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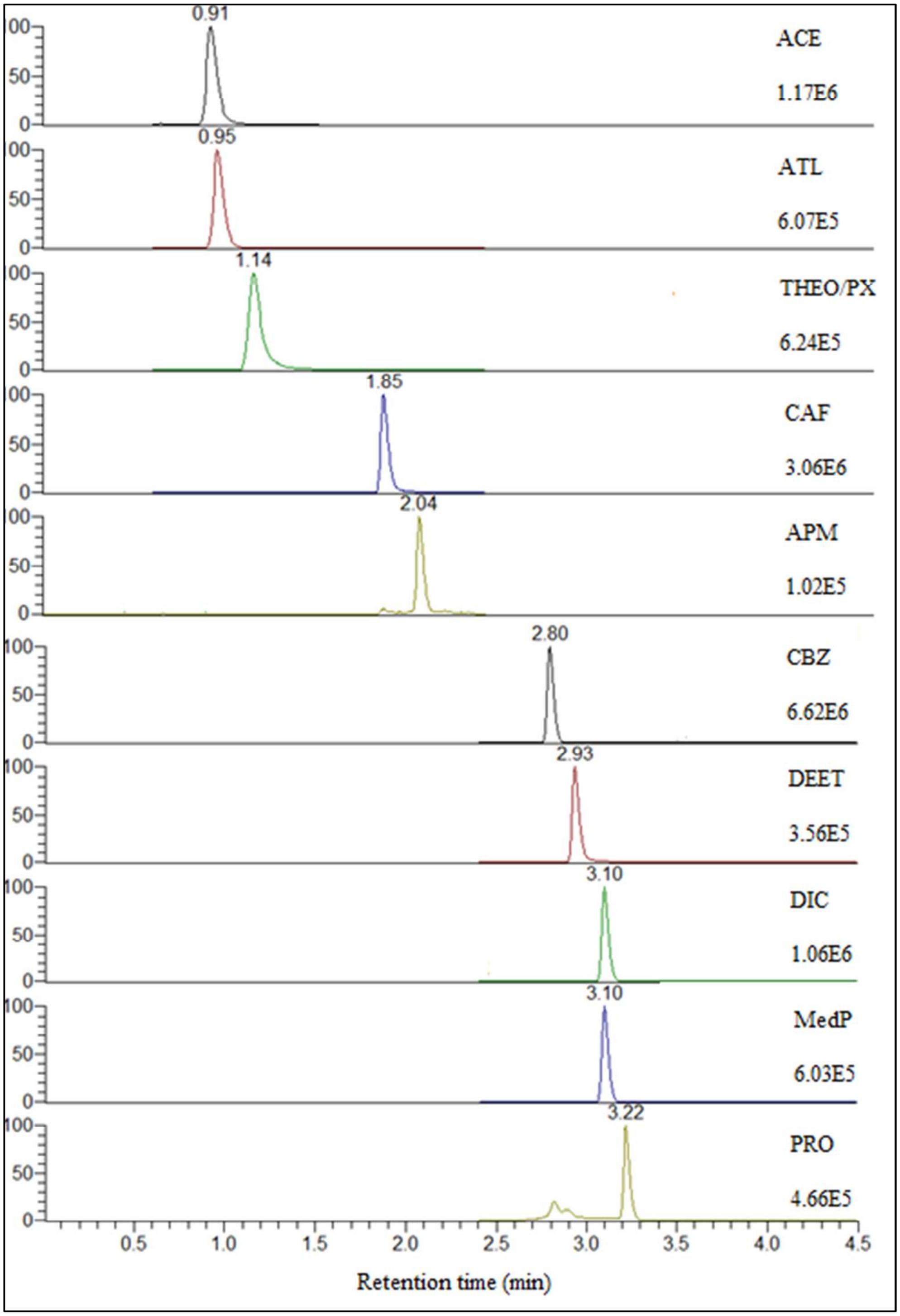

Graphical abstract

This work presents the first measurement of wastewater micropollutants in combined sewer sediments and compares with measurements from water and sediments in natural streams.

Environmental Impact Statement

A sensitive method was developed to measure the sediment concentration of 10 wastewater micropollutants selected as potential sanitary tracers of sewage contamination. This method was applied to an investigation of stream and combined sewer overflow sediment samples that differed in organic carbon contents and particle size distributions. The ratio of the average concentration to the limit of detection (C:LOD) in sediments for a subset of compounds were compared to their C:LOD in water. In waters with a large capacity for dilution relative to fecal sources, the C:LOD in sediments were greater than in water. Thus monitoring programs for fecal source tracking using wastewater micropollutants should consider sediment sampling, particularly for waters with highly diluted sources of fecal contamination.

Wastewater micropollutants as tracers of sewage contamination: Analysis of combined sewer overflow and stream sediments

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ABSTRACT

A sensitive method was developed to measure the sediment concentration of 10 wastewater micropollutants selected as potential sanitary tracers of sewage contamination and include: nonsteroidal anti-inflammatory drugs (acetaminophen – ACE and diclofenac – DIC), an anti-epileptic drug (carbamazepine – CBZ), a ß-blocker (atenolol – ATL), a stimulant (caffeine – CAF), a bronchodilator (theophylline – THEO), steroid hormones (progesterone – PRO and medroxyprogesterone – MedP), an artificial sweetener (aspartame – APM) and personal care products (N,N-diethyl-3-methylbenzamide – DEET). Natural sediments (combined sewer overflow and stream sediments) were extracted by ultrasonic-assisted extraction followed by solid-phase extraction. Analyses were performed using ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) using atmospheric pressure chemical ionisation in positive mode (APCI+) with a total analysis time of 4.5 min. Method detection limits were in the range of 0.01 to 15 ng/g dry weight (dw) for the compounds of interest, with recoveries ranging from 75% to 156%. Matrix effects were observed for some compounds, never exceeding |±18%|. All results displayed a good degree of reproducibility and repeatability, with relative standard deviations (RSD) of less than 23% for all compounds. The method was applied to an investigation of stream and combined sewer overflow sediment samples that differed in organic carbon contents and particle size distributions. Acetaminophen, caffeine and theophylline (as confounded with paraxanthine) were ubiquitously detected at 0.13-22 ng/g dw in stream bed sediment samples and 98-427 ng/g dw in combined sewer overflow sediment samples. Atenolol (80.5 ng/g dw) and carbamazepine (54 ng/g dw) were quantified only in combined sewer overflow sediment samples. The highest concentrations were recorded for DEET (14 ng/g dw) and progesterone (11.5 ng/g dw) in stream bed and combined sewer overflow sediment samples, respectively. The ratio of concentration to its limit of detection (C:LOD) in sediments for a subset of compounds were compared to their C:LOD in water. In waters with a large capacity for dilution relative to fecal sources, the C:LOD ranges in sediments were greater than in water. Thus monitoring programs for fecal source tracking using wastewater micropollutants should consider sediment sampling, particularly for waters with highly diluted sources of fecal contamination.

Keywords

Fecal source tracking; Sewer cross-connections; Wastewater micropollutants; Ultrasonic-assisted extraction; APCI-MS/MS.

1. Introduction

Wastewater micropollutants (WWMPs) have the potential to produce detrimental effects in the environment [1]. Their presence in various matrices such as wastewater influents and effluents, combined sewer overflow (CSO) effluents, surface waters, sources of drinking waters and public water supply has been widely documented [2-13]. Recent research has indicated that while some compounds displace easily within the water column, others are hydrophobic and have a tendency to adsorb onto sediments [14-22]. Thus, to account for and bring both hydrophylic and hydrophobic compounds into consideration, it is necessary to sample the water column and bed sediments. Water samples and sediments were also analysed to source track fecal sewage pollution in discharges into aquatic environment [1, 23, 24]. Measured concentrations of WWMPs normally vary from ng/L to µg/L (water samples) or ng/g to µg/g (sediment samples) [25-

35]. However, their concentrations remain unknown in CSO sediments which play a role of vector for WWMPs [36] in sewer systems. Such data are needed for investigating the contribution of storm waters and combined sewer overflows to the accumulation of fines and associated contaminants in the bed sediments of the receiving streams. Such deposited sediments could also contribute to the desorption of sorbed contaminants into receiving waters. The perturbations in contaminant inputs caused by combined sewer overflow (CSO) events can disrupt steady-state conditions and could confound the use of wastewater tracers [2]. Furthermore, knowledge about the concentrations of WWMPs in stream sediments is also necessary to understand the routing, transport and fate of these contaminants in the environment and for estimating their persistence and environmental risks.

There are no standard methods for extraction, elution, concentration and detection for many compounds. To identify and measure WWMPs in sediments, adequate analytical methods with sufficiently low detection limits need to be developed, due to the high sulphur content of anoxic sediments and the potentially high contaminant loadings [37]. LC–MS/MS has become the preferred analytic technique for determining polar environmental pollutants [38-40]. Atmospheric pressure chemical ionisation (APCI) is employed in a few studies but its use has increased since it seemed to be less prone to matrix effects than standard electrospray ionization (ESI) [41-43]. It is commonly used as an interface for the LC–MS analysis of medium and low polarity substances [44-46].

It is nearly impossible to analyse all WWMPs. A preselection of target analytes is therefore crucial in developing an index of human fecal pollution. The standards for preselection that must be considered for WWMPs are: extensive and increased annual use (3–4% by weight per annum) [47], dissimilar structural and physico-chemical properties, pharmacokinetic behavior, frequent detection in wastewaters, some affinity with solids, potential toxic effect doses/concentrations, relative environmental persistence, usage as anthropogenic waste indicators (AWIs) and presence at trace concentrations in real samples, hence requiring more advanced and laborious analytical tools for their accurate determination.

Given that our focus is to find good tracers of anthropogenic impact on waters and sediments, we have chosen to focus on ten WWMPs belonging to the following groups: ß-blockers, analgesics, anti-inflammatory drugs, stimulants, diuretics, a sweetener, an antiepileptic drug, personal care products and hormones (see details in the Supplementary material section).

The objectives of this study were to: (1) develop a sensitive method for the separation and quantification of WWMPs in different types of solids (e.g., sewer and stream sediments) based on an ultra-high-performance liquid chromatography–atmospheric pressure chemical ionization tandem mass spectrometry (UHPLC–APCI–MS/MS), (2) compare concentrations in sediments with concentrations in water to evaluate the use of sediment sampling for fecal source tracking.

2. Methods and materials

2.1 Description of study sites

Five study sites were selected for the analysis of sediments and water: two urban streams (US_1 and US_2), a large river (US_3), an urban drinking water supply canal and 1 CSO which is discharged upstream of the sampling site (US_3). The two small ungauged urban streams in the Greater Montréal Area with mean measured dry weather flow rates of less than 0.1 m^3/s were selected because of elevated dry weather fecal indicator bacteria (*Escherichia coli* concentrations greater than 400 MPN/100 mL) potentially contaminated from cross-connected sewers. Both urban streams are upstream of drinking water supplies. The large river with a mean flow rate of 1000 m^3/s is used for drinking water supply as described by Madoux-Humery *et al.* [48] and receives discharges from storm sewers and combined sewer overflows. The selected CSO receives a mixture of sewage and precipitation primarily from foundation and roof drains. The CSO consists of a 355 mm round pipe draining into a chamber with an overflow structure that channels flow to a 450 mm round pipe draining to a separate storm sewer. The urban canal was selected as a site with very low concentrations of fecal indicator bacteria (dry weather concentrations generally less than 50 MPN/100 mL) with suspected inputs of sewage from sewer exfiltration. Details regarding the urban canal including WWMP results are available in Guérineau *et al.* [23] and are presented in this study for method validation and evaluation of WWMPs in sediments as tracers for field sites with varying degrees of fecal contamination.

2.2 Apparatus

The system set-up for analysis of WWMPs is described in Supplementary material.

2.3 Procedure

2.3.1 Sample collection and pretreatment

Sediment samples were collected from the upper 3 cm of the stream bed in urban streams (US_1) (n = 5), (US_2) (n = 11), (US_3) (n = 5), in canal (n = 15) and CSO (C, n = 3) in the Greater Montréal area. They were taken during dry weather in the summer and fall of 2011 and 2012. Samples were collected in 1-L pre-cleaned amber glass jars and kept cold on ice during transport to the laboratory. Upon arrival, sediment samples were homogenized, divided into several sub-samples, sealed in polypropylene jars, wrapped with aluminium foil, and stored at -20 °C.

Surface water samples were collected under different hydraulic conditions. Samples were taken in clean bottles (capacity 1 L) typically up to 30 cm depth, and filled up to the top to eliminate air bubbles. Forty one surface water samples were collected from urban streams (US_1) (n = 10), (US_2) (n = 11), (US_3) (n = 20) under dry weather conditions and fifty eight samples under wet weather conditions (US_1) (n = 30), (US_2) (n = 6), (US_3) (n = 28). Water samples were filtered and stored at 4 °C after adding formic acid as a preservative (see details in Madoux-Humery *et al.* [48].

Physico-chemical and microbial analysis of the samples (detailed data not shown) revealed a clear sanitary contamination of the waters and sediments.

2.3.2 Sediment sample extraction

Preparation and spiking of sediment samples are detailed in Supplementary material. The final optimized method for simultaneous extraction of 10 selected WWMPs used various extraction solvents. Sediment samples were successively extracted with 4 and 2 mL of the mixture of methanol/water (9:1, v/v, pH 11), followed by two extractions using 2 mL of acetone and ultimately with 4 mL of water with 0.1% formic acid (pH 2.65). There was five operating cycles in the extraction process. In each extraction step, the sample was vigorously vortexed for 1 min, ultrasonicated for 20 min in an ultrasonic bath (frequency 40 KHz, Bransonic 5510, Connecticut, USA) at 30 °C and centrifuged at 4000 *g* for 10 min. The supernatants obtained from each extraction step were combined, filtered using a 0.2-µm polypropylene syringe filter and concentrated to dryness by evaporation under a nitrogen stream. After the addition of 250 µL of methanol, the extract was diluted to 10 mL with HPLC Grade water (UPW) adjusted to pH 7 with sodium hydroxide 0.5 M and subjected to the SPE procedure. The developed extraction method with previously developed method for stream sediment analysis was also applied to CSO sediments.

2.3.3 SPE procedure: Cleanup and preconcentration

To reduce matrix interference, further cleanup of sediment samples is normally required. In this study, specific solid phases were used as a clean-up and preconcentration treatment. Generally, polymeric adsorbents have a higher adsorption capacity than C18 adsorbent for polar analytes [19, 39, 49-58]. As indicated above, SPE cleanup was performed using an Oasis HLB cartridge (30 µm, 60 mg/3 cc). The cartridge was preconditioned successively with 3 × 1 mL of methanol and UPW prior to sample load. After sample passage, the cartridge was washed with 10 mL of UPW and dried under vacuum for 30 min. The analytes were then eluted successively with 1 mL of methanol and 1 mL of 0.5 M formic acid–methanol mixture. The eluate was evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved with the initial mobile phase condition (0.5 mL). Before analysis, 2 µL of instrument internal standard containing 5 isotope-labeled compounds (1 mg/L) was added to correct for variations in sample recovery and instrumental performance [59].

2.3.4 Analytical methods

The optimized method was applied to the determination of WWMP concentrations in CSO and stream sediment samples. The four WWMPs (ACE, THEO, CAF and CBZ) selected by Madoux-Humery *et al.* [48] were analysed during this study in surface water samples by an on-line solid-phase extraction combined with liquid chromatography electrospray tandem mass spectrometry with positive electrospray ionisation (SPE-LC-ESI-MS/MS) [48]. Detailed information on preservation and analytical methods are published and available [48, 60]. Detection limits were estimated as three times the standard deviation of 5 replicate measurements of a field sample and were 10 ng/L for ACE, 6.50 ng/L for CAF, 6 ng/L for THEO and 0.52 ng/L for CBZ. All samples were analyzed in duplicate.

3. Results and discussion

3.1 Optimization of UHPLC–APCI–SRM/MS analysis and quantification

Atmospheric pressure chemical ionisation tandem mass spectrometry provides high sensitivity and selectivity for the identification and quantitative analysis of selected compounds. The collision gas pressure and the offset energy for the collision quadrupole Q2 were two important factors for determining the major product ion intensity for each compound; they were optimized at 1.5 mTorr and between 13 and 27 eV, respectively (Tables S3 and S4, Supplementary material).

The separation of the ten studied compounds occurred within 3.6 min with good resolution and the total run time was 4.5 min. Detailed description and discussion of the optimization of UHPLC–APCI–SRM/MS method are included in Supplementary material.

3.2 Optimization of extraction and SPE steps

Our study was carried out on the most relevant parameters that affect the recovery of target compounds (e. g. extraction solvent, cycle number, contact time and temperature of sonication, sample pH, type of SPE sorbent and volume and type of elution solvent). Detailed description and discussion of the optimization of extraction and SPE steps are included in Supplementary material.

The developed method (see Methods and materials) was applied to CSO sediment samples. The results of quantitative extraction showed that 63− 122% of the total extractable amounts in both sediment samples with the exception of atenolol (46% from stream sediment) and aspartame (53% from CSO sediments) were recovered in the first five cycles (Figure 1). In a subsequent extraction step with 2 mL of acidified water, none of the analytes could be detected anymore. The differences in the extraction recoveries between WWMPs and sample matrices are consistent with those reported by Martin *et al.* [50].

3.3 Analytical method validation

In order to assess the performance of the proposed method, the main analytical quality parameters were thoroughly evaluated by determination of recoveries, linearity, precision, repeatability, matrix effects and detection limits. Matrix-matched calibration curves prepared in every type of sample showed good linearity between 0 and 100 µg/L, with a correlation coefficient (R^2) ≥ 0.9946 and ≥ 0.9653 for stream and CSO sediments respectively (Table 2). These R^2 values were of the same order of magnitude than those reported by Pérez-Carrera *et al.* [61].

Relative recoveries and precision data are also listed in Table 2 for stream and CSO sediments. Satisfactory relative recoveries and good repeatability in spiked extract samples illustrated the suitability of the internal standards. Relative recoveries ranged from 75.5% to 156% in stream sediment extracts as well as in CSO sediment extract samples for all analytes, indicating good performance of the proposed method. Our proposed method achieved a significantly better recovery for acetaminophen in comparison with methods developed by Martin *et al.* and Radjenovic *et al.* [50, 54] for its determination in sample matrices which may have similar properties as CSO sediments.

The repeatability values varied in the range of 2.19–17.4% for stream sediments and 1.80–22.6% for CSO sediments and reproducibility was of 0.04–20.0% for stream sediments and of 0.82–22.9% for CSO sediments. These results did not show apparent differences between stream and CSO sediment samples and are similar to those reported by other studies [50, 54, 62].

Table 2 also outlines limits of detection (LODs) for stream and CSO sediment extracts that were in the range of 0.01–0.41 ng/g in stream sediment extracts and 0.21–14.8 ng/g in CSO sediment extracts. The sensitivity for stream sediment samples was better than for CSO sediment samples. The caffeine registered a higher LOD in comparison with the other compounds. Thus, our method is less sensitive to analyse caffeine as compared to the other analytes but given the very high concentrations of caffeine observed, this is a non-issue. LODs for stream sediments were better than reported in previous studies using LC [49, 61, 62].

3.4 Matrix effects

We successfully reduced matrix effects by using selective extraction and cleanup procedures and using an APCI interface as the ionisation source instead of the more standard ESI interface (see details in Supplementary material).

3.5 Method applicability in sediment samples and comparison with water samples

After the optimization and validation, the developed method was applied to real samples with different matrices, to evaluate its applicability in the determination of the investigated WWMPs in stream and CSO sediments. To the best of our knowledge, this is the first time that such compounds were measured in CSO sediments.

With the exception of medroxyprogesterone, almost all of the target compounds were detected in sieved sediment samples (80 mesh) with concentrations ranging from 0.13 to 427 ng/g dw and the most abundant compound was theophylline/paraxanthine (Table 3). Comparison among the concentrations of compounds in combined sewer overflow sediments (CSO) and sediments from the river downstream of CSOs (US_3) show that the majority of compounds are effectively removed by natural attenuation (e.g. dilution, hydrolysis, sorption, biotransformation and phototransformation).

Table 4 presents mean concentrations of 4 compounds measured in surface water samples during dry and wet weather conditions. Our results were compared with data, reported by Madoux-Humery *et al.* [48] and Guérineau *et al.* [23], in order to compare the water and sediment samples from sites having different degrees of human fecal contamination relative to the available dilution (CSOs > US_2 = US_1 > canal > US_3).

Figure 2 shows the ratio between the average concentrations of WWMPs measured in water and sediment samples for each of the sites and their limits of detection. This ratio indicates the range over which a particular compound (ACE, THEO, CAF or CBZ) could be useful as a wastewater tracer similar to the recommendation of Benotti and Brownawell for comparing various WWMPs as tracers of wastewater contamination using dynamic ranges of the WWMPs [2] see Table S5 (Supplementary material). In contrast to the dynamic range of Benotti and Brownawell [2], the concentration:LOD ratio (C:LOD) is defined here with average concentrations rather than the maximum concentration measured in order to reduce the bias from extreme values that are not representative of environmental conditions:

$$\mathrm{C{:}\,LOD} = \frac{\text{Average measured concentration in environmental sample}}{\text{LOD}} \qquad (1)$$

For highly concentrated sampling locations such as sewers (SA and SB) in dry weather and one of the CSOs in wet weather (OA, the overflow of sewer SA), the C:LOD was greater (from 5 to 43 times higher for THEO and CAF, respectively) in water than in sediments for all WWMPs. In general, as the degree of dilution increased, the C:LOD in sediments increased relative to the C:LOD in water. For example, OB, the overflow from combined sewer SB is highly diluted because it receives runoff from a large impermeable surface [48]. For all WWMPs in OB except for CAF, the C:LOD of CSO sediments (C) was greater than in water. For ACE, the C:LOD in sediments was always greater than in water with the exception of the highly concentrated sewage samples (SA, SB, and OA). In contrast, the C:LOD for CBZ in water was higher than in sediments with the exception of site OB because of the higher LOD for CBZ in sediments. In CSO sediments, the WWMP with the highest C:LOD was THEO followed by ACE. For urban stream and canal sediments, ACE was the best tracer of fecal contamination followed by CAF and THEO. For water, CAF appeared most frequently as the WWMP with the highest C:LOD followed by ACE. However, ACE was below the detection limit in water samples from the most highly diluted urban streams.

Benotti and Brownawell [2] have shown the potential of using some of the selected compounds (acetaminophen, caffeine, paraxanthine and carbamazepine) as wastewater tracers of a highly sewage-impacted estuary bay. By determining the dynamic range of LC-ToF-MS analysis in waters, they found that caffeine and paraxanthine were some of the compounds with the largest dynamic ranges. Unique to our study, was the analysis and comparison of WWMPs concentrations in sediment samples with their concentrations in water samples.

The dynamic range as defined by Benotti and Brownawell [2] or the C:LOD depend strongly on the method used for measurements. The comparison of the dynamic ranges or C:LOD of WWMPs in water versus sediments strongly supports the use of sediment sampling in addition to water sampling for fecal source tracking. Because the C:LOD of some WWMPs (specifically ACE in our study) in sediments can be higher than the C:LOD in water, sediment sampling can be more useful for establishing gradients related to contaminant sources, particularly for highly diluted water sources with wastewater sources that are intermittent [23]. The disadvantages of sediment sampling include the greater heterogeneity of the samples with regards to particle size, natural organic matter, etc. that can influence WWMP sorption [21, 63-66] and the smaller volumes of samples collected. Advantages of sediment sampling include the lower mobility of WWMPs in sediments at specific locations, particularly in relation to wastewater discharges that are intermittent such as CSOs, cross-connections or spills that are difficult to monitor in water because of their highly dynamic nature. Many factors influence the concentrations of WWMPs in water and sediments, including human consumption patterns and excretion rates, discharge patterns, sorption processes, degradation rates and dilution processes [67-69]. The relative importance of these factors for a given system, in addition to the LOD of WWMPs will determine the most appropriate WWMP tracers to select and whether they should be measured in both the aqueous and sediment phases. Results of this study showed that even WWMPs considered to have a relatively low sorption potential, such as ACE [70] can serve as useful tracers in sediments because they had a relatively high C:LOD ratio. Dilution processes often dominate when travel times are short, discharges are intermittent or highly variable, and flow rates are low compared to the receiving water. In these cases, where the C:LOD is low, water sampling alone will not likely provide meaningful results and sediment sampling should be considered.

4. Conclusions

A method using ultrasonication–assisted extraction and UHPLC–APCI–MS/MS detection was successfully developed for the simultaneous analysis of 10 WWMPs from a diverse group of markers of sanitary contamination, including pharmaceuticals, hormones and personal care products. Our work helps to demonstrate the versatility of USE methods to target a more diverse range of compounds. Optimisation of the ultrasonic extraction, SPE and analytical parameters are required for more efficient and reproducible extractions, purifications and analyses. Ultimately, the choice of the extraction, cleanup and analytical methods was dependent on the effectiveness, capital cost, operating cost, simplicity of operation, and waste production. The optimized ultrasonic extraction and cleanup procedures were found to extract WWMPs at ng/g levels from stream and CSO sediments with recoveries greater than 70% for most analytes. All selected compounds were eluted within a 3.6 minute period; with a short chromatography run (4.5 min). It allows for significant improvement over previously published works in terms of matrix effect for the analysis of the target compounds in sediments (especially acetaminophen). The method has been used in our laboratory to extract WWMPs from field-collected sediments from rivers, creeks and combined sewer overflows. The range of WWMPs extracted and its complete separation obtained by the optimized method was found to be very useful in the application of fingerprinting and source determination of human fecal contaminated samples. Chromatographic separation of theophylline and paraxanthine was necessary for accurate quantitation of the theophylline used as a medication on one hand and of the primary metabolite of caffeine on the other hand. This method has excellent extraction efficiency, precision and recovery of WWMPs. In addition, when combined with easy sample preparation, it makes it an ideal technique for laboratories engaged in analyzing a large number of sediment samples. Based on the optimized conditions, the level of selected WWMPs in the sediment samples (≤ 80 µm) collected in the Greater Montreal area was found to be between 0.13 and 427 ng/g dw. Our results support the hypothesis of Madoux-Humery *et al.* [48] who suggested that internal sewer sediments were the source of WWMPs that were remobilized with the increase of flow rate associated with rain events. Sediment sampling of WWMPs should accompany water sampling for fecal source tracking for systems where dilution rates are high and the C:LOD is low. Thus confirmation of concentrations in sediments is necessary to understand their environmental fate and potential ecological effects, in addition to their use as tracers of sewage contamination.

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SUPPLEMENTARY INFORMATION

Supplementary data associated with this article can be found in the online version at

5. References

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FIGURE CAPTIONS

Figure 1. Absolute and relative extraction recoveries for selected WWMPs from spiked stream sediment (top) and CSO sediment (bottom). Error bars represent standard deviations (n=3).

Figure 2. Average concentration to LOD ratios of WWMPs in CSOs (C, SA, SB, OA and OB), urban streams (US_1, US_2 and US_3) and canal sediment (S) and water (W) samples under dry (DW) and wet (WW) weather conditions.

Table 1. Characteristics of the extraction method (USE) described in the literature for the determination of the target compounds in solid environmental samples.

Sample	Compound	Extraction solvents	Total solvent volume (mL)	Ultrasonication cycles	pH extract	Clean-up	Analytical determination	Recoveries (%)	References
Sewage sludge, river and estuary sediments	ATL CBZ MedP	Acetonitrile–water (5:3, v/v)	24	3 x 15 min	7	Oasis HLB	UHPLC–MS/MS (+ESI, MRM)	80–100% except for atenolol	[71]
Sea sediments	CBZ DIC	Acetone–McIlvaine buffer (1:1,v/v, pH 4)	80	2 x 15 min	–	Evolute ABN and Oasis HLB	UHPLC–MS/MS (+ESI, -ESI, MRM)	60–70% 50–60%	[39]
Sewage sludge, compost and sediments	ACE CBZ CAF DIC	Methanol Methanol Acetone	9	3 x 15 min	2	Oasis HLB	HPLC, UV–DAD	10–20% 80–100% 80–100% 60–80%	[50]
Primary and excess sludge	ACE DIC CBZ ATL THEO CAF DEET	Methanol–water (1:9,v/v, pH 11)	25	1 x 15 min and 2 x 10 min	–	Oasis HLB	HPLC–MS/MS (API)	80–120% except for atenolol (40%)	[72]
Activated and digested sludge	CBZ DIC	Methanol Acetone	10	4 x 5 min	7 2	RP-C_{18}ec Oasis MCX	HPLC–MS/MS (+ESI, -APCI, MRM)	76–85%	[73]

Table 2. Recoveries in stream and CSO sediment extracts, repeatability, reproducibility, linearity (regression coefficient) and detection limit (LOD) for the method.

Compound	Recovery (%, n=2)	Intra-day RSD (%, n=5)	Inter-day RSD (%, n=3)	R^2	LOD (ng/g)
ACE	96.6^a	2.29^a	4.67^a	0.9984^e	0.01^e
	101^b	2.97^b	6.99^b		
	96.9^c	2.30^c	0.72^c		
	107.6^d	8.08^d	6.43^d	0.9995^f	3.41^f
ATL	93.3	5.98	3.33	0.9972	0.17
	100	6.92	14.45		
	88.7	2.67	0.04		
	112	10.51	5.30	0.9653	3.48
THEO	103	3.32	4.05	0.9990	0.33
	112	8.9	16.32		
	100	3.18	4.20		
	156	8.43	5.53	0.9992	3.15
CAF	124	10.00	2.84	0.9975	0.41
	121	8.60	11.82		
	104	5.20	5.31		
	118	6.87	6.13	0.9995	14.79
APM	111	4.00	6.54	0.9971	0.34
	107	9.00	9.20		
	99.0	15.00	3.57		
	99.8	1.80	6.94	0.9991	0.21
CBZ	105	11.94	7.38	0.9972	0.32
	113	10.99	16.06		
	103	2.94	2.40		
	87.6	10.57	17.63	0.9991	3.89
DEET	113	3.38	3.43	0.9995	0.21
	114	6.68	14.39		
	98.8	2.19	10.02		
	81.1	7.50	8.96	0.9991	0.90
DIC	82.6	17.42	6.10	0.9988	0.25
	85.0	17.37	19.98		
	75.5	9.11	2.59		
	104	5.96	18.68	0.9988	1.50
MedP	106	6.77	7.49	0.9946	0.13
	104	4.08	15.34		
	91.8	8.18	6.05		
	85.7	22.62	22.90	0.9991	0.84
PRO	109	15.8	10.24	0.9998	0.23
	85.6	10.37	3.53		
	88.7	7.43	0.18		
	94.9	6.05	11.87	0.9995	2.32

Where a, b and c represent respectively 10, 20 and 30 µg/L as nominal concentrations of analytes doped into stream sediment extract and d represents a concentration of 100 µg/L in CSO sediment extract. The linearity ranged from 0 to 30 µg/L in stream sediment extract (e) and between 0 and 100 µg/L in CSO sediment extract (f). This nomenclature is also applied to the other rows of the table.

Table 3. WWMP content of real sediment samples (CSO, urban streams and canal) under dry weather conditions, means are given with standard deviations.

Compound	Mean concentration (ng/g)				
	CSO	US$_1$	US$_2$	US$_3$	Canal^b
ACE	97.69 ± 16.8	0.87 ± 0.03	2.45 ± 1.08	0.13 ± 0.05	8.23 ± 4.55
ATL	80.46 ± 9.26	nd	Trace	nd	Na
THEO/PX	426.63 ± 13.0	0.69 ± 0.05	0.44 ± 0.04	Trace	1.35 ± 0.77
CAF	297.04 ± 16.2	22.34 ± 0.72	1.59 ± 1.19	1.59 ± 0.55	1.31 ± 0.39
APM	nd	nd	Trace	nd	Na
CBZ	53.91 ± 6.78	Trace	Trace	nd	Nd
DEET	2.30 ± 1.17	0.68 ± 0.01	13.82 ± 10.6	nd	Na
DIC	Trace	nd	nd	nd	Na
MedP	nd	nd	nd	nd	Na
PRO	11.49 ± 1.05	nd	nd	0.59 ± 0.11	Na

na and nd represent not analysed and not detected respectively; trace refers to cases where an MS transition peak was observed, but it was below the LOD; ^{b} refers to results (n = 15) reported during the study of Guérineau *et al.* [23].

Table 4. WWMP content of water samples (CSOs, urban streams and canal) under dry and wet weather conditions, means are given with standard deviations.

Compound	**Mean concentration (ng/L)**											
	Dry weather (DW)						**Wet weather (WW)**					
	SA[a]	**SB**[a]	**US_1**	**US_2**	**US_3**	**Canal**[b]	**OA**[a]	**OB**[a]	**US_1**	**US_2**	**US_3**	**Canal**[b]
ACE	8460 ± 5270	3280 ± 1683	170 ± 126	508 ± 243	nd	nd	6420 ± 6808	1 ± 0	124 ± 20	72.6 ± 36.9	nd	nd
THEO/PX	4460 ± 1613	3200 ± 3049	80.7 ± 31.9	130 ± 58.4	22.6 ± 15.1	14.1 ± 3.38	3630 ± 3203	128 ± 190	53.6 ± 15.6	nd	20 ± 8.74	11.7 ± 4.48
CAF	7740 ± 5561	810 ± 504	92.2 ± 26.9	318 ± 51.1	21.3 ± 5.30	55.3 ± 24.0	5520 ± 4968	336 ± 190	165 ± 24.5	36.2 ± 5.35	26.6 ± 24.7	35.1 ± 5.53
CBZ	310 ± 239	101 ± 136	6.61 ± 1.29	0.97 ± 0.16	2.12 ± 0.65	1.65 ± 0.17	207 ± 204	8.79 ± 14	3.68 ± 2.56	1.32 ± 0.53	2.12 ± 0.62	1.83 ± 0.13

nd represents not detected; [a] and [b] refer to data and results reported by Madoux-Humery *et al.* [48] and Guérineau *et al.* [23] respectively.

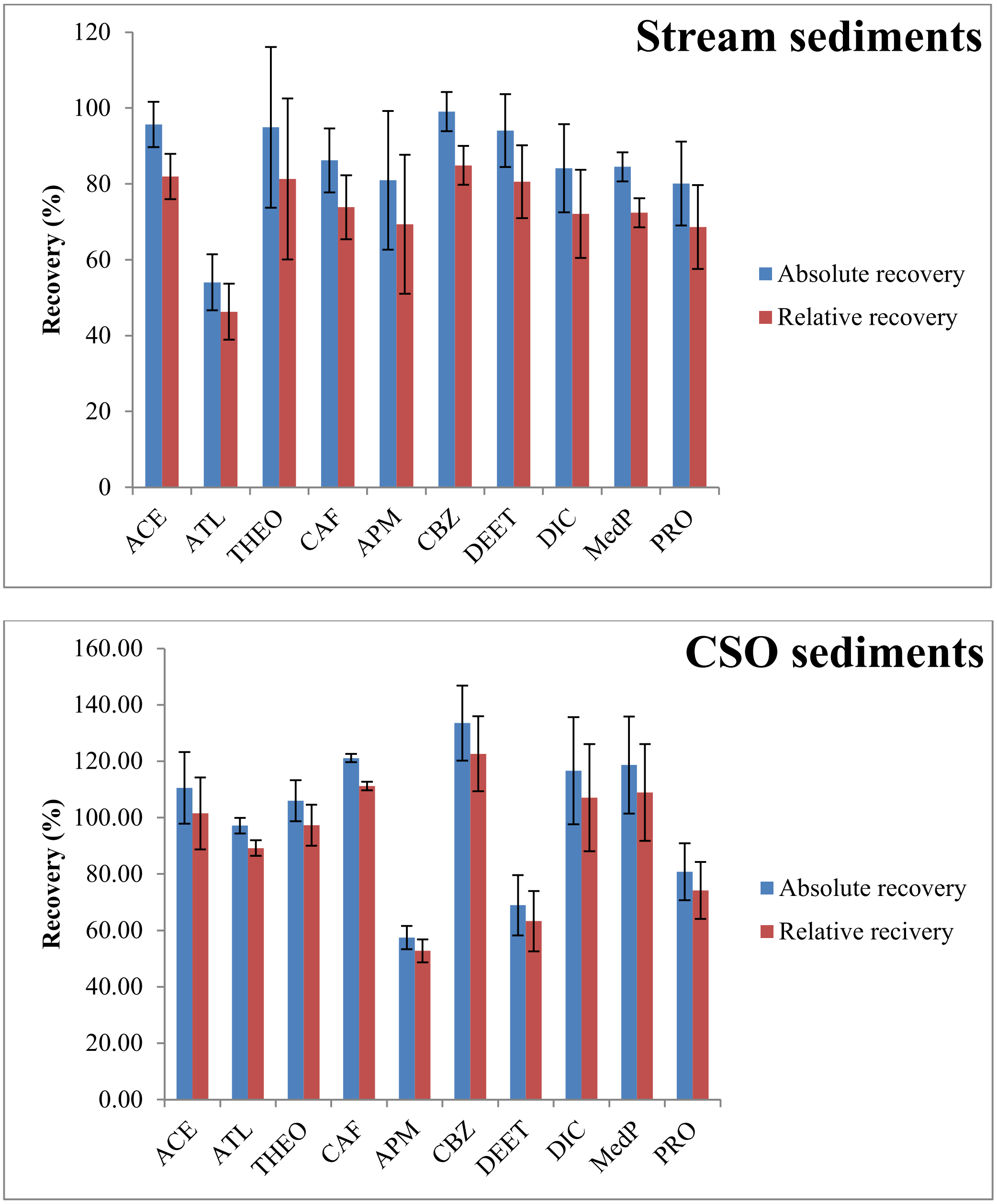
Stream sediments
Recovery (%)
120
100
80
60
40
20
0
ACE
ATL
THEO
CAF
APM
CBZ
DEET
DIC
MedP
PRO
Absolute recovery
Relative recovery
CSO sediments
Recovery (%)
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
ACE
ATL
THEO
CAF
APM
CBZ
DEET
DIC
MedP
PRO
Absolute recovery
Relative recivery

Figure 1

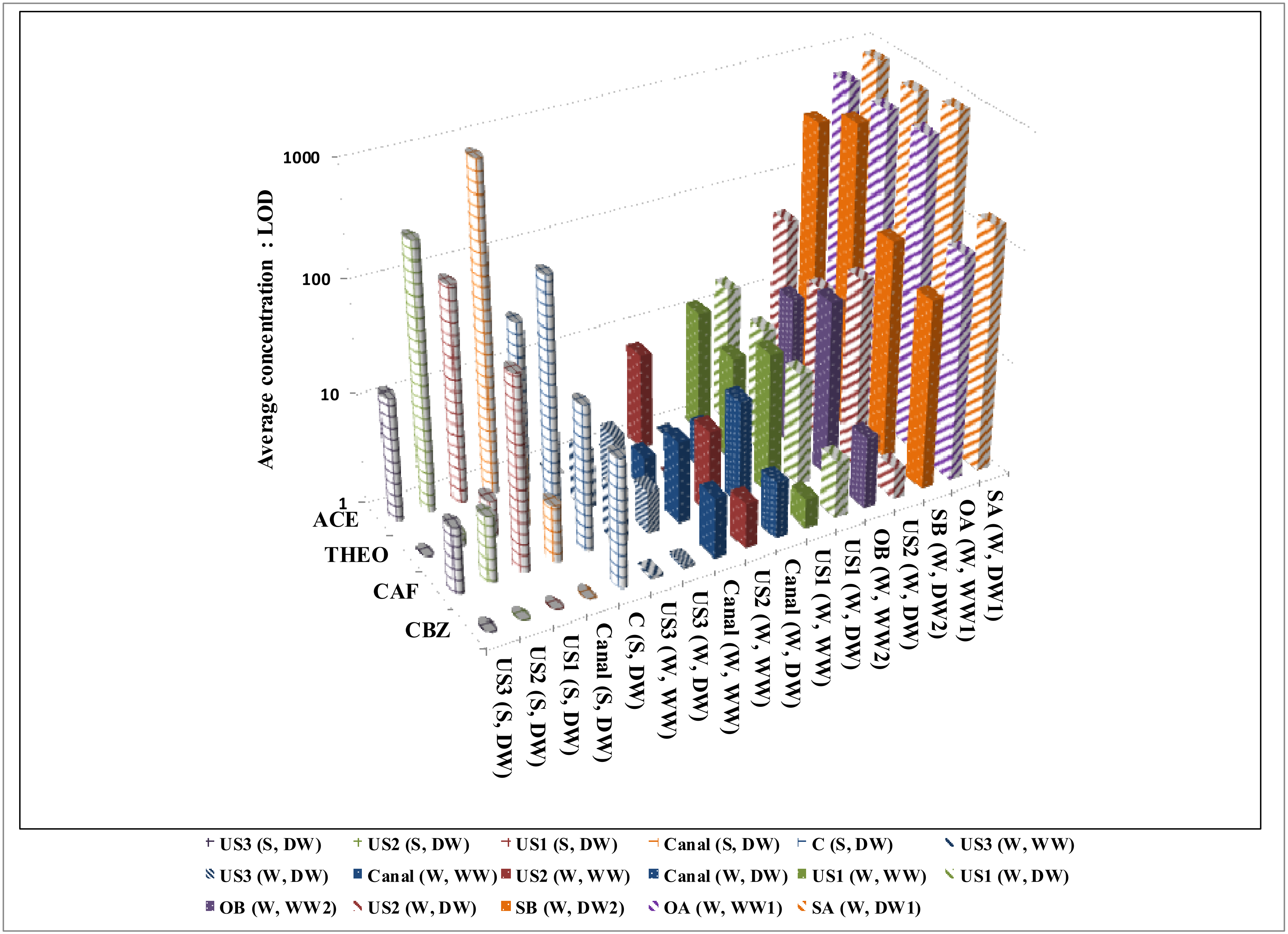
Average concentration : LOD
1000
100
10
1
ACE
THEO
CAF
CBZ
US3 (S, DW)
US2 (S, DW)
US1 (S, DW)
Canal (S, DW)
C (S, DW)
US3 (W, WW)
US3 (W, DW)
Canal (W, WW)
US2 (W, WW)
Canal (W, DW)
US1 (W, WW)
US1 (W, DW)
OB (W, WW2)
US2 (W, DW)
SB (W, DW2)
OA (W, WW1)
SA (W, DW1)
US3 (S, DW)
US2 (S, DW)
US1 (S, DW)
Canal (S, DW)
C (S, DW)
US3 (W, WW)
US3 (W, DW)
Canal (W, WW)
US2 (W, WW)
Canal (W, DW)
US1 (W, WW)
US1 (W, DW)
OB (W, WW2)
US2 (W, DW)
SB (W, DW2)
OA (W, WW1)
SA (W, DW1)

Figure 2