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Simultaneous determination of endocrine-disrupting phenols and steroid estrogens in sediment by gas chromatography–mass spectrometry

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Abstract

A simple and effective method has been developed to simultaneously determine endocrine-disrupting phenolic xenoestrogens and steroid estrogens in sediment by using ultra-sonicated extraction in combination with silica gel fractionation, derivatization with pentafluropropionic anhydride, and gas chromatography–mass spectrometry (GC–MS) in selected ion monitoring mode (SIM). Satisfactory recoveries have been obtained for phenolic xenoestrogens and steroid estrogens. The method enables the determination of targets at concentrations of lower nanogram-per-gram in sediments. The method has been successfully applied to the sediments collected from Pearl River Estuary (PRE), South China Sea, China. Nonylphenol and bisphenol-A (BPA) were detected in the range from 204.2 to 664.5 ng/g and 0.6 to 4.0 ng/g, respectively. None of the estrogens were found in the sediment samples.
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Keywords: Endocrine-disrupting compounds; Phenolic xenoestrogens; Steroid estrogens; GC–MS (SIM); Sediment

1. Introduction

The potential adverse effects of endocrine disrupting compounds (EDCs), mainly on sex-specific characteristics in various organisms have been well documented in literature, such as feminization and imposex of aquatic organisms [1–6]. These impacts may even be cumulative, possibly will only appear in subsequent generations and irreversible, endangering the sustainable development of humans and the ecosystem.

EDCs encompass a wide range of chemicals, most of which are introduced into the environment by anthropogenic activities. Steroid estrogens, which include natural and synthetic ones, are most potent EDCs and their estrogenic effects have been observed in laboratory studies at very low concentrations [5,7]. Natural (e.g. 17β-estradiol and estrone) and synthetic estrogens (e.g. mestranol and 17α-ethynilestradiol, active components of oral contraceptives) enter environment predominantly through sewage discharge after they have been excreted by women [8–11]. Phenolic compounds, such as alkylphenols (APs) and bisphenol-A (BPA), are known as xenoestrogens because they are also suspected to influence the hormonal system of aquatic organisms [5,12]. The main pathways for phenolic EDCs into environment are domestic and industrial wastewater discharges because they are widely used for household and industrial detergents [2,5,12]. Steroid estrogens and xenoestrogenic phenols have been detected in a variety of waters [7–12].

Several analytical methods have been developed for separation and determination of steroid and phenolic EDCs in aqueous matrixes [13–19]. However, phenols and steroids have a high tendency to accumulate in solid matrices due to their lipophilicity indicated by their higher log K_{OW} values (2.81–4.67, Table 1), which implies that sediment may adsorb considerable amounts of phenolic EDCs and estrogens, posing a potential threat to sediment biota [20–26]. Therefore, a precise quantification of phenolic EDCs and sex hormones in sediment is necessary for their risk assessment. Li et al. [27] reported analysis of APs and BPA in sediments based on acidic digestion followed by solvent extraction and derivatization with bis(trimethylsilyl)trifluoroacetamide (BSTFA) before detection by gas chromatography–mass spectrometry (GC–MS). Ternes et al. [28] measured estrogens in sediment and sewage sludge by solvent extraction combined successively with silica gel

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Table 1
Target phenols and steroid estrogens and their characteristics ions (as PFPA derivatives)

Compounds	Abbreviation	Log K_{OW} [23,24]	pK_a	RT[a] (min)	Characteristics ions (m/z)[b]
Nonylphenol	NP	4.48	10.7 [30]	11.19	253, 267, 281, 295
Bisphenol-A-d16	BPA-d16	–[c]	–[c]	14.39	271, 516
Bisphenol-A	BPA	3.32	9.59–11.3 [31]	14.46	265, 505
Estrone	E1	3.13	10.3–10.4 [17]	19.42	306, 416, 372, 119
17β-estradiol	E2	4.01	10.3–10.4 [17]	18.93	237, 401, 359
17 α-estradiol	α-E2	–[c]	–[c]	18.39	237, 401
Estriol	E3	2.81	10.3–10.4 [17]	19.07	235, 399
Mestranol	MeEE2	4.67	13.1 [17]	19.91	292, 173, 160
17β-estradiol acetate	E2AC	–[c]	–[c]	20.35	306, 460
Terphenyl-d14	I.S	–[c]	–[c]	17.21	244

[a] RT, retention time.
[b] Underlined ions are used for quantification.
[c] No reported.

cleanup, solid phase extraction, HPLC fractionation, derivitazation with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA)/trimethylsilylimidazole (TMSI)/dithioerytrol (DTE) (1000:2:2, v/v/w) and detection by GC–MS–MS. The detection limits can be down to 0.2 ng/g for estrogens in freshwater sediments. Liu et al. [29] used microwave-assisted extraction followed by derivatization with pyridine and BSTFA with trimethylchlorosilane (TMCS, 1%) and GC–MS analysis to determine phenolic and steroid EDCs in river sediments. However, there had few reports on the simultaneous determination of phenolic xenoestrogens and steroid estrogens in solid matrices to date, albeit they usually co-occur in environment due to their similar origins. The main objective of this study is to develop a simple and effective method to simultaneously determine the steroid estrogens and phenols in sediment samples.

2. Experimental

2.1. Chemicals, reagents, and glassware

Table 1 lists the target EDCs including two phenolic compounds, three natural and one synthetic estrogens. Nonylphenol (NP, technical mixture), bisphenol-A (>99%), estrone (E1), 17β-estradiol (E2), 17α-estradiol (α-E2), estriol (E3), mestranol (MeEE2), surrogate standards bisphenol A-d16 (98% atom D) and 17β-estradiol acetate (E2AC), and derivatizing reagent pentafluropropionic anhydride (PFPA) were purchased from Sigma–Aldrich Canada Ltd. (Oakville, Ont.). Silylation reagents BSTFA and BSTFA with TMCS (1%) were obtained from Supelco (Bellefonte, PA, USA). Internal standard terphenyl-d14 was from Supelco too. The molecular structures of the investigated EDCs are shown in Fig. 1.

Distilled chromatographic-grade solvents including dichloromethane (DCM), methanol (MeOH), hexane, and acetone were purchased from Caledon Laboratories Ltd. (Georgetown, Ont., Canada). Silica gel (100–200 mesh, pore size 150 Å, >99%, Aldrich), sodium sulfate and glass wool were sequentially rinsed with acetone, DCM and hexane for three times each, respectively, and completely dried in the fume hood. The dried silica gel and sodium sulfate were then activated at 180–200 °C for 20 h in a shallow tray that was loosely covered with aluminum foil. All glassware were rinsed successively with MeOH, DCM, and hexane for three times prior to use.

2.2. Standard solutions

Stock standard solutions were prepared by dissolving 10 mg of each target compound into 10 mL of acetone and stored in an amber glass vial at −20 °C. The working standard solutions were diluted from the stock solution with acetone and stored at 4 °C.

2.3. Preparation of spiked sediments and environmental samples

Sediment samples of approximate 10 g each were thoroughly extracted for 24 h with DCM using Soxhlet extraction and then dried in a fume hood. These pre-extracted sediments were spiked with the standard solution at the level of 100 ng/g of each targets and surrogate standards (BPA-d16 and E2AC), and then stirred using a votex mixer for 2 h in order to ensure the sufficient contact of the targets with the solid matrix. Upon completion of mixing, the samples were stored in a freezer prior to use. Environmental samples were collected from Pearl River Estuary (PRE), South China Sea, where is surrounded by one of the most industrially-developed and heavily-populated areas in China. The environmental sediment samples were freeze-dried (Freeze Dryer ALPHA 1-4, Martin Christ, Germany), homogenized, and stored in dark at −20 °C.

2.4. Extraction

To compare the extraction efficiency, ultra-sonication, mechanical shaking, and Soxhlet extraction with acetone/DCM (1:1, v/v) were performed on the spiked sediments.

2.4.1. Sonication extraction

An aliquot of the spiked sediment samples (∼10 g) was put into a 40-mL amber glass vial with PTFE screw cap. Five milliliters of acetone/DCM and 3 mL of Milli-Q water (Millipore, Canada) with 0.1 M sodium chloride were added. The

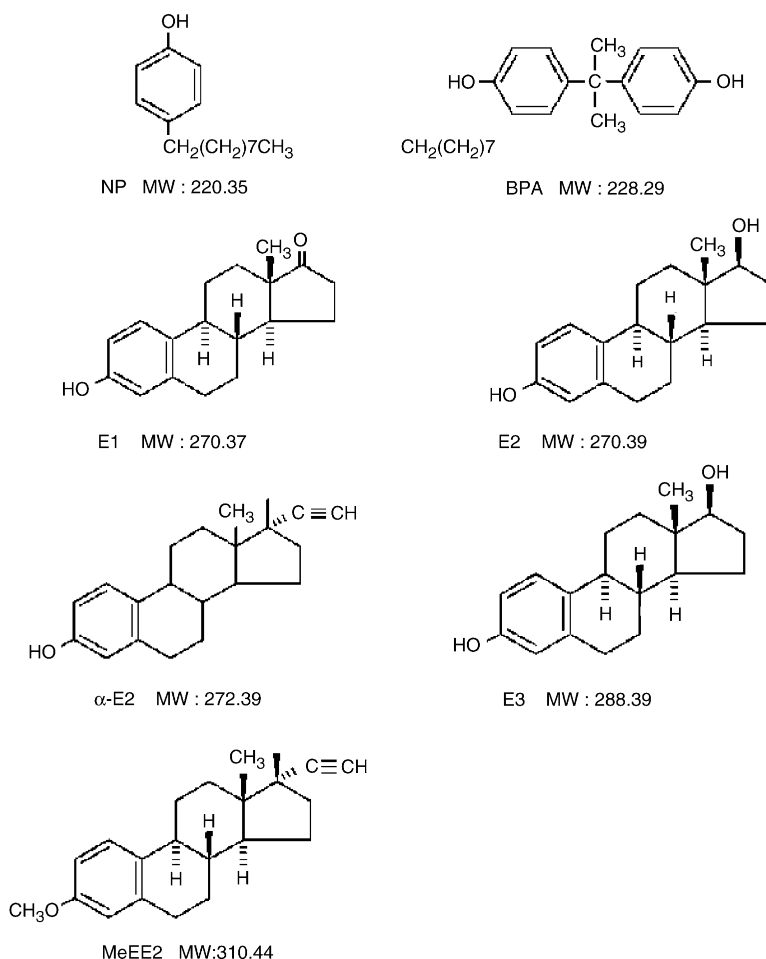

Fig. 1. Molecular structures of the investigated phenolic and steroid EDCs.

mixture was then ultrasonicated (Bransonic Ultrasonic Cleaner, Branson Cleaning Equipment Company, USA. 60 HZ, 117 V, 1.3 A) for 15 min. The supernatant was transferred to a glass separatory funnel that contained about 50 mL of Milli-Q water. The extraction was repeated two more times. The extracts were combined and the organic phase was thereafter back-extracted three times with 15 mL of DCM each time.

2.4.2. Soxhlet extraction

Another aliquot (∼10 g) of the spiked sediments was extracted by Soxhlet extraction with 200 mL of acetone/DCM for 24 h.

2.4.3. Mechanical extraction

Mechanical extraction was performed in a 50-mL glass centrifuge tube. Ten milliliter of acetone/DCM was added into the sample (∼10 g) and the mixture was then vigorously shaken with a votex mixer for 15 min. The mixture was centrifuged for 3 min at 3000 rpm. The procedure was repeated for two more times. Upon completion of extractions, the supernatants were combined, filtered and dried by passing through anhydrous sodium sulfate.

All extracts were concentrated to small volumes using rotary evaporation, and then further concentrated under a gentle flow of nitrogen to about 1 mL. Acid digestion was also conducted to spiked sediment samples, as described in detail by Li et al. [27], to evaluate its effect on the extraction efficiency.

2.5. Column chromatographic fractionation

A chromatographic column with a Teflon stopcock (200 mm × 10.5 mm I.D.) was plugged with glass wool at the bottom, serially rinsed with methanol, hexane and DCM, and allowed to dry. The column was dry-packed with 3 g of activated silica gel with tapping to settle the silica gel and topped with about 0.5 cm anhydrous sodium sulfate. The column was preconditioned with 10 mL of hexane and the eluant was discarded. The concentrated extract was quantitatively transferred onto the column. The column was then eluted successively with 10 mL of hexane, 12 mL of DCM and 10 mL of MeOH. Both phenols and steroids were in the MeOH fraction. The MeOH eluant was concentrated to a small volume, transferred to an amber vial, and further blown down to just dryness under a gentle flow of high purity nitrogen.

2.6. Derivatization

The derivatization of the MeOH eluant was performed by addition of 100 μL of PFPA and sealed. After a reaction at 60 °C

for 2 h, the derivatives were then cooled and blown down to just dryness under a gentle stream of nitrogen and reconstituted in hexane that contained 1 μg/mL of terphenyl-d14 as internal standard. The PFPA derivatives were stored at −20 °C prior to instrumental analysis within 2 days.

2.7. Capillary gas chromatography–mass spectrometry

The target compounds were determined by an HP 5890 capillary gas chromatograph equipped with a 5972 mass selective detector (MS) in the selective ion monitoring (SIM) mode. System control and data acquisition were achieved with an enhanced HP ChemStation. One microliter of sample was injected into an HP-5 MS column (30 m × 0.25 mm × 0.25 μm film thickness) in splitless mode. Helium was used as carrier gas and the flow rate was set at 1 mL/min. The oven temperature was programmed as: 60 °C for 1 min, ramp to 290 °C at a rate of 10 °C/min, and 10 min held at 290 °C. The injector and detector temperatures were set at 280 and 300 °C, respectively. For routine quantification, duplicate injections were performed for all samples. The mean values were adopted. The characteristics ions for identification and quantification of all target EDCs were also listed in Table 1.

2.8. Calibration and quantification

Derivatized working solutions containing all analytes (including surrogates) of 1 μg/mL were injected in duplicate before and after a set of five samples. The relative response factor (RRF) for each analyte was calculated relative to the internal standard. The relative standard deviations (RSDs) were determined to be in the range of 4–17.8% ($n \geq 4$) for target analytes. The average RRFs were used for quantification of target compounds in this work.

2.9. Quality assurance and quality control (QA/QC)

Procedural blanks that were constituted of DCM/acetone (1:1, v/v) mixture spiked with the surrogate standards BPA-d16 and E2AC, solvent blanks and control samples were included in each batch of analyses. Blanks and controls were treated in the same manner as the samples. GC–MS was tuned with perfluorotributylamine (PFTBA) and a calibration standard solution of 1 μg/mL was injected in duplicate to monitor the instrumental sensitivity and reproducibility every time before sample analyses.

3. Results and discussion

3.1. Extraction efficiency

Recoveries of the target EDCs were quantified to determine the extraction efficiencies of the methods. The reported recoveries (Table 2) have been corrected by surrogate standards (BPA-d16 for phenols and E2AC for estrogens). Satisfactory recoveries were achieved for phenolic compounds using both Soxhlet extraction and ultra-sonification, ranging from 91 to 135% for NP and 89 to 92% for BPA after corrected by the recovery of the surrogate BPA-d16 (recovered at 73–77%). In the case of estrogens, better recoveries were obtained by ultra-sonification except for E3 (27–32%, Table 2). Recovery of E1 was as high as 130–140% using both extractions. As the surrogate for steroid estrogens, E2AC was recovered at 87–106% and 107–110% from spiked sediment samples during Soxhlet extraction and ultrasonication, respectively. Poor recoveries were found using mechanical shaking extraction (results not listed here).

Table 2
Recoveries (%±SD) of phenols and steroid estrogens obtained by different extraction[a]

Compounds	Soxhlet extraction[b]		Ultra-sonication[c]	
	Digested	Non-digested	Digested	Non-digested
NP	114 ± 15	135 ± 7	91 ± 2	114 ± 8
BPA	91 ± 5	91 ± 2	89 ± 6	92 ± 7
E1	133 ± 8	141 ± 5	132 ± 3	134 ± 2
E2	37 ± 8	30 ± 1	71 ± 3	68 ± 7
α-E2	72 ± 3	77 ± 23	79 ± 5	82 ± 4
E3	73 ± 14	45 ± 10	32 ± 5	27 ± 3
MeEE2	43 ± 13	35 ± 10	66 ± 3	70 ± 2

[a] Sediment spiked at 100 ng/g dry weight. Recoveries were corrected by surrogate standards.
[b] $n = 6$.
[c] $n = 3$.

Li et al. [27] reported that acid digestion with hydrochloric acid (0.1 M) could improve the extraction efficiency of APs and BPA from sediments. However, in our work, acidic digestion caused no significant difference in the recoveries during both the Soxhlet extraction and ultra-sonification. This is consistent with the very weak acidic properties of the target EDCs as shown by their higher pK_a values (Table 1).

In order to find the reasons why E1 showed abnormally high recovery, while E2 and MeEE2 showed relatively low recoveries during the Soxhlet extraction (30–43%), we spiked pre-extracted sediment samples with E1, E2, and MeEE2 individually and then extracted by the Soxhlet extraction for 24 h, respectively. The recovery of E1 was found to be about 120%, while those of E2, and MeEE2 were in the ranges of 39–40% and 28–37%, respectively. It has been reported that both E2 and MeEE2 can degrade easily, 95% E2 transforming into E1 in 1–3 h and 80% MeEE2 vanished during 24 h, partly converting into 17α-ethinylestradiol [20]. That means that the longer-time Soxhlet extraction is not optimal for extracting steroid estrogens from solid matrices because they are likely to lose significantly due to their easy degradation. On the contrary, the ultra-sonication gives better results because it was accomplished in a much shorter time. In addition, the ultra-sonication is also solvent-saving. Therefore, the ultra-sonication without acidic digestion was thereafter used to extract phenolic xenoestrogens and steroid estrogens from environmental samples in this work.

Ultrasonicated extraction was optimized by addition of NaCl (0.1 M) solution and the following back-extraction of the extracts with DCM. Liu et al. [18] reported that the presence of NaCl enhanced the extraction efficiency for APs. Addition of NaCl

was also useful to prevent sorption of the analytes onto the sides of the vessels [32]. The following liquid–liquid extraction with DCM helped to decrease the strongly polar substances in the ultrasonicated extracts. Strongly polar substances such as humic and fulvic acids widely present in environmental sample may interfere the analysis of the target compounds during GC–MS.

3.2. Fractionation and derivatization

Fractionation and purification is necessary to remove unwanted matrix interference compounds from solvent extracts prior to derivatization and instrumental analysis. In this work, we used simple activated silica gel column for sample fractionation and cleanup. The method using activated silica gel column has been proved to be effective in removal of potential interference substances such as humic and fulvic acids by adsorption of these strongly polar compounds on the surface of silica gel particles [18]. As for non-polar compounds, they can be readily removed by sequential elution with hexane and DCM.

Derivatization is mandatory for the investigated EDCs prior to the GC–MS (SIM) analysis in order to improve the chromatographic separation and the sensitivity. Several derivatizing agents have been employed for derivatization of the hydroxyl functional groups present in the molecular structure of phenols and steroids (Fig. 1), including BSTFA with a small proportion of catalyzer [29], *N*-methyl-*N*-(*tert*-butyldimethylsilyltrifluoracetamide) (MTBSTFA) [33], and MSTFA alone [17] or with some kind of catalyzers [28]. BSTFA, BSTFA + TMCS (1%) and PFPA were tested to derivatize the target analytes under the same condition (60 °C for 2 h). The three reagents had comparable derivatizing effects on phenolic compounds. Natural estrogens obtained much better separation and higher sensitivity after being derivatized by PFPA than by silylation reagents (BSTFA and BSTFA + TMCS (1%)). Mestranol appeared only partially derivatized by all the three derivatizing reagents evidenced by the less improvement of the sensitivity. However, this is a common phenomenon as has been reported by other researchers [34]. PFPA was, therefore, chosen as the derivatizing reagent in this work.

3.3. Method validation

Linearity of the method was checked with standard mixtures containing all target EDCs including surrogate standards at 10 levels of concentration in the range of 0.1–50 μg/ml with terphenyl-d14 (1.0 μg/ml) as internal standard. Phenols and most natural estrogens (E1, E2, α-E2, and E3) were linear from 0.1 to 50 μg/ml with the correlation coefficients (R^2) from 0.980 (BPA-d16) to 0.999. The linear range was 0.5–50 μg/ml for MeEE2 ($R^2 = 0.940$).

Standard mixtures of 10, 100, and 1000 ng/g were spiked into pre-extracted sediment in order to test the reproducibility of recoveries of the investigated EDCs. No statistically significant differences in recoveries were obtained, which means that the recoveries of the target compounds are not concentration dependent.

Table 3
Occurrence of phenolic and estrogenic EDCs in the sediment of PRE, South China Sea (ng/g dry weight)[a]

	NP	BPA	E1	E2	α-E2	E3	MeEE2
S1	204.2	3.8	ND	ND	ND	ND	ND
S2	229.8	0.6	ND	ND	ND	ND	ND
S3	664.5	4.0	ND	ND	ND	ND	ND

ND, not detected.
[a] S1, S2, S3 are sediment samples numbers.

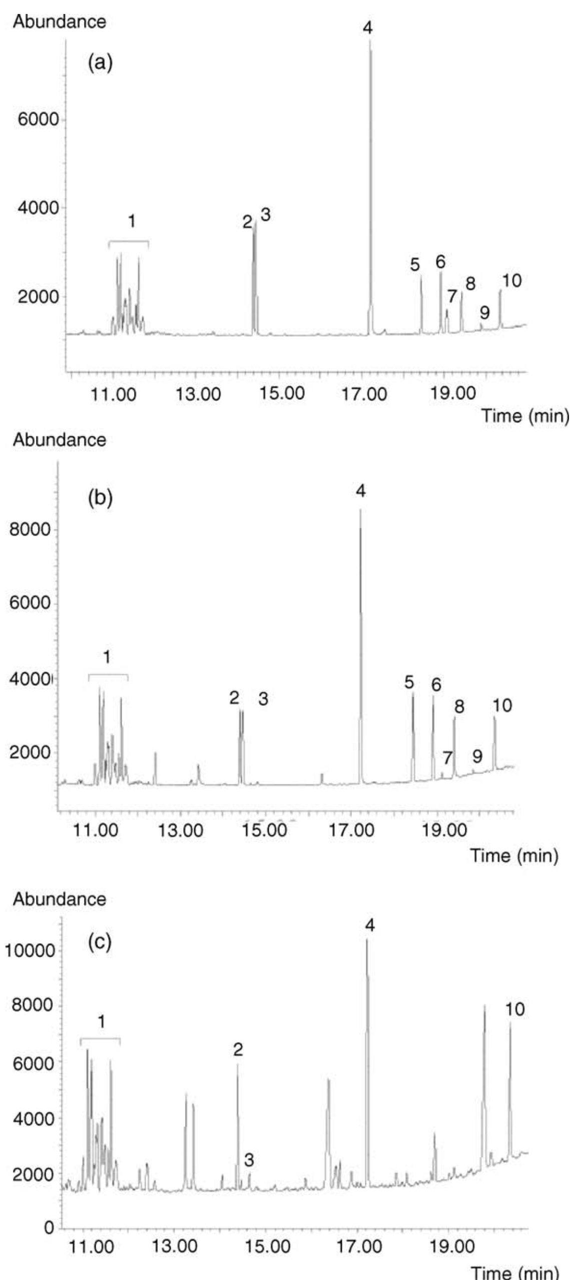

Fig. 2. Chromatogram of target EDCs in (a) standard solution (1 ng injection); (b) sediment spiked with 10 ng/g standard mixture (final volume of 0.1 mL); (c) sediment sample from Peral River Estuary. Peak numbers refer to (1) NP, (2) BPA-d16 (S.S), (3) BPA, (4) terphenyl-d14 (I.S), (5) α-E2, (6) E2, (7) E3, (8) E1, (9) MeEE2, (10) E2AC (S.S).

Deuterated bisphenol-A (BPA-d16) demonstrated excellent repeatability in recoveries, and they were very close to that of investigated phenols. Hence, BPA-d16 is a good choice as the surrogate for the phenolic xenoestrogens. However, recoveries of steroid estrogens vary to some extent from compound to compound (Table 2) due to the difference in their chemical stabilities. Therefore, it is not ideal to use an identical surrogate for all steroid estrogens. Compound-specific isotope-labeled surrogates would be preferred if possible.

The instrumental detection limits (LODs) and quantification limits (LOQs) for analytes were estimated on the basis of signal/noise ratios of 3 and 10, respectively. Generally, the method quantification limit (MQL) depends upon the mass of the sample extracted, the extraction efficiency, and instrumental LOQ as well. MDLs were determined to be 0.1 ng/g dry weight for BPA, 0.2 ng/g for NP, 0.6 ng/g for E1 and α-E2, 0.8 ng/g for E2, 1.5 ng/g for E3, and 2.5 ng/g for MeEE2 on the basis of 10 g of sediment sample in this work.

3.4. Application of the method to environmental samples

Three environmental sediment samples were randomly collected from Pearl River Estuary, South China Sea. They were extracted by ultra-solication, purified, derivatized and analyzed by GC–MS (SIM) as described in detail above. NP and BPA were detected in the three samples, ranging from 204 to 664 ng/g and 0.6 to 4.0 ng/g, respectively (Table 3, Fig. 2). None of estrogens were found in the sediments. This may be related with the fact that the sampling sites were not adjacent to sewage effluent discharge points. Unlike xenoestrogenic phenols, estrogens are not persistent, with half-lives of only a few days in environment [20]. Therefore, they are not likely to transport long distances in the environment.

4. Conclusion

The method consisted of ultra-sonicated extraction, silica gel fractionation and purification, PFPA derivatization, and GC–MS (SIM) analysis. This method enables simultaneous determinations of phenolic EDCs and steroid estrogens in sediments down to nanogram per gram of sediment (dry weight). The results are comparable with those using methods separately for phenolic EDCs and sex hormones [27,28]. The method was demonstrated to be simple, effective and economic. This method can also expect to be used for determination of phenolic xenoestrogens and sex hormones in other solid matrices, such as suspended particles and sewage sludge without substantial modification. The method has been successfully used to analyze NP, BPA and steroid estrogens in sediment samples collected from Pearl River Estuary, South China Sea, China. NP and BPA were detected in the range of 204–664 ng/g and 0.6–4.0 ng/g, respectively, while no detectable steroid estrogens were found in these sediments.

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