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Analysis of endocrine disrupting compounds, pharmaceuticals and personal care products in sewage sludge by gas chromatography–mass spectrometry

Yong Yu*, Laosheng Wu

Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

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ABSTRACT

Endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) have been acknowledged as emerging pollutants due to widespread contamination in environment. A rapid and reliable analytical method, based on ultrasonic extraction, clean up on Envi-carb cartridge, derivatized with *N*-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA), and analyzed by gas chromatography–mass spectrometry (GC–MS), was developed for determination of 4 EDCs (bisphenol A, estrone, nonylphenol and octylphenol) and 10 PPCPs (acetylsalicylic acid, carbamazepine, clofibric acid, diclofenac, gemfibrozil, ibuprofen, ketoprofen, naproxen, paracetamol and triclosan) in sewage sludge. Mean recoveries of the target analytes, at different spike levels (40, 300 and 2000 ng/g), ranged from 57.9% to 103.1%. Relative standard deviations (RSDs) were in the range of 1.3–9.5% at different spiked levels. The limit of quantification (LOQ) ranged from 4.7 to 39 ng/g. The method was applied to sewage sludge samples from sewage treatment plants (STPs) in southern California. High concentrations of PPCPs and EDCs were found in sewage sludge, ranging from 1502 to 5327 ng/g dry weight. Appropriate disposal of sewage sludge was required to avoid secondary contamination.

1. Introduction

Endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) are emerging pollutants that have attracted much public attention [1–3]. They are challenging to detect in the environment. Increasing numbers of water samples obtained from lakes, streams, aquifers and municipal supplies are found to be contaminated by trace quantities of these compounds. The concentrations are typically in the microgram to nanogram per liter ranges [4–6]. To track their fate and transport in the terrestrial and aquatic environment, and to assess the consequences of aquatic ecosystems and human health due to chronic exposure to compounds way below the therapeutic thresholds, protocols are needed for their expedient detections and there is no easy straightforward answer [7].

Pharmaceutical residues excreted by patients, in addition to discarded medicines, eventually end up in sewage treatment plants (STPs), which are the primary sources of these chemicals to the aquatic environment [8]. During the course of wastewater treatment process, the PPCPs and EDCs may be adsorbed by the suspended solids and subsequently removed from water stream by sedimentation [9]. Municipal sewage sludge, the solid fractions separated from the wastewater stream, therefore is potentially a sink of the wastewater-borne PPCPs and EDCs [10]. Many studies [9,11–13] showed that the concentrations of PPCPs and EDCs were reduced as the influent wastewater underwent purification in STPs and much of them were removed by the activated sludge process. Municipal sewage sludge is conventionally land disposed. To track the fate and transport of sludge-borne PPCPs and EDCs in terrestrial and aquatic ecosystems, it is imperative to develop reliable and accurate analytical methods for detection of these compounds in municipal sewage sludge that has complex organic matrices that would bond with these compounds by surface adsorption.

Currently analytical methods emphasized detection of the compounds in aqueous matrices, such as surface water and wastewater [14]. A few studies were on measuring PPCPs and EDCs present in solid matrices, such as sewage sludge, soil and sediment from which the targeted chemicals must be extracted. Durán-Alvarez et al. [15] separated pharmaceuticals from wastewater irrigated soils by accelerated solvent extraction. Xu et al. [16] recovered selected pharmaceuticals, EDCs and hormonal compound using acetone and ethyl acetate ultrasonic extractions. Huang et al. [17] determined azole antifungal chemicals in municipal sewage sludge that was sonicated to extract the analytes. Minten et al. [18] extracted pharmaceuticals in sediment using liquid–liquid extraction and ultra-sonication followed by solid-phase extraction.

* Corresponding author at: Department of Environmental Sciences, University of California, 900 University Ave., Riverside, CA 92521, USA. Tel.: +1 951 827 4664; fax: +1 951 827 4664.
E-mail address: yuyong.env@gmail.com (Y. Yu).

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Cleaning up the extracts is crucial for the subsequent analytical process employed. Matrix components of the samples could mask responses of target compounds in the instrumental determination. Solid phase extraction (SPE) is the most common used method for cleaning up the extracts, SPE products such as Oasis HLB, MCX and C18 are frequently used [16,19,20]. The Envi-carb cartridge has been reported to effectively clean up trace organic pollutants in solid matrices [21,22]. It is however unclear whether the existing SPE products are equally effective for different pharmaceutical classes and under matrices of different complexity.

The actual analytical determinations involving trace quantities of pharmaceutical chemicals would employ high/ultra performance liquid chromatography coupled with detection by tandem mass spectrometry (LC–MS/MS). Tandem mass spectrometry (MS/MS), such as triple-quadruples (QqQ) and quadruple time-of-flight (QTof), are the most widely used [23–25]. However, the matrix effect is problematic in the analyzing PPCPs involving electrospray ionization (ESI) source. The co-eluting substances present in the extract may lead to ion suppression or enhancement resulting in relatively high detection limits and decreased reproducibility [26,27]. In contrast, gas chromatography in combination with electron impact (EI) ionization mass spectrometry (GC–MS) operating in the selected ion monitoring (SIM) mode are applicable for analyses of PPCPs and no apparent matrix effect has been found [28–30]. The GC–MS allows less costly and easier operation than LC–MS/MS. However, the challenge of GC–MS to analyze for PPCPs and EDCs lies in the compounds' low volatility and presence of polar functional groups with active hydrogens, such as –OH, amines and amides that require the use of derivatization procedure to reduce polarity and enhance their volatility [31–33].

In this study, we tested the conditions of extracting PPCPs and EDCs from solid phase matrices, including different organic solvents for the extraction and extract clean up methods and selected the optimal protocols for the analysis of these compounds in municipal sewage sludge. The method was applied to detect PPCPs and EDCs in the sewage sludge of four STPs in southern California.

2. Experimental procedures

2.1. Chemicals and materials

Acetylsalicylic acid, carbamazepine, clofibric acid, diclofenac (sodium salt), ketoprofen and naproxen were purchased from MP Biomedicals (Solon, OH). Bisphenol A, estrone, gemfibrozil, ibuprofen, nonylphenol, octylphenol and paracetamol were obtained from Sigma–Aldrich (St. Louis, MO) and triclosan from Fluka (St. Louis, MO). The surrogate standard, [$^2H_3$]-ibuprofen (D3-ibuprofen) and [$^2H_3$]-paracetamol (D3-paracetamol) were purchased from C/D/N Isotopes Inc. (Quebec, Canada). Chemical structures, CAS registry numbers of the compounds are summarized in Table S1 (Supplementary material). Stock solutions of the reference compounds were prepared in methanol and stored at −20 °C. *N-tert*-Butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) (Sigma–Aldrich, St. Louis, MO) was used as the derivatization reagent.

Acetone, ethyl acetate, methanol (pesticide grade), and formic acid were purchased from Fisher Scientific (Pittsburgh, PA). Deionized water was prepared by a Milli-Q water purification system. SPE products Oasis HLB (500 mg, 6 mL) was purchased from Waters (Milford, MA). Supelclean Envi-carb (500 mg, 6 mL) were obtained from Supelco (St. Louis, MO).

2.2. Sampling

In June 2010, sewage sludge samples were collected from four STPs serving different communities in southern California. The sewage sludge samples were approximately 80% in water weight. After collection, the samples were air-dried at room temperature, finely ground to pass through a sieve with 0.5 mm openings, and stored at 0 °C until the analyses (less than 15 h).

2.3. Extraction and clean up procedures

2.3.1. Ultrasonic extraction method

1 g aliquot of prepared sludge sample was spiked with 0.1 mL 2000 ng/mL of the surrogates. 5 mL of methanol containing 1% (v/v) formic acid were added, vortex mixed (Fisher Vortex Genie 2, Pittsburgh, PA) for 2 min, ultrasonicated (FS30H, Fisher Scientific, Pittsburgh, PA) for 20 min, centrifuged at 3000 rpm for 10 min, and then decanted the supernatant. The sludge was extracted two additional times respectively with 4 and 3 mL of the solvent. The supernatants were combined.

2.3.2. Extract clean up and derivatization

For extract cleaning using HLB cartridges, the supernatants were evaporated under nitrogen in a 37 °C water bath to about 1 mL. The concentrated extract was re-dissolved into 100 mL of deionized water. The cartridges were conditioned with 2 mL methanol and 2 mL deionized water, followed by loading of the sample at a flow rate of 5 mL/min. Afterwards, the cartridges was first dried under nitrogen and then eluted with 4 × 1 mL methanol [16,19].

For using the Envi-carb extract clean up cartridges, the supernatants were evaporated to about 2 mL. The clean up columns were conditioned with 2 mL methanol and then the concentrated extract was introduced at a rate of 1 drop/s and the drainage collected. At the end, the cartridge was eluted with 1 mL of methanol and 1 mL of methanol containing 1% (v/v) formic acid. The drainage and elute were combined [21].

The extracts were evaporated to dryness with a gentle stream of nitrogen gas at 37 °C, and re-dissolved in 900 μL of ethyl acetate, transferred into the GC vial, and then 100 μL of MTBSTFA was added. The GC vials were placed into GC oven at 70 °C for 60 min for derivatization prior to GC–MS analysis [16,33].

2.4. Detection with GC–MS

The chemicals in the prepared samples were determined by using an Agilent 6890N GC interfaced to a 5975C MSD, equipped with an Agilent 7683B automatic liquid sampler. The instrument was equipped with a HP-5MS GC column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) for chromatographic separation with helium (purity > 99.999%) as the carrier gas at a constant flow rate of 1.2 mL/min. Injector temperature was 250 °C. The GC oven temperature was programmed from 70 °C (held for 1 min) to 120 °C at 20 °C/min, raised to 250 °C at 10 °C/min and then to 280 °C at 5 °C/min and held for 3 min. 1 μL sample was injected in pulsed splitless mode and the total analysis time for a GC run was 25 min. MS was operated in EI ionization mode (70 eV) with SIM mode and a solvent delay time of 11 min. The GC–MS interface, ion source and quadruple temperatures were set at 280, 230 and 150 °C, respectively. The retention time and fragment ions were identified by injecting single compound standard under the full scan. Primary and secondary ions used for quantification and monitoring are shown in Table 1.

2.5. Quantification

A seven point calibration curve with concentrations of the compound in ethyl acetate spanning from 2 to 2000 ng/mL. Solvent blanks were used to monitor the procedural and instrument background. A constant amount of deuterium labeled surrogate

Table 1
Retention times (min) and mass spectrometric data (m/z) for *tert*-BDMS derivatives of the chemicals.

Compound	Retention time	Molecular weight	Primary ions	Secondary ions
Acetylsalicylic acid	11.83	180.2	195	237, 196
Bisphenol A	20.93	228.3	441	207, 442
Carbamazepine	18.97	236.3	193	194, 293
Clofibric acid	12.43	214.6	143	273, 271
Diclofenac-Na	19.41	318.1	352	214, 409
Estrone	23.37	270.4	327	328, 384
Gemfibrozil	15.98	250.3	243	179, 307
Ibuprofen	12.79	206.3	263	264, 161
Ketoprofen	18.39	254.3	311	295, 312
Naproxen	17.16	230.3	287	185, 288
Nonylphenol	15.84	220.4	277	278, 334
Octylphenol	13.15	206.3	249	250, 320
Paracetamol	15.20	151.2	322	379, 248
Triclosan	17.67	289.5	347	200, 345
D3-ibuprofen	12.81	209.3	266	267, 268
D3-paracetamol	15.22	154.2	325	251, 326

standards (200 ng/g) was added before extraction. The labeled surrogates compensates for differences in extraction yields between analytes and for variations between sludge samples that possess different physico-chemical properties. D3-ibuprofen and D3-paracetamol were used as surrogates. D3-ibuprofen was selected for the quantification of acetylsalicylic acid, bisphenol A, clofibric acid, diclofenac, estrone, gemfibrozil, ibuprofen, ketoprofen and naproxen, while D3-paracetamol was used for carbamazepine, nonylphenol, octylphenol, paracetamol and triclosan. Quantification was performed using the calibration curves with an inverse weighing factor ($1/x$) of the surrogates.

2.6. Method validation

The recovery of the method was evaluated by determining the sludge samples (triplicates each) spiked with low, medium and high levels of analytes namely 40, 300 and 2000 ng/g, respectively. Aliquots of the analytes in methanol were mixed with sewage sample, vortex mixed for 5 min, then the solvents were evaporated at 21 °C in a darkened fume hood for 12 h. The absolute recovery was calculated as the ratio of the peak area difference of spiked and non-spiked sample to the peak area in a non-enriched external standard. The instrumental detection limit (IDL) was set as signal to noise (S/N) ratio of 3, obtained from serial dilution of standards. The limit of detection (LOD) and the limit of quantification (LOQ) were determined by calculating the S/N ratios of 3 and 10 for the compound in sewage sludge matrices, respectively. The accuracy of method was evaluated by intra-day and inter-day reproducibility. The precision of method were determined by calculating the relative standard deviation (RSD). Statistical treatment of data (significance level) was carried out using the statistical software SPSS 16.

3. Results and discussion

3.1. GC–MS quantification

No quantifiable amounts of the analytes were detected in procedural and instrumental blanks. Fig. 1(a) shows the typical chromatogram for a standard solution (100 ng/mL). The peak area repeatability obtained from five repeated injections of a spiked sludge sample, and RSD were less than 6% (Table 2), reflecting the stability of the instrument. Values of IDL for the analytes ranged from 1 to 10 pg (Table 2). The linearity of the calibration curve for each analyte was tested in the range shown in Table 2. Linearity was evaluated by statistical methods measuring the coefficient of determination (R^2) which quantify the goodness of fit of the linear regression. The GC–MS exhibited satisfactory linearity ($R^2 > 0.983$) for all the analytes [24,34].

3.2. Method performance

3.2.1. Optimization of extraction

Different solvents, including acetone, ethyl acetate, methanol, acidified ethyl acetate and methanol, were evaluated for their ability of extracting the PPCPs and EDCs from sludge samples that was spiked at 300 ng/g dry weight (dw) of each target compound. As shown in Fig. 2(a), acetone gave poor recoveries to most compounds. Ethyl acetate, methanol and acidified ethyl acetate were acceptable in recovering some of the compounds. However, their performance on recoveries of some compounds such as acetylsalicylic acid, carbamazepine, clofibric acid and diclofenac were not acceptable. The acidified solvent, methanol with 1% formic acid, showed the best outcomes with recoveries ranging from 57.9 to 103.1% and was selected as the extraction solvent.

To investigate the effect of extraction time on the recoveries, extraction times of 10, 20 and 30 min were tested. The recovery of the targeted analytes significantly increased when the extraction time extended from 10 to 20 min ($p < 0.01$) while no significant increase was observed when the extraction time was extended to 30 min ($p > 0.05$). The sewage sludge samples were extracted at 20 min optimal contact time.

The results of sequential extraction tests revealed that more than 97% of the total extractable chemicals in sewage sludge were released in three extraction cycles. Therefore, for optimal conditions the sewage sludge samples were extracted three successive cycles and the extracts were combined.

The effects of sample size on the analytical precision were evaluated by extracting 0.5, 1 and 3 g of sludge samples under the previously described optimized conditions. High concentrated factor is widely used to obtain low LOQ for analytes, however, higher sample size could cause more matrix interference [17,26]. In this study, the extraction efficiency did not vary appreciably at 0.5 and 1 g sample ($p > 0.05$), when 3 g of sludge sample was extracted, poor peaks shape appeared for some analytes, and more importantly, the recovery of method were lower for most analytes and the RSD rose up to 28%. Finally, for optimal results the sample size of 1 g sewage sludge sample was used in quantification of the analytes.

3.2.2. SPE clean up

HLB is the most common used SPE for clean up. In this study, HLB and Envi-carb cartridges were tested for their one-step recovery in clean up of the sewage sludge extracts that were spiked at 300 ng/g dw. As shown in Fig. 2(b), recoveries were good using HLB cartridge with the exception of nonylphenol, octylphenol and paracetamol. The recoveries of all targeted analytes were acceptable using Envi-carb, ranging from 75.3 to 95.5%. Moreover, Envi-carb cartridge reduced the color of the extracts much more efficient than HLB indicating efficient removal of background organic substances. Using Envi-carb also reduces the operation and the sample preparation time. Therefore, Envi-carb was selected as SPE cleaning up the extracts. Fig. 1(b) and (c) shows the chromatogram for a sludge sample with and without clean up by Envi-carb. Without clean up, the peak heights and areas were much lower and the baselines were less stable than those with clean up. The lower responses of the analytes without clean up are likely due to the incomplete derivatization of the extracts, because co-extractive substances present in the extracts may compete with the target analytes for the silylating reagent [16]. Moreover, some non-target peaks appeared, indicating the Envi-carb clean up procedure was effective to remove the matrix components from the extracts.

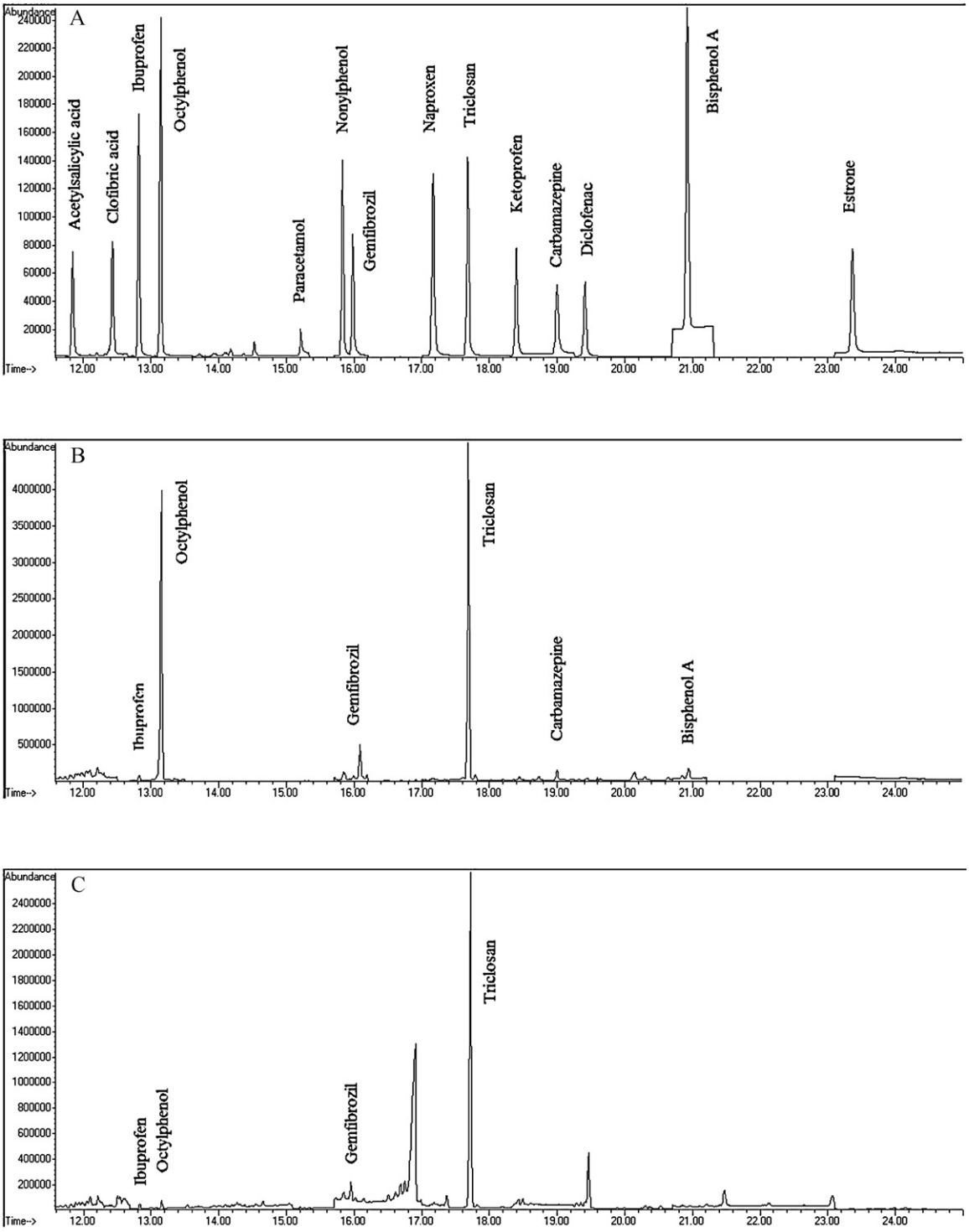

Fig. 1. GC–MS-SIM chromatograms of analytes: (a) standard solution, 100 ng/mL; (b) real sample clean up with Envi-carb; (c) real sample without clean up.

3.3. Method validation

The recovery and precision of the method, based on the analyses of sludge samples spiked at 40, 300 and 2000 ng/g dw levels are shown in Table 3. Acceptable recoveries were obtained for the analytes, varied from 57.9% (acetylsalicylic acid) to 103.1% (clofibric acid). The RSD was less than 9.5% indicating a high level of precision in the recovery. Lower recoveries were observed for acetylsalicylic acid (57.9–64.1%), carbamazepine (60.3–67.0%) and paracetamol (62.7–69.7%), that are hard to elute from Envi-carb partially related to their lower log K_{ow} and relatively weaker polarity. The results obtained were comparable to those reported by Xu et al. [16].

Method accuracy was calculated as the RSD of concentrations obtained from intra-day and inter-day determination (Table 3). The RSD of intra-day reproducibility were less than 9%. While inter-day RSD were slightly higher, such as 10.4, 10.7 and 13.3% for

Table 2
Instrumental performance and validation data.

Compound	Repeatability of peak area (RSD, %) (n = 5)	IDL (pg)	Instrumental linear range (pg)	R^2
Acetylsalicylic acid	3.5	4.0	10.0–2000	0.9898
Bisphenol A	2.2	1.0	2.0–2000	0.9926
Carbamazepine	1.7	2.0	4.0–2000	0.9942
Clofibric acid	4.6	4.0	10.0–2000	0.9858
Diclofenac	5.7	10.0	20.0–2000	0.9833
Estrone	4.8	4.0	10.0–2000	0.9875
Gemfibrozil	2.2	4.0	10.0–2000	0.9887
Ibuprofen	3.2	2.0	4.0–2000	0.9938
Ketoprofen	4.5	4.0	10.0–2000	0.9878
Naproxen	5.3	2.0	4.0–2000	0.9899
Nonylphenol	2.4	2.0	4.0–2000	0.9913
Octylphenol	1.9	1.0	2.0–2000	0.9908
Paracetamol	5.9	10.0	20.0–2000	0.9891
Triclosan	1.4	2.0	4.0–2000	0.9903

acetylsalicylic acid, naproxen and paracetamol, respectively. Finally, LOQ of the 14 targeted analytes in the extracts were below 20 ng/g with the exception of declofenac and paracetamol (Table 3), demonstrating that the method is suitable for detection of trace levels (ng/g) of these chemicals in solid matrix. We compare our results with other studies. Durán-Alvarez et al. [15] showed that LOD (S/N = 3) varied from 0.1 to 25 ng/g, where they used a concentrated factor of 10 or 100 by concentrating soil samples from 10 g to 1 mL or 0.1 mL. Minten et al. [18] indicated that LOQs were in the range of 0.4–8 ng/g sediment, when they employed a concentrated factor of 10. Vazquez-Roig et al. [35] reported that MQLs (S/N = 10) ranged from 0.5 to 23 ng/g when the concentrated factor is 3.

3.4. Application to real samples

The method developed in this work was applied in the analysis of sewage sludge samples from four STPs in southern California. As shown in Table 4, 14 chemicals were found in these four STPs with exception of clofibric acid that was absent in STP2, estrone and ketoprofen that was absent in STP2 and STP3. Triclosan and octylphenol were the most abundant compounds, with mean value of 1416 and 1293 ng/g dw, respectively; while estrone, ketoprofen and naproxen were present in relative low levels in sewage sludge, with mean value of 13.7, 10.4 and 17.7 ng/g, respectively. High concentrations of PPCPs and EDCs found in sewage sludge suggest that suspended solids have potential capability to absorb these chemicals in influent, reducing the possibility of being discharged into natural water body. It also demonstrates the need to investigate the fate and transport of PPCPs and EDCs when sewage sludge is land applied.

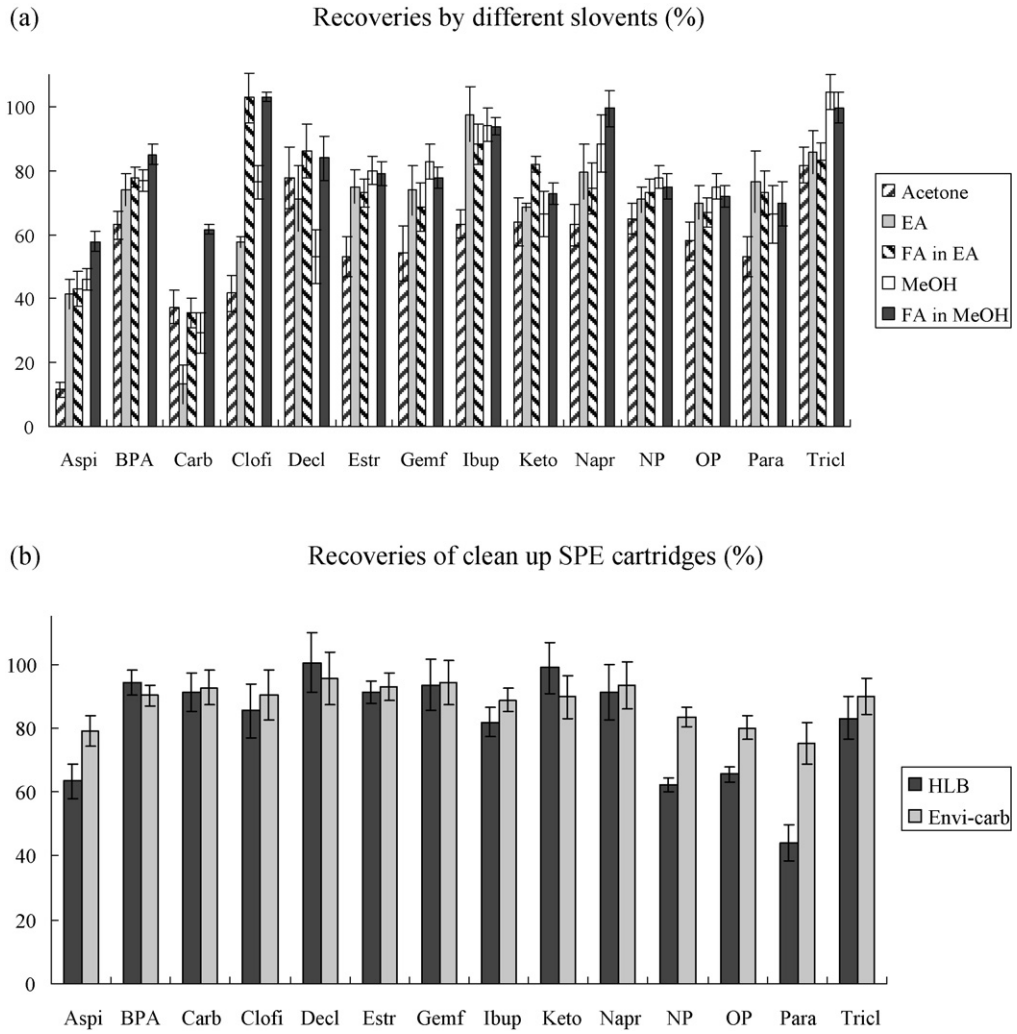

Fig. 2. Recovery and precision of the method optimized by (a) different solvents, and (b) HLB and Envi-carb, for spiked level at 300 ng/g. FA in EA: 1% formic acid in ethyl acetate; FA in MeOH: 1% formic acid in methanol.

Table 3
Analytical method performance and validation data.

	Recovery (mean ± SD, %)			Intra-day RSD, % (n = 3)	Inter-day RSD, % (n = 6)	LOD (ng/g)	LOQ (ng/g)
	Low level spiked, 40 ng/g	Medium level spiked, 300 ng/g	High level spiked, 2000 ng/g				
Acetylsalicylic acid	64 ± 6.2	58 ± 3.0	64 ± 4.9	7.4	10.4	6.0	20
Bisphenol A	83 ± 2.2	85 ± 2.0	80 ± 4.2	3.7	4.8	1.4	4.7
Carbamazepine	67 ± 5.3	62 ± 1.4	60 ± 6.0	4.4	5.8	2.7	9.5
Clofibric acid	99 ± 7.3	103 ± 1.3	93 ± 8.8	7.7	9.9	3.9	13
Diclofenac	n.a.	84 ± 6.7	88 ± 9.3	6.5	9.7	11	37
Estrone	78 ± 7.5	79 ± 2.4	80 ± 4.7	6.2	9.1	4.8	16
Gemfibrozil	72 ± 6.4	78 ± 3.3	77 ± 8.2	7.1	10.0	5.0	17
Ibuprofen	87 ± 4.5	94 ± 2.6	82 ± 2.8	3.8	4.3	2.0	6.7
Ketoprofen	74 ± 6.1	73 ± 3.4	79 ± 5.9	5.5	8.7	5.0	17
Naproxen	91 ± 8.2	99 ± 5.6	95 ± 6.6	7.0	10.7	2.2	7.6
Nonylphenol	73 ± 2.6	75 ± 2.7	76 ± 3.0	5.8	8.1	2.3	7.7
Octylphenol	72 ± 2.4	72 ± 3.4	72 ± 4.5	4.6	6.4	1.6	5.4
Paracetamol	n.a.	70 ± 7.0	63 ± 6.5	8.5	13.3	11	39
Triclosan	89 ± 6.1	100 ± 4.9	86 ± 5.8	5.3	7.8	2.1	7.2

n.a., not available.

Table 4
Concentrations (ng/g) of PPCPs and EDCs in sewage sludge from 4 sewage treatment plants (STPs) in southern California.

Compound	STP1	STP2	STP3	STP4
Acetylsalicylic acid	143	184	79.9	78.4
Bisphenol A	145	217	66.4	95.4
Carbamazepine	251	162	60.6	371
Clofibric acid	155	<LOQ	56.9	24.1
Diclofenac	184	86.6	421	129
Estrone	31.1	<LOQ	<LOQ	23.8
Gemfibrozil	222	57.1	209	41.8
Ibuprofen	208	27.1	58.1	133
Ketoprofen	23.2	<LOQ	<LOQ	18.3
Naproxen	35.1	12.7	11.9	11.1
Nonylphenol	45.6	83.8	36.8	27.6
Octylphenol	1656	2413	157	947
Paracetamol	41.2	119	72.6	54.0
Triclosan	1703	1965	271.9	1724

4. Conclusion

We present a sensitive and reliable analytical protocol to determine the PPCPs and EDCs present in solid phase environmental matrices based on ultrasonic extraction, Envi-carb cartridge for cleaning up the extracts, derivatized with MTBSTFA, followed by GC–MS for the analysis of target chemicals. It gave satisfactory recovery for all the target compounds at concentrations ranging from ng/g to μg/g levels. The method was successfully applied to analyze several sewage sludge samples. High concentrations of PPCPs and EDCs were found in the municipal sewage sludge. Appropriate disposal of sewage sludge was also required to avoid them entering the environment. The method we developed provides a valuable tool to study occurrence, behavior and fate of PPCPs and EDCs in environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.12.023.

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