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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

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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

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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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