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Simultaneous determination of pharmaceuticals, endocrine disrupting compounds and hormone in soils by gas chromatography–mass spectrometry

Jian Xu[a,b,*], Laosheng Wu[a], Weiping Chen[a], Andrew C. Chang[a]

[a] Department of Environmental Sciences, University of California, Riverside, CA 92521, USA
[b] College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

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ABSTRACT

Analytical methods have been developed for simultaneous determination of six different pharmaceuticals and personal care products (PPCPs) (clofibric acid, ibuprofen, naproxen, ketoprofen, diclofenac, and triclosan), three endocrine disrupting compounds (EDCs) (4-*tert*-octylphenol, 4-*n*-nonylphenol, and bisphenol A (BPA)) and one estrogenic compound (estrone) in soil matrix. The soils were extracted by different solvents with the help of an ultrasonic treatment at 42 kHz, followed by a solid phase extraction (SPE) as a cleanup procedure. The purified extracts were derivatized with *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) and then analyzed by GC–MSD (SIM mode). The method was evaluated by testing the following variables: initial spiking levels, extraction solvents, solvent volumes, and soil types (sandy and clay soils). For 5 g of soil, four successive extraction steps with the mixture of acetone–ethyl acetate provided satisfactory recoveries. In the sandy soil, the recoveries of all the compounds were from 63.8 to 110.7% for the spiking level of 100 ng/g dry soil, and from 52.2 to 108.2% for 5 ng/g dry soil, respectively. Result was similar for the clay soil. The precision across all recoveries was high, suggesting that this method has a good reproducibility. The method was successfully employed to soil samples collected from a golf course irrigated with reclaimed wastewater in southern California, and resulted in the detection of clofibric acid, ibuprofen, naproxen, triclosan, bisphenol A, and estrone at ng per gram dry weight concentration levels. The method is robust and simple, and provides straightforward analyses of these current-emerging trace organic pollutants in solid matrices.

1. Introduction

The fate of trace organic contaminants present in treated wastewater effluents, such as pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs) including estrogenic compounds, has attracted considerable attentions of both scientific and regulatory communities [1–8]. The PPCPs include medications ranging from analgesics and antibiotics to contraceptives and lipid regulators, in addition to the active ingredients in soaps, detergents, perfumes, and skin, hair, and dental care products [9]. The EDCs such as alkylphenol ethoxylates, bisphenol A (BPA) and phthalates mainly originate from industrial production and consumer products, while estrogenic hormones are metabolic byproducts of humans and animals [10]. Effluents (reclaimed water) released from wastewater treatment plants are the primary sources for these compounds found in the environment [11–13], because the conventional wastewater treatment processes are not specifically designed to remove these trace organic contaminants. During the course of water reuses, depending on the destinations, the consumers and the aquatic and terrestrial eco-systems may advertently be exposed to low levels of therapeutic, personal care, and endocrine disrupting chemicals potentially for extended period of time. While a large number of compounds have been detected in reclaimed municipal wastewater, there is no telling which compound is actually present and in what concentration when the treated wastewater effluents are released.

At trace levels, each chemical may not be harmful in the natural environment. Mixtures of multiple chemicals though each at very low concentrations may exert additive effects that result in significant detrimental impacts on wildlife and humans. Pomati et al. showed that a mixture of 13 pharmaceuticals all present at levels comparable to those commonly found in the environment resulted in a 10–30% reduction in growth of human embryonic kidney cells after 48 h of exposure *in vitro*, while no effects were observed when each chemical was presented individually [14]. Thus, developing a method allowing simultaneous detection of diverse, low-level

* Corresponding author at: College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China. Tel.: +1 951 827 2565; fax: +1 951 827 5325.
E-mail address: xujian@nankai.edu.cn (J. Xu).

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Table 1
CAS registry numbers, chemical structures of selected chemicals

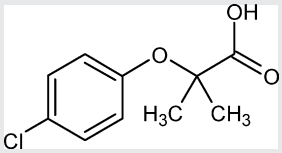
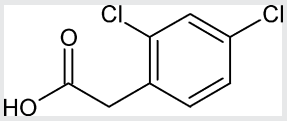
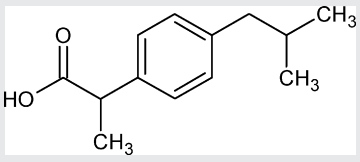
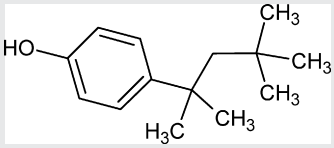
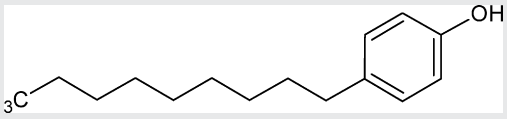
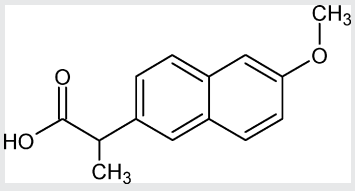
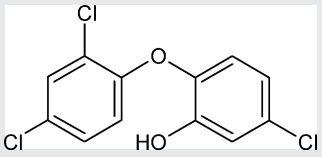
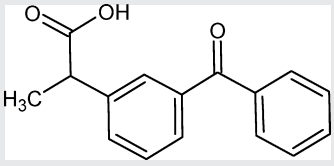
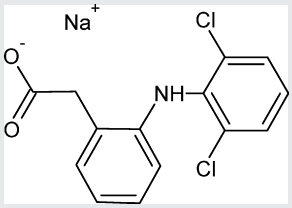
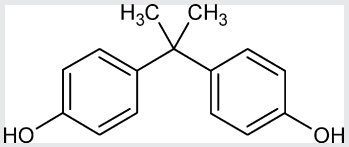
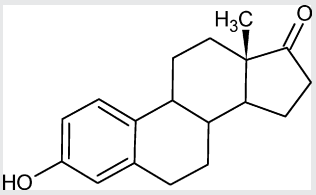
Compounds (manufacturer)	CAS number	Structure
---	---	
Clofibric acid (MP Biomedicals)	882-09-7	
2,4-Dichlorophenylacetic acid (Spex CertiPrep)	19719-28-9	
Ibuprofen (Acros)	15687-27-1	
4-*tert*-Octylphenol (Aldrich)	140-66-9	
4-*n*-Nonylphenol (Riedel-de-Haën)	104-40-5	
Naproxen (MP Biomedicals)	22204-53-1	
Triclosan (Fluka)	3380-34-5	
Ketoprofen (MP Biomedicals)	22071-15-4	
Diclofenac sodium salt (MP Biomedicals)	15307-79-6	
Bisphenol A (Aldrich)	80-05-7	

Table 1 (*Continued*)

Compounds (manufacturer)	CAS number	Structure
Estrone (Acros)	53-16-7	

contaminants is needed in order to determine their concentrations present in the environmental media, and evaluate their consequent fate and impact.

Several extraction methods have been developed for determining the concentrations of pharmaceuticals and endocrine disrupting compounds in environmental samples. For liquid samples, such as wastewater, river water or drinking water, solid phase extraction (SPE) is the most commonly used method [10,11,28–30,43]. Others such as liquid–liquid extraction [15–17], and solid phase microextraction (SPME) [15,18,19] have also been reported. Extraction methods used for solid samples include ultrasonic solvent extraction (USE) [30,31,38,39], microwave assisted solvent extraction (MASE) [9,20], pressurized liquid extraction (PLE) [21–23], and supercritical fluid extraction (SFE) [24]. Quantification of contaminants in the extracts might be achieved by employing GC/MS, GC/MS/MS, LC/MS, or LC/MS/MS techniques [4–6,10,25–29]. A few investigated the presence of multiple contaminants in complex matrices of the river sediments and sewage sludge. For example, Gatidou et al. [30] used sonication to extract 4-*n*-NP, NP1EO, NP2EO, BPA and triclosan from sewage sludge, with recoveries ranging from 47.6 to 106% for all the compounds. Most of the studies however, focused on a single or a subclass of PPCP and EDC contaminant in solid matrices [9,31–36]. Ramirez et al. reported the extraction of pharmaceuticals from soil samples using solvents adjusted to different pH or polarity [37]. Rice and Mitra [9] developed a method using solvent of 2:1 (v/v) dichloromethane:methanol which could give the optimum recovery rate from natural soils spiked with PPCP mixtures with microwave-assisted solvent extraction. Ternes et al. extracted estrogens in sediment samples using ultrasonication followed by GC/MS/MS analysis [38]. They also reported the determination of pharmaceuticals and musk fragrances in activated sludge samples [39].

There is no telling which PPCP and EDC contaminants would be present, for environmental monitoring, so it necessitates the development of methods that are capable of detecting several classes of chemicals in solid matrices simultaneously. We tested an effective and time-efficient analytical protocol that simultaneously detected multiple PPCP, EDC and hormonal compounds in soils. Specifically, clofibric acid, ibuprofen, naproxen, ketoprofen, diclofenac, triclosan, 4-*tert*-octylphenol, 4-*n*-nonylphenol, bisphenol A and estrone were selected due to their frequent presence in the reclaimed wastewater and soils receiving reclaimed water irrigation. USE was employed to separate the chemicals from the soils, followed by SPE cleanup procedure and analyses by GC/MS. Due to the high polarities of selected compounds, derivatization was conducted prior to GC/MS to reduce the polarity and enhance their mobility on the GC column. The method was optimized by analyzing chemicals in two types of soil (sandy and clay soils) with varying the spiking levels, extraction solvents, and solvent volumes. The final method was applied to soil samples collected from a golf course which was irrigated with reclaimed wastewater for a long period of time.

2. Experimental

2.1. Reagents and standards

The PPCPs, EDCs and hormonal compounds used in the experiment included naproxen, ketoprofen, clofibric acid and diclofenac sodium salt, estrone and ibuprofen, 4-*tert*-octylphenol, bisphenol, 4-*n*-nonylphenol, and triclosan. The surrogate standard, 2,4-dichlorophenylacetic acid was purchased from Spex CertiPrep. Chemical structures, CAS registry numbers and the manufacturers of the compounds are shown in Table 1. Stock solutions of the reference compounds were prepared in ethyl acetate and stored at −20 °C. *N*-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) (Sigma–Aldrich) was used as the derivatizing reagent.

Solvents used in the study, ethyl acetate and acetone, dichloromethane, and methanol were all pesticide grade and were used as received. De-ionized water was prepared with a Milli-Q water purification system.

2.2. Soil spiking

Two soils were used as receiving solid matrices of the compounds. Both were obtained from croplands in southern California. One represents the clay and the other represents the sandy soil. Selected properties of the two soils are summarized in Table 2. The soils were air-dried and crushed to pass through a sieve with 0.5 mm openings. Aliquots of the chemicals in ethyl acetate solutions were mixed with 10 g of soil. Acetone was added to ensure the spiked compounds were evenly distributed in the soil [38]. The solvents in the spiked soils were allowed to evaporate at room temperature in a darkened fume hood for 15 h. The spiked samples were then thoroughly mixed with a sufficient mass of untreated soil to attain the desired concentration. To inhibit the microbial activities, the prepared soils were treated with 0.1% $HgCl_2$.

Table 2
Selected physical and chemical properties of the two test soils

Soil	pH	CEC (meq/100 g)	Clay content (%)	Silt content (%)	Sand content (%)	Organic matter content (%)
Imperial silty clay	8.2	6.0	50	44.7	5.3	0.50
Arlington fine sandy loam	7.0	7.5	12.5	16.6	70.9	0.75

2.3. Soil extraction

Five gram aliquots of the prepared soil were mixed with the surrogated standard and selected solvents (5 ml) in 50 ml of screw-top Teflon centrifuge tube, ultrasonicated at 42 kHz for 15 min, centrifuged at 6000 rpm for 10 min, and decanted the supernatant. The soil was extracted three additional times with 4 ml, 5 ml, and 4 ml of solvent, respectively at each successive time. The supernatants were combined and were nitrogen-evaporated in a water bath at 40 °C to about 1 ml.

To test the recoveries, individual solvent and their combinations, including acetone–methanol, acetone–ethyl acetate, acetone–dichloromethane, methanol–ethyl acetate, methanol–dichloromethane, and ethyl acetate–dichloromethane were tested. For extractions involving more than one solvent, the sample was extracted successively for two times with the first solvent and then successively two times with the next solvent. Extracts were combined, cleaned, and concentrated for analysis. Because most of the chemicals selected were acidic, a solvent combination of acetone–ethyl acetate (consisting of 10% acetic acid (v/v)) was included to test whether the extraction at acidic pH would be effective for their recoveries.

2.4. Solid phase extraction/cleanup and derivatization

The concentrated extract (~1 ml) was re-dissolved into 500 ml of de-ionized water, and the pH of the solution was adjusted to 3 with concentrated sulfuric acid. Solution was loaded onto the HyperSep C18 cartridge (500 mg/6 ml, Thermo Electron Corporation) at a flow rate of 15 ml/min, which was pre-conditioned with 3 ml of ethyl acetate, 3 ml of methanol, and 3 ml of de-ionized water (pH 3) in sequence. The cartridge was dried by nitrogen for 20 min after sample loading, and was eluted with two aliquots of 4 ml of ethyl acetate. The eluates were dried over anhydrous sodium sulfate, and reduced to 0.5 ml with a gentle stream of nitrogen at 40 °C, then transferred into the GC vial. 100 μl of MTBSTFA was added, and the volume was brought to 1 ml with ethyl acetate. MTBSTFA was selected as the derivatization reagent because of its greater thermal and hydrolytic stability of the *tert*-butyldimethylsilyl (TBDMS) derivatives for the studied compounds [10,11,29,40], and the $[M-57]^+$ ions had strong responses in the SIM mode for all of the target compounds in this study. The GC vials were put into GC oven at 70 °C for 60 min for derivatization.

2.5. Detection with GC/MSD

Target chemicals were determined using an Agilent 6890N GC with 5975C MSD equipped with an Agilent 7683B automatic liquid sampler and an HP-5MS GC column (30 m, 0.25 mm i.d., 0.25 um film thickness). Helium was used as the carrier gas, with a column flow rate of 1.2 ml/min in constant-flow mode. Injector temperature was 250 °C. The GC–MSD interface and the ion source temperatures were set at 280 and 230 °C, respectively. The GC oven temperature was kept at 50 °C for 1 min, followed by the first ramp at 20 °C/min to 120 °C, second ramp at 10 °C/min to 280 °C, and holding for 11 min.

Prior to quantification process, mass spectra and GC retention times of each compound from *m*/*z* 50 to 500 were obtained in full scan mode. From these the base peak ion was selected for quantification, and two or more qualifier ions were used for confirmation if applicable (Table 3). For quantification, the mass spectrometer was operated in the selected ion monitoring mode with electron impact ionization voltage of 70 eV. A 2 μl sample was injected in pulsed splitless mode.

Table 3
Retention times and mass spectrometric data for *tert*-BDMS derivatives of selected compounds

Compound	Retention time (min)	Molecular weight	Primary ions	Secondary ions
Clofibric acid	13.34	215	143	273, 271
2,4-Dichlorophenylacetic acid (surrogate standard)	13.65	205	261	159, 263
Ibuprofen	13.78	206	263	161, 264
4-*tert*-Octylphenol	14.10	206	263	165, 320
4-*n*-Nonylphenol	16.79	220	277	165, 334
Naproxen	18.15	230	287	185, 288
Triclosan	18.63	290	347	200, 345
Ketoprofen	19.29	254	311	295, 312
Diclofenac-Na	20.14	318	352	214, 409
Bisphenol A	21.33	228	441	207, 456
Estrone	23.65	270	327	163, 384

The schematic depiction of the analytical method used for the analyses of the target compounds in the spiked soils is shown in Fig. 1.

3. Results and discussion

3.1. GC/MSD quantification

Seven-point calibration curves were prepared by spiking corresponding amounts of target compounds into 500 ml of de-ionized water. The spiked water samples were analyzed as the procedure described above. Water sample with addition of blank soil extract was analyzed to provide a calibration blank. The calibration curves were quite good for all the target compounds ($R^2 > 0.99$).

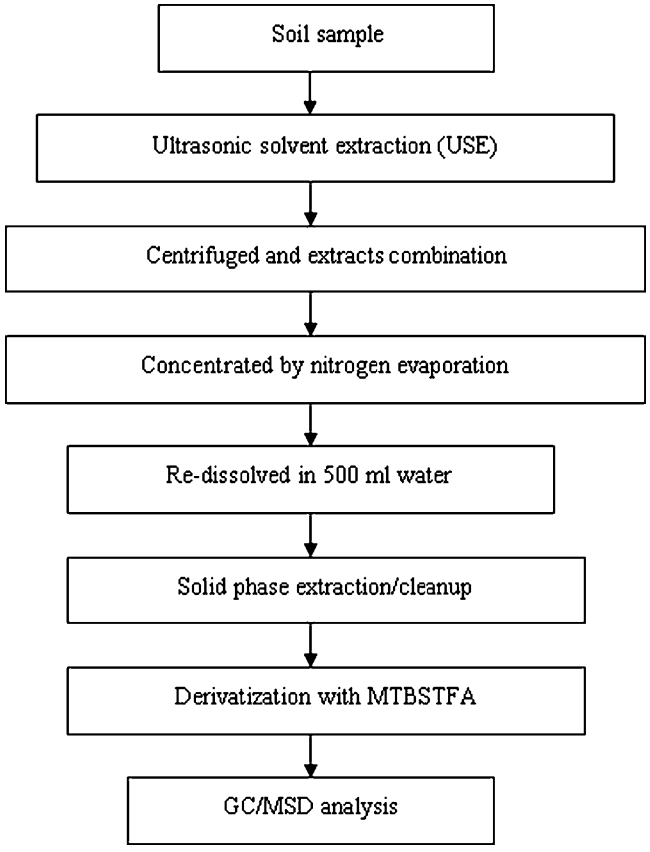


Fig. 1. Scheme of the analytical procedure used for analyzing the target compounds in soil samples.

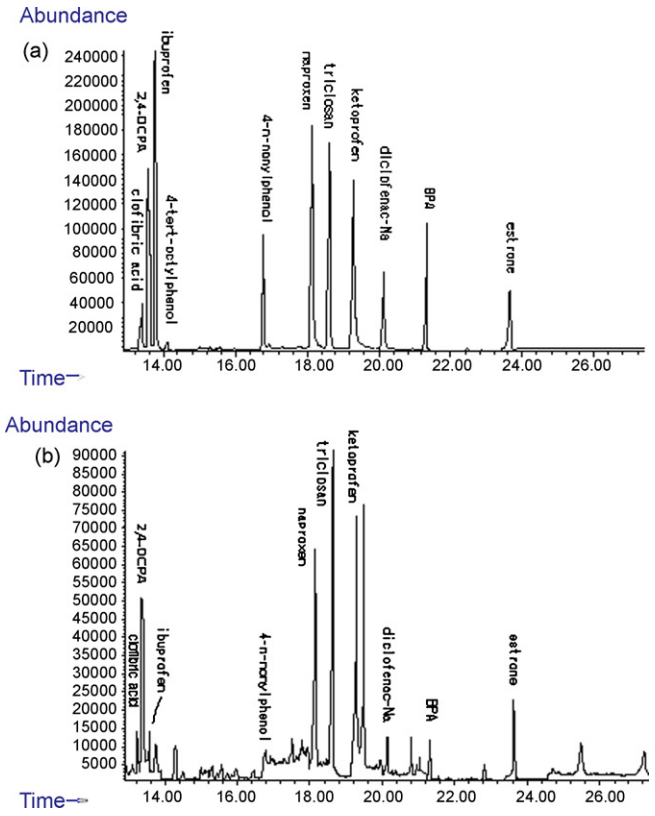


Fig. 2. GC/MSD/SIM chromatograms of extracts from spiked sandy soils (100 ng/g) sample. (a) Extracts with SPE cleanup; (b) without SPE cleanup procedure.

Limits of quantification (LOQ) were set as the second lowest calibration point within the linear correlation curve, with a signal-to-noise (S/N) ratio of at least 10 using the baseline in the chromatogram. The LOQ of the method were 0.2 ng/g for ibuprofen, 2.4 ng/g for 4-*tert*-octylphenol, 0.4 ng/g for clofibric acid, 4-*n*-nonylphenol, naproxen, triclosan, ketoprofen, and bisphenol A; 1.2 ng/g for diclofenac sodium salt and estrone, respectively. Fig. 2(a) shows a typical chromatogram for a spiked soil sample (100 ng/g for the sandy soil).

3.2. Method performance

Spiking experiments are frequently employed for the development of analytical method by determining the recovery rates and extraction yields. During the spiking process, two major challenges for the determination of the extraction yields of organic analytes in solid matrices are the attainment of sorption–desorption equilibrium prior to extraction, and the inhibition of microbial activities [31]. In our method, the ultrasonic solvent extraction took place 15 h after spiking. The 15 h duration was sufficient to ensure that the ethyl acetate/acetone were completely evaporated and the sorption–desorption reached [38].

Research indicated that the recovery rates of ibuprofen, trimethoprim and paracetamol were lower in non-autoclaved sediment than autoclaved samples [31], indicating the influence of bio-transformation process on recovery rates. The microbial activities might also influence the binding of the analytes to the soil/sediment by incorporation into the organic matter [31]. Therefore, the soils must be sterilized to minimize any bio-transformation during the course of extraction. Methods commonly used to sterilize solid matrices included γ-radiation, autoclaving, and addition of microbial inhibitors such as sodium azide

Table 4
Percent recovery of target compounds from spiked sandy soil (100 ng/g) with different solvents ($n = 3$)

Compounds	Mean ± SD (%)										
	ACE	ME	ET	DCM	ACE-ME	ACE-ET	ACE-DCM	ME-ET	ME-DCM	ET-DCM	ACE-ET[a]	ACE-ET[b]
Clofibric acid	29.2 ± 6.3	16.3 ± 4.2	102.0 ± 4.2	9.1 ± 0.4	14.2 ± 2.5	63.9 ± 2.3	31.9 ± 5.6	22.5 ± 2.2	4.5 ± 1.0	73.1 ± 1.2	63.2 ± 1.5	68.6 ± 3.2
Ibuprofen	62.6 ± 5.4	38.5 ± 3.3	98.7 ± 7.9	0.7 ± 0.2	38.8 ± 5.4	103.4 ± 8.5	65.5 ± 7.5	12.3 ± 1.4	19.3 ± 2.2	106.5 ± 3.5	99.3 ± 5.7	100.4 ± 4.9
4-*tert*-Octylphenol	39.2 ± 3.5	–	7.74 ± 2.1	40.2 ± 2.3	–	63.8 ± 3.9	38.4 ± 1.6	–	–	20.3 ± 0.6	67.9 ± 4.2	65.3 ± 3.6
4-*n*-Nonylphenol	65.1 ± 5.3	15.2 ± 3.1	37.6 ± 5.2	65.9 ± 3.1	25.2 ± 1.1	73.7 ± 6.7	68.2 ± 4.5	36.5 ± 2.2	10.8 ± 1.6	44.2 ± 1.2	88.8 ± 4.8	78.6 ± 6.1
Naproxen	63.5 ± 6.2	24.5 ± 4.6	92.5 ± 8.5	–	26.3 ± 3.3	110.7 ± 7.2	60.6 ± 6.2	60.1 ± 5.6	–	73.5 ± 1.0	103.6 ± 6.2	116.5 ± 6.9
Triclosan	86.9 ± 3.3	79.3 ± 0.8	91.4 ± 7.5	77.0 ± 3.0	77.9 ± 3.5	95.7 ± 8.4	86.9 ± 6.4	88.6 ± 3.6	29.0 ± 3.1	81.3 ± 1.0	93.9 ± 6.2	93.3 ± 5.9
Ketoprofen	92.6 ± 5.6	–	80.2 ± 7.2	–	–	89.0 ± 7.6	90.4 ± 8.2	–	–	92.5 ± 6.3	90.4 ± 3.3	92.8 ± 4.6
Diclofenac-Na	90.4 ± 6.5	–	76.3 ± 5.3	–	–	89.1 ± 6.9	75.2 ± 2.6	–	–	88.3 ± 2.5	95.2 ± 2.2	95.8 ± 6.3
Bisphenol A	93.3 ± 1.8	6.2 ± 0.9	36.1 ± 4.2	37.0 ± 2.2	14.4 ± 2.6	104.3 ± 6.8	94.9 ± 5.4	11.3 ± 2.2	3.9 ± 0.5	45.2 ± 1.3	94.9 ± 4.5	92.7 ± 3.6
Estrone	69.1 ± 6.2	32.6 ± 3.2	47.3 ± 4.4	46.2 ± 0.8	38.6 ± 1.8	77.7 ± 3.6	73.4 ± 3.4	22.9 ± 4.1	29.1 ± 1.9	46.3 ± 0.9	78.4 ± 4.6	75.3 ± 6.1

–: Not detected; (a) soil sample was extracted six times; (b) acetic acid was added in acetone. ACE: acetone; ME: methanol; ET: ethyl acetate; DCM: dichloromethane.

and mercuric chloride. Mercuric chloride was employed in this study. It was considered the most effective soil sterilization method as it caused the least changes in the soil properties [41,42].

3.2.1. Solvent selection

There have been studies examining the recovery rates for extracting target analytes from soil samples using solvents different in pH or polarity [37]. Rice and Mitra reported 2:1 (v/v) dichloromethane:methanol could give the optimum recovery rate from natural soils spiked with PPCP mixtures with microwave-assisted solvent extraction [9]. We examined the recovery rates of the target compounds by acetone, methanol, ethyl acetate, dichloromethane, and their mixtures with the ultrasonic solvent extraction procedures. To test the solvent combinations, the soil was first extracted with 5 ml and then 4 ml of the first solvent, followed by another 5 and 4 ml successively of the second solvent. Table 4 summarized the recoveries with different solvents for the sandy soil spiked at 100 ng/g level.

Some compounds such as 4-*tert*-octylphenol, naproxen, ketoprofen and diclofenac-Na could not be recovered when the soils were extracted with methanol or dichloromethane alone. All the compounds could be extracted with acetone or ethyl acetate, but the recovery rates for some compounds were low. Our results indicated that combination of acetone and ethyl acetate resulted in the optimum recovery for ibuprofen, naproxen, triclosan, ketoprofen, diclofenac-Na, and bisphenol A, and substantial recovery for clofibric acid, 4-*tert*-octylphenol, 4-*n*-nonylphenol, and estrone. Mean recoveries of the analytes extracted with this combination ranged from 63.8 to 110.7% at the spiking level of 100 ng/g, which is comparable to or better than the results obtained by other studies, for example, the recovery range of 47.6–106% by Gatidou et al. for 4-*n*-NP, NP1EO, NP2EO, BPA and triclosan from sewage sludge [30]; 70 and 90% for estrogens in sludge and sediments, respectively by Ternes et al. [38], who used ultrasonication followed by GC/MS/MS analysis; 43 to 78% in activated sludge for some pharmaceuticals by Ternes et al. [39]; and 89.6 ± 2.89% for three of the seven diverse PPCPs by Rice and Mitra using a microwave-assisted solvent extraction (MASE-based) method [9].

Other solvent combinations, such as acetone–dichloromethane and ethyl acetate–dichloromethane combinations could also recover most of the target compounds with an acceptable recovery rates. However, their efficiency was lower than the acetone–ethyl acetate combination. Compounds like 4-*tert*-octylphenol, ketoprofen and diclofenac-Na could not be recovered by methanol or dichloromethane alone, neither the solvent combinations of acetone–methanol, methanol–ethyl acetate, or methanol–dichloromethane. The acidified solvent combination of acetone (with 10% acetic acid added)–ethyl acetate could extract all of the compounds from spiked soils, with similar performance to un-acidified acetone–ethyl acetate combination, but did not significantly improve the recovery of individual chemicals (see Table 4). Acidification has little influence on the extraction efficiency under current experimental conditions.

To investigate whether a higher solvent/soil ratio could enhance the compound recovery rates from the soil, the samples were extracted one traditional time with 5 ml of acetone and 5 ml of ethyl acetate. The subsequent two extractions however did not significantly increase the recovery rates for any compound, except for 4-*n*-nonylphenol (see Table 4). Given that the initial recovery rate of 73.7% was acceptable for 4-*n*-nonylphenol, the four times of extraction with acetone and ethyl acetate combination would be cost- and time-effective for simultaneously analyzing the 10 selected compounds in a single soil sample.

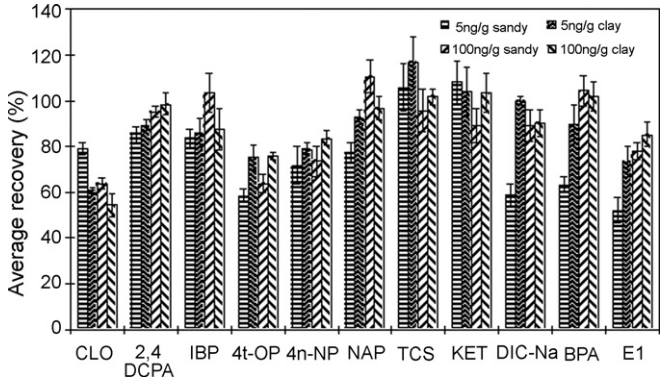


Fig. 3. Percent recovery of target compounds from spiked soil samples extracted with combination of acetone and ethyl acetate ($n = 3$).
CLO: clofibric acid; 2,4-DCPA: 2,4-dichlorophenylacetic acid; IBP: ibuprofen; 4-*t*-OP: 4-*tert*-octylphenol; 4-*n*-NP: 4-*n*-nonylphenol; NAP: naproxen; TCS: triclosan; KET: ketoprofen; DIC-Na: diclofenac sodium salt; BPA: bisphenol A; E1: estrone.

3.2.2. Soil types and initial spiking levels

To demonstrate the efficiency of the extraction procedures, recovery rates from two types of soils spiked with chemicals at two spiking levels were examined. The results were shown in Fig. 3. The mean recovery rates of all compounds at two spiking levels were in the range from 52.2 to 117.0% in the two soils, while the recovery of the surrogates was within the range of 85.4–98.6%. The standard deviations ($n = 3$) were lower than 9% for all the cases, indicating that the precision of the extraction procedure was good.

ANOVA analysis was conducted to compare the differences of the recovery rates for each group chemicals under two different soil matrix and spiking levels. Results of the statistical analyses showed that no significant difference of the recovery rates was found among the treatments at $p > 0.05$. The soil matrix (clay soil vs. sandy soil) as well as the spiking levels of chemicals (5 ng/g vs. 100 ng/g) had no impact on extraction of these chemicals.

3.3. SPE/cleanup

For environmental samples, cleaning up the extracts is crucial in the subsequent analytical process. The matrix components in samples, such as in soils, wastewaters, or in biomass samples, can mask the response of target compounds in the chromatography. In this study, the SPE was used to cleanup soil extracts. The recovery rates following the SPE cleanup procedures ranged from 80.8 to 118.3% for the target chemicals (Table 5). As illustrated in Fig. 2(b), without SPE cleanup procedure, the peak heights and areas were much lower and the baselines were much less stable for all target compounds than those with the SPE cleanup. The lower responses of the target compounds before SPE cleanup are likely due to the incomplete derivatization of the uncleaned extracts, because sam-

Table 5
Recovery (%) of target compounds from SPE at spiking level of 1 μg/L ($n = 3$)

Compounds	Recovery (%)
Clofibric acid	105.5 ± 3.3
Ibuprofen	100.0 ± 4.5
4-*tert*-Octylphenol	87.9 ± 5.2
4-*n*-Nonylphenol	80.8 ± 6.1
Naproxen	118.3 ± 6.6
Triclosan	107.2 ± 2.1
Ketoprofen	99.5 ± 4.0
Diclofenac-Na	114.0 ± 5.5
Bisphenol A	94.5 ± 2.5
Estrone	103.3 ± 3.6

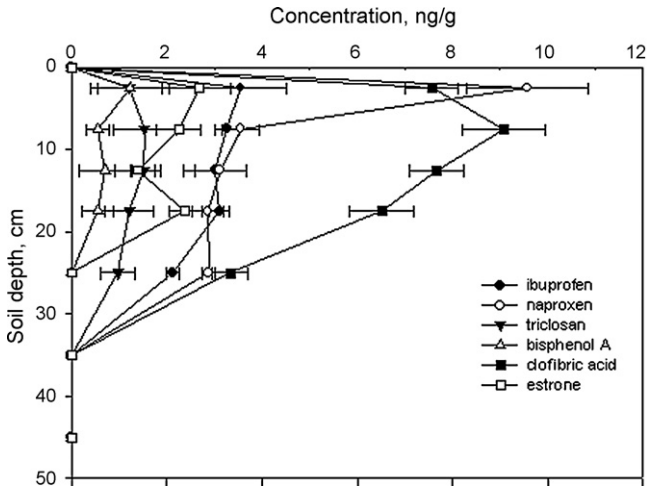


Fig. 4. Vertical concentration profiles of examined compounds in sandy loam soil in a golf course irrigated with reclaimed wastewater.

ple co-extractives and solvent residues competed with the target compounds for the silylating reagent. The SPE cleanup procedure was effective to remove the matrix components from the extracts. The recoveries of the SPE were almost quantitative for many acidic pharmaceutical compounds and a range of potential EDCs in water [11,31,43].

3.4. Application of the analytical method to natural soil samples

The method was applied to soil samples collected from a golf course fairway in southern California, which was irrigated with reclaimed wastewater. The PPCPs, EDCs and hormonal contaminants were known to be present in the applied water. Five soil core samples were taken to a depth of 40 cm, and each core was sliced into 5 cm segments according to the depth. Same-depth segments were combined and mixed thoroughly. The soil was a fine sandy loam that contained 70.7% sand, 19.8% silt, and 11.3% clay. Fig. 4 shows the concentration of the compounds in the soil profiles. The application of the method allowed the detection of clofibric acid, ibuprofen, naproxen, triclosan, bisphenol A and estrone at levels ranging from 0.55–9.08 ng/g dry weight soil. The result indicates that trace organic contaminants in the reclaimed wastewater may accumulate in the surface soils during the course of reclaimed wastewater irrigation, consequently exposing the groundwater to potential contamination.

The analytical method is an appropriate protocol for environmental monitoring when multiple PPCP, EDC, and hormonal contaminants are expected. The laboratory testing demonstrated the accuracy and precision of the method. During the field case study the method showed its robust performance and easiness in sample handling.

4. Conclusion

Potential ecological and human health risks associated with the presence of human pharmaceuticals and personal care products, hormones and endocrine disrupting compounds in soil matrix necessitate the development of rapid, sensitive and direct analytical methods to support research of their occurrences and environmental behavior. The presence of these compounds in soils may be simultaneously determined by ultrasonic assisted solvent extractions to recover the contaminants from soils followed by solid phase separation to free the compounds from the background matrices of the soils and finally analysis of the chemicals by GC/MS. It was able to detect simultaneously six PPCPs (clofibric acid, ibuprofen, naproxen, ketoprofen, diclofenac, and triclosan), three EDCs (4-*tert*-octylphenol, 4-*n*-nonylphenol, and bisphenol A) and one estrogenic compound (estrone) in soils. The protocol involved extracting the soils four successive times alternating the acetone and ethyl acetate as the solvent; the recovered extracts were combined and separated from the background matrices by SPE, and concentrated and derivatized with MTBSTFA, and analyzed by GC-MS. It gave satisfactory recovery rates for all the target compounds in different soil matrixes and concentration levels. The method is potentially applicable to other PPCPs, EDCs and estrogenic compounds if they are present in the soils.

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