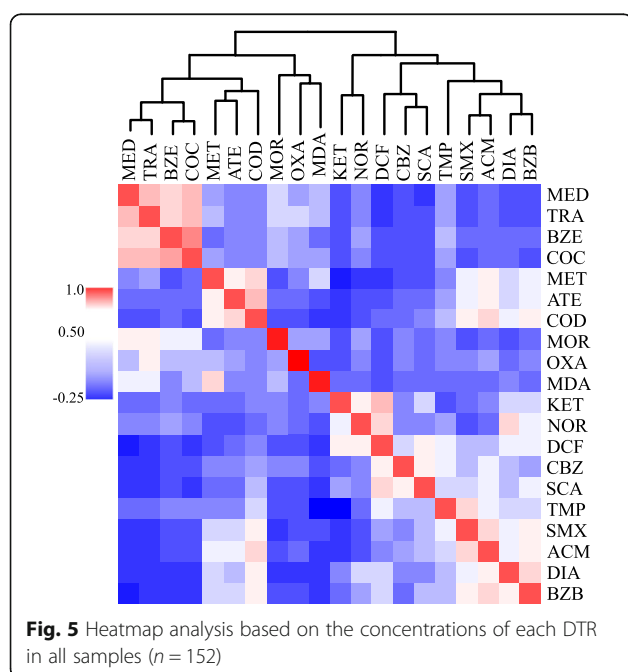
a high sand and gravel content and displays low TOC values, whereas (ii) in the lower part of the core, both TOC and fine-grain contents are high (Fig. 4). The total amount of DTRs followed this pattern, with limited cumulated concentration in the upper part of the core and higher total concentrations in the lower part of the core. However, this increase varied depending on the DTR. For example, ACM and BZB concentrations were very limited in the upper part of the core, whereas an opposite pattern was observed for MET.

DTR concentration in sediment: what are the driving factors?

The correlation between the concentrations of each DTR in all the sediments was assessed. From the resulting heatmap (Fig. 5) and correlation matrix (Table S4), two clusters were distinguished. The first one comprises COD, ATE, MET, OXA, MDA, MOR, MED, TRA, BZE and COC, and the second one KET, NOR, BZB, DIA, DCF, SUL, TMP, CBZ, SCA and ACM. The most striking feature of these two clusters is that they correspond exactly to the speciation of DTRs. If one excepts OXA, which is theoretically neutral, the first cluster is exclusively composed of cationic DTRs (with a pH value = 7.5, Table S3), whereas the second cluster is exclusively composed of neutral and anionic DTRs (and NOR, zwitterionic).

As a result, the vertical distribution of DTR concentrations in these sediments appears to be mainly driven by the charge state of the DTR. This parameter strongly controls the possible adsorption mechanisms according to the type of solids in interaction (mineral or organic).

Beyond the impact of the type of sediments on the recording conditions, some concurrent patterns between DTRs may enlighten us on the historical loads of DTRs in the catchment, given that the presence of these mostly hydrophilic DTRs in the dissolved phase (i.e., wastewater) is mandatory for them to accumulate in contaminated sediments. In this respect, several very significant correlations are especially informative. The correlation coefficient between COC and BZE was 0.94 (Table S4). This high value can be attributed to the fact that COC and BZE are both cationic, and are also DTRs of the same parent compound, cocaine. In sewage epidemiology studies, BZE is preferred to assess the consumption of cocaine, due to its greater stability than that of COC [30]. Our results confirm these



observations, with a detection frequency of BZE that was always higher than that of COC, and BZE concentrations that were systematically higher than those of COC, despite a theoretical higher affinity of COC for solids in general (Table S3). The correlation between COC and BZE therefore reflects both the same origin (i.e., excretion) and a close affinity for solids. Lower concentrations for COC compared to BZE are attributed to its lower excretion ratio and its lower stability in the sewer system [28, 31].

The second most significant statistical correlation was displayed between SCA and ACM (Fig. 5). The occurrence of these two DTRs in wastewater derives from the consumption of analgesics, which are considered as the most commonly used medications. Moreover, their temporal excretion dynamics was demonstrated to be close, and impacted by the same controlling factors (e.g., the same type of use, [32]). Again, this correlation indicates both an obvious (albeit limited) affinity with solids (SCA is anionic, ACM neutral) and a possible impact of the temporal dynamic of excretion in the catchment.

Finally, the third most significant statistical correlation was between SMX and TMP, with a correlation coefficient of 0.64. These two antibiotics are often consumed in association in a single medicinal product: cotrimoxazole [33]. As a result, the daily loads of both in wastewater influents are correlated [22, 34], and this correlation remains valid in sediments, despite distinct theoretical affinities with solids.

These three correlations are good examples of the potential of such sedimentary archives in sewer networks to reconstruct the temporal evolution of licit and illicit drug consumption over a catchment, as some classical

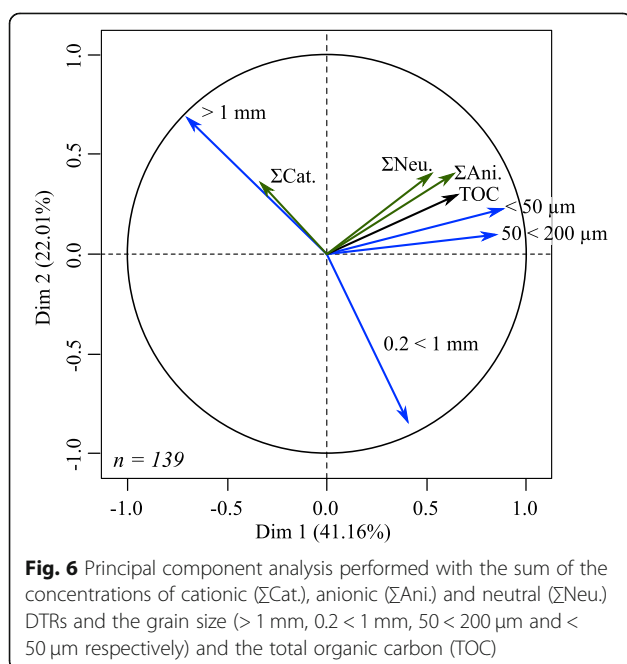
correlations found in the dissolved phase were also recorded in sediments. However, two main types of information are merged and hard to distinguish; (i) the sediment composition and (ii) the excretion dynamic.

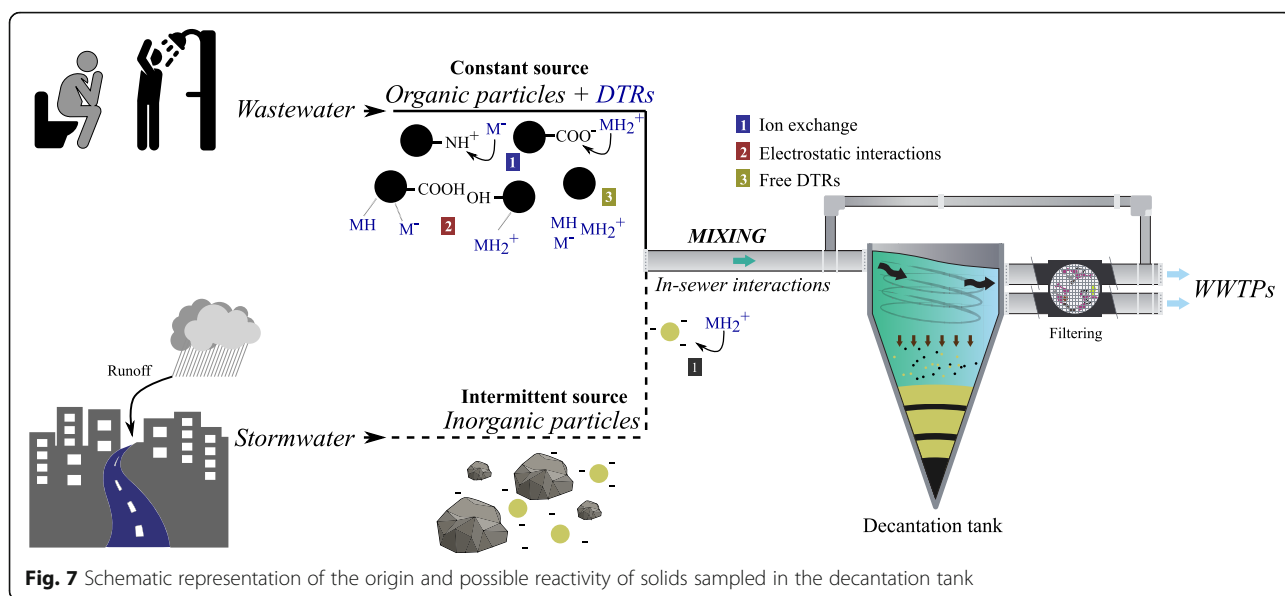
In order to deepen our understanding of the impact of sediment composition on the concentrations of DTRs, a PCA analysis was performed with grain size, TOC and the sum of DTRs with the same charge state at the working pH. The PCA analysis confirms the heatmap clusters based on theoretical charge. Moreover, neutral and anionic DTRs are correlated with TOC and fine grain content, whereas cationic DTRs are correlated with coarse grain content (Fig. 6).

In these cores, two main types of sedimentary facies were present: on the one hand, organic and fine sediments, mainly originating from wastewater inputs; on the other hand, mineral and coarse sediments mostly coming from stormwaters. As a result, the sediment composition has a strong impact on the distribution of DTRs. Yet, the correlation of cationic contaminants with the coarse fraction should be understood through the non-correlation with fine grain content rather than as a pure correlation with sand or gravel content, which are not especially renowned for their adsorption capacity of DTRs, even cationic ones.

Adsorption mechanisms vs. excreted amount

Initially, the decision to analyze such sediments was driven by the possibility to back-calculate the historical consumption of licit and illicit drugs over the watershed. Several studies have conducted these types of investigation in riverine or lacustrine sedimentary archives, despite the significant removal of numerous DTRs during wastewater treatment and dilution in water bodies, limiting their occurrences in sedimentary records [11]. In these more natural sediment accumulations, the vertical variations in composition (i.e., grain size, TOC) were weak. An almost identical affinity between solids and DTRs was thus expected, whatever the deposition time [10, 23]. Yet, in the “Chambre à Sable” decantation tank, the vertical composition of the sediments varies dramatically (Figs. 3 and 4), depending on the respective inputs of wastewater-derived (continually produced in the watershed and carrying organic-rich particles) and stormwater-derived (carrying high amounts of mineral solids during specific events) material. These two types of waters contain very different suspended solids (Fig. 7). Stormwaters contain mostly inorganic particles (i.e., sand, gravel, clay) as a result of the washout of urban areas and are theoretically depleted in DTRs [16], whereas wastewaters contain mostly organic particles and are the primary source of DTRs [18, 35]. However, during rain events, a mix between wastewater and stormwaters in sewers occurred, potentially allowing





interaction between DTRs present in wastewater with stormwater particles.

These two types of particles however display different affinities for DTRs, especially as a function of the charge state at their surfaces. Inorganic surfaces such as those of clay minerals and silica may display two types of charges: permanent negative charges due to isomorphous substitutions, and amphoteric charges due to hydroxyl radicals [36]. The latter type of charge is strongly impacted by the pH, and under slightly alkaline conditions as in sewers it is expected that most of these charges will be negative. As a result, it can be considered that most of the inorganic surfaces are negatively charged. These charges are therefore compensated by cations. DTRs could play this role [37]. However, the affinity of non-cationic DTRs with such surfaces is considered as very weak, and mainly driven through weak electrostatic interactions such as Van der Waals interactions [38]. Hence, it can be assumed that the spontaneous cation exchange adsorption mechanism of cationic DTRs is the main interaction mechanism between DTRs and inorganic surfaces.

Surfaces of organic particles are more complex due to their high chemical functionalization and strongly hydrophobic nature. As a result, many types of interactions can be expected between DTRs and such surfaces. Among them, ion exchange can be both anionic and cationic, depending on the nature of the chemical functions. But the most important adsorption mechanism between DTRs and organic surfaces that can also concern neutral DTRs is the organic carbon water partition, due to the affinity of hydrophobic moieties for organic matter in general [39]. Hence, the adsorption of all types of DTRs can be significant onto organic surfaces, even if organic surfaces are considered as unfavorable for the

adsorption of cationic DTRs, in comparison with inorganic ones [40, 41].

This was confirmed by the statistical analyses, as it was obvious that neutral and anionic DTRs were correlated with TOC (Fig. 6), emphasizing that the organic carbon hydrophobicity was favorable for the adsorption of anionic and neutral DTRs. However, no correlation was found between cationic DTRs and TOC. This can be explained by the possible interactions between cationic DTRs and inorganic surfaces after the mixing between wastewaters and stormwaters. From the results, it can therefore be assumed that inorganic surfaces mainly adsorb cationic DTRs, and organic surfaces potentially adsorb all DTRs (Fig. 7) to a larger extent. This is therefore the main reason why both the DTR diversity and concentrations are higher in more organic layers.

This strong variation in the sedimentary occurrence of DTRs according to their charge is also visible on their vertical distribution and hinders the correct understanding of the historical variation in the amount excreted in the catchment. Hence, on the basis of current knowledge, the potential of this archive is primarily to enable the exploration of the interactions between suspended solids and DTRs rather than to reconstruct the historical excretion of DTRs in the catchment. To elucidate the latter, some clues remain to be explored, such as for example organic carbon normalization for anionic and neutral DTRs, although the back-calculation of cationic DTR consumption necessitates further research.

Conclusions

In this study, the sampled sediments were very close to the primary source of DTRs (i.e., households), making it possible to detect a wider variety of compounds such as,

for the first time, illicit drugs compared to river or lacustrine sediments, in which only highly concentrated or persistent DTRs can be detected. This wider DTR diversity emphasized the potential of such sediments for the reconstruction of the consumption/excretion history. However, due to sudden vertical variations in the composition of the sediments that are attributed to respective inputs of wastewater and stormwater materials depending on meteorological events, the affinity of DTRs with sediments was obviously impacted as well.

Specific vertical distributions of DTRs according to their molecular charge were revealed by statistical analyses and evaluated based on general knowledge of the adsorption mechanisms of organic contaminants onto organic and inorganic surfaces. As a result, before expecting a complete understanding of the historical excretion within this catchment based on sedimentary accumulations in sewer networks, several corrections have to be performed on these vertical distributions, based on the affinity between DTRs and sediments/suspended solids.

Finally, although this archive displays the first distribution pattern for most DTRs, further work remains necessary in order to better understand the historical deposition dynamics and potential local remobilization.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s42834-021-00092-w>.

Additional file 1: Table S1 Presentation of all the samples used in the main manuscript and the associated results with the sediment properties (grain size and total organic carbon) and DTR concentrations. n.d. indicated non available data. **Table S2** Physico-chemical properties of the targeted DTRs. **Table S3** Analytical parameters and performance of the selected DTRs with the abbreviation Abb., the Multiple Reaction Monitoring transition with the Precursor and the Quantification Ion (QI), Ce the collision energy, RF Lens, RT the Retention Time, the extraction recovery Rec. and LOQ the limit of quantification. **Table S4** Correlation matrix of the DTR concentrations within sediments ($n = 108$) with italic/colored, colored and colored/bold corresponding to p -values < 0.05 , 0.01 and 0.001 respectively, with positive correlation red and negative correlation in blue. SC, SA, SN and ZC corresponds to sum of cationic, sum of anionic, sum of neutral and zwitterionic compound respectively. **Fig. S1** Chemical structure of the investigated DTRs.

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Authors' contributions

JJ and AS carried out coring operations and sample preparation and description. TT, JJ, CLM and LF conducted laboratory experimental studies. TT and JJ drafted the manuscript. AS, CLM, ED and LF critically reviewed and edited the final version of the manuscript. All authors have read and approved the final manuscript.

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Availability of data and materials

All the data generated or analyzed during this study are fully available in the supplementary materials.

Declarations

Competing interests

The authors declare they have no competing interests.

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