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Determination of household and industrial chemicals, personal care products and hormones in leafy and root vegetables by liquid chromatography-tandem mass spectrometry

Irene Aparicio*, Julia Martín, Concepción Abril, Juan Luis Santos, Esteban Alonso

Department of Analytical Chemistry, Escuela Politécnica Superior, University of Seville, C/ Virgen de África 7, E–41011 Seville, Spain

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ABSTRACT

A multiresidue method has been developed for the determination of emerging pollutants in leafy and root vegetables. Selected compounds were 6 perfluoroalkyl compounds (5 perfluorocarboxylic acids and perfluorooctanesulfonic acid), 3 non-ionic surfactants (nonylphenol and nonylphenolethoxylates), 8 anionic surfactants (4 alkylsulfates and 4 linear alkylbenzene sulfonates), 4 preservatives (parabens), 2 biocides (triclosan and triclocarban), 2 plasticizers (bisphenol A and di-(2-ethylhexyl)phthalate), 6 UV-filters (benzophenones) and 4 hormones. The method is based on ultrasound-assisted extraction, clean-up by dispersive solid-phase extraction (d-SPE) and liquid chromatography-tandem mass spectrometry analysis. Due to the diversity of the physico-chemical properties of the target compounds, and to better evaluate the influence of sample treatment variables in extraction efficiencies, Box-Behnken design was applied to optimize extraction solvent volume, number of extraction cycles and d-SPE sorbent amount. Linearity (R^2) higher than 0.992, accuracy (expressed as relative recoveries) in the range from 81 to 126%, precision (expressed as relative standard deviation) lower than 19% and limits of detection between 0.025 and 12.5 ng g^{-1} dry weight were achieved. The method was applied to leafy vegetables (lettuce, spinach and chard) and root vegetables (carrot, turnip and potato) from a local market. The highest concentrations corresponded to the surfactants reaching levels up to 114 ng g^{-1} (dry weight), in one of the lettuce samples analyzed.

1. Introduction

Vegetables cultivated in soils irrigated with reclaimed wastewater, or amended with sewage sludge from wastewater treatment plants, may uptake organic pollutants through their roots [1–3]. Irrigation with reclaimed wastewater is a widespread disposal option, especially in arid and semi-arid regions, whereas sludge application onto soils allows agronomic benefits due its organic matter content. Wastewater treatments are not specifically designed to remove emerging pollutants, therefore, depending on soil properties, such as organic matter content, and on pollutant properties, such as pK_a and K_{ow}, they can be accumulated into soils to much higher concentrations than in the irrigation water [2]. Once in the soil, plant uptake, root accumulation or translocation within the plant can occur depending on the physico-chemical properties of the pollutants and also on soil characteristics. Linear relationship, between root uptake and chemical hydrophobicity, has been reported for neutral compounds whereas electrical attraction, or repulsion, and ion trap, affect root accumulation of ionizable compounds [2]. Root bioaccumulation follows the order anionic ≥ neutral ≥ cationic whereas leaf bioaccumulation follows the opposite order [4]. Pollutant accumulation in roots and leaves can affect crops and can constitute a potential health risk when affecting edible plants [5,6] especially those with endocrine disrupting properties that can cause reproductive damage, cancer and metabolic disorders [7,8]. Plant uptake studies of emerging pollutants have been mainly focused on pharmaceuticals and personal care products [1,2,5,9–14] and in a lower extent on other emerging pollutants such as plastizicers [15–18], perfluoroalkyl compounds [19,20], disinfection by-products [15], the flame retardant tributylphosphate [15] and the antioxidants BHT and BHA [15]. To evaluate plant uptake and bioaccumulation, sensitive and accurate analytical methods are needed. Nevertheless, for years, analytical methods have been focused on the presence of pesticides and multiresidue methods allowing the determination of hundreds of compounds have been reported [21–23]. Analytical

* Corresponding author.
E-mail address: iaparicio@us.es (I. Aparicio).

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methods for the determination of emerging pollutants in vegetables are scarce and focused on pharmaceuticals and personal care products [24,25] and, in a lower extent, on other pollutants such as alkylphenols [26,27], bisphenol A and hormones [26–28] and perfluorinated compounds [29]. Different extraction methods, such as ultrasound-assisted extraction (UAE) [26], focused ultrasound solid-liquid extraction (FUSLE) [27,29], pressurized solvent extraction (PLE) [25], matrix solid-phase dispersion (MSPD) [28,30] and QuEChERS (quick, easy, cheap, effective, rugged and safe) extraction [25] have been reported for the determination of emerging pollutants in vegetables. After extraction, clean-up by solid-phase extraction (SPE) [29], dispersive solid-phase extraction (d-SPE) [25] and enrichment of the target compounds on a polymeric material using an ion-pair reagent [31] have been applied. Nevertheless, sample treatment is usually based on solid-liquid extraction and clean-up by SPE [32]. Then, analytical determination by liquid chromatography-tandem mass spectrometry (LC–MS/MS) [25,27,29] or by gas chromatography-tandem mass spectrometry (GC–MS/MS) [26,28,30] is carried out.

The aim of this work was to develop a multiresidue analytical method for the determination of a wide group of emerging pollutants (35 compounds from 8 groups) in leafy and root vegetables. Target compounds were 6 perfluoroalkyl compounds, 3 non-ionic surfactants, 8 anionic surfactants (4 alkylsulfates and 4 linear alkylbenzene sulfonates), 4 preservatives, 2 biocides, 2 plasticizers, 6 UV-filters and 4 hormones. Selection was done taking into account their environmental persistence, bioaccumulation, toxicity, relevance in treated wastewater [33–36] and/or sewage sludge and/or endocrine disruption properties [37,38]. Sample treatment is based on affordable and low-cost techniques: UAE and d-SPE clean-up. Analytical determination was carried out by LC–MS/MS. The method was applied to the analysis of the pollutants in three leafy vegetables (lettuce, spinach and chard) and in three root vegetables (carrot, turnip and potatoes).

2. Experimental

2.1. Chemicals and reagents

HPLC-grade acetone, acetonitrile (ACN), ethyl acetate (EtAc), hexane, methanol (MeOH) and water were supplied by Romil (Barcelona, Spain). Analytical grade ammonium acetate (≥98%) was supplied by Panreac (Barcelona, Spain). High purity standards of perfluorobutanoic acid (PFBuA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluroroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), 4-nonylphenol (NP), Igepal® CO-210 technical mixture of nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO), methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP), benzylparaben (BzP), triclocarban (TCB), triclosan (TCS), bisphenol A (BPA), benzophenone-1 (BP-1), benzophene-2 (BP-2), benzophenone-3 (BP-3), benzophenone-6 (BP-6), benzophenone-8 (BP-8), 4-hidroxibenzophenone (4-OH-BP) were supplied from Sigma-Aldrich (Steinheim, Germany). A commercial linear alkylbenzene sulfonate (LAS) mixture containing LAS C10 (12.3%), LAS C11 (32.1%), LAS C12 (30.8%) and LAS C13 (23.4%) was kindly supplied by Petroquímica Española (PETRESA, Spain). Di-(2-ethylhexyl) phthalate (DEHP) was obtained from Riedel-de Haën (Seelze, Germany). Estrone (E1), 17β-estradiol (E2), estriol (E3) and 17α-ethinylestradiol (EE2) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sodium dodecylsulfate (AS-C12), sodium tetradecylsulfate (AS-C14), sodium hexadecylsulfate (AS-C16) and sodium octadecylsulfate (AS-C18) were supplied by Alfa Aesar (Barcelona, Spain). Isotopically labelled compounds used as internal standards (I.S.) were supplied by Sigma-Aldrich (Madrid, Spain) (EtP-d_5, BP-d_{10}, and BPA-d_{16}) and by Cambridge Isotope Laboratories (MA, USA) (PFOA-$^{13}C_4$). Alumina, florisil and silica used as d-SPE sorbents were provided by Sigma-Aldrich (Madrid, Spain). Primary-secondary amine (PSA) and C18 were provided by Scharlab (Barcelona, Spain). Individual stock standard solutions were prepared at 1000 μg mL^{-1} in MeOH and stored at −18 °C. Working solutions were prepared by dilution of the stock standard solutions in MeOH.

2.2. Liquid chromatography-tandem mass spectrometry

Chromatographic conditions were those previously reported [39]. Instrument settings are summarized in Supplementary material Table S1. Chromatographic determination was performed on an Agilent 1200 series HPLC (Agilent, USA) coupled to a 6410 triple quadrupole (QqQ) mass spectrometer (MS) equipped with an electrospray ionization source (ESI). Chromatographic separation was carried out on HALO C_{18} column (50 mm × 4.6 mm i.d., 2.7 μm particle size) (Teknokroma, USA) thermostated at 25 °C by gradient elution with 10 mM ammonium acetate aqueous solution and MeOH at a flow rate of 0.6 mL min^{-1}. Gradient elution was carried out by a linear increase of MeOH proportion from 23% to 70% in 14 min, then to 80% in 19 min and to 100% in 25 min (held for 3 min). Back to initial conditions was carried out by a linear decrease of MeOH proportion from 100% to 23% in 2 min, held for 4 min to stabilization. The injection volume was 10 μL. MS parameters were as follows: capillary voltage, 3000 V; drying gas flow rate; 9 L min^{-1}; drying gas temperature; 350 °C; and nebulizer pressure; 40 psi. Instrument control and data acquisition were carried out with MassHunter software (Agilent, USA).

2.3. Sample collection and treatment

Leafy and root vegetables were purchased from a local market. Fresh vegetables were cut into small pieces, homogenized in a grinder, freeze-dried in a Cryodos-50 lyophilizer (Telstar, Terrasa, Spain), sieved (particle size <100 μm), kept in glass bottles and maintained at −18 °C until analysis. Lyophilized samples (0.2 g dry weight (d.w.)) were transferred into 12 mL glass centrifuge tubes and spiked with the I.S. (EtP-d_5, BP-d_{10}, BPA-d_{16} and PFOA-$^{13}C_4$) (final concentration 125 ng g^{-1} d.w.). Samples were extracted with 3 mL of ACN by sonication for 10 min in an ultrasonic bath. After extraction, tubes were centrifuged for 10 min at 2900 × *g* and the liquid phase was transferred to clean 50 mL polypropylene conical tubes. The extraction procedure was repeated three times. The extracts were combined and subjected to clean-up by d-SPE by adding 0.6 g of C18. The tubes were shaken vigorously for 1 min and centrifuged at 2900 × *g* for 15 min. The organic phase was transferred to a clean tube, evaporated to dryness under a gentle nitrogen stream, reconstituted in 250 μL of MeOH:water solution (1:1, v/v), filtered through a 0.2 μm cellulose syringe filter and transferred into an automatic injector vial for LC–MS/MS analysis.

3. Results and discussion

3.1. Method optimization

Method was optimized with spiked samples (0.2 g d.w.) at 125 ng g^{-1} d.w. Samples were extracted in an ultrasonic bath for 10 min, centrifuged at 2900 × *g* for 10 min and subjected to clean-up by d-SPE. Overall recoveries, involving extraction efficiencies and matrix effect, were applied for method optimization. Blank samples were simultaneously analyzed and their signals were subtracted to spiked sample extract signals.

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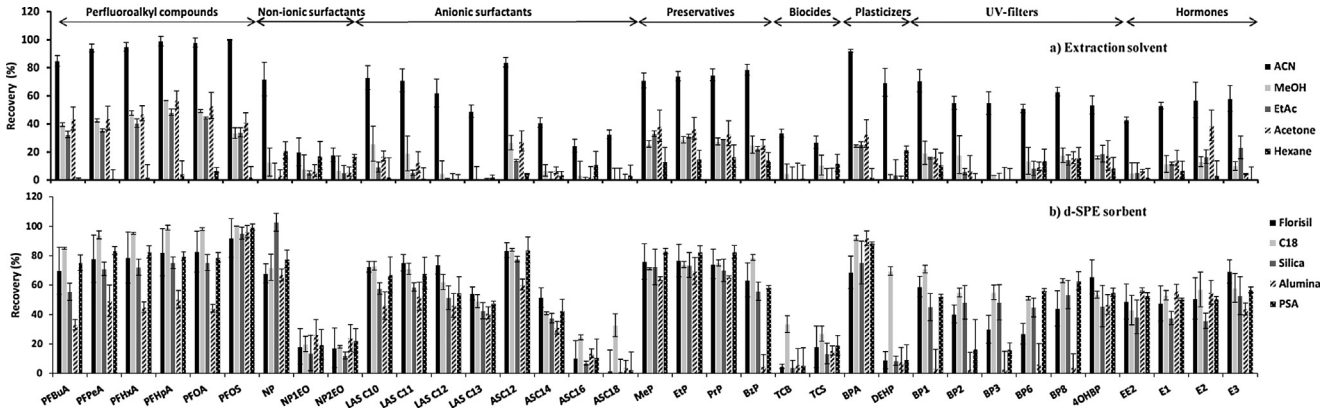

Fig. 1. Optimization of a) extraction solvent and b) d-SPE sorbent (n = 3).

3.1.1. Optimization of the extraction solvent

Extraction solvents tested were ACN, MeOH, EtAc, acetone and hexane. Optimization was carried out in triplicate with 3 mL of the tested solvent. After sample extraction and centrifugation, clean-up with 0.6 g of C18 was applied. Overall recoveries were calculated by comparison of the signal of the spiked vegetable, after subtracting blank sample signals, with that of a standard solution at the same spiking concentration. As can be seen in Fig. 1a, the best overall recoveries were obtained with ACN, so ACN was selected as extraction solvent.

3.1.2. Optimization of the d-SPE sorbent

A reverse phase sorbent (C18), a weak anion exchanger sorbent (PSA) and three normal phase sorbents (florisil, alumina and silica) were evaluated. C18 is commonly used to remove nonpolar and moderately polar compounds such as lipophilic compounds; PSA sorbent is used to remove polar organic acids, polar pigments, sugars and fatty acids; florisil, alumina and silica are suitable to remove polar compounds. As can be seen in Fig. 1b, the best overall recoveries were obtained with C18. Therefore, it was selected as d-SPE sorbent.

3.1.3. Optimization of extraction solvent volume, number of extraction cycles and d-SPE sorbent amount

Box-Behnken design (BBD) was applied to optimize extraction solvent volume, number of extraction cycles and d-SPE sorbent amount. Three levels were evaluated for each variable: ACN volume (3, 4 and 5 mL), number of extraction cycles (1, 2 and 3) and C18 amount (300, 600 and 800 mg). The number of experiments (N) required is defined by the equation: $N = 2\,k(k-1) + C_0$, where k is the number of variables and C_0 is the number of central points. In this study, both k and C_0 values were set at 3 resulting in a total of 15 experiments. The experiments were randomly performed to minimize the effects of uncontrolled variables. BBD matrix is shown in Supplementary material Table S2. The data were evaluated by ANOVA test and by standardized (P = 0.05) Pareto charts. Pareto charts showed that the number of extraction cycles and C18 amount had a higher effect on extraction efficiency than ACN volume. Pareto charts of some of the target compounds can be seen in Figure<-- --> S1 in Supplementary material. To better evaluate the effects of the variables, and their interactions, on overall recoveries, response surfaces were plotted for each group of compounds. First, a desirability value, between 0 (least desirable) and 1 (most desirable), was assigned to the response of each compound in each group. Then, the global desirability function (D) was obtained as a geometric mean of the individual desirability functions [40–42]. In Fig. 2, response surface plots for the global desirability function versus ACN volume and C18 amount (Fig. 2a) and versus ACN volume and the number of extraction cycles (Fig. 2b) are shown for three groups of pollutants. Response surface plots for the other groups, and for the number of extraction cycles versus C18 amount, can be seen in Supplementary material (Fig. S2). To select the best conditions for the 35 target compounds, the global desirability function for ten of the target compounds, at least one from each group, was also plotted (Fig. 3). The highest values of the global desirability functions were obtained for 3 mL of ACN and three extraction cycles whereas C18 amount affected in a different way to each group. For instance, the increase of C18 amount resulted in an increase of the extraction efficiencies of biocides and anionic and non-ionic surfactants whereas the extraction efficiencies of other compounds (preservatives and UV-filters) decreased or were not affected by C18 amount (perfluoroalkyl compounds). The increase of overall recoveries with the increase of C18 amount can be explained by the removal of matrix interfering compounds causing LC–MS/MS signal suppression. The decrease of overall recoveries with the increase of C18 amount can be due to a loss of the target compounds by adsorption onto C18 sorbent. According to the results, 3 mL of ACN, three extraction cycles and 600 mg of C18 were selected for sample extraction and clean-up.

3.2. Method validation

The method was validated in terms of linearity, method detection limits (MDL), method quantification limits (MQL), precision and accuracy. Previously, matrix effect was evaluated in a leafy vegetable (chard) and in a root vegetable (carrot) by comparison of the calibration curve slopes in pure solvent (external calibration curves) and in sample extract (matrix-matched calibration curves). The calibration curves were prepared at eight concentration levels in triplicate in the range from 0.025 to 250 ng g^{-1} d.w. Calibration curves were constructed using analyte-I.S. area ratio versus analyte concentration. Matrix effect (ME), calculated from the slopes (b) of the calibration curves according to Eq. (1) [43], was in the range from 10 to 70%.

$$ME(\%) = \left[1 - \frac{\left({}^{b}matrix - matched\ calibration\ curve\right)}{{}^{b}external\ calibration\ curve}\right] \times 100 \qquad (1)$$

Student's *t*-test, at 95% of confidence, showed statistical differences between slopes, therefore, matrix-matched calibration curves were used for quantitation.

The method was validated for leafy and root vegetables by using spiked chards and carrots. To evaluate the linearity, eight-point matrix-matched calibration curves were prepared in triplicate in the range from method quantitation limit (MQL) to 250 ng g^{-1}. Correlation coefficients were equal or higher than 0.9920 for all

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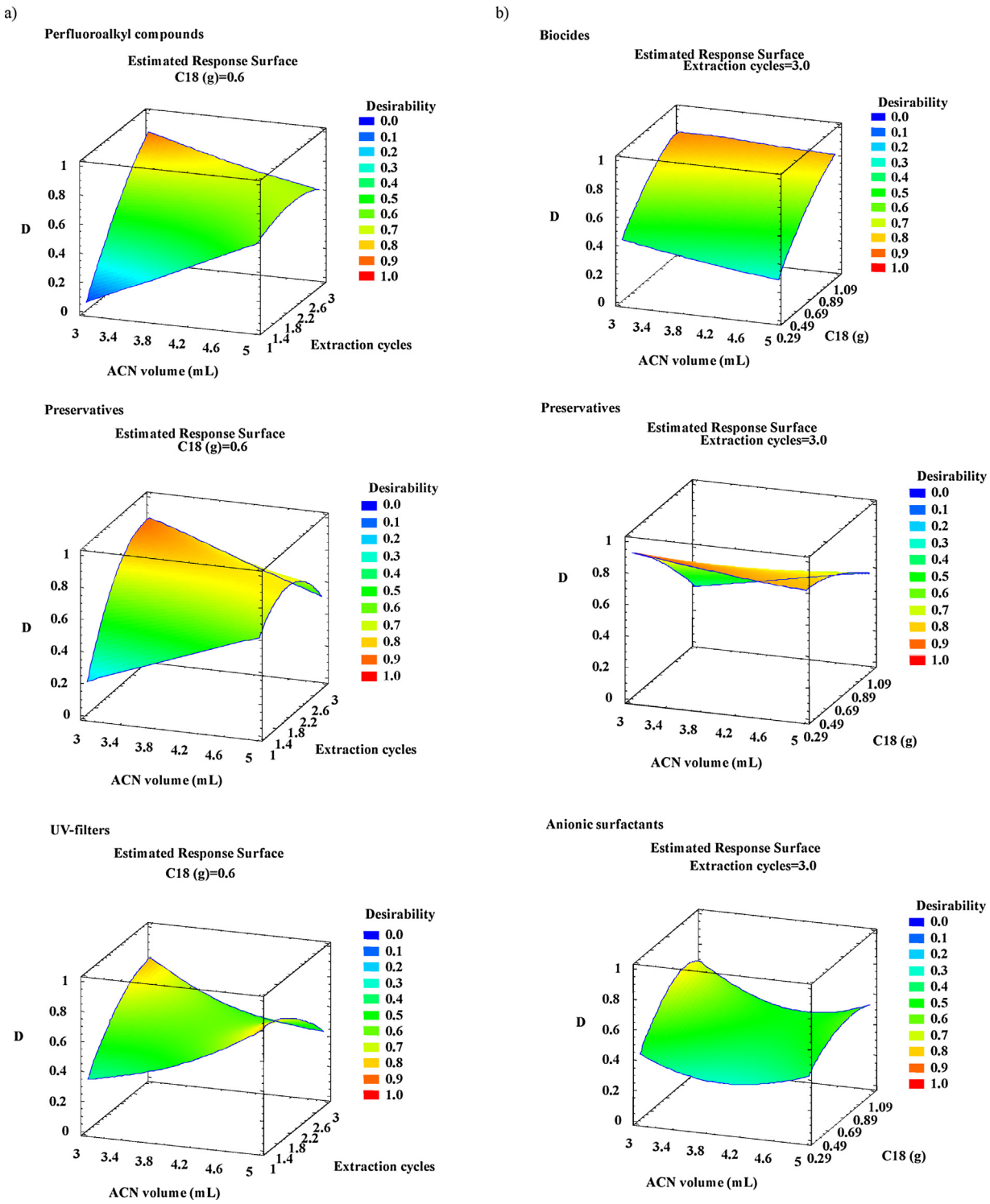

Fig. 2. Response surface plots corresponding to the global desirability function versus a) ACN volume and number of extraction cycles; b) ACN volume and C18 amount.

the compounds in both matrices (Table 1). Method detection limits (MDL) and MQL values were estimated as the concentrations corresponding to signal-to-noise ratios of 3 and 10, respectively, by means of spiked samples at low concentration levels. Blank samples, for which no target compound was detected, were used to evaluate MDL and MQL. MDL values were in the range from 0.025 ng g^{-1} (BP-1 and BP-8) to 2.5 ng g^{-1} (E2) in chards and from 0.025 ng g^{-1} (BP-1) to 12.5 ng g^{-1} (E2) in carrots (Table 1). Accuracy and precision were evaluated from spiked samples at three concentration levels (50, 125 and 250 ng g^{-1}) in triplicate. Accuracy was calculated as the percentage of analyte extracted, quantified using matrix-matched calibration curves, in relation to the spiking level. Accuracy was in the range from 87% and 113% for leafy vegetables and in the range from 81% to 126% for root vegetables (Table 2). Precision, expressed as relative standard deviation (%RSD), was determined from the analysis of spiked samples in triplicate on two

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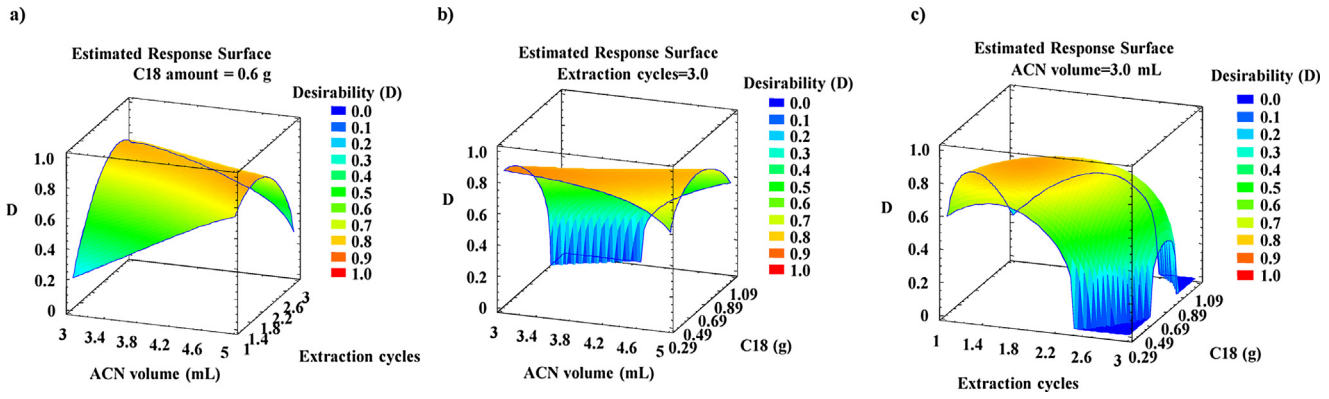

Fig. 3. Response surface plots, corresponding to the global desirability function of PFOS, PrP, BP-3, BPA, E2, TCB, TCS, LAS C13, AS C12, NP2EO, versus a) ACN volume and number of extraction cycles; b) ACN volume and C18 amount; c) number of extraction cycles and C18 amount.

Table 1
Method detection limits (MDL), method quantification limits (MQL) and matrix-matched calibration curve correlation coefficients (R^2).

Group	Compound	Chard			Carrot		
		MDL (ng g^{-1} dm)	MQL (ng g^{-1} dm)	R2	MDL (ng g^{-1} dm)	MQL (ng g^{-1} dm)	R2
Perfluoroalkyl compounds	PFBuA	0.050	0.167	0.9991	0.025	0.083	0.9983
	PFPeA	0.050	0.167	0.9991	0.025	0.083	0.9971
	PFHxA	0.050	0.167	0.9974	0.025	0.083	0.9957
	PFHpA	0.050	0.167	0.9972	0.025	0.083	0.9974
	PFOA	0.050	0.167	0.9995	0.025	0.083	0.9942
	PFOS	0.050	0.167	0.9986	0.025	0.083	0.9982
Non-ionic surfactants	NP	0.025	0.083	0.9991	0.025	0.083	0.9996
	NP1EO	0.025	0.083	0.9990	0.050	0.167	0.9997
	NP2EO	0.025	0.083	0.9992	0.050	0.167	0.9997
Anionic surfactants	LAS C10	0.025	0.083	0.9997	0.025	0.083	0.9990
	LAS C11	0.025	0.083	0.9991	0.025	0.083	0.9994
	LAS C12	0.025	0.083	0.9992	0.025	0.083	0.9991
	LAS C13	0.025	0.083	0.9994	0.025	0.083	0.9982
	AS-C12	0.025	0.083	0.9998	0.025	0.083	0.9990
	AS-C14	0.025	0.083	0.9994	0.025	0.083	1.0000
	AS-C16	0.025	0.083	0.9995	0.050	0.167	0.9994
	AS-C18	0.050	0.167	0.9996	0.050	0.167	0.9979
Preservatives	MeP	0.050	0.167	0.9991	0.025	0.083	0.9993
	EtP	0.050	0.167	0.9997	0.050	0.167	0.9994
	PrP	0.025	0.083	0.9997	0.050	0.167	0.9990
	BzP	0.025	0.083	0.9995	0.025	0.083	0.9964
Biocides	TCB	0.050	0.167	0.9992	0.025	0.083	0.9991
	TCS	0.500	1.667	0.9997	0.050	0.167	0.9990
Plasticizers	BPA	0.025	0.083	0.9995	0.050	0.167	0.9995
	DEHP	0.025	0.083	0.9985	0.025	0.083	0.9970
UV-filters	BP-1	2.500	8.333	0.9991	12.50	41.67	0.9920
	BP-2	0.025	0.083	0.9994	0.050	0.167	0.9991
	BP-3	0.025	0.083	0.9999	0.025	0.083	0.9986
	BP-6	0.025	0.083	0.9992	0.050	0.167	0.9991
	BP-8	2.500	8.333	0.9991	0.025	0.083	0.9981
	4-OH-BP	0.025	0.083	0.9991	2.500	8.333	0.9946
Hormones	EE2	0.025	0.083	0.9991	0.050	0.167	0.9997
	E1	2.500	8.333	0.9992	0.025	0.083	0.9993
	E2	0.500	1.667	0.9972	12.50	41.67	0.9995
	E3	0.050	0.167	0.9994	2.500	8.333	0.9987

different days. RSD values were below 21% for both types of matrices at the three spiked concentration levels. Accuracy and precision were similar for both types of vegetables.

3.3. Method application

The method was applied to the determination of the target compounds in three types of leafy (lettuce, spinach and chard) and in root vegetables (carrot, turnip and potato). Four samples of each type of vegetable were purchased from local markets and analyzed. In Supplementary material, chromatograms of a chard and a potato sample (Figs. S3 and S4, respectively) and concentrations found in samples (Table S3) are shown. PFBuA, LAS and TCB were detected in all the analyzed samples at mean concentration levels in the ranges 1.4–2.2 ng g^{-1}, 8.4–45.6 ng g^{-1} and 1.4–6.0 ng g^{-1}, respectively, in leafy vegetables, and in the ranges 2.0–6.8 ng g^{-1}, 1.3–15.8 ng g^{-1} and 0.3 ng g^{-1}, respectively, in root vegetables. BzP, UV-filters (except BP-2 and BP-3) and E3 were not detected. The

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Table 2
Accuracy (%) and precision, expressed as relative standard deviation (RSD%), for chard and carrot matrices at four spiking levels.

Compoud	Chard								Carrot							
	0.5 ng g^{-1}		50 ng g^{-1}		125 ng g^{-1}		250 ng g^{-1}		0.5 ng g^{-1}		50 ng g^{-1}		125 ng g^{-1}		250 ng g^{-1}	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
PFBuA	87	10	88	8	89	2	100	2	99	12	98	7	94	6	101	11
PFPeA	101	12	102	8	101	2	99	8	103	5	96	4	96	1	107	1
PFHxA	95	8	99	4	92	5	102	6	89	6	93	6	94	1	108	1
PFHpA	92	6	98	1	92	3	102	7	93	4	98	7	94	1	107	1
PFOA	97	10	98	9	97	4	101	6	97	8	92	9	95	3	107	1
PFOS	95	9	102	1	101	8	99	7	99	11	92	6	98	18	108	1
NP	98	8	97	8	97	2	101	7	103	8	93	5	106	6	114	4
NP1EO	100	6	113	2	103	7	99	11	97	11	102	9	98	8	103	18
NP2EO	95	8	93	3	101	11	100	6	92	12	88	13	101	16	98	8
LAS C10	101	5	95	4	103	7	99	10	96	11	99	10	126	3	100	1
LAS C11	98	13	103	11	100	8	100	8	104	5	113	2	98	1	88	3
LAS C12	97	6	103	2	100	5	100	8	96	4	104	1	92	1	88	2
LAS C13	99	6	97	2	100	1	100	4	103	3	114	4	90	1	96	1
AS-C12	103	5	98	4	100	3	100	7	98	13	125	15	125	21	100	2
AS-C14	98	8	102	2	100	6	100	6	95	8	116	6	90	2	100	12
AS-C16	98	3	98	7	100	1	100	10	103	5	90	6	111	2	100	15
AS-C18	97	7	95	6	99	4	100	7	98	6	92	4	120	2	75	14
MeP	99	4	95	5	101	6	98	2	102	4	126	3	107	17	98	5
EtP	103	10	108	3	99	3	104	6	89	5	81	6	109	4	102	1
PrP	97	9	105	4	101	6	98	1	97	12	94	8	101	19	100	5
BzP	93	8	89	6	100	5	100	9	92	8	90	7	96	2	101	7
TCB	96	9	88	5	102	5	100	6	89	4	92	2	96	1	84	5
TCS	99[a]	5[a]	105	2	98	1	100	3	87	3	93	1	99	2	89	5
BPA	97	6	102	8	99	2	100	7	97	8	96	10	94	9	98	1
DEHP	102	8	98	4	100	3	100	11	93	7	90	5	102	10	101	1
BP-1	96[a]	7[a]	106	2	101	6	99	1	–	–	112	1	99	1	97	2
BP-2	95	9	97	8	100	5	100	8	98	13	117	12	91	6	105	5
BP-3	101	6	103	2	100	3	100	4	92	12	94	13	97	11	100	3
BP-6	96	8	90	5	100	5	100	6	89	6	92	5	96	3	102	4
BP-8	108[a]	9[a]	113	4	100	8	100	9	92	6	90	4	93	3	115	4
4-OH-BP	92	11	87	3	99	10	101	4	103[a]	11[a]	121	8	99	6	100	5
EE2	92	5	101	3	98	13	100	17	97	8	98	7	92	4	191	1
E1	103[a]	6[a]	107	5	97	19	101	14	92	12	95	14	95	6	100	8
E2	99	4	104	1	101	3	99	7	–	–	99	4	98	2	104	8
E3	95	3	92	4	102	9	100	8	107[a]	10[a]	115	9	111	3	109	1

[a] Data for 10 ng g^{-1} dm.

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highest concentrations in leafy vegetables corresponded to LAS (mean values in the range from 8.4 ng g^{-1} to 45.6 ng g^{-1}) whereas in root vegetables the highest concentrations corresponded to NP (mean values in the range from 7.9 ng g^{-1} to 22.9 ng g^{-1}). Different occurrence pattern was observed between leafy vegetables and root vegetables for some compounds such as PFPeA, NP, NP1EO, AS homologues and DEHP, that were not detected in leafy vegetables but were detected in 92–100% of the root vegetables analysed, and for BP-2, that was not detected in root vegetables but was detected in the 100% of leafy vegetables at concentrations in the range from 0.17 to 0.19 ng g^{-1}. Compounds detected in both types of vegetables (LAS homologues and BP-3) were found at higher concentrations in leafy vegetables than in root vegetables. These results are consistent with the scarce data about concentration of emerging pollutants in vegetables from local markets. For instance, BPA has been detected in carrots from local markets by Lu et al. [26] (2.0 ng g^{-1}); Mijangos et al. [27] (9.1 ng g^{-1}) and by Albero et al. [28] (5.1–16.3 ng g^{-1}) and in lettuce by Mijangos et al. [27] (10.9 ng g^{-1}) and Albero et al. [28] (3.4–8.0 ng g^{-1}). Albero et al. [28] detected also the presence of EE2 in onion (1.5–3.4 ng g^{-1}) but not in carrot, tomato or lettuce whereas Lu et al. [26] reported concentrations of 1.9 ng g^{-1}, 1.36 ng g^{-1} and 2.31 ng g^{-1} of E2 in lettuce, potato and citrus, respectively. The World Health Organization recommends a daily intake of five servings of fruit and/or vegetables corresponding to 400–500 g d^{-1} [44]. Assuming a 300 g d^{-1} intake of vegetables, the worse-case scenario for daily intake of PFBuA, LAS, TCB would be 0.7, 14, 1.8 μg d^{-1}, respectively, from ingestion of leafy vegetables, and 2.0, 4.7 and 0.09 μg d^{-1}, respectively, from ingestion of root vegetables. A further research, with a higher number of samples, is needed to better estimate the potential human exposure to emerging compounds. Nevertheless, due to the lack-of-agreement associated with health effects-thresholds of the target emerging compounds, risk assessment to human health cannot be properly evaluated yet [45].

4. Conclusions

A sensitive and accurate analytical method has been developed for the determination of household and industrial chemicals (perfluoroalkyl compounds, non-ionic surfactants, anionic surfactants and plasticizers), personal care products (biocides and UV-filters) and hormones in leafy and root vegetables. The method is, to the best of our knowledge, the first analytical method for multiclass determination of so wide group of health concern pollutants in vegetables. Sample treatment is based on affordable, easy to perform, and low-cost extraction (UAE) and clean-up (d-SPE) techniques. Analytical determination is carried out by LC–MS/MS avoiding derivatization step required for GC–MS/MS analysis. The method was successfully validated for leafy and root vegetables. MDLs were in the range from 0.025 to 0.050 ng g^{-1} for 88% of the target compounds, accuracy was in the range 81–126% and precision was lower than 19%. The method was satisfactorily applied to lettuce, spinach, chard, carrot, turnip and potato from local markets. Different occurrence pattern was observed between leafy vegetables and root vegetables. Some compounds were detected in both types of vegetables whereas others were detected just in leafy or root vegetables. The proposed method can constitute a useful tool to evaluate emerging pollutant uptake, their bioaccumulation and can be used to estimate daily intake of pollutants by consumption of vegetables.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2017.12.011

References

[1] E.L. Miller, S.L. Nason, K.G. Karthikeyan, J.A. Pedersen, Root uptake of pharmaceuticals and personal care product ingredients, Environ. Sci. Technol. 50 (2016) 525–541.
[2] X. Wu, L.K. Dodgen, J.L. Conkle, J. Gan, Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: a review, Sci. Total Environ. 536 (2015) 655–666.
[3] C. Hurtado, C. Domínguez, L. Pérez-Babace, N. Cañameras, J. Comas, J.M. Bayona, Estimate of uptake and translocation of emerging organic contaminants from irrigation water concentration in lettuce grown under controlled conditions, J. Hazard. Mater. 305 (2016) 139–148.
[4] L.K. Dodgen, A. Ueda, X. Wu, D.R. Parker, J. Gan, Effect of transpiration on plant accumulation and translocation of PPCP/EDCs, Environ. Pollut. 198 (2015) 144–153.
[5] T. Malchi, Y. Maor, G. Tadmor, M. Shenker, B. Chefetz, Irrigation of root vegetables with treated wastewater: evaluating uptake of pharmaceuticals and the associated human health risks, Environ. Sci. Technol. 48 (2014) 9325–9333.
[6] R.S. Prosser, P.K. Sibley, Human health risk assessment of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, and wastewater irrigation, Environ. Int. 75 (2015) 223–233.
[7] E.R. Kabir, M.S. Rahman, I. Rahman, A review on endocrine disruptors and their possible impacts on human health environ, Toxicol. Pharmacol. 40 (2015) 241–258.
[8] M. Giulivo, M. Lopez de Alda, E. Capri, D. Barceló, Human exposure to endocrine disrupting compounds: their role in reproductive systems, metabolic syndrome and breast cancer. A review, Environ. Res. 151 (2016) 251–254.
[9] M.B.M. Ahmed, A.U. Rajapaksha, J.E. Lim, N.T. Vu, I.S. Kim, H.M. Kang, S.S. Lee, Y.S. Ok, Distribution and accumulative pattern of tetracyclines and sulphonamides in edible vegetables of cucumber, tomato, and lettuce, J. Agric. Food Chem. 63 (2015) 398–405.
[10] D. Azanu, C. Mortey, G. Darko, J.J. Weisser, B. Styrishave, R.C. Abaidoo, Uptake of antibiotics from irrigation water by plants, Chemosphere 157 (2016) 107–114.
[11] H. Dolliver, K. Kumar, S. Gupta, Sulfamethazine uptake by plants from manure-amended soil, J. Environ. Qual. 36 (2007) 1224–1230.
[12] P.A. Herklotz, P. Gurung, B.V. Heuvel, C.A. Kinney, Uptake of human pharmaceuticals by plants grown under hydroponic conditions, Chemosphere 78 (2010) 1416–1421.
[13] L. Sabourin, P. Duenk, S. Bonte-Gelok, M. Payne, D.R. Lapen, E. Topp, Uptake of pharmaceuticals, hormones and parabens into vegetables grown in soil fertilized with municipal biosolids, Sci. Total Environ. 431 (2012) 233–236.
[14] D. Shargil, Z. Gerstl, P. Fine, I. Nitsan, D. Kurtzman, Impact of biosolids and wastewater effluent application to agricultural land on steroidal hormone content in lettuce plants, Sci. Total Environ. 505 (2015) 357–366.
[15] D. Calderón-Preciado, V. Matamoros, J.M. Bayona, Occurrence and potential crop uptake of emerging contaminants and related compounds in an agricultural irrigation network, Sci. Total Environ. 412–413 (2011) 14–19.
[16] L.K. Dodgen, J. Li, D.R. Parker, J.J. Gan, Uptake and accumulation of four PPCP/EDCs in two leafy vegetables, Environ. Pollut. 182 (2013) 150–156.
[17] C. Hurtado, N. Cañameras, C. Domínguez, G.W. Price, J. Comas, J.M. Bayona, Effect of soil biochar concentration on the mitigation of emerging organic contaminant uptake in lettuce, J. Hazard. Mater. 323 (2017) 386–393.
[18] T. Eggen, E.S. Heimstad, A.O. Stuanes, H.R. Norli, Uptake and translocation of organophosphates and other emerging contaminants in food and forage crops, Environ. Sci. Pollut. Res. 20 (2013) 4520–4531.
[19] A.C. Blaine, C.D. Rich, E.M. Sedlacko, L.S. Hundal, K. Kumar, C. Lau, M.A. Mills, K.M. Harris, C.P. Higgins, Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils, Environ. Sci. Technol. 48 (2014) 7858–7865.
[20] E. Bizkarguenaga, I. Zabaleta, L. Mijangos, A. Iparraguirre, L.A. Fernández, A. Prieto, O. Zuloaga, Uptake of perfluorooctanoic acid, perfluorooctane sulfonate and perfluorooctane sulphonamide by carrot and lettuce from compost amended soil, Sci. Total Environ. 571 (2016) 444–451.
[21] V. Hanot, S. Goscinny, M. Deridder, A simple multi-residue method for the determination of pesticides in fruits and vegetables using a methanolic extraction and ultra-high-performance liquid chromatography-tandem mass spectrometry: optimization and extension of scope, J. Chromatogr. A 1384 (2015) 53–66.
[22] Ł. Rajski, M.M. Goímez-Ramos, A.R. Fernaíndez-Alba, Large pesticide multiresidue screening method by liquid chromatography-orbitrap mass spectrometry in full scan mode applied to fruit and vegetables, J. Chromatogr. A 1360 (2014) 119–127.
[23] A. Masiá, M.M. Suarez-Varela, A. Llopis-Gonzalez, Y. Picó, Determination of pesticides and veterinary drug residues in food by liquid

chromatography-mass spectrometry:a review, Anal. Chim. Acta 936 (2016) 40–46.
[24] X. Wu, J.L. Conkle, J. Gan, Multi-residue determination of pharmaceutical and personal care products in vegetables, J. Chromatogr. A 1254 (2012) 78–86.
[25] Y. Chuang, Y. Zhang, W. Zhang, S.A. Boyd, H. Li, Comparison of accelerated solvent extraction and quick, easy, cheap, effective, rugged and safe method for extraction and determination of pharmaceuticals in vegetables, J. Chromatogr. A 1404 (2015) 1–9.
[26] J. Lu, J. Wu, P.J. Stoffella, P.C. Wilson, Isotope dilution-gas chromatography/mass spectrometry method for the analysis of alkylphenols, bisphenol A, and estrogens in food crops, J. Chromatogr. A 1258 (2012) 128–135.
[27] L. Mijangos, E. Bizkarguenaga, A. Prieto, L.A. Fernández, O. Zuloaga, Simultaneous determination of a variety of endocrine disrupting compounds in carrot, lettuce and amended soil by means of focused ultrasonic solid–liquid extraction and dispersive solid-phase extraction as simplified clean-up strategy, J. Chromatogr. A 1389 (2015) 8–18.
[28] B. Albero, C. Sánchez-Brunete, E. Miguel, J.L. Tadeo, Application of matrix solid-phase dispersion followed by GC–MS/MS to the analysis of emerging contaminants in vegetables, Food Chem. 217 (2017) 660–667.
[29] I. Zabaleta, E. Bizkarguenaga, A. Iparragirre, P. Navarro, A. Prieto, L.A. Fernández, O. Zuloaga, Focused ultrasound solid-liquid extraction for the determination of perfluorinated compounds in fish, vegetables and amended soil, J. Chromatogr. A 1331 (2014) 27–37.
[30] E. Bizkarguenaga, I. Zabaleta, A. Iparraguirre, J. Aguirre, L.A. Fernández, U. Berger, A. Prieto, O. Zuloaga, Enrichment of perfluorinated alkyl substances on polyethersulfone using 1-methylpyperidine as ion-pair reagent for the clean-up of carrot and amended soil extracts, Talanta 143 (2015) 263–270.
[31] A. Iparraguirre, R. Rodil, J.B. Quintana, E. Bizkarguenaga, A. Prieto, O. Zuloaga, R. Cela, L.A. Fernández, Matrix solid-phase dispersion of polybrominated diphenyl ethers and their hydroxylated and methoxylated analogues in lettuce, carrot and soil, J. Chromatogr. A 1360 (2014) 57–65.
[32] V. Matamoros, D. Calderón-Preciado, C. Domínguez, J.M. Bayona, Analytical procedures for the determination of emerging organic contaminants in plant material: a review, Anal. Chim. Acta 722 (2012) 8–20.
[33] D. Camacho-Muñoz, J. Martín, J.L. Santos, I. Aparicio, E. Alonso, Occurrence of surfactants in wastewater: hourly and seasonal variations in urban and industrial wastewaters from Seville (Southern Spain), Sci. Total Environ. 468–469 (2014) 977–984.
[34] J.L. Wilkinson, J. Swinden, P.S. Hooda, J. Barker, S. Barton, Markers of anthropogenic contamination: a validated method for quantification of pharmaceuticals, illicit drug metabolites, perfluorinated compounds, and plasticisers in sewage treatment effluent and rain runoff, Chemosphere 19 (2016) 638–646.
[35] D. Montes-Grajales, M. Fennix-Agudelo, W. Miranda-Castro, Occurrence of personal care products as emerging chemicals of concern in water resources: a review, Sci. Total Environ. 595 (2017) 601–614.
[36] S.D. Richardson, S.Y. Kimura, Emerging environmental contaminants: challenges facing our next generation and potential engineering solutions, Environ. Technol. Innov. 8 (2017) 40–56.
[37] B.O. Clarke, S.R. Smith, Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, Environ. Int. 37 (2011) 226–247.
[38] M. Mezcua, M.A. Martínez-Uroz, M.M. Gómez-Ramos, M.J. Gómez, J.M. Navas, A.R. Fernández-Alba, Analysis of synthetic endocrine-disrupting chemicals in food: a review, Talanta 100 (2012) 90–106.
[39] J. Martín, A. Zafra-Gómez, F. Hidalgo, A.J. Ibáñez-Yuste, E. Alonso, J.L. Vilchez, Multi-residue analysis of 36 priority and emerging pollutants in marine echinoderms (Holothuria tubulosa) and marine sediments by solid-liquid extraction followed by dispersive solid phase extraction and liquid chromatography–tandem mass spectrometry analysis, Talanta 166 (2017) 336–348.
[40] C. Stalikas, Y. Fiamegos, V. Sakkas, T. Albanis, Developments on chemometric approaches to optimize and evaluate microextraction, J. Chromatogr. A 1216 (2009) 175–189.
[41] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandão, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Box-Behnken design: an alternative for the optimization of analytical methods, Anal. Chim. Acta 597 (2007) 179–186.
[42] A. Luque-Muñoz, J.L. Vílchez, A. Zafra-Gómez, Multiclass method for the determination of pharmaceuticals and personal care products in compost from sewage sludge using ultrasound and salt-assisted liquid-liquid extraction followed by ultrahigh performance liquid chromatography-tandem mass spectrometry analysis, J. Chromatogr. A 1507 (2017) 72–83.
[43] M.J. García-Galán, M. Petrovic, S. Rodríguez-Mozaz, D. Barceló, Multiresidue trace analysis of pharmaceuticals, their human metabolites and transformation products by fully automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry, Talanta 158 (2016) 330.
[44] World Health Organization (WHO), Effectiveness of Interventions and Programs Promoting Fruit and Vegetable Intake, 2005, Accessed 28 September, 2017 http://www.who.int/dietphysicalactivity/publications/f&v_promotion_effectiveness.pdf.
[45] J. Lu, J. Wu, P.J. Stoffella, P.C. Wilson, Uptake and distribution of bisphenol A and nonylphenol in vegetable crops irrigated with reclaimed water, J. Hazard. Mat. 283 (2015) 865–870.

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