Journal of Chromatography A, 1352 (2014) 29–37

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Analysis of endocrine disrupters and related compounds in sediments and sewage sludge using on-line turbulent flow chromatography–liquid chromatography–tandem mass spectrometry☆

Marina Gorga[a], Sara Insa[b], Mira Petrovic[b,c,*], Damià Barceló[a,b]

[a] Water and Soil Quality Research Group, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
[b] Catalan Institute for Water Research (ICRA), Girona, Spain
[c] Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain

ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 10 April 2014
Accepted 13 May 2014
Available online 17 May 2014

Keywords:
Endocrine disruptors
Online turbulent flow chromatography
Sediment and sewage sludge
Matrix effects

ABSTRACT

A novel fully automated method based on dual column switching using turbulent flow chromatography followed by liquid chromatography coupled to tandem mass spectrometry (TFC–LC–MS/MS) was applied for the determination of endocrine disruptors (EDCs) and related compounds in sediment and sewage sludge samples. This method allows the unequivocal identification and quantification of the most relevant environmental EDCs such as natural and synthetic estrogens and their conjugates, antimicrobials, parabens, bisphenol A (BPA), alkylphenolic compounds, benzotriazoles, and organophosphorus flame retardants, minimizing time of analysis and alleviating matrix effects. Applying this technique, after the extraction of the target compounds by pressurized liquid extraction (PLE), sediment and sewage sludge extracts were directly injected to the chromatographic system and the analytes were concentrated into the clean-up loading column. Using six-port switching system, the analytes were transferred to the analytical column for subsequent detection by MS–MS (QqQ). In order to optimize this multiplexing system, a comparative study employing six types of TurboFlow™ columns, with different chemical modifications, was performed to achieve the maximum retention of analytes and best elimination of matrix components. Using the optimized protocol low limits of quantification (LOQs) were obtained ranging from 0.0083 to 1.6 ng/g for sediment samples and from 0.10 to 125 ng/g for sewage sludge samples (except for alkylphenol monoethoxylate). The method was used to evaluate the presence and fate of target EDCs in the Ebro River which is the most important river in Spain with intensive agricultural and industrial activities in the basin that contribute to deteriorating soil and water quality.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The endocrine disrupting compounds (EDCs) interfere with the endocrine system and disrupt the physiological function of hormones [1]. These compounds can act in a low dose in a variety of organisms producing disorders such as sexual development problems, feminizing of males or masculine effects on females and infertility [2].

Some EDCs, with different structures and properties, are found in a high variety of products commonly used in the daily life (detergents, personal care products such as cosmetics, pharmaceuticals and in different industrial formulations). Consequently, they are detected in the aquatic environment, being wastewater treatment plants (WWTPs) effluents and run-offs from farmlands the main sources for their introduction into the aquatic environment [3–7]. Because the potential effects in the environment may occur at very low concentrations, their analysis needs to reach very low detection limits, especially difficult to achieve in complex matrices such as in solid environmental samples (sediments and sewage sludge).

In the literature, there are several analytical methodologies already available for the determination of EDCs in sediments and

☆ Presented at the XIII Scientific Meeting of the Spanish Society of Chromatography and Related Techniques (SECyTA2013), 8–11 October 2013, Puerto de la Cruz, Tenerife, Canary Islands, Spain.

* Corresponding author at: Catalan Institute for Water Research (ICRA), Emili Grahit, 101, 17003 Girona, Spain. Tel.: +34 972183380; fax: +34 972183248.
E-mail addresses: mglqam@cid.csic.es (M. Gorga), sinsa@icra.cat (S. Insa), mpetrovic@icra.cat (M. Petrovic), dbcqam@cid.csic.es (D. Barceló).

http://dx.doi.org/10.1016/j.chroma.2014.05.028
0021-9673/© 2014 Elsevier B.V. All rights reserved.

sewage sludge samples with acceptable limits of detection (LODs) [8–13]. Most commonly used procedures applied for the extraction of the target compounds in solid samples are based on pressurized liquid extraction (PLE), ultrasonic extraction (USE) or liquid extraction (LLE). Clean up of the samples is generally performed using classical approaches such as solid phase extraction (SPE) or using semi-automatic techniques such as a gel permeation chromatography (GPC). Another methodology reported in the literature is on QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) technique [14]. However, majority of previously reported protocols involve time and labour consuming multi-step clean-up that often constitute the bottleneck of the analytical method. Nowadays, it is recognized that the growing number of samples to be analyzed in the laboratories carrying out monitoring studies requires employment of high-throughput and automated techniques. Consequently, different on-line and automated techniques have been developed during the last years, coupling sample preparation units with detection systems [15].

In this work 30 EDCs and related compounds (suspect EDCs), belonging to different groups of chemical substances (10 estrogens, natural and synthetic, in free and conjugated form, 8 alkylphenolic compounds and their metabolites, 4 preservatives, 2 antimicrobials, 3 organophosphorous flame retardants, 2 anticorrosives and bisphenol A (BPA)) and the chemical biomarker caffeine were determined in sediment and sewage sludge samples.

For these purposes, an on-line technology based on turbulent flow chromatography – TFC (TurboFlow^{TM}), a robust, fast and high-throughput method, was applied [16]. This online automated system uses the TFC column to separate the analytes of interest from their complex matrices, combining principles of diffusion, chemistry and size exclusion. Chromatographic separation is subsequently achieved in the second analytical column. Therefore, an online clean up is achieved, minimizing the sample preparation and reducing the ion suppression due to higher specificity. This dual column technology has been previously optimized and applied for the determination of BPA, pesticides, perfluoroalkyls, drugs substances and other environmental contaminants in biological and food samples [17–21], but there are no methods developed for environmental matrices such as sediment and sewage sludge. For all of these, the objective was to optimize TFC parameters and also the LC separation which included the selection of TurboFlow^{TM} purification column and the switching times as defined by the matrix elution profile, breakthrough time of analytes and analyte elution profile.

2. Experimental

2.1. Materials and standards

Pure standard of the target estrogens estradiol (E2), estrone (E1), estriol (E3), ethinylestradiol (EE2), diethylstilbestrol (DES), estriol 3-sulfate (E3-3S), estradiol 17-glucuronide (E2-17G), estrone 3-glucuronide (E1-3G), estriol 16-glucuronide (E3-16G), triclosan (TCS), methylparaben (MeP), ethylparaben (EtP), Propilparaben (PrP), benzylparaben (BeP), d_{16} (BPA)-d_{16}, 4-tert-octylphenol (OP), OP-d_2, 4-tert-octylphenol-3,5 d_2-diethoxylate (OP_2EO-d_2), triphenyl-d_{15}-phosphate, Caff, Caff-C_{13} were purchased from Sigma–Aldrich (St Louis, MO, USA). Triclorocaraban (TCC), benzylparaben (BeP), BPA, tolyltriazole (TT), tris(butoxyethyl) phosphate (TBEP), tris(2-chloroethyhl) phosphate (TCEP) were supplied by Aldrich (Milwaukee, WI, USA). Nonylphenol (NP), NP-d8, octylphenol mono- and dicarboxylate (OP_1EC and NP_1EC), octylphenol mono- and diethoxylate (OP_1EO and NP_1EO), octyl- and nonylphenol diethoxylate (OP_2EO and NP_2EO), NP1EO d_2 were purchased from Dr. Ehrenstorfer (Germany). E2-d_5, E1-d_4, EE2-d_4, E1-3S-d_4, were also obtained from CDN Isotopes (Pointe-Claire, Quebec, Canada). 1H-benzotriazole (BT), tris(chloroisopropyl) phosphate (TCPP), ethyl hydroxybenzoate C_{13}, BT ring d_4 were purchased from Fluka (Buchs, Switzerland) (see the Supporting information (Table 1)).

Individual stock solutions of the analytes were initially prepared at 1 mg/mL in methanol and subsequently diluted in order to obtain an appropriate analyte concentration. Standard mixtures, one of them for the target compounds analyzed in negative ionization (NI) mode and the other one for the target compounds analyzed in positive ionization (PI) mode, were prepared in methanol at different concentrations by appropriate dilution of individual stock solutions.

SPE cartridges (3 mL, 3 mg, hydrophilic–lipophilic balance (HLB)) were obtained from Waters Corp. (Millford, MA). All the solvents (water and methanol) were HPLC grade and were purchased from Merck (Darmstadt, Germany), and ammonium formate (95% of purity), formic acid (98%), acetic acid (99.5%) and ammonia (30%) were from Panreac (Barcelona, Spain). Nitrogen for drying 99.995% of purity was from Air Liquide (Spain).

2.2. Sample collection

Sediment samples were collected from the Ebro River basin (NE Spain) during a sampling campaign in 2010. The following samples were taken: ARG, downstream Pamplona WWTP (WWTP1); NAJ, an important agricultural wine area, upstream Logroño WWTP (WWTP2); EBR4, downstream to WWTP2; GAL2 in the agricultural area and HUE, inside the city of Zaragoza, receives the effluents from several industrial areas, both sampling points upstream Zaragoza WWTP (WWTP3); EBR6 downstream Lleida WWTP (WWTP4); SEG downstream to WWTP4; EBR9 in the Ebro delta with rice fields, downstream Tortosa WWTP (WWTP5) (see Supporting information (Fig. 1)).

Sewage sludge for five major WWTP in the basin were also collected. Samples were wrapped into aluminium foil, frozen and transported at −20 °C to the laboratory, and finally lyophilized. The lyophilized samples were ground, homogenized using a mortar and pestle and stored at −20 °C. In the case of sediment samples before freezing sediments sieved through a 125-μm sieve.

2.3. Analytical method

2.3.1. Extraction conditions

2 g dry weight (dw) of sediment sample and 1 g dw sewage sludge sample were spiked with 100 μL of a surrogate standard solution at a concentration of 250 μg/L and 2500 μg/L, respectively.

Before the extraction, the spiked samples were kept overnight to equilibrate and then a PLE was carried out using a fully automated ASE 200 system (Dionex, Sunnyvale, CA, USA). Samples were placed into the extraction cell, provided with two cellulose filters in the bottom and any void space was filled with Hydromatrix (Varian Inc., Palo AQlto, USA) and the cell was sealed with the top cell cap. The cell was heated up to 50 °C. The extraction solvent employed was water:methanol:acetone (1:2:1, v/v) mixture and the pressure reached 1500 psi. After an oven heat-up time of 5 min under these conditions, three static extractions of 5 min at constant pressure and temperature were applied. The resulting extract volume was about 20 mL and the time required for the extraction was 25 min.

The extract was reduced under a gentle nitrogen stream and redissolved in 1 mL and 10 mL of methanol for sediment and sewage sludge samples, respectively. The approximate time required in this step was about 20 min. This solution was centrifuged, collecting 0.5 mL of the top of the centrifuge vial for the LC–LC–MS/MS analysis.

Download English Version:

https://daneshyari.com/en/article/1202997

Download Persian Version:

https://daneshyari.com/article/1202997

Daneshyari.com