Journal of Chromatography B 1072 (2018) 25–33

Contents lists available at ScienceDirect

Journal of Chromatography B

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

Determination of perfluoroalkyl acid isomers in biosolids, biosolids-amended soils and plants using ultra-high performance liquid chromatography tandem mass spectrometry

Hongna Zhang[a], Bei Wen[a,*], Wen Wen[b], Yibing Ma[c], Xiaoyu Hu[d], Yali Wu[a], Lei Luo[a], Shuzhen Zhang[a]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] College of Electrical Engineering, Zhejiang University, Hangzhou 310027, China
[c] Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China
[d] Beijing Center for Disease Prevention and Control, Beijing 100020, China

ARTICLE INFO

Keywords:
Perfluoroalkyl acids
Isomer
Biosolid
Soil
Plant
UHPLC–MS/MS

ABSTRACT

Isomer-specific analysis of perfluoroalkyl acids (PFAAs) is important to accurately assess their environmental source, fate, and human risks. In this study, a method was developed for the determination of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorohexane sulfonate (PFHxS) isomers in biosolids, biosolids-amended soils and plants using ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC–MS/MS). The separation efficiencies of two chromatographic columns and extraction capacities of different methods were tested. Compared with the C18 column (ACQUITY UPLC BEH Shield RP18 column), the column with an alkyl perfluorinated C8 stationary phase (Epic FO LB column), in combination with the distinct MS/MS transitions of analytes, allowed better separation of most isomers. The ion-pair extraction method showed more effective matrix separation than that of the alkaline digestion method, with recoveries ranging from 79.6-105% for biosolids, 80.4-116% for soils, and 68.0-114% for plant tissues. The method detection limits ranged from 10 to 55, 3–13, and 8–58 pg/g dry weight for biosolids, soil, and plants, respectively. This method was applied successfully to quantify individual isomers in biosolids, biosolids-amended soils and plants. Six PFOA, eight PFOS, and two PFHxS isomers were found in the samples, with linear isomers being the dominant species. Further analysis revealed that the translocation potentials of branched isomers within plants were higher than those of linear isomers.

1. Introduction

Perfluoroalkyl acids (PFAAs) have been incorporated into numerous industrial and consumer products for over 60 years. They have received great scientific and chemical regulatory attention due to their ubiquitous occurrence, environmental persistence, chain length-dependent bioaccumulation, and potential toxicity [1]. The main manufacturing processes for PFAA products include electrochemical fluorination (ECF) and telomerization. The telomerization process yields almost exclusively linear perfluoroalkyl isomers, whereas the ECF process typically leads to a mixture of 70–80% linear and 20–30% branched perfluoroalkyl isomers [2]. After the phase-out of ECF perfluorooctyl chemistries by the 3 M Company in 2002, telomerization became the dominant method for producing PFAAs in Western Europe and North America, but the ECF process is still used in some Asian countries, especially China [3,4].

PFAA isomers have been proven to widely exist in the environment, and show significantly different transport, bioaccumulation, and toxicity properties in organisms [2]. Linear isomers of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have higher bioaccumulation and biomagnification potential than the corresponding branched isomers in aquatic food webs [5,6]. In human serum, branched PFOS isomers were generally preferentially accumulated [7,8], while PFOA isomer profiles were predominantly linear [8,9]. In addition, branched PFAA isomers generally had a higher renal clearance rate than did the corresponding linear isomers in humans [10,11]. The toxicity of PFAAs may also be isomer-specific. Loveless et al. [12] reported that linear PFOA or mixed linear/branched PFOA were more

* Corresponding author.
E-mail address: bwen@rcees.ac.cn (B. Wen).

https://doi.org/10.1016/j.jchromb.2017.09.036
Received 30 July 2017; Received in revised form 20 September 2017; Accepted 21 September 2017
Available online 06 November 2017
1570-0232/ © 2017 Elsevier B.V. All rights reserved.

toxic than branched PFOA in rodents. However, O'Brien et al. [13] found that mixed linear/branched PFOS altered the expression of more transcripts and elicited a greater transcriptional response in cultured chicken embryonic hepatocytes than those of linear PFOS alone. Therefore, unless PFAAs are considered as individual isomers, much of the information could potentially lead to inaccuracies in environmental and human risk assessment [2].

Sewage sludge is considered to be an important sink of PFAAs [14]. The land application of biosolids (treated sewage sludges) as fertilizer in agriculture can cause PFAA contamination in soils [15,16]. PFAAs in the contaminated soils may enter into the food chain by plant uptake and pose a potential threat to the ecological environment and human health. Uptake, translocation, and distribution of PFAAs in plant tissues from biosolids-amended soils have been demonstrated [17,18]. However, limited information is available about isomer-specific PFAA transport and bioaccumulation in biosolids-amended soil-plant systems. Naile et al. [19] demonstrated the existence of PFOA isomers in biosolids, soils, sediments, and grass. However, individual PFOA isomers were not quantified. To elucidate the isomer-specific transport and bioaccumulation behaviors of PFAAs, it is essential to develop a fast, sensitive, and reliable methodology for PFAA isomer quantification in these matrices.

Polar organics with carboxylic groups can be analyzed by gas chromatography system through derivatization [20]. In-port derivatization-gas chromatography-mass spectrometry (GC–MS) showed promise for isomer-specific analyses of perfluoroalkyl carboxylates (PFCAs) [21] and PFOS [22] in environmental samples. However, PFCAs and PFOS could not be determined simultaneously due to their different derivatization methods. High performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS) has been applied to detect PFCA, perfluoroalkyl sulfonate (PFSA), and perfluorooctane sulfonamide (FOSA) isomers in multiple matrixes [11,23–25]. Ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC–MS/MS) offers significant theoretical advantages in resolution, speed, and sensitivity for analytical determinations. Ullah et al. [26] utilized this technique to analyze linear and branched PFOS and FOSA in herring from the Swedish west coast; however, information on individual branched isomers was not available. Kärrman et al. [27] applied UHPLC–MS/MS to analyze PFOA and PFOS isomers in the environment of aqueous film forming foam-impacted sites, but some of the monomethyl branched isomers could not be individually quantified due to the unsatisfactory resolution. In this study, a method for the analysis of linear and branched PFOA, PFOS, and perfluorohexane sulfonate (PFHxS) isomers using UHPLC–MS/MS was developed. The extraction efficiencies and matrix separation of the ion-pair extraction and alkaline digestion methods followed by solid phase extraction (SPE) clean-up were compared. The optimized method was then applied to determine the levels of PFOA, PFOS, and PFHxS isomers in biosolids, biosolids-amended field soils and plants. To the best of our knowledge, this is the first isomer-specific analysis of PFAAs in these environmental matrices.

2. Materials and methods

2.1. Chemicals and reagents

Detailed information on analyte nomenclature and acronyms are listed in Table S1. Standards of *n*-, 3*m*-, 4*m*-, 5*m*-, *iso*-, *tb*-, (4,4)m_2-, (4,5)m_2-, and (3,5)m_2-PFOA; *n*-, 1*m*-, 3*m*-, 4*m*-, 5*m*-, *iso*-, *tb*-, (4,4)m_2-, (4,5)m_2-, and (3,5)m_2-PFOS; brPFHxSK, a *n*-/*br*-PFHxS mixture; stable isotope-labeled MPFOA ([1,2,3,4-$^{13}C_4$]-PFOA), MPFOS ([1,2,3,4-$^{13}C_4$]-PFOS), and MPFHxS ($^{18}O_2$-PFHxS) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Details of isomer standards are shown in Table S2. HPLC-grade methanol (MeOH) and methyl *tert*-butyl ether (MTBE) were purchased from Fisher Chemical (Fair Lawn, NJ, USA). HPLC-grade formic acid and ammonium hydroxide were purchased from CNW Technologies GmbH (Düsseldorf, Germany). Tetra-butyl ammonium hydrogen sulfate (TBAHS), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and sodium acetate were purchased from Sigma-Aldrich Inc. (Milwaukee, WI, USA). Weak anion exchange (Oasis® WAX, 6 cm^3, 150 mg, 30 μm) solid phase extraction (SPE) cartridges were purchased from Waters Corp. (Milford, MA, USA). Water obtained from a Milli-Q Advantage A10 system (Millipore, Bedford, MA, USA) was used throughout the experiment.

2.2. Biosolids, soil, and plant samples

Biosolids, soils, and maize plants were sampled from biosolids-amended agricultural fields in Dezhou Experiment Station, Chinese Academy of Agricultural Sciences (Dezhou, Shandong province, China) in September 2016. Uncontaminated soils and maize plants (blanks) were collected from an experimental field at Beijing Academy of Agriculture and Forestry Sciences. A commercial peat soil purchased from Jilin Changbai Mountain Peat Moss Development Co., Ltd. (Changchun, Jilin Province, China) was used as a surrogate for the blank biosolids matrix in terms of organic components, because we did not find biosolids without detectable concentrations of our PFAA analytes. The organic matter contents of peat soil and biosolids were 46.5% and 45.2%, respectively. The pH values measured at these two matrixes were 6.6 and 7.1, respectively. Soil samples were taken from the cultivated surface layer (0–20 cm). Biosolids and soils were freeze-dried, finely ground, and screened through a MeOH-washed, 0.3 mm stainless-steel sieve. Plant samples were divided into roots, stems, and leaves. The subsamples of maize were washed thoroughly with Milli-Q water, freeze-dried, and ground. All dried samples were stored at −20 °C before analysis.

2.3. Extraction and clean-up procedure

Studies have shown that the ion-pair extraction method (IPE) and alkaline digestion method (ADM) are efficient in the extraction of PFAA homologues from solid and biological samples [28–31]. To evaluate the capacity of the two methods, recovery tests for PFOA, PFOS, and PFHxS isomers in blank biosolids, soils, and maize plants were conducted. A solution mixture of PFOA, PFOS, and PFHxS isomers prepared by blending the single standards was used in the recovery experiments. In the solution mixture, *n*-, 3*m*-, 4*m*-, 5*m*-, *iso*-, *tb*-, (4,4)m_2-, (4,5)m_2-, and (3,5)m_2-PFOA were 200, 190, 220, 196, 310, 195, 314, 122, and 60 ng/mL, respectively; *n*-, 1*m*-, 3*m*-, 4*m*-, 5*m*-, *iso*-, *tb*-, (4,4)m_2-, (4,5)m_2-PFOS were each 100 ng/mL, (3,5)m_2-PFOS was 50 ng/mL; *n*-PFHxS was 81.1 ng/mL, and *br*-PFHxS was 18.9 ng/mL. Two g of blank soils, 0.5 g of blank biosolids or plant tissues (roots, stems, and leaves) were weighed in 15 mL polypropylene (PP) centrifuge tubes. Before extraction, 30 μL of the PFOA, PFOS, and PFHxS isomer solution mixture was added to blank samples and aged for 24 h. The corresponding spiked levels for *n*-, 3*m*-, 4*m*-, 5*m*-, *iso*-, *tb*-, (4,4)m_2-, (4,5)m_2-, (3,5)m_2-PFOA were 6.00, 5.70, 6.60, 5.88, 9.30, 5.85, 9.42, 3.66, 1.80 ng, respectively; *n*-, 1*m*-, 3*m*-, 4*m*-, 5*m*-, *iso*-, *tb*-, (4,4)m_2-, (4,5)m_2-PFOS were 3.00 ng each, (3,5)m_2-PFOS was 1.50 ng; *n*-PFHxS was 2.454 ng, while *br*-PFHxS was 0.567 ng. All extractions were performed in triplicate for each sample type.

For the IPE, 1.5 mL of 0.4 M NaOH solution was added to the samples. Then 2 mL of 0.25 M Na_2CO_3/$NaHCO_3$ buffer (pH 10) and 1 mL of 0.5 M TBAHS solution were added. After thorough mixing, 5 mL of MTBE was added to the solution. The samples were then kept in a constant-temperature shaker (200 rpm, 25 °C) for 8 h. The samples were then centrifuged (3000*g*, 20 min) and the top MTBE layer was transferred to a second PP tube. The extraction was repeated twice with 5 mL MTBE. The organic supernatants of the three extractions were combined, evaporated to dryness under a gentle stream of nitrogen, and then reconstituted in 1.0 mL MeOH.

For the ADM, the samples were extracted with 6 mL of 0.05 M

Download English Version:

https://daneshyari.com/en/article/7615580

Download Persian Version:

https://daneshyari.com/article/7615580

Daneshyari.com