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

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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.

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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.

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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

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