Conference paper

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Accurate determination of pesticides, hormones and endocrine disruptor compounds in complex environmental samples using matrix dilution and matrix matching with dispersive liquid–liquid microextraction

<https://doi.org/10.1515/pac-2018-0206>

Abstract: Quantitative determination of contaminants in environmental samples is usually hampered by low analyte recovery which results from the complex nature of the sample matrix. This study presents the application of a developed dispersive liquid–liquid microextraction method for the determination of 12 analytes in environmental samples including sea water, fresh water (lake, well and tap water), brackish water and soil samples. Matrix matched standards were used to compensate for the low analyte recovery recorded by the conventional calibration method. The effect of matrix dilution on analyte recovery was also tested. All matrix matched and matrix diluted spiked recoveries were done concurrently with calibration standards prepared in deionized water. Percent recoveries recorded for the analytes according to deionized water calibration standards ranged between 66 and 137 %. Matrix matching and matrix dilution yielded close to 100 % recovery results, but the later lowered the detection limit according to the dilution factor.

Keywords: DLLME; endocrine disruptor; ICGC-7; matrix matching; pesticides.

Introduction

Contamination of natural resources keeps rising due to rapid urbanization and advancement in technology, which directly or indirectly release pollutants into the environment [1]. The application of pesticides to improve the quality and yield of farm products result in contamination of the environment [2]. A greater concern is the presence of pesticide residues in consumable products such as fruits, vegetables and cereals after harvest [3, 4]. Hormones are naturally produced in the human body to regulate various functions such as growth, reproduction, metabolism and tissue formation [5]. Hormones including estradiol and estrone are prescribed to treat or prevent medical conditions such as vaginal atrophy [6], but they could cause several side effects such as nausea, vomiting and abdominal pain [7]. Bisphenol A (BPA) is a synthetic organic compound widely used

Article note: A collection of invited papers based on presentations at the 7th International IUPAC Conference on Green Chemistry (ICGC-7), Moscow, Russia, 2–5 October 2017.

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to make common consumer products such as plastic bottles, sports equipment, medical devices and coatings for food/beverage cans [8]. Recent discovery of BPA's endocrine disruptor property led to its ban in the US by the Food and Drug Administration (FDA) for products meant for infants and young children [9].

Chemical spillage and waste disposal are the main means by which natural resources such as the soil and water bodies become contaminated. Accidental spillage of chemicals such as pesticides during transport and application results in contaminated soil surfaces which require cleaning. Water soluble chemicals which are not cleaned leach down into ground water through soil pores and can also be taken up by plant roots [10]. Marine outfalls are tunnels or pipelines through which municipal and industrial treated wastes are released into the sea. However, wastewater treatment plants do not completely remove pollutants before being released into the ocean [11]. Other wastes are directly disposed into the open ocean, both legally and illegally. Pollutants accumulate in the fat tissues of aquatic organisms and the concentration increases as it moves up the food chain into humans [12]. Fresh water is a general term for water sources besides sea water or brackish water (salinity between fresh water and sea water). Fresh water is classified into still water or lentic systems (ponds, lakes), running water or lotic systems (rivers, streams) and groundwater (wells) [13]. Fresh water is a very important resource for humans (portable drinking water, irrigation and industrial applications) and other living organisms. Water reaching homes through pipelines are considered safe due to the treatment processes (coagulation, sedimentation, filtration, disinfection/chlorination) it undergoes. Contaminants in tap water may be within allowable concentration limits but processes such as boiling can lead to the preconcentration of these contaminants as the water volume reduces significantly [14].

Threat of these contaminants on the endocrine system calls for accurate analytical methods for their determination in environmental samples. Trace analyte determinations require very sensitive instrumentation and sample preparation methods. Chromatographic methods working on the principles of adsorption, partition, ion exchange, exclusion and affinity are useful in separating organic compounds [15]. Gas chromatography mass spectrometry (GC-MS) is a powerful tool for the determination of low molecular weight/volatile organic compounds [16]. The mass selective detector also offers selectivity for a group of compounds and specificity for a particular compound when run in the selected ion monitoring (SIM) mode [17]. In order to get the lower detection limits and eliminate/reduce the matrix effect on analyte(s) signals, different extraction strategies and quantification strategies have been used in literature [18]. Recent development of microextraction methods has cut down the amount of toxic solvents used while significantly increasing the preconcentration factor for trace analyte determinations [19]. Dispersive liquid-liquid microextraction as one of the most popular microextraction method was developed by Rezaee et al. and has been widely used for the determination of both organic and inorganic analytes [20, 21].

The aim of this study was to apply a dispersive liquid-liquid microextraction method for the determination of 12 selected analytes in environmental samples with a proper calibration strategies to get high accurate results. Due to the complicated nature of these samples' matrices, matrix matching and matrix dilution were used to improve analyte recovery and accuracy of quantitative determination.

Materials and methods

Reagents

4-n-Octylphenol, diazinon, estrone, aldrin, bisphenol-A, 4-n-nonylphenol, 17- β -estradiol, cis-chlordane, heptachlor, endosulfan α - β and dieldrin standards were all obtained from Dr. Ehrenstorfer (Augsberg, Germany). A mixed standard stock solution (80 mg L⁻¹) of these analytes was prepared in acetonitrile and appropriate aliquots diluted to prepare aqueous working standard solutions. Methanol, chloroform, potassium iodide and acetonitrile all obtained from Merck (Germany) were used in the extraction processes.

Instrument

Separation, identification and quantitative determination of analytes was achieved with an Agilent 6890 gas chromatography system (HP-5MS column – 30 m; 250 μm ; 0.25 μm) coupled to a mass selective detector. Chromatographic data was obtained in the scan mode and peak area integration of each analyte was done with the most prominent ion (m/z). All injections (1.0 μL) were carried out in the splitless mode and helium gas was kept at a constant flow rate of 1.8 mL min^{-1} . Temperatures of the injection port and detector transfer line were 250 $^{\circ}\text{C}$ and 280 $^{\circ}\text{C}$, respectively. The oven was programmed to increase from an initial temperature of 70 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$, 210 $^{\circ}\text{C}$ and 290 $^{\circ}\text{C}$ at rates of 60, 4.0 and 40 $^{\circ}\text{C min}^{-1}$, respectively. Other apparatus used in this study were vortex (ISOLAB – M1010002), centrifuge (Hettich Zentrifugen – EBA 20) and mechanical shaker (Kermanlab – 51).

Procedure

Optimized extraction conditions of a previous study was adopted in this work [22]. Potassium iodide was added to 8.0 mL sample solutions and vortexed for about 10 s to facilitate dissolution. A mixture of chloroform (200 μL) and methanol (2.0 mL) was injected into the sample solution and hand shaken for 30 s. The solution was then centrifuged for 2.0 min at 3461 g and a sufficient amount withdrawn from the bottom chloroform phase into insert vials for GC-MS determination. For the soil sample, 1.0 g was weighed and washed into a 15 mL centrifuge tube with 10 mL acetonitrile and then agitated for 10 min on a mechanical shaker. Soil and solvent phase separation was quickened by centrifugation at 3461 g for 2.0 min and then filtered to obtain a clean soil extract. Matrix matching calibration standards were prepared by diluting appropriate stock standard solutions with samples of a similar matrix composition after blank determinations showed analytes were not present. Matrix dilution of soil sample extracts was performed to reduce matrix effects and allow application of dispersive liquid–liquid microextraction.

Samples

Surface soil was sampled in the university campus and crushed into small particles using a laboratory scale ceramic mortar and pestle. The crushed soil was then passed through a 100 μm sieve to obtain very fine particles. Prior to each analysis, weighed soil samples were kept in an oven below 70 $^{\circ}\text{C}$ for 1.0 h to ensure complete dryness. In the sampling of water samples, plastic bottles were thoroughly rinsed with the samples before being filled to the brim. The water samples included two sea water (Turkey), two well water (Turkey), three tap water (one from North America and two from Turkey), and three lake water (Turkey) samples. All samples were successively filtered through 125 mm paper and 0.45 μm RC filter to remove particulate materials. The water samples were stored in cabinets under ambient laboratory conditions and analyzed within 1 month of sampling.

Results and discussion

In order to determine the effect of matrix dilution and matching, aqueous standard solutions prepared in ultrapure deionized water were run along each set of matching samples as a comparator. The average peak area of triplicate measurements were used to develop charts to depict the closeness in results. All samples were spiked at three different concentrations (10, 20 and 50 ng mL^{-1}) and the percent recoveries of analytes were determined using one sample as standard relative to the other for matrix matching. Analytical figures of merit for the method used are presented in Table 1 [22].

Table 1: Analytical figures of merit of the analytes under study [22].

Analyte	LOD, ng mL ⁻¹	LOQ, ng mL ⁻¹	%RSD	Linear range, ng mL ⁻¹	R ²
4-n-Octylphenol	0.09	0.31	2.2	0.50–500	0.9995
Diazinon	0.27	0.70	4.5	0.50–100	0.9998
4-n-Nonylphenol	0.16	0.55	3.9	0.50–250	0.9996
Heptachlor	1.3	4.1	4.1	5.0–250	0.9965
Aldrin	1.4	4.7	2.4	5.0–1000	0.9975
Endosulfan α	3.4	11.19	6.1	10–500	0.9970
cis-Chlordane	0.18	0.61	5.4	0.50–250	1.000
Bisphenol A	0.33	1.10	4.4	1.0–500	0.9995
Dieldrin	0.31	1.04	8.0	1.0–250	0.9997
Endosulfan β	2.1	6.85	9.2	5.0–500	0.9992
Estrone	0.24	0.80	4.8	1.0–250	0.9995
17- β -Estradiol	0.30	1.01	7.4	1.0–1000	0.9992

Effect of experimental process on analytes

Sample preparation is a very crucial step in the determination of analytes because it can alter the accuracy, precision and sensitivity of the method being used. Errors recorded in analytical analysis mainly originate from sample preparation processes [16]. The loss of analytes during sample preparation is a major concern and as such, the effect of all processes used in this study was tested. The processes tested were filtration through 125 mm and 0.45 μ m pores, vortexing, mechanical shaking, and centrifugation. A 2.0 ng mL⁻¹ standard solution was taken through 10 s of vortexing, 10 min of mechanical shaking, 2.0 min of centrifugation at 3461 g and successively filtered through 125 mm and 0.45 μ m pore sized filter papers into GC vials. In comparison to this, a 2.0 ng mL⁻¹ standard solution was directly taken into a GC vial for triplicate measurements. The standard solution taken through the processes above recorded slightly higher peak area values. This could be a result of minimal solvent evaporation and a subsequent increase in concentration. The percentage difference between treated and untreated standard solutions (Fig. 1) was less than 4.0 % for all samples, except for bisphenol A which was about 6.4 % based on the mean value. These percentage differences were not statistically significant to affect the overall results of the method.

Tap water

Contaminants are rarely transmitted from water treatment facilities to households but leakages in the distribution lines near contaminated land sites can result in contaminated tap water. A more common mode of

Fig. 1: A chart of average peak area values showing closeness in results for treated and untreated standards, $n = 3$ standard deviation (* and ** represent 2 times scaled down and 2–5 times scaled up results, respectively).

contamination is the leaching of pipe materials over time into the water stream [23]. Bisphenol A, nonylphenol and octylphenol can be found in plastic and polymer compounds used in pipes and other materials. Old pipelines are prone to corrosion and leaching of several contaminants into water. The tap water samples, representing three geographical regions as Europe, Asia and North America were sampled and analyzed under the optimum experimental conditions. None of the 12 analytes were detected in the tap water samples, and they were therefore spiked at the three different concentrations. Percent recoveries obtained ranged between 76 and 93 % for all spiked concentrations, with the lowest recoveries being recorded for 10 ng mL⁻¹ spiked samples. The presence of some interferants could have slightly hindered the extraction of analytes from the tap water samples. Figure 2 is an overlay chromatogram of 50 ng mL⁻¹ aqueous standard and tap water samples spiked at 50 ng mL⁻¹ for diazinon. The signals of the three samples can be seen to be lower than the signal of the standard solution. The tap water sample from North America recorded peak area values that were between the values of the other two samples and was therefore used to prepare matrix matched calibration standards. The percent recoveries calculated using the matched standard ranged between 96–104, 94–106 and 95–106 % for 10, 20 and 50 ng mL⁻¹ spiked samples, respectively, as presented in Table 2.

Fig. 2: An overlay chromatogram of 50 ng mL⁻¹ aqueous standard and tap water samples spiked at 50 ng mL⁻¹ for 4-n-octylphenol (m/z 107).

Table 2: Percent recoveries for tap water samples calculated by matrix matching.

Analyte	Europe			Asia		
	10 ng mL ⁻¹ (%)	20 ng mL ⁻¹ (%)	50 ng mL ⁻¹ (%)	10 ng mL ⁻¹ (%)	20 ng mL ⁻¹ (%)	50 ng mL ⁻¹ (%)
4-n-Octylphenol	98.8 ± 3.2	97.3 ± 1.8	99.1 ± 0.1	100.0 ± 0.9	102.6 ± 0.7	106.3 ± 2.0
Diazinon	99.5 ± 10.9	96.9 ± 0.2	103.0 ± 2.4	104.1 ± 2.9	101.3 ± 1.4	105.9 ± 2.5
4-n-Nonylphenol	99.3 ± 2.3	94.2 ± 1.1	95.9 ± 0.2	98.5 ± 0.7	102.8 ± 4.1	102.0 ± 1.9
Heptachlor	96.4 ± 7.8	99.6 ± 0.5	101.1 ± 5.0	98.5 ± 12.8	103.5 ± 4.1	100.2 ± 3.5
Aldrin	99.7 ± 7.4	100.5 ± 2.4	100.9 ± 5.6	98.0 ± 3.0	103.1 ± 2.8	101.3 ± 1.6
Endosulfan α	^a	96.0 ± 4.6	96.5 ± 1.2	^a	101.8 ± 0.5	98.9 ± 0.1
cis-Chlordane	97.7 ± 2.1	101.9 ± 2.1	96.7 ± 4.6	100.8 ± 9.4	106.0 ± 0.3	99.5 ± 1.2
Bisphenol A	99.3 ± 1.4	100.9 ± 1.9	102.1 ± 1.2	98.8 ± 5.1	99.0 ± 6.4	102.7 ± 0.1
Dieldrin	96.3 ± 0.4	100.2 ± 2.6	99.2 ± 0.2	99.3 ± 3.3	103.1 ± 0.7	100.6 ± 0.2
Endosulfan β	104.1 ± 12.2	103.7 ± 3.6	103.7 ± 2.4	95.9 ± 6.2	103.0 ± 4.6	104.3 ± 1.9
Estrone	97.9 ± 10.9	106.2 ± 0.7	99.6 ± 0.1	101.6 ± 8.0	101.7 ± 0.1	98.5 ± 0.4
17-β-Estradiol	98.3 ± 14.9	101.1 ± 6.9	102.5 ± 1.9	99.2 ± 12.7	106.3 ± 2.5	101.7 ± 0.1

^aBelow quantification limit, n = 3 uncertainty (±), North American sample was used as matrix matched standard, thus, no recovery data given in the table.

Fresh water samples

The type of aquifer of a water body determines the mineral content of the water, where those with high calcium and magnesium content are generally termed hard water which has been reported to hinder the extraction efficiency of analytes [24], thus, low analyte recovery affects accurate analyte quantification. The lake and well water samples were spiked after blank determinations, and their respective percent recoveries were determined with deionized water standards. The percent recoveries calculated for the analytes in the two well water samples ranged between 75 and 116 %, but using one well sample as standard relative to the other gave results between 90 and 103 % as shown in Table 3. Two of the lake water samples are fresh water but the third lake water sample is a brackish water, which has salinity levels between sea water and fresh water. Its high salt content makes it inconvenient for drinking or irrigation but supports only limited aquatic life such as darekh (herring species). Presented in Fig. 3 is an overlay chromatogram of 4-n-nonylphenol for the three lake water samples spiked at 50 ng mL^{-1} . The high salinity content (29.2 mS/cm) of the third lake sample can be seen to have lowered the extraction efficiency of 4-n-nonylphenol and similarly the other analytes. The salinity level determined for the two fresh lake water samples based on electrical conductivity was 6.29 and 3.7 mS/cm. The closeness in results of the fresh lake samples makes them suitable for matrix matching as presented in Table 3.

Table 3: Percent recovery for fresh water samples spiked at 50 ng mL^{-1} obtained by matrix matching.

Analyte	Spiked well water	Spiked lake water
4-n-Octylphenol	$91.6 \pm 2.4 \%$	$97.4 \pm 0.9 \%$
Diazinon	$93.8 \pm 6.2 \%$	$95.3 \pm 4.0 \%$
4-n-Nonylphenol	$92.6 \pm 3.3 \%$	$97.0 \pm 2.2 \%$
Heptachlor	$95.3 \pm 1.7 \%$	$95.1 \pm 2.8 \%$
Aldrin	$92.3 \pm 1.4 \%$	$102.5 \pm 3.9 \%$
Endosulfan α	$103.6 \pm 5.1 \%$	$96.1 \pm 3.5 \%$
cis-Chlordane	$93.2 \pm 2.3 \%$	$96.9 \pm 3.3 \%$
Bisphenol A	$103.6 \pm 0.7 \%$	$97.0 \pm 1.7 \%$
Dieldrin	$90.7 \pm 1.0 \%$	$104.0 \pm 1.1 \%$
Endosulfan β	$93.8 \pm 7.7 \%$	$99.3 \pm 6.4 \%$
Estrone	$96.8 \pm 4.5 \%$	$93.3 \pm 3.1 \%$
17- β -Estradiol	$100.8 \pm 2.4 \%$	$97.4 \pm 0.9 \%$

n = 3 uncertainty ($\pm$).

Fig. 3: An overlay chromatogram of 50 ng mL^{-1} aqueous standard lake water samples spiked at 50 ng mL^{-1} for 4-n-nonylphenol (m/z 107).

Sea water

Salinity and density of matrix are two important properties affecting the mass transfer of analytes from aqueous solution into extraction solvents. Analyte mass transfer is hindered by high density, resulting in low extraction efficiencies. Salinity on the other hand when in the right amount could lower analyte solubility and enhance its migration into extraction solvent, and also facilitate phase separation [25]. Two sea samples were sampled from different regions in İstanbul. The sampling depth was about one meter for both samples. The pH and density determined for sea sample A were 7.39 (at 24 °C) and 1.026 g mL⁻¹, respectively, and 7.45 (at 24 °C) and 1.019 g mL⁻¹, respectively for sea sample B.

The sea samples were spiked to 10, 20 and 50 ng mL⁻¹ after analytes were not detected in blank determinations. Due to the wide applicability of alkylphenols (nonylphenol and octylphenol) and BPA, they are commonly detected in industrial waste sites and sea water [26]. Special attention was given to the blanks of these analytes due to their possible presence in the plastic tubes used. Potassium iodide was not added to the sea samples due to their natural salinity content, but the aqueous standard solutions were extracted with the addition of salt according to the optimized method. Integrated peak area values of both sea water samples were lower than their aqueous standard analogues of similar concentrations. The effect of potassium iodide was therefore investigated by adding 0.50, 1.0 and 2.0 g to both samples spiked at 50 ng mL⁻¹. The extraction efficiencies decreased with increasing salt amount and average percentage differences calculated between saltless extraction, and 0.50, 1.0 and 2.0 g were 14, 25 and 39 %, respectively. The decrease in extraction output for the salt added samples might be due to saturated sea samples hindering analytes movement into the extraction solvent.

The percent recoveries recorded for the analytes were similar at all concentrations, having less than 7 % percent difference. The lowest percent recovery (67 %) was obtained for Endosulfan α as presented in Table 4. Sea sample B, with lower salinity content and density had a relatively higher percent recovery and was thus used as a matching standard to calculate percent recoveries of the sea sample A. The matrix matched percent recoveries obtained were between 90 and 110 % as presented in Table 4. The increased percent recovery signifies an increase in accuracy for quantitative determinations.

Soil

Soil is a typical environmental sample having complex matrix. This complexity is a result of its composition which includes minerals, gases, liquids, organic matter, and several living organisms that help maintain the

Table 4: Percent recovery for sea water samples spiked at 20 ng mL⁻¹ and their matrix matched recoveries.

Analyte	Sea sample A	Sea sample B	Matrix matching
4-n-Octylphenol	84.8 ± 1.5 %	91.8 ± 1.4 %	92.4 ± 1.6 %
Diazinon	87.1 ± 3.7 %	93.0 ± 3.9 %	93.6 ± 4.0 %
4-n-Nonylphenol	85.0 ± 2.3 %	84.9 ± 2.8 %	100.1 ± 2.7 %
Heptachlor	86.7 ± 4.5 %	87.9 ± 6.3 %	98.5 ± 5.1 %
Aldrin	88.3 ± 3.9 %	90.7 ± 9.8 %	97.3 ± 4.3 %
Endosulfan α	67.7 ± 7.5 %	75.0 ± 5.6 %	90.2 ± 10.0 %
cis-Chlordane	88.5 ± 4.8 %	90.9 ± 1.8 %	97.4 ± 5.3 %
Bisphenol A	113.5 ± 10.4 %	102.5 ± 7.2 %	110.8 ± 10.2 %
Dieldrin	87.7 ± 7.3 %	93.2 ± 2.3 %	94.1 ± 7.8 %
Endosulfan β	92.2 ± 4.1 %	97.0 ± 3.4 %	95.0 ± 4.2 %
Estrone	86.1 ± 3.4 %	94.4 ± 4.5 %	91.2 ± 3.6 %
17- β -Estradiol	92.6 ± 6.9 %	98.0 ± 3.2 %	94.5 ± 7.0 %

n = 3 uncertainty (±).

Table 5: Percent recovery for spiked soil sample at 10, 20 and 50 ng mL⁻¹.

Analyte	10 ng mL ⁻¹	20 ng mL ⁻¹	50 ng mL ⁻¹
4-n-Octylphenol	96.0 ± 4.8	100.7 ± 2.6	98.9 ± 2.2 %
Diazinon	98.6 ± 8.7	99.2 ± 3.2	94.3 ± 2.7 %
4-n-Nonylphenol	102.7 ± 5.9	101.8 ± 5.0	97.1 ± 3.4 %
Heptachlor	103.3 ± 7.3	99.5 ± 5.2	95.9 ± 2.9 %
Aldrin	99.6 ± 6.2	94.7 ± 3.5	96.0 ± 7.4 %
Endosulfan α	^a	97.4 ± 6.4	93.7 ± 8.0 %
cis-Chlordane	96.1 ± 5.3	96.9 ± 3.3	98.3 ± 4.2 %
Bisphenol A	94.4 ± 3.7	103.5 ± 1.8	102.7 ± 1.0 %
Dieldrin	101.7 ± 9.4	96.2 ± 2.9	95.7 ± 1.9 %
Endosulfan β	96.1 ± 5.7	102.4 ± 5.6	94.9 ± 4.1 %
Estrone	103.5 ± 2.2	95.6 ± 4.9	97.4 ± 1.4 %
17- β -Estradiol	98.0 ± 4.8	101.4 ± 4.5	96.3 ± 2.6 %

^aBelow quantification limit, n = 3 uncertainty ($\pm$).

balance of the ecosystem [27]. Components of soil can either suppress the determination of an analyte or boost its output, both a misinterpretation of the true amount. Some pesticides and other chemicals having very low solubility in water do not easily leach down the layers of soil into the water table. Nonporous soils also tend to retain chemicals for longer periods. Acetonitrile is an appropriate solvent for most pesticides and was therefore used as extraction solvent to extract 1.0 g soil samples spiked at 10, 20 and 50 ng mL⁻¹ as final concentration in the extraction solvent.

Due to the miscibility of chloroform and acetonitrile, the extraction method could not be directly applied to the soil extract. Appropriate aliquots from extracted soil sample were diluted 4.0, 8.0 and 16 folds in deionized water. The dilution facilitated application of dispersive liquid–liquid microextraction, and at the same time diluted the soil extract for less matrix effects. High dilution factors decrease or eliminate matrix effects but it also pose the risk of diluting analytes below their detection limits. The 8.0 fold dilution presented the best extraction output for all 12 analytes. The 4.0 fold dilution was expected to give the highest extraction output due to its lower dilution factor, but the amount of acetonitrile in the diluted sample turned out to be too high. This resulted in nearly complete loss of chloroform after extraction and the settled phase could not be taken for analysis. Acetonitrile on its own is a good dispersive solvent and its high amount resulted in over dispersion of chloroform. Using the 8.0 folds dilution, spiked samples were compared to their calibration analogues prepared in deionized water. The spiked soil samples recorded very high signals and their percentage recoveries were accordingly higher than 120 %. However, blank determination of the soil sample did not record a signal for all analytes. The amount of acetonitrile in the diluted soil sample clearly increased the extraction efficiency of analytes with respect to aqueous standards. To overcome this effect, 1.0 g of unspiked soil sample was taken through the same extraction procedure performed for spiked samples. Equivalent amounts from the blank soil extracts was then used to prepare calibration standards. This resulted in the matching of both acetonitrile amount (12.5 %) and soil matrix. The percent recoveries recorded with this method therefore was close to 100 % for all analytes as shown in Table 5.

Conclusions

Sensitive and accurate analytical approach was applied to different environmental samples to eliminate the matrix effect. Dispersive liquid–liquid microextraction was used to preconcentrate 12 analytes with endocrine disruptor properties from soil and water samples. Poor analyte recovery confirmed the complexity of the samples' matrices and this was overcome by using matching samples to prepare calibration standards. Dilution of the more complex soil sample resulted in a more effective application of the extraction method and

improved analyte recovery. Matrix dilution resulted in high analyte recovery but it also diluted most analytes out of their detection limits. It was observed that properties such as density, pH and salt content affected the recovery of most analytes in sea samples but the use of matching samples corrected these effects. Matrix matching therefore paves way for high analyte recovery for an accurate quantitative determination of analytes.

Acknowledgements: Authors duly acknowledge Yildiz Technical University for the financial support (Scientific Research Project, 2016-01-02-KAP04).

Conflict of interest statement: All authors declare that there is no conflict of interest with this study.

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