

DETERMINATION OF PERFLUORINATED COMPOUNDS IN SURFACE SOILS

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Abstract

Much attention has recently been focused on the investigation of perfluorinated compounds (PFCs), including perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and other related homologues. A growing number of studies have demonstrated the widespread presence of PFCs in environmental and biological matrices. However, little has been done to date to characterize the environmental distributions of these compounds at the local, regional, or world-wide scales. Surface soils are an easily acquired matrix that can be used to evaluate patterns of PFC contamination. Moreover, soils are intricately linked with hydrologic and atmospheric cycling, both of which have been shown to be important factors in the distribution and fate of the PFCs. A new method has been developed for the analysis of 10 related PFCs (Table 1) in surface soils at the sub ng/g concentration range. This method involves ultrasonic extraction of soils in methanol followed by a graphitized carbon SPE cleanup and LC/MS-MS analysis.

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Introduction

Perfluorinated compounds (PFCs) have been detected world wide in a variety of environmental and biological matrices.¹⁻³ Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the best known of these compounds as they have been demonstrated to be bio-accumulative, persistent, and toxic.^{4,5} While almost all humans living in industrialized regions of the world have measurable concentrations of the PFCs in their blood, the routes of human exposure are still not well understood. Recent evidence for transport of PFCs from a manufacturing facility to nearby soil and water has been demonstrated.⁶ In addition, consumption of PFC contaminated water has been shown to increase the body burden of individuals drinking that water.⁷ The net negative charge of soils and negative charge of the more common PFCs acids and sulfonates may lead to mobility through soils to ground water. Little to no information exists concerning the translocation of PFCs from contaminated soils into plant matter. Few studies have investigated the analysis of PFCs in soils^{8,9}, but given the central role that soil is likely to play in the contamination of water and food supplies, a well characterized analytical method for PFCs in soils is a very high priority.

Materials and Methods

Standards and reagents: Potassium salts of perfluorobutane sulfonate (PFBS, 98% purity), perfluorohexane sulfonate (PFHS, 93%), and perfluorooctane sulfonate (PFOS, 93%) were provided by 3M Company (St. Paul, MN). Perfluorohexanoic acid (C6, 97%), perfluoroheptanoic acid (C7, 99%), perfluorooctanoic acid (C8 or PFOA, 96%), perfluorononanoic acid (C9, 97%), perfluorodecanoic acid (C10, 98%), were purchased from Sigma-Aldrich (St. Louis, MO). Perfluoroundecanoic acid (C11, 96%), and perfluorododecanoic acid (C12, 96%) were purchased from Oakwood Products (West Columbia, SC). ¹⁸O₂-Ammonium perfluorooctane sulfonate (18O-PFOS) was purchased from Research Triangle Institute (Research Triangle Park, NC). 1,2-¹³C₂-labeled PFOA (13C-PFOA) was purchased from Perkin Elmer Life and Analytical Sciences (Boston, MA). Deionized (DI) water, HPLC grade methanol, and ammonium acetate were determined to be free of PFCs prior to use.

PFC measurement: Surface soils were obtained from various sources world-wide and stored at 4°C prior to being sieved to 2 mm at field moisture before analysis. Sub-samples were extracted with methanol via shaking and sonication. Extracts were then subjected to cleanup using SPE (graphitized carbon). The final sample eluate was

reduced in volume under N₂ gas and then injected on a high-performance liquid chromatography coupled with quadrupole tandem mass spectrometer (LC/MS/MS) for quantitation. Mass transitions of each analyte and HPLC/MS/MS conditions are listed in Table 1 and 2, respectively. Quantitation was carried out using surface soil/solvents fortified with a series of PFC standards (6 points). Recoveries were calculated using matrix matched solutions.

Table 1. Mass transitions of each analyte

Perfluorinated Compounds	Parent Ion, m/z	Fragment Ion, m/z	Perfluorinated Compounds	Parent Ion, m/z	Fragment Ion, m/z
C6 (perfluorohexanoic acid)	313	269	PFBS (perfluorobutane sulfonate)	299	80
C7 (perfluoroheptanoic acid)	363	319	PFHS (perfluorohexane sulfonate)	399	80
C8 (perfluorooctanoic acid)	413	369	PFOS (perfluorooctane sulfonate)	499	80
C9 (perfluorononanoic acid)	463	419		Parent Ion, m/z	Fragment Ion, m/z
C10 (perfluorodecanoic acid)	513	469	Labeled Compounds		
C11 (perfluoroundecanoic acid)	563	519	¹³ C ₂ -PFOA (¹³ C labelled PFOA)	415	370
C12 (perfluorododecanoic acid)	613	569	¹⁸ O ₂ -PFOS (¹⁸ O labelled PFOS)	503	84

Table 2. HPLC and MS/MS conditions

HPLC		MS/MS	
Instrument	Agilent 1100	Instrument	API 3000
Column	Waters Sunfire C18 5 μm, 3.0×50 mm	Ionization	Negative ESI
		Scan mode	MRM
Mobile phase	77:23 methanol:2 mM ammonium acetate	Curtain gas	N ₂ (9 arbitrary units, au)
		Nebulizer gas	N ₂ (8 au)
Flow rate	200 μL/min	Dryer gas	Zero air (8 L/min, 350°C)
Injection volume	10 μL	Ion spray	-1500 V
		Ionization and collision cell voltages	Optimized for individual analytes

Results and Discussion

Methanolic extracts of soils are inherently dirty due to co-extraction of matrix interferences. The SPE cleanup with graphitized carbon (GL Sciences, Carbograph) with no modifiers removed much of the matrix interference and allowed the extracts to be reduced in volume enough to provide sensitivity and precision in the sub ng/g range.

Recovery experiments using solvent based standards and soils spiked with methanolic PFC standards indicated that SPE cleanup with graphitized carbon generally lead to recoveries in the range of 70–130%. Duplicate analysis of soils resulted in coefficients of variation ranging between 2.2–15.1% at spike levels of 50 and 200 pg/g soil. Extraction of between 2–5 grams of soils appeared to be adequate for determination of low level (sub ng/g) contamination. Application of the method to a soil sub-set indicates a wide range in concentrations and composition of PFC in these samples. An assessment of the performance characteristics of this method and application to an international collection of soils (USA, Japan, China, Greece, Norway) for PFC analysis will be presented.

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