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ScienceDirect
Chemosphere 70 (2008) 858–864
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Application of ultrasonic assisted extraction of chemically diverse organic compounds from soils and sediments

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Received 5 January 2007; received in revised form 27 June 2007; accepted 30 June 2007
Available online 5 September 2007

Abstract

The objective of this research was the development, optimization, and demonstration of an ultrasonic assisted extraction (UAE) based method for organic anthropogenic waste indicators (AWIs) with a range of physicochemical properties from soil and sediment samples. The optimized method was designed to be cost effective compared to existing extraction methods, which may require large quantities of consumables, produce substantial volumes of organic waste, or require costly instrumentation or equipment. Reagent grade sand, soil collected from the native grassland in proximity to Eastern Washington University (EWU), and sediment samples collected from the Spokane river were used as sample matrices during method development. These matrices were fortified with eight AWIs of varying chemical properties that are representative of a variety of household, industrial, and agricultural sources. The recoveries of the AWIs spiked onto these matrices were determined in the extracts using gas chromatography/mass spectrometry (GC/MS). These values reflect the efficiency of the method for extraction of these analytes from representative environmental matrices. Recoveries ranged from 46.1% to 110% in the fortified soil and from 49.2% to 118.6% in the fortified sediment samples, which is comparable with existing methods for the study analytes. The optimized method was then used to quantify AWIs in a biosolid-amended soil. Indole and *p*-cresol were detected in the biosolid-amended soil.

Keywords: Pharmaceuticals; Endocrine disruptors; Wastewater treatment; PAHs; Biosolid

1. Introduction

Organic anthropogenic waste indicators (AWIs) are a broad range of industrial, agricultural, and household chemicals which include products of oil and combustion, prescription and non-prescription drugs, detergent metabolites, personal care products, hormones, steroids, and pesticides, which can enter the municipal waste stream. Some of these compounds are discharged into the environment in controlled applications such as during pesticide use; however, others are released through regulated and unregulated processes associated with industry (Kolpin et al., 2002). The incomplete removal of AWIs present in the wastewater stream during the wastewater treatment process can result in detectable concentrations of these compounds in surface waters downstream of effluent discharge from wastewater treatment facilities (WWTFs) and in soils irrigated with reclaimed water (Jorgensen and Halling-Sorensen, 2000; Kolpin et al., 2002; Castiglioni et al., 2005; Kinney et al., 2006a). Furthermore, depending on their hydrophobic/lipophilic nature, many AWIs will remain sequestered to sewage sludge (Rogers, 1996; Jorgensen and Halling-Sorensen, 2000; Golet et al., 2003; Kinney et al., 2006b) and can later enter the environment via leaching after the sludge is dispersed on agricultural fields

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0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.06.088

as biosolids. Consequently, there are a number of pathways by which AWIs may enter into the environment.

A number of researchers have detected AWIs in environmental soil and sediment samples throughout North America and Europe, where, as noted previously, they have generally originated from discharge of treated wastewater effluent, use of reclaimed water for irrigation, or soil application of biosolids. Kinney et al. (2006a) measured individual pharmaceuticals in Colorado soils irrigated with reclaimed wastewater ranging from 0.02 to 15 μg/kg (dry soil). In biosolid products the AWI content may constitute more 1800 mg/kg of the dry weight of land applied products (Kinney et al., 2006b). Research conducted by Bright and Healey (2003) identified the presence of several petroleum-based hydrocarbons such as *p*-cresol and phenanthrene (among others) in biosolids destined for land application. Some AWIs such as benzalkonium chlorides (BACs) and pharmaceuticals have been found in environmental sediment samples downstream of treated wastewater discharge throughout the United States (Ferrer and Furlong, 2002; Furlong et al., 2004).

Until recently, there have been few analytical methods available for extracting and quantifying trace levels of a broad range of AWIs in environment matrices. As a result, the origin, transport, and fate as well as possible synergistic and antagonistic effects of mixtures of AWIs are not clearly understood (Halling-Sorensen et al., 1998; Kolpin et al., 2002). The potential for AWIs to bioaccumulate and persist in the environment has lead to concerns about their potential effects on human and ecosystem health, such as disruption of endocrine system functions, promoting the natural selection of antibiotic-resistant bacteria, cancer, and genetic mutations (Martinez et al., 2004; Kampioti et al., 2005; Santos et al., 2005; Burkhardt et al., 2005a; Kinney et al., 2006a). Given these concerns the development of analytical methods for the detection of trace concentrations of AWIs in the environment is highly warranted (Kolpin et al., 2002; Burkhardt et al., 2005a,b; Kinney et al., 2006a,b). Ultimately, the choice of the extraction method may depend on effectiveness, capital cost, operating cost, simplicity of operation, and waste production (Banjoo and Nelson, 2005).

Soxhlet is recommended by the United Stated Environmental Protection Agency (USEPA) to extract semi-volatile and non-volatile organics from solid matrices (Sun et al., 1998; Banjoo and Nelson, 2005). Soxhlet extraction is relatively costly, time consuming, labor intensive, requires the use of large volumes of solvent, and may result in large volumes of toxic organic waste (Sun et al., 1998; Burkhardt et al., 2005a). For these reasons, a number of robust alternative methods, such as pressurized liquid extraction (PLE), microwave assisted extraction (MAE), and ultrasonic assisted extraction (UAE), have been used to reduce time, expenses, and solvent volumes (Sun et al., 1998; Pino et al., 2000, 2001; Martinez et al., 2004; Parera et al., 2004; Burkhardt et al., 2005a,b; Morales-Muñoz et al., 2005). With rare exception, such methods have primarily focused on compounds of a limited number of legacy chemicals such as PAHs and PCBs.

Ultrasonic assisted extraction (UAE) has a proven comparable extraction efficiency for a limited number of anthropogenic chemical classes with other conventional extraction methods (Sun et al., 1998; Martinez et al., 2004; Banjoo and Nelson, 2005; Filipkowska et al., 2005; Kawata et al., 2005; Yang et al., 2005). For example, UAE has comparable performance to traditional extraction methods for the extraction of PAHs from environmental soil and sediment samples (Sun et al., 1998; Pino et al., 2001; Martinez et al., 2004; Banjoo and Nelson, 2005). Studies have shown that recoveries and reproducibility using UAE of PAHs are equivalent to, or better than those obtained by other extraction techniques (Sun et al., 1998; Martinez et al., 2004; Banjoo and Nelson, 2005). General application of UAE has focused on the extraction of specific chemical groups, such as PAHs or specific classes of pesticides (Sun et al., 1998; Martinez et al., 2004; Banjoo and Nelson, 2005; Filipkowska et al., 2005; Kawata et al., 2005; Yang et al., 2005), however AWIs consists of a suite of contaminants with diverse physicochemical properties (Kolpin et al., 2002; Kinney et al., 2006b).

Ultrasound assisted extraction is unique because it aids in chemical as well as physical extraction of analytes from solid matrices. Cavitation bubbles produced during the UAE process may attain significant internal temperature and pressure that eventually collapse causing the extraction solvent to propagate outward with considerable velocity and on a collision course with matrix particles. These collisions break up the matrix and cause smaller particles to be produced, thereby exposing more surface area to the extraction solvent (Capelo and Mota, 2005); therefore, UAE is a robust method for extracting organic contaminants from solid matrices comparable to other commonly used methods such as Soxhlet, PLE, and MAE.

A subset of AWIs with varying physicochemical properties was used during the extraction method development in this project (Table 1). Though these compounds are few in number, they represent many possible AWIs in their physical and chemical behavior in environmental solid matrices. Ottawa sand, eastern Washington native grassland soil (NG soil), and wet Spokane river sediment samples were fortified with a mixture of the AWI method compounds. Isopropanol:water (IPA:H_2O) mixtures have proven to be efficient extraction solvents for a range of physicochemically diverse AWIs by other researchers (Burkhardt et al., 2005a,b), and proved to be true for the method presented here. Method recoveries were used as a measure of method performance for the various matrices, which are representative of those commonly impacted by AWIs (Ferguson et al., 2001; Ferrer and Furlong, 2002; Bright and Healey, 2003; Kinney et al., 2006a,b). The present research describes a cost effective alternative method for the extraction of AWIs from soil and sediment samples based UAE followed by SPE clean-up and analyses using GC–MS.

Table 1
OWC analytes and physicochemical properties

Compound name	Use	HSA[a]	CAS number	Log K_{ow}[b]	Vapor pressure (mm Hg)[b]	Water solubility (mg/l)[b]
4-*tert*-Octylphenol	Detergent metabolite	E	140-66-9	5.28	4.78×10^{-4}	5
Benzo[*a*]pyrene	PAH	A	50-32-8	6.13	5.49×10^{-9}	0.00162
Bisphenol A	Fire retardant	E	80-05-7	3.32	3.91×10^{-7}	120
Carbamazepine	Antiepileptic	–	298-46-4	2.45	1.84×10^{-7}	17.7
Indole	Fragrance	–	120-72-9	2.14	0.0122	3.560×10^{3}
p-Cresol	Preservative	–	106-44-5	1.97	0.11	2.15×10^{4}
Phenanthrene	PAH	–	85-01-8	4.52	1.21×10^{-4}	1.15
Triclosan	Disinfectant	–	3380-34-5	4.53	6.45×10^{-7}	10

[a] HSA = hormone system affected (E = estrogen/testosterone, A = Androgen).

[b] Physical chemical properties from the following online database http://www.syrres.com/ese.

2. Experimental

2.1. Chemicals and reagents

HPLC grade isopropanol (IPA) and water and class 1A diethyl ether (DEE) were purchased from Fisher Scientific (Fairlawn, NJ, USA). Dipotassium hydrogen phosphate and potassium dihydrogen phosphate used to prepare a phosphate buffer (pH 7.0), sodium sulfate, and acetone were purchased from J.T. Baker Chemical Company (Phillipsburg, NJ, USA). Dichloromethane, and AWI method compounds bisphenol A, indole, triclosan, *p*-cresol, phenanthrene, carbamazepine, and 4-*tert*-octylphenol were purchased from Sigma Aldrich (St. Louis, MO, USA). Oasis™ HLB 6 cm^3, 550 mg LP extraction cartridges (polystyrene-divinylbenzene packing material) and Honeywell Burdick & Jackson florisil cartridges (1 g florisil packed in a 6 ml barrel) were used for solid phase extraction clean-up. Bisphenol-A-d_{16} used as an internal standard was purchased from Sigma Aldrich (St. Louis, MO, USA).

2.2. Matrices

Ashed Ottawa sand (400 °C, >4 h), soil core samples taken from an eastern Washington native grassland (NG) field near EWU, and Spokane river sediment samples taken upstream from the Spokane WWTF were used as the solid matrices for method development. Three, 15 cm deep NG soil core samples, 5 cm in diameter, were collected in fall 2005. The cores were combined and homogenized to make a bulk sample. A sediment grab sample was taken about 1800 m upstream of the Spokane WWTF and about 7 m from the river bank (April 2006) and stored in amber glass jars at −4 °C until use.

Soil collected on August 16, 2006 from a site in Central Oregon with an extended history (20+ years) of biosolid application as an organic soil amendment was selected to validate the application of this method on environmental samples likely impacted by AWIs. The date of soil collection was 22 days after the most recent application of biosolid to this site. The soil was transported from the field site to the laboratory in an ice filled cooler. Once in the laboratory the soil was stored at −4 °C until analysis.

2.2.1. Matrix characterization

The organic carbon content of the NG soil and wet Spokane river sediment was estimated by loss on ignition using the universal conversion coefficient 0.58 (Schulte and Hopkins, 1996). Calcium carbonate was used to control for loss of inorganic carbon. Textural analysis of the NG soil was completed using standard soil hydrometry testing and pH (1:1 soil:water by mass mixture) was determined using a portable Hanna pHep® (model: HI98107) pH meter. The NG soil estimated to contain 1.92% organic carbon and contained 43.1% sand (>0.05 mm), 39.1% silt, and 17.8% clay. The Spokane river sediment is estimated to contain 0.23% organic carbon. The pH of the soil was 5.4.

2.3. Ultrasonic assisted extraction

The initial method was developed using 2 g samples of soil or sediment placed in replicate ($n = 6$) ashed (400 °C, >4 h) Corex® centrifuge tubes and fortified with 200 μg of each method compound. A second set of extraction experiments used 10 g of each matrix ($n = 6$) fortified with 50 μg of each method compound. The fortified matrices were allowed to rest for ~24 h before extraction. Five millilitres of the 80:20 IPA:H_2O extraction solvent was added to the samples to the 2-g fortified matrices while 15-mL of extraction solvent was added to the 10-g fortified samples. The mixtures were then placed in an ultrasonic bath (Branson 1510) for 10 min at room temperature. The samples were centrifuged at 3000 rpm for 5 min and the extraction solvent was decanted into a ashed (400 °C, >4 h) test tube. Each sample was then extracted a second time using the same volume of solvent at elevated temperature (55 °C) for 10 min. Following centrifugation the solvent from the second extraction step was decanted combined with first prior to the clean-up and preconcentration steps.

The triplicate soil samples (10 g) from the Central Oregon field site were extracted using the optimized method as described above. In addition, triplicate soil samples (10 g) from this field site were fortified with 50 μg of each study compound (matrix spike), extracted, and quantified to verify method performance.

2.4. Clean-up and preconcentration

The clean-up and preconcentration steps used as part of this method were adapted from an existing method developed by Burkhardt et al. (2005a,b). Oasis^{TM} HLB solid phase extraction (SPE) cartridges were conditioned with 25 ml of 80:20 DCM:DEE. The extract was loaded into the barrel of the SPE cartridges followed by the addition of 20 ml of phosphate buffer. A vacuum was applied to the SPE block until all the liquid was drawn through the cartridges. The cartridges were dried for 10 min under vacuum. Florisil cartridges conditioned with 10 ml of acetone were placed on the SPE block, and about 4 g of ashed (400 °C, >4 h) sodium sulfate was added into the barrel of each florisil cartridge. The HLB cartridges were stacked on top of the florisil cartridges. Ashed test tubes were used to collect the eluted samples. The SPE stack was eluted with three, 5 ml aliquots of 80:20 DCM:DEE. The eluted samples were evaporated under a gentle stream of air to 1 ml, and quantitatively transferred to 2-ml amber vials. Prior to analysis, 50 μl of the 4 mg ml^{-1} bisphenol-A-d$_{16}$ internal standard was added to the sample and the blank extracts. The extracts were either immediately analyzed or they were stored at 4 °C until analysis.

2.5. Gas chromatography/mass spectrometry (GC/MS)

Final extracts were quantified on Hewlett Packard HP 5890 series II gas chromatograph/mass spectrometer (HP-5972) using external calibration. The column used was a Hewlett Parkard-5, 30 m × 0.25 mm inside diameter fused-silica capillary column coated with 0.25 μm thick cross-linked 5% phenylmethylsilicone. A 2 μl volume was injected in a splitless mode. The injection port temperature was 290 °C, the purge flow was 6.1 ml/min, and the transfer line was maintained at 250 °C. The oven temperature was programmed as follows: 40 °C (hold 3 min), ramped at 8.00 °C/min to 100 °C (hold 4.50 min), then ramped at 9.00 °C/min to 290 °C; with pressure control set for a constant flow of helium carrier gas of 3.0 ml/min. The MS was operated in full scan mode, but extracted ion chromatograms were used for calibration and quantification.

2.6. Quality control

Several measures of quality control were used during UAE method development. Internal standard (bisphenol-A-d$_{16}$) was added to each sample after preconcentration and prior to analysis. Multiple characteristic ion monitoring was used in addition to retention time and quantification ions to assure proper compound identification during quantitative analysis. Field soil and sediment blanks were extracted and analyzed along with their respective fortified soil or sediment samples. In addition with each set of samples, a laboratory blank and fortified sand sample were analyzed. None of the AWI analytes were detected in the field or laboratory blanks.

3. Results and discussion

3.1. Initial method development

Optimization of the present method was carried out during the initial stages of research. The variables considered during this process include extraction solvent, the length of extraction, the number of extraction cycles, as well as extraction temperature, which have been considered for variation in other UAE method development research (Pino et al., 2001; Banjoo and Nelson, 2005). For the present method, it was found that optimal AWI extraction from sand or soil occurred when an 80:20 IPA:H_2O was used as the extraction solvent and two extraction cycles (one at ambient temperature, the other at 55 °C) were used.

The temperature of the ultrasonic bath during UAE of sand or soil was varied to evaluate whether heat was beneficial for extraction of certain AWIs, such as the high molecular weight, non-polar compounds. The results of these tests indicate that a second extraction at 55 °C significantly improves the recovery of bisphenol A, which is the most non-polar compound included in this study. As a consequence, a dual extraction technique was employed where the samples were extracted first at room temperature, and re-extracted a second time at elevated temperature. The two extracts were then combined and run through the clean-up and preconcentration steps, as described in Section 2.4.

3.2. Method recoveries

Method recoveries of analytes using the optimized method are listed in Table 2. Recoveries ranged from 46.1% to 110% for analytes from the NG soil to 49.2–118.6% in the Spokane river sediment. The recovery of bisphenol A was consistently the lowest for the study compounds from all of the matrices tested suggesting the poor recovery may be independent of the matrix. Burkhardt et al. (2005a) reported similarly low recoveries for bisphenol A using a PLE based extraction method. Given the matrix and extraction method independence of the relatively poor recovery of bisphenol A, we hypothesize that the post extraction clean-up step and preconcentration steps may be responsible for the lower recovery of bisphenol A. It is worth noting that the clean-up and preconcentration steps used in this study were adapted from those developed by Burkhardt et al. (2005a,b), giving further credence to this hypothesis.

Generally, greater recoveries were obtained for analytes extracted from the fortified sediment than from the fortified native grassland soil samples. Furlong et al. (2004) showed that naturally-occurring organic matter in a sample may sequester analytes, diminishing their recovery. The sorption of analytes to the relatively higher organic carbon content in the soil samples may therefore have affected the efficiency of UAE of organic contaminants from the soil,

Table 2
Method quantitation values and mean method recoveries of fortified matrices ($n = 6$)

Compound name	Fortification (µg)	Retention time (min)	Quantitation ion (*m*/*z*)	Confirmation ion (*m*/*z*)	Confirmation ion (*m*/*z*)	Mean % recovery soil	Initial method detection limit (µg/g soil)[a]	Mean % recovery sediment[b]	Initial method detection limit (µg/g sediment)[a]
p-Cresol	200	9.66	107	108	77	88.2 (17)		102 (8)	
	50					62.5 (12)	16.5	91.2 (6)	12.2
Indole	200	15.51	117	90	89	77.2 (17)		110 (6)	
	50					81.6 (4)	7.6	80.1 (4)	7.1
4-*tert*-Octylphenol	200	21.99	135	107	–	90.9 (16)		118 (8)	
	50					74.9 (10)	16.7	59.3 (14)	18.5
Phenanthrene	200	24.35	178	176	89	97.2 (14)		118 (7)	
	50					56.9 (48)	60.7	90.4 (5)	10.5
Triclosan	200	27.96	288	290	218	96.1 (21)		118 (7)	
	50					59.0 (19)	25.7	52.3 (13)	15.4
Bisphenol A	200	28.79	213	228	119	58.5 (42)		57.7 (16)	
	50					46.1 (16)	17.1	49.2 (12)	13.7
Carbamazepine	200	30.52	193	236	165	81.2 (38)		96.4 (12)	
	50					67.6 (19)	27.8	87.5 8)	15.9
Benzo[*a*]pyrene	200	34.54	252	126	250	110 (27)		115 (7)	
	50					50.0 (17)	18.4	88.4 (6)	11.7
Bisphenol-A-d_{16}[c]		28.67	224	242	125				

[a] US Environmental Protection Agency (1997).

[b] Value in parentheses are the relative standard deviation ($n = 6$).

[c] Internal standard.

and may contribute to the decrease in AWI recoveries from the soil compared to the sediment. It is also possible that co-extracted compounds from the fortified soil not removed during the clean-up step may in part account for lower recoveries compared to the fortified sediment.

While direct comparison of method recoveries with other published methods is complicated by differences in the compounds and the quantities studied, we can make some qualitative comparisons. The method recoveries of most of the compounds included in this work (all but carbamazepine) are generally comparable to those reported by Burkhardt et al. (2005a,b). However, it is important to note that the lowest fortified concentration of compounds used in this study are about an order of magnitude higher than those published by Burkhardt et al. (2005a,b). These results illustrates that UAE may be a viable alternative to PLE for some matrices and AWIs with a range of physicochemical properties for researchers without access to the equipment required for PLE.

There are numerous reports of successful use of UAE for the extraction of PAHs from soils and sediments, which used similar quantities of the PAHs included in this project (phenanthrene and benzo[*a*]pyrene). For example, Martinez et al. (2004) and Filipkowska et al. (2005) used UAE based methods to extract PAHs from fortified environmental sediment samples. Martinez et al. (2004) used hexane:acetone (1:1) as the extraction solvent and reported a 63% recovery for benzo[*a*]pyrene and 85% for phenanthrene. Filipkowska et al. (2005) used acetonitrile as the extraction solvent for PAHs and found that using high pressure liquid chromatography (HPLC) for quantification to be comparatively superior to GC/MS analysis. Filipkowska et al. (2005) reported recoveries of 78% and 87% benzo[*a*]pyrene and phenanthrene using HPLC, respectively, which are similar to the recoveries reported in the present work. Although, the basic selection of UAE as the extraction method is common with other studies (Martinez et al., 2004; Filipkowska et al., 2005) and the present one, there are some considerable differences, such as the extraction solvent, the clean-up steps, and the physicochemical diversity of the compounds for which the method has been developed. While existing UAE methods have generally targeted analytes of a specific chemical class, as in the work by Filipkowska et al. (2005) and Martinez et al. (2004), our work helps demonstrate the versatility of UAE methods to target a more diverse range of compounds.

Analyte recovery using UAE may yield results comparable to MAE based methods and Soxhlet extractions (Budzinski et al., 1999; Letellier et al., 1999; Pino et al., 2001; Parera et al., 2004). Using MAE, Pino et al. (2000,2001) and Budzinski et al. (1999) extracted benzo[*a*]pyrene and phenanthrene from soil and sediment samples fortified with similar quantities of the PAHs as used in this study. In the two Pino et al. works, phenanthrene recovery was consistently near 49, while the recoveries of benzo[*a*]pyrene differed between the two works at 84.37% and 93.8%. Budzinski et al. (1999) used DCM to extract PAHs from soil and sediment samples and obtained about 80% recovery of both phenanthrene and benzo[*a*]pyrene. In the present method, we report 56.9% and 90.4% recovery of phenanthrene and 50.0% and 88.4% recovery of benzo[*a*]pyrene from soil and sediment fortified with 50 µg of each compound, respectively.

Table 3
AWI content of biosolid-amended soil

Compound name	Concentration (μg/g)[a]	Mean % recovery matrix spike[a]	Limit of detection (μg/g)[b]
p-Cresol	1.3 (17)	82.7 (11)	0.09
Indole	3.7 (21)	79.9 (8)	0.06
4-*tert*-Octylphenol	ND[c]	81.0 (13)	0.07
Phenanthrene	ND	89.4 (6)	0.08
Triclosan	ND	84.2 (9)	0.07
Bisphenol A	ND	49.5 (24)	0.09
Carbamazepine	ND	78.8 (8)	0.11
Benzo[*a*]pyrene	ND	87.6 (12)	0.08

[a] Values in parentheses are the relative standard deviation ($n = 3$).
[b] Limit of detection calculated based on empirical results of blank ashed sand extracts fortified with method compounds.
[c] "ND" = not detected.

3.3. Method application

Soil collected from a site within Central Oregon likely to have the presence of AWIs as a result of biosolid application from a local municipal WWTF was selected to test the optimized extraction method. Two of the study compounds, indole and *p*-cresol, were detected at low concentrations in the soil samples (Table 3). The matrix spike samples from this site had similar recoveries to the NG soil used during method development (Table 3). These results further validate the utility of the method described in this paper.

4. Conclusion

The method recoveries obtained using the present method, demonstrate that UAE is an attractive, affordable, and effective alternative to existing extraction methods for organic contaminants from solid matrices. Major advantages of UAE in comparison to other extraction methods such as PLE or Soxhlet, include ease of use, cost, and in some cases extraction time. From the start of the extraction of a set of samples ($n = 9$) to final preconcentrated extract ready for quantitation was typically about 2 h. The developed method was then successfully applied to environmental samples collected from a biosolid-amended soil. Our work provides evidence that UAE can be effectively employed to extract organic contaminants that vary considerably in their physicochemical properties.

Acknowledgements

The authors thank Dr. Stephen Warren and Pete Black in the Department of Chemistry at Gonzaga University for providing access to vital instrumentation for the completion of this project. Funding for this project was provided in part from an Eastern Washington University Faculty Research Grant awarded to the corresponding author.

References

Banjoo, D., Nelson, P., 2005. Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments. J. Chromatogr. A. 1066, 9–18.

Bright, D.A., Healey, N., 2003. Contaminant risks from biosolids land application: contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia. Environ. Pollut. 126, 39–49.

Budzinski, H., Letellier, M., Garrigues, P., Menach, K., 1999. Optimisation of the microwave-assisted extraction in open cell of polycyclic aromatic hydrocarbons from soils and sediments study of moisture effect. J. Chromatogr. A. 837, 187–200.

Burkhardt, M., ReVello, R., Smith, S., Zaugg, S., 2005a. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment. Anal. Chim. Acta 534, 89–100.

Burkhardt, M., Zaugg, S., Burbank, T., Olson, M., Iverson, J., 2005b. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for semivolatile organic compounds, polycyclic aromatic hydrocarbons (PAH), and alkylated PAH homolog groups in sediment. Anal. Chim. Acta 549, 104–116.

Capelo, J.L., Mota, A.M., 2005. Ultrasonication for analytical chemistry. Curr. Anal. Chem. 1, 193–201.

Castiglioni, S., Bagnati, R., Calamari, D., Fanelli, R., Zuccato, E., 2005. A multiresidue analytical method using solid-phase extraction and high-pressure liquid chromatography tandem mass spectrometry to measure pharmaceuticals of different therapeutic classis in urban wastewaters. J. Chromatogr. A. 1092, 206–215.

Ferrer, I., Furlong, E., 2002. Accelerated solvent extraction followed by on-line solid-phase extraction coupled to ion trap LC/MS/MS for analysis of benzalkonium chlorides in sediment samples. Anal. Chem. 2002, 1275–1280.

Ferguson, P.L., Iden, C.R., Brownawell, B.J., 2001. Analysis of nonylphenol and nonylphenol ethoxylates in environmental samples by mixed-mode high-performance liquid chromatography-electrospray mass spectrometry. J. Chromatogr. A. 938, 79–91.

Filipkowska, A., Lubecki, L., Kowalewska, G., 2005. Polycyclic aromatic hydrocarbon analysis is different matrices of the marine environment. Anal. Chim. Acta 547, 243–254.

Furlong, E., Kinney, C., Ferrer, I., Werner, S., Cahill, J., Ratterman, G., 2004. Pharmaceuticals and personal care products in solids: analysis and field results for sediment, soil and biosolid samples. Abstr. Pap. Am. Chem. S. 228, U620.

Golet, E., Xifra, I., Siegrist, H., Alder, A., Giger, W., 2003. Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil. Environ. Sci. Technol. 37, 3243–3249.

Halling-Sorensen, B., Nielsen, S., Lanzky, P.F., Ingerslev, F., Lützhoft, H.C., Jorgensen, S.E., 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere. 36, 357–393.

Jorgensen, S.E., Halling-Sorensen, B., 2000. Drugs in the environment. Chemosphere 40, 691–699.

Kampioti, A., Borba da Cunha, A., López de Alda, M., Barceló, D., 2005. Fully automated multianalyte determination of different classes of pesticides, at picogram per litre levels in water, by on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry. Anal. Bioanal. Chem. 382, 1815–1825.

Kawata, K., Asada, T., Oikawa, K., 2005. Multiresidue determination of pesticides in sediment by ultrasonically assisted extraction and gas chromatography/mass spectrometry. J. AOAC Int. 88, 1440–1451.

Kinney, C., Furlong, E., Werner, S., Cahill, J., 2006a. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. Environ. Toxicol. Chem. 25, 317–326.

Kinney, C., Furlong, E., Zaugg, S., Burkhardt, M., Werner, S., 2006b. Survey of organic wastewater contaminants in biosolids destined for land application. Environ. Sci. Technol. 40, 7207–7215.

Kolpin, D., Furlong, E., Meyer, M., Thurman, E., Zaugg, S., Barber, L., Buxton, H., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. Environ. Sci. Technol. 36, 1202–1211.

Letellier, M., Budzinski, H., Charrier, L., Capes, S., Dorthe, A.M., 1999. Optimization by factorial design of focused microwave assisted extraction of polycyclic aromatic hydrocarbons from marine sediment. Fresen. J. Anal. Chem. 364, 228–237.

Martinez, E., Gros, M., Lacorte, S., Barceló, D., 2004. Simplified procedures for the analysis of polycyclic aromatic hydrocarbons in water, sediments and mussels. J. Chromatogr. A. 1047, 181–188.

Morales-Muñoz, S., Vreuls, R.J.J., Luque de Castro, M.D., 2005. Dynamic ultrasound-assisted extraction of environmental pollutants from marine sediments for comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection. J. Chromatogr. A. 1086, 122–127.

Parera, J., Santos, F.J., Galceran, M.T., 2004. Microwave-assisted extraction versus Soxhlet extraction for the analysis of short-chain chlorinated alkanes in sediments. J. Chromatogr. A. 1046, 19–26.

Pino, V., Ayala, J., Afonso, A., González, V., 2000. Determination of polycyclic aromatic hydrocarbons in marine sediments by high-performance liquid chromatography after microwave-assisted extraction with micellar media. J. Chromatogr. A. 869, 515–522.

Pino, V., Ayala, J.H., Afonso, A.M., González, V., 2001. Cloud-point preconcentration and HPLC determination of polycyclic aromatic hydrocarbons in marine sediments. Fresen. J. Anal. Chem. 371, 526–531.

Rogers, H., 1996. Sources, behavior and fate of organic contaminants during sewage treatment and in sewage sludges. Sci. Total Environ. 185, 3–26.

Santos, J.L., Aparicio, I., Alonso, E., Callejón, M., 2005. Simultaneous determination of pharmaceutically active compounds in wastewater samples by solid phase extraction and high-performance liquid chromatography with diode array and fluorescence detectors. Anal. Chim. Acta 550, 116–122.

Schulte, E.E., Hopkins, B.G., 1996. Estimation of organic matter by weight loss-on-ignition. P. 21-31. In: Magdoff, F.R. et al. (Eds.), Soil organic matter: analysis and interpretation. Soil Science Society of America, Madison, WI, pp. 21–31.

Sun, F., Littlejohn, D., Gibson, M., 1998. Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection. Anal. Chim. Acta 364, 1–11.

United States Environmental Protection Agency. 1997. Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136): definitions and procedures of the determination of the method detection limit, Fed. Reg., vol. 40, pp. 265–267.

Yang, R., Jiang, G., Zhou, Q., Yuan, C., Shi, J., 2005. Occurrence and distribution of organochlorine pesticides (HCH and DDT) in sediments collected from East China Sea. Environ. Int. 31, 799–800.