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RESEARCH PAPER

Polyfluorinated substances in abiotic standard reference materials

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Abstract The National Institute of Standards and Technology (NIST) has a wide range of Standard Reference Materials (SRMs) which have values assigned for legacy organic pollutants and toxic elements. Existing SRMs serve as homogenous materials that can be used for method development, method validation, and measurement for contaminants that are now of concern. NIST and multiple groups have been measuring the mass fraction of a group of emerging contaminants, polyfluorinated substances (PFASs), in a variety of SRMs. Here we report levels determined in an interlaboratory comparison of up to 23 PFASs determined in five SRMs: sediment (SRMs 1941b and 1944), house dust (SRM 2585), soil (SRM 2586), and sludge (SRM 2781). Measurements presented show an array of PFASs, with perfluorooctane sulfonate being the most frequently detected. SRMs 1941b, 1944, and 2586 had relatively low concentrations of most PFASs measured while 23 PFASs were at detectable levels in SRM 2585 and most of the PFASs measured were at detectable levels in SRM 2781. The measurements made in this study were used to add values to the Certificates of Analysis for SRMs 2585 and 2781.

Keywords Polyfluorinated substances · Standard reference materials · Sediment · Sludge · House dust · Interlaboratory comparison exercise

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Introduction

Polyfluorinated substances (PFASs) are a group of persistent compounds that have been measured in biotic and abiotic samples worldwide [1–9]. Since PFASs are resistant to degradation and ubiquitous in the environment, some are candidate persistent organic pollutants under the Stockholm Convention and some are listed on Annex B of the Stockholm Convention [10]. Included in this class of compounds are perfluoroalkyl sulfonates (PFSAs) and perfluoroalkylcarboxylic acids (PFCAs), with the most recognizable compounds being perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

PFASs were manufactured worldwide and used in a variety of consumer products (e.g. waxes, firefighting foams, lubricants, plastics) [11, 12]. The phase-out of PFOS and PFOS-based materials started in 2000 has resulted in a decline in the amount and assortment of products using PFASs in the United States and Europe [13]. The reduction and regulation of PFAS production and emissions has resulted in the decline of certain PFASs, but this trend tends to be location and analyte specific. For example, while the United States and Europe have declined production of longer chain PFAS, Asian countries, such as China, have increased manufacturing of PFOS-based materials [13]. To better understand trends of PFASs in the environment, multiple countries have been conducting retrospective studies of PFAS concentrations focusing on environmental media [14–21]. These retrospective studies are useful in themselves, but comparing data among the studies tends to be difficult. There are differences in analytical techniques used among the laboratories, which pose challenges when data users, like modelers and epidemiologists, want to investigate global patterns and environmental hot spots.

The number of laboratories measuring PFASs in environmental media has increased in the past years. Some laboratories have tried to show proficiency in measuring PFASs by participating in interlaboratory comparison studies [22–24]; however, these studies bring to light that many laboratories still need improvements in their analytical methodology. The use of reference materials as a quality control material can serve as a way to assess comparability within and among laboratories and potentially minimize analytical bias and help to establish a comparable global perspective when talking about chemicals of concern, like PFASs.

In early interlaboratory comparison studies measuring PFASs, data quality varied widely [23–25]. With the issues in PFAS measurements, Martin et al. [26] pleaded for reference materials to help in method development and validation. The National Institute of Standards and Technology (NIST) has provided Standard Reference Materials (SRMs) in human matrices (serum, plasma, milk) [27, 28] and biological matrices (fish tissue, bovine liver) [29] with values assigned for

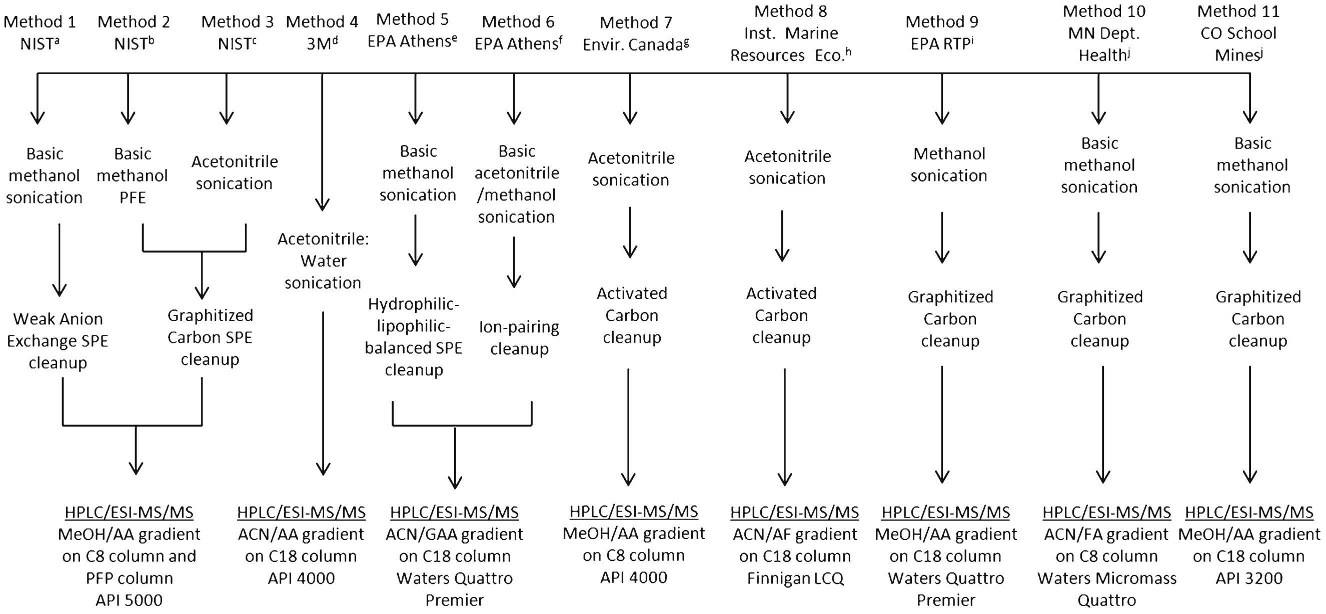

Fig. 1 Methods used for the determination and quantification of PFASs in SRMs. Abbreviations: pressurized fluid extraction (PFE); solid-phase extraction (SPE); methanol-ammonium acetate mobile phase (MeOH/AA); acetonitrile-ammonium acetate mobile phase (ACN/AA); acetonitrile-formic acid mobile phase (ACN/FA). [a]Method modified from Taniyasu et al. [30]. [b]Method modified from Reiner et al. [28]. [c]Method similar to Hansen et al. [42]. [d]Method similar to Malinsky et al. [43]. [e]See Yoo et al. [44] for method details. [f]See Washington et al. [45] for method details. [g]Method similar to Muller et al. [46]. [h]See Kwadijk et al. [47] for method details. [i]See Strynar et al. [40] for method details. [j]See Sepulvado et al. [9] for extraction method details

Table 1 Mass fraction of PFASs (ng/g as received) measured in SRM 1941b (Organics in Marine Sediment) by six laboratories using different methods. Values represent the mean and one standard deviation. Range is reported for *n* =2

Compound	NIST method 1 *(n= 6)*	3M *(n= 9)*	EPA Athens *(n= 6)*	Environ. Canada *(n-3)*	Inst. Marine Resources Eco. *(n= 2)*	MN Dept. Health *(n= 6)*
PFBA	< 0.778	< 13.1	NM	NM	NM	< 0.0750
PFPeA	< 0.201	< 1.29	NM	NM	NM	0.0663±0.0067
PFHxA	< 0.650	< 0.258	1.03±0.06	NM	NM	0.0715±0.0067
PFHpA	< 0.253	< 0.516	0.220±0.017	< 0.180	NM	NM
PFOA	< 0.185	< 0.518	0.414±0.035	0.972±0.061	0.173–0.227	0.345±0.037
PFNA	< 0.200	< 0.519	0.290±0.016	0.528±0.062	NM	NM
PFDA	< 0.191	< 0.518	0.0550±0.0051	0.177±0.020	NM	NM
PFUnA	< 0.745	< 0.259	0.152±0.014	0.296±0.039	NM	NM
PFDoA	< 0.690	< 0.259	0.612±0.001	0.237±0.098	NM	NM
PFTriA	< 0.199	NM	0.0754±0.0110	NM	NM	NM
PFTA	< 0.188	NM	0.0323±0.0046	NM	NM	NM
PFBS	< 0.236	< 0.259	NM	NM	NM	< 0.100
PFHxS	< 0.206	< 0.258	NM	0.429±0.189	NM	< 0.0750
PFHpS	NM	NM	NM	NM	NM	NM
PFOS	< 0.346	0.471±0.094	0.803±0.288	1.20±0.15	< 0.800	0.350±0.014
PFDS	NM	NM	NM	0.745±0.176	NM	NM
PFOSA	< 0.226	< 0.259	NM	NM	NM	NM

Values shown as "<" a specified number describe the actual reporting limit

NM not measured

Table 2 Mass fraction of PFASs (ng/g as received) measured in SRM 1944 (New York/New Jersey Waterway Sediment) by seven laboratories using different methods. Values represent the mean and one standard deviation. Range is reported for *n* =2

Compound	NIST method 1 *(n= 6)*	NIST method 2 *(n= 6)*	3M *(n= 9)*	EPA Athens *(n= 6)*	Environ. Canada *(n= 3)*	Inst. Marine Resources Eco. *(n= 2)*	MN Dept. Health *(n= 6)*	CO school mines *(n= 8)*
PFBA	< 0.902	< 0.153	2.42±0.42	NM	NM	NM	0.147±0.046	0.0920±0.0189
PFPeA	< 0.233	< 1.19	< 0.574	NM	NM	NM	0.163±0.008	< 0.0500
PFHxA	< 0.754	< 1.00	< 0.230	2.65±0.19	NM	NM	0.228±0.019	0.318±0.133
PFHpA	< 0.293	< 0.791	0.402±0.072	1.05±0.11	< 0.180	NM	NM	0.0463±0.0095
PFOA	< 0.215	< 1.32	0.823±0.038	0.892±0.078	1.75±0.31	0.422–0.554	0.843±0.050	0.633±0.082
PFNA	< 0.232	< 0.461	< 0.115	0.122±0.014	< 0.320	NM	NM	< 0.0500
PFDA	< 0.222	< 0.531	0.242±0.061	0.117±0.017	0.303±0.012	NM	NM	< 0.100
PFUnA	< 0.864	< 1.45	0.386±0.057	0.418±0.022	1.48±0.53	NM	NM	< 0.100
PFDoA	< 0.800	< 0.791	0.239±0.047	0.302±0.019	0.613±0.077	NM	NM	0.485±0.119
PFTriA	3.82±1.01	< 0.923	NM	1.02±0.07	NM	NM	NM	NM
PFTA	< 0.219	< 0.251	NM	0.230±0.023	NM	NM	NM	NM
PFBS	< 0.274	< 0.140	0.744±0.187	NM	NM	NM	< 0.100	< 0.0500
PFHxS	< 0.239	< 0.122	< 0.115	NM	< 0.200	NM	< 0.0750	0.0937±0.0216
PFHpS	NM	NM	NM	NM	NM	NM	NM	< 0.0500
PFOS	0.959±0.245	1.50±0.19	1.31±0.20	3.31±0.71	2.98±0.09	< 0.500	1.27±0.05	1.40±0.14
PFDS	NM	NM	NM	NM	3.10±0.13	NM	NM	1.40±0.05
PFOSA	< 0.262	< 0.183	0.235±0.030	NM	NM	NM	NM	NM
N-MeFOSAA	NM	NM	NM	NM	NM	NM	NM	1.44±0.21
N-EtFOSAA	NM	NM	NM	NM	NM	NM	NM	4.49±0.38

Values shown as "<" a specified number describe the actual reporting limit

NM not measured

PFASs on the Certificates of Analysis. Since recent focus on PFAS measurements has been in abiotic matrices including soil and dust, NIST, in conjunction with a number of other laboratories, has been working with existing abiotic SRMs (including sediments, house dust, and wastewater sludge) to determine concentrations of PFASs with the goal of adding values (concentrations) for PFASs to the Certificates of Analysis. Specifically, the aims of this study were to coordinate an interlaboratory comparison study measuring PFASs in a variety of existing abiotic SRMs and value assign PFAS mass fractions for these SRMs. Adding values of PFASs on the Certificates of Analysis for these existing SRMs will aid the analytical community and support future PFAS measurements.

Material and methods

Twenty-three PFASs were examined in this study (Electronic Supplementary Material Table S1). These include perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTriA), perfluorotetradecanoic acid (PFTA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), PFOS, perfluorodecane sulfonate (PFDS), perfluorooctane sulfonamide (PFOSA), 6:2 Fluorotelomer sulfonic acid (6:2 FTS), 8:2 Fluorotelomer sulfonic acid (8:2 FTS), bis(1H,1H,2H,2H-perfluorooctyl)phosphate (6:2 diPAP), bis(1H,1H,2H,2H-perfluorodecyl)phosphate (8:2 diPAP), N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA), and N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA).

The SRMs were prepared by NIST using methods described in their respective Certificates of Analysis and have previously been certified for concentrations of persistent organic pollutants and metals (http://www.nist.gov/srm/). For this study, PFASs were measured in SRM 1941b Organics in Marine Sediment, SRM 1944 New York/New Jersey Waterway Sediment, SRM 2585 Organic Contaminants in House Dust, SRM 2586 Trace Elements in Soil, and SRM 2871 Domestic Sludge.

Eight laboratories including NIST, Colorado School of Mines, Minnesota Department of Health, US Environmental Protection Agency (EPA), Wageningen IMARES (Institute for Marine Resources and Ecosystem Studies), 3M, and Environment Canada participated in an interlaboratory

Table 3 Mass fraction of PFASs (ng/g as received) measured in SRM 2585 (Organic Contaminants in House Dust) by three laboratories using different methods. Values represent the mean and one standard deviation

Compound	NIST method 1 *(n=6)*	NIST method 2 *(n=9)*	NIST method 3 *(n=6)*	EPA RTP *(n=6)*	CO school mines *(n=8)*
PFBA	265±38	227±26	218±17	270±2	283±18
PFPeA	195±15	238±22	179±13	243±10	259±21
PFHxA	251±20	261±29	236±18	400±13	474±31
PFHpA	268±22	251±31	227±13	440±53	220±12
PFOA	626±30	567±83	430±25	760±39	512±62
PFNA	95.9±5.1	101±12	103±8	96.5±6.7	86.1±9.9
PFDA	47.6±4.8	38.1±3.9	23.9±1.3	65.7±3.9	34.7±4.3
PFUnA	55.8±13.7	37.8±14.2	45.2±4.0	NM	26.1±2.1
PFDoA	40.6±5.8	36.5±9.6	34.3±4.2	NM	37.3±6.2
PFTriA	27.9±5.4	28.1±7.4	29.3±1.5	NM	NM
PFTA	22.4±6.0	21.0±2.9	10.7±1.2	NM	NM
PFBS	130±12	40.8±3.0	21.1±1.0	18.8±2.3	112±7
PFHxS	1340±110	1500±290	1170±70	1480±85	1510±120
PFHpS	NM	NM	NM	22.5±1.9	43.4±4.7
PFOS	2410±510	2350±280	2020±100	2000±150	2290±120
PFDS	NM	NM	NM	902±138	375±43
PFOSA	11.6±0.8	8.67±3.63	7.78±0.48	NM	NM
6:2 FTS	NM	NM	NM	90.0±9.5	NM
8:2 FTS	NM	NM	NM	169±58	NM
6:2 diPAP	NM	NM	NM	421±83	NM
8:2 diPAP	NM	NM	NM	868±30	NM
N-MeFOSAA	NM	NM	NM	NM	150±12
N-EtFOSAA	NM	NM	NM	NM	675±77

NM not measured

comparison study by analyzing selected SRMs for the PFASs routinely measured in their laboratories (Table S1, Electronic Supplementary Material). In all cases, the laboratories used their existing extraction and cleanup methods coupled with liquid chromatography tandem mass spectrometry (LC-MS/MS) for the quantification of PFASs.

Analytical methods

Participating laboratories were asked to determine the concentrations of the PFASs, in the SRMs, they currently measure in their laboratory (Table S1, Electronic Supplementary Material). They were asked to measure at least three replicates of the SRMs using their current methods and own standards. A brief description of sample extraction, cleanup, and instrumental technique was provided by the participating laboratories along with the results. Participants were asked to provide the reporting limit (RL) for each compound, in each matrix. Seven participating laboratories measured PFASs in SRM 1944. Six participating laboratories measured PFASs in SRMs 1941b and 2586. Five participating laboratories measured PFASs in SRM 2781. Three laboratories provided PFAS measurements for SRM 2585.

Extraction and cleanup methods used included alterations of established methods (Fig. 1). Extraction methods included an acetonitrile extraction (sonication or accelerated solvent extraction) and basic methanol (potassium hydroxide or sodium hydroxide) extraction. Some participants chose no further cleanup after extraction while other participants chose to use different solid-phase extraction columns (i.e. Waters Oasis WAX or Supelco ENVI-Carb) or the addition of activated carbon to the extraction solution for the cleanup of their extracts. All laboratories used an internal standard approach for quantification using current mass-labeled internal standards and liquid chromatography-tandem mass spectrometry (LC-MS/MS) for quantification. It is important to note that most calibration standards and internal standards are only available from a single source and not all analytes have complementary mass-labeled internal standards. The branched and linear isomers of PFOA, PFHxS, and PFOS were integrated together and the concentrations of these compounds are reported as totals of all isomers.

NIST method two is newly adapted from previous methods [28, 30]. Briefly, the SRMs were extracted with 0.01 mol/L potassium hydroxide in methanol using pressurized fluid extraction (Dionex Accelerated Solvent Extractor (ASE) 350, Sunnyvale, CA, USA) in two cycles of 5 min each at 70 °C. Extracts were cleaned up using a graphitized carbon SPE column [28].

Table 4 Mass fraction of PFASs (ng/g as received) measured in SRM 2586 (Trace Elements in Soil) by six laboratories using different methods. Values represent the mean and one standard deviation. Range is reported for $n=2$

Compound	NIST method 1 *(n= 6)*	NIST method 2 *(n= 6)*	EPA Athens *(n= 6)*	Env. Canada *(n= 3)*	Inst. Marine Resources Eco. *(n= 2)*	MN Dept. Health *(n= 6)*	CO school mines *(n= 8)*
PFBA	< 0.621	< 0.315	NM	NM	NM	0.0828±0.0076	0.181±0.084
PFPeA	< 0.160	< 2.45	NM	NM	NM	0.130±0.000	0.145±0.033
PFHxA	< 0.519	< 2.06	0.238±0.021	NM	NM	0.145±0.010	0.448±0.080
PFHpA	< 0.202	< 1.62	0.131±0.024	< 0.180	NM	NM	0.0817±0.0107
PFOA	< 0.148	< 2.72	0.544±0.046	1.30±0.04	0.311–0.490	0.573±0.023	0.568±0.037
PFNA	< 0.160	< 0.949	0.101±0.007	< 0.320	NM	NM	0.0984±0.0150
PFDA	< 0.153	< 1.09	0.125±0.013	0.308±0.035	NM	NM	< 0.100
PFUnA	< 0.595	< 2.98	0.0777±0.0073	0.189±0.020	NM	NM	< 0.100
PFDoA	< 0.551	< 1.62	0.0798±0.0084	0.189±0.020	NM	NM	< 0.200
PFTriA	< 0.159	< 1.89	0.0429±0.0086	NM	NM	NM	NM
PFTA	< 0.150	< 0.517	0.0329±0.0062	NM	NM	NM	NM
PFBS	< 0.189	< 0.289	NM	NM	NM	< 0.100	0.0947±0.0130
PFHxS	< 0.164	< 0.252	NM	< 0.200	NM	0.0712±0.0061	0.107±0.012
PFHpS	NM	NM	NM	NM	NM	NM	< 0.0500
PFOS	2.13±0.21	3.64±0.30	4.43±0.42	5.84±0.13	2.94–3.16	3.17±0.08	3.71±0.23
PFDS	NM	NM	NM	0.418±0.024	NM	NM	0.108±0.018
PFOSA	< 0.180	< 0.377	NM	NM	NM	NM	NM
N-MeFOSAA	NM	NM	NM	NM	NM	NM	< 0.0500
N-EtFOSAA	NM	NM	NM	NM	NM	NM	0.454±0.048

Values shown as "<" a specified number describe the actual reporting limit

NM not measured

Determining reference values

The method that has previously been used for value assigning organic contaminants in SRMs was used for value assigning PFASs in these SRMs. This method combines the data from at least two different analytical methods. In the present study, PFAS values were obtained by combining the results from the extraction methods used by NIST with results from the interlaboratory study. The results reported in this study were used to assign reference values for some PFASs in SRMs 2585 and 2781. The reference value is a weighted mean of the results from the analytical methods [31]. The expanded uncertainties about the mean were calculated according to Rukhin [32] using a coverage factor equal to 2 (approximately 95 % confidence), calculated by combining a pooled within method variance with a between method variance [33] following the ISO Guide [34, 35].

Results and discussion

PFASs were detected in all the SRMs studied (Tables 1, 2, 3, 4, and 5). Depending on the matrix, the PFAS values varied significantly, ranging over several orders of magnitude (from sub ng/g mass fractions in the sediment to μg/g mass fractions in the house dust). The agreement among laboratories varied widely depending on the matrix and analytes, especially compared to previous interlaboratory studies using SRMs [28, 29]. PFOS was the most frequently detected analyte, and in general, there was better agreement among the results from most laboratories for measurements of PFOS. Results for the other analytes among laboratories were less consistent with relative standard deviations (RSDs) greater than 15 %.

Concentrations of PFASs measured in sediment SRMs were similar to concentrations of PFASs measured in sediment samples collected around the world [36–38]. SRM 1941b was prepared from marine sediment collected from Baltimore Harbor (MD, USA). SRM 1944 was prepared from marine sediment collected near urban areas in New York and New Jersey. Both materials were made from naturally occurring marine sediments from urban areas. In SRM 1941b, PFOS was the most frequently detected PFAS measured by all laboratories; however, some laboratories were not able to make measurements of PFOS above the limit of detection (Table 1). Very few other PFASs were consistently detected in SRM 1941b (Table 1), and if detectable, the mass fractions were sub ng/g levels. All laboratories measured detectable amounts of PFOS in SRM 1944 (Range < RL to 3.31 ng/g,

Table 5 Mass fraction of PFASs (ng/g as received) measured in SRM 2781 (Domestic Sludge) by five laboratories using different methods. Values represent the mean and one standard deviation. Range is reported for $n=2$

Compound	NIST method 1	NIST method 2	NIST method 3	3M	EPA Athens	Inst. Marine Resources Eco.	CO school mines
	(n=6)	*(n=9)*	*(n=6)*	*(n=9)*	*(n=4)*	*(n=2)*	*(n=8)*
PFBA	23.3±1.4	18.9±2.4	23.4±1.9	3.34±0.47	35.9±5.7	NM	12.5±1.0
PFPeA	4.12±0.61	< 2.99	3.98±0.33	9.56±1.00	< 3.50	NM	5.65±1.13
PFHxA	9.97±1.61	12.1±1.8	11.4±1.1	13.9±0.7	16.9±1.8	NM	16.4±1.8
PFHpA	6.23±0.86	7.76±2.31	7.57±0.47	7.38±0.75	8.23±0.52	NM	4.83±0.54
PFOA	30.8±4.6	24.0±3.3	30.3±1.6	25.7±2.0	31.0±4.4	21.8–23.0	18.7±1.8
PFNA	3.20±0.55	6.59±1.05	< 30.8	2.56±0.27	3.47±0.62	NM	2.82±0.55
PFDA	2.98±0.48	5.85±1.19	3.42±0.21	5.33±0.45	6.05±1.38	NM	2.67±0.54
PFUnA	2.74±0.56	7.13±1.75	23.6±2.6	2.89±0.32	< 1.50	NM	2.43±0.13
PFDoA	2.02±0.19	2.60±0.36	2.20±0.16	2.01±0.23	< 1.50	NM	4.81±2.34
PFTriA	1.37±0.39	3.25±0.99	24.4±2.4	NM	< 1.50	NM	NM
PFTA	0.556±0.113	< 0.631	1.00±0.20	NM	< 3.50	NM	NM
PFBS	< 0.186	< 0.353	< 0.405	< 1.25	< 1.50	NM	34.9±4.0
PFHxS	7.34±1.08	9.70±2.89	10.0±0.4	5.04±1.67	NM	NM	9.28±1.01
PFHpS	NM	NM	NM	NM	< 5.00	NM	0.964±0.120
PFOS	166±14	205±23	263±13	219±11	373±25	227–234	218±30
PFDS	NM	NM	NM	NM	NM	NM	290±50
PFOSA	5.23±0.63	5.78±0.91	6.70±0.35	4.11±0.52	NM	NM	NM
N-MeFOSAA	NM	NM	NM	NM	NM	NM	73.6±14.5
N-EtFOSAA	NM	NM	NM	NM	NM	NM	463±63

Values shown as "<" a specified number describe the actual reporting limit

NM not measured

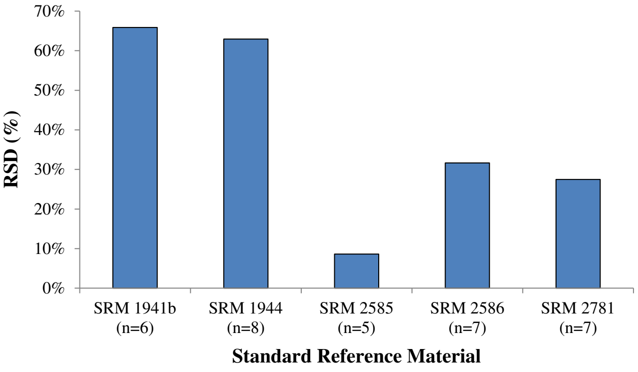

Fig. 2 Relative standard deviation (RSD) of PFOS reported for all SRMs

as received; Table 2). The agreement among the laboratory means in SRM 1944 was relatively poor (RSD greater than 60 %; Fig. 2). Since sediment is not a matrix routinely measured and the concentrations of PFASs are relatively low, difficulties may arise during the measurements of PFOS. Also important to note, most laboratories used the same method to measure all abiotic matrices, even though the matrices are not equivalent. Although there is no clear indication that the variance is based on the extraction and cleanup methods employed, it can be a possible source of the poor agreement. In addition to PFOS, other PFASs were detected and measured by the participating laboratories in SRM 1944 (Table 2). The concentrations of other PFASs ranged from below the laboratories' reporting limits to 4 ng/g as received.

SRM 2585 Organic Contaminants in House Dust was prepared from dust taken from vacuum cleaner bags collected during 1993 and 1994 from houses, cleaning services, motels, and hotels in Maryland, Montana, New Jersey, North Carolina, Ohio, and Wisconsin [39]. Concentrations of PFASs measured in SRM 2585 were much higher compared to the concentrations of PFASs measured in the other SRMs in this study (Table 3). All 23 compounds were detected in this SRM, and the concentrations of PFOS and PFOA determined in SRM 2585 were similar (same range) to concentrations measured in house dust samples collected around the world [40, 41]. PFOS was detected at the highest concentrations in this SRM, with the agreement among laboratory means for PFOS being relatively good (RSD was less than 10 %; Fig. 2). The agreement among measurements of the other compounds ranged from 7 % to 37 % (RSDs of the laboratory means) except for measurements of PFBS for which there was very poor agreement among laboratories (81 % RSD). It is important to note that an isotopically paired internal standard for PFBS is not commercially available. The poor agreement for PFBS measurements many be dependent on the internal standard each laboratory used for quantification of PFBS. The NIST methods used $^{13}C_3$-PFHxS, the EPA method used $^{18}O_2$-PFOS, and the Colorado School of Mines method used $^{18}O_2$-PFHxS. With each laboratory using a different internal standard for quantification, it is hard to determine which, if any of the measurements are accurate. This reiterates the need for matching mass-labeled internal standards for high quality, accurate measurements.

SRM 2586 Trace Elements in Soil is a mixture of soil samples collected from Baltimore, MD in 1990. In this SRM, PFOS was the only PFAS detected by all participating laboratories (Table 4). The mass fraction of PFOS measured in SRM 2586 ranged from 2.13 ng/g to 5.84 ng/g, as received with an RSD of 32 % (Fig. 2). Similar to SRMs 1941b and 1944, these data show that there are still issues in measurements of PFOS from rarely analyzed matrices. Other PFASs were infrequently detected in SRM 2586, and when detected, the values were at sub ng/g levels.

SRM 2781 Domestic Sludge was prepared from sewage cake material collected at a wastewater treatment plant in Denver, CO. The concentrations of PFASs measured in SRM 2781 were similar to concentrations of PFASs measured in previous studies [37]. PFOS was detected at the highest concentrations; however, the agreement among the means of

Table 6 Reference (± expanded uncertainties; ng/g, dry mass) and information values (ng/g, dry mass) for selected PFASs in abiotic SRMs

Compound	SRM 2781 Domestic sludge	SRM 2585 House dust
Reference[a]		
PFBA		249±25
PFPeA		226±31
PFHxA	13.0±2.0	
PFHpA	7.96±1.50	
PFOA	28.5±3.3	
PFNA		101±5
PFHxS	9.39±1.76	1400±170
PFOS[b]	225±41	2280±200
PFOSA	6.31±1.02	
Information[c]		
PFHxA		279
PFHpA		259
PFOA		561
PFNA	5.09	
PFDA	4.76	38.6
PFUnA		47.0
PFDoA		37.0
PFTriA		30.0
PFTA		19.3
PFOSA		9.84

[a] The reference value is a weighted mean of the results from the interlaboratory exercise [31]. The expanded uncertainties about the mean were calculated according to Rukhin [32] using a coverage factor equal to 2 (approximately 95 % confidence)

[b] PFOS values are inclusive of branched and linear isomers

[c] The information value is a mean of the results from the interlaboratory exercise

the laboratories' measurements was slightly less than 30 % (Table 5; Fig. 2). Other PFASs were detected in SRM 2781 with laboratory agreement fairly poor among the laboratories (RSDs ranging between 10 % and 165 %). As shown in Fig. 1, there are only slight differences among laboratory methods, and although sludge is rarely analyzed for PFASs right now, this is a matrix that will, most likely, be measured in many future studies.

Reference values, along with the expanded uncertainties, for PFASs measured in SRMs 2585 and 2781 can be found in Table 6. The reference values were calculated using the results from this interlaboratory study. Information values, rather than reference values, are provided for those PFASs which had a higher relative standard deviation (greater than 15 %) and were reported by less than three laboratories. All reference and information values are reported in dry mass. For comparison, the reference and information values for PFASs in SRM 2585 are found in the same range as concentrations of legacy pollutants (polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers) previously measured in the SRMs.

Conclusions

This study showed that participating laboratories were able to measure PFASs in a variety of abiotic matrices. With the high variability of PFAS measurements in some of the abiotic material, there are concerns about the extraction and cleanup methods currently used. The interlaboratory comparability was best for the matrices that had relatively high concentrations of PFASs, mainly house dust and domestic sludge, compared to the matrices that had much lower concentrations of PFASs, sediment and soil. Compounds with matching isotopically labeled internal standards tended to have better agreement among laboratory measurements compared to compounds without a paired internal standard. As a result of this interlaboratory exercise, reference and information values for some PFASs will be added to the Certificates of Analysis for SRMs 2585 and 2781 (Table 6). These materials which are representative of current day PFAS environmental concentrations provide much needed reference materials for environmental studies.

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Disclaimer Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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