Certification of Standard Reference Material® 1936
Great Lakes Sediment

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Abstract

Standard Reference Material (SRM) 1936 Great Lakes Sediment is intended for 1) use in validating calibration and validation materials for sediment analysis methods and 2) value assigning in-house produced control materials analyzed using those methods. A unit of SRM 1936 consists of one bottle containing approximately 50 g of radiation-sterilized, dried sediment from Milwaukee Bay, WI, USA. This publication documents the production, analytical methods, and statistical evaluations used to characterize this material.

Keywords

Fresh-water sediment; Perfluorooctane sulfonate (PFOS); Polyaromatic Hydrocarbons (PAHs); Standard Reference Material (SRM).

Technical Information Contact for this SRM

Please address technical questions you may have about this SRM to srms@nist.gov where they will be assigned to the appropriate Technical Project Leader responsible for support of this material. For sales and customer service inquiries, please contact srminfo@nist.gov.

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1. Introduction

The National Institute of Standards and Technology (NIST) has developed a number of Standard Reference Material®s (SRM®s) to address the needs of the environmental community. These materials deliver well-characterized amount-of-substance values for a broad range of organic and inorganic contaminants in diverse matrices, including whale blubber, fish and mussel tissues, human blood, house dust, and salt-water sediments. Recently various government agencies and independent laboratories have requested a fresh-water sediment reference material certified for organic contaminants to be used for quality assurance and traceability of contaminants. To satisfy this need, SRM 1936 Great Lakes Sediment has been produced to provide a fresh-water sediment material characterized for legacy and emerging organic contaminants.

Section 2 of this publication describes the sourcing, production, and packaging of SRM 1936, Sections 3 and 4 the NIST measurements, and Section 5 the results from a 2017 interlaboratory study conducted by the Northern Contaminants Program (NCP) Quality Assurance/Quality Control Program to support laboratories in maintaining and developing capabilities for high quality environmental analyses. Section 6 describes the statistical analysis used to certify values for various polycyclic aromatic hydrocarbon (PAH) analytes.

2. Material, Preparation, and Packaging

2.1. Sediment

A total of 481.5 kg (wet mass) of sediment was collected in three batches, corresponding to three slightly different sites, during a single day from Milwaukee Bay, WI, on the west shore of Lake Michigan. The sediment consistency was uniform between sites and was similar to the consistency of peanut butter. Little organic matter was observed in the sediment throughout the collection process. Figure 1 is a Google Earth satellite image of the sampling area.
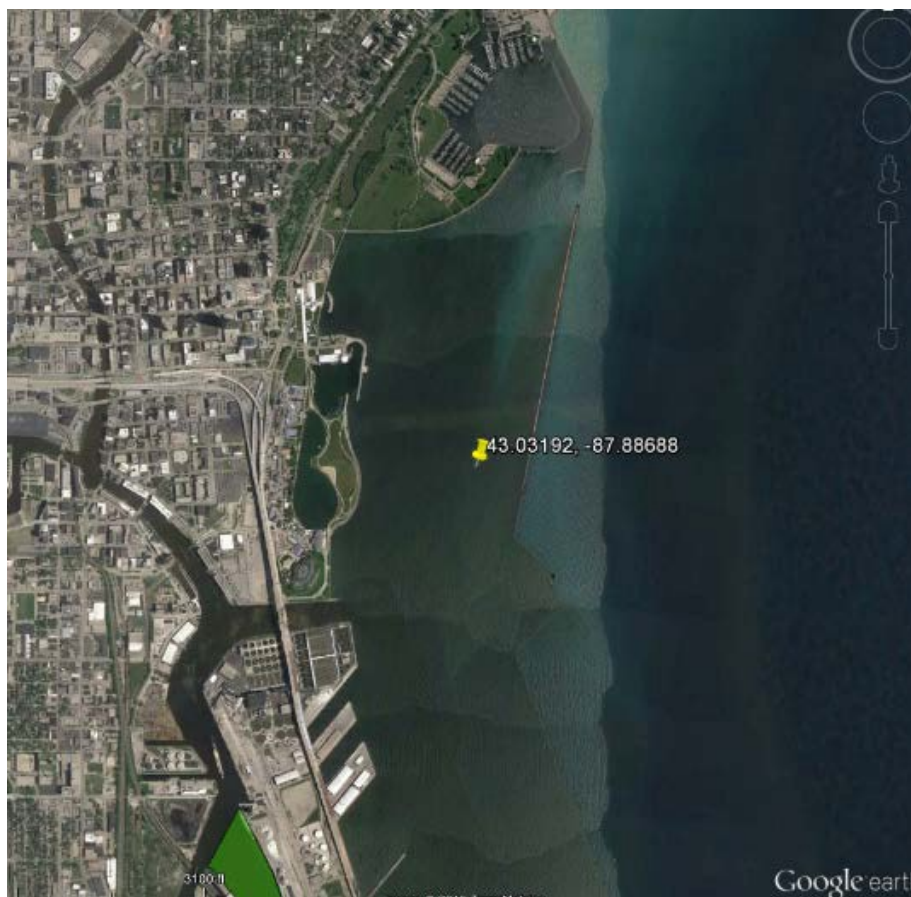
Figure 1. Image of Milwaukee Bay, WI Sampling Area (Google Earth). Individual sampling sites are not provided in this image

2.1.1. Collection Vessels

Ten 10 gallon (3.79 L) stainless steel milk transport cans (Hamby Dairy Supply, Maysville, MO; Product: 30192) were used for sediment storage and transport. These collection vessels were cleaned prior to sediment collection. The silicone gaskets were removed from the stainless-steel lids and cleaned separately with Liqui-Nox detergent (Alconox, White Plains, NY). The gaskets were rinsed three times with tap water followed by two rinses with high purity 18.2 MΩ/cm Milli-Q water (Millipore). The gaskets were then placed on a Bytac sheet and allowed to air dry.

The collection vessels and lids were cleaned with detergent and water as described above; with the addition that following the final high purity water rinse, they were rinsed with acetone and hexane (Honeywell International, Muskegon, MI). The residual solvents were collected and properly disposed of as waste. A low lint Tex-Wipe was placed over the mouth of the vessels and the vessels were allowed to air dry overnight. Once all the supplies were dry, the silicone gaskets were replaced in the lids and the lids were sealed with the vessel's latching system until further use.

2.1.2. Sediment Collection

On the day of collection (May 4, 2016), the weather was overcast with an air temperature of approximately 5 °C and windy. The Mudpuppy II, a U.S. EPA research ship, equipped with a Ponar grab sampler and crane, was used for sediment collection. Due to space restrictions aboard the ship, the sediment was collected in three batches. Following collection of each batch, the collection vessels were taken ashore, loaded in the open bed of a truck, and secured under lock and key.

For sample collection, the Ponar grab was deployed and retrieved from the bow of the ship via a crane, collecting an approximately 50 cm long by 30 cm wide by 20 cm deep sample from the surface of the bay floor with each Ponar grab (Figure 2A). The bay floor was approximately 7.77 m (25.5 ft) below the surface. Excess water was decanted from the top of the Ponar (Figure 2B) and the sample was transferred to a stainless-steel pan (Figure 2C). The sample was then transferred to the collection vessel with a stainless-steel scoop (Figure 2D). Following the fifth Ponar grab sample transfer, the lid of the collection vessel was resealed and the stainless-steel pan and scoop were rinsed with lake water to remove any residual sediment between collections.
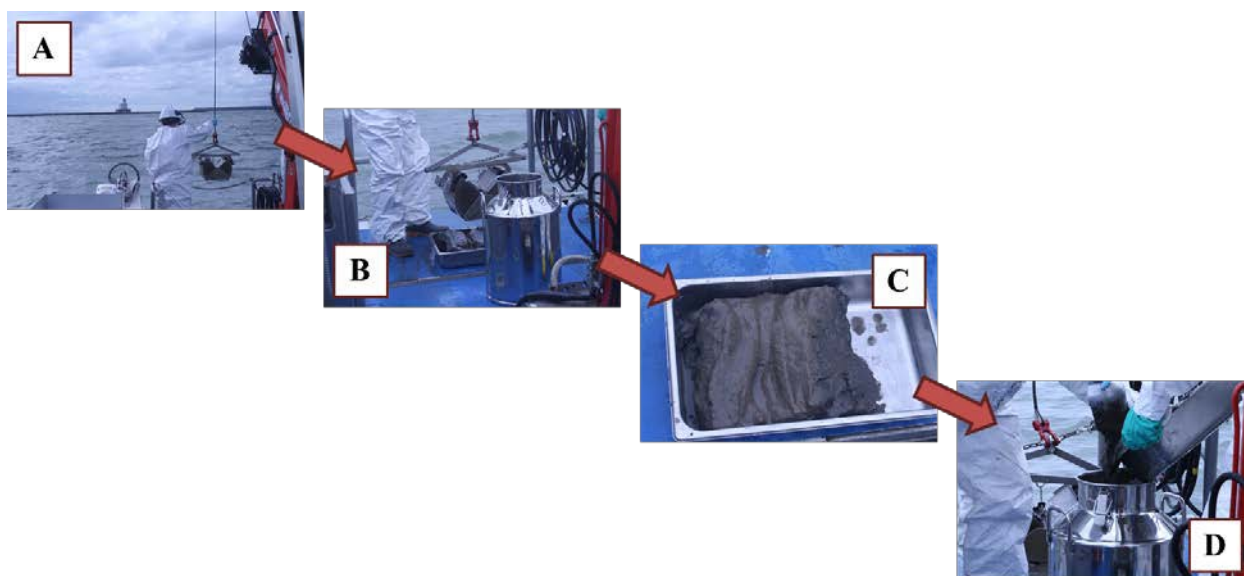
Figure 2. Ponar sampling of sediment from Milwaukee Bay, WI

Following collection, the collection vessels were transported back to Charleston, SC over two days and stored at 4 °C in a walk-in cooler at the Hollings Marine Laboratory until the drying process began. Table 1 lists the time, site, and quantity information for each collection vessel.

Table 1. Collection Times, Location, and Mass Collected

Vessel	Start Time	End Time	Collection Site	Mass kg
1	8:30	8:55	43° 01.9343' N 87° 53.1729' W	48.1
2	8:55	9:15	43° 01.9343' N 87° 53.1729' W	47.9
3	9:15	9:25	43° 01.9343' N 87° 53.1729' W	49.1
4	9:25	9:40	43° 01.9343' N 87° 53.1729' W	48.7
5	10:49	11:00	43° 01.9249' N 87° 53.2010' W	47.8
6	11:00	11:15	43° 01.9249' N 87° 53.2010' W	47.5
7	11:15	11:31	43° 01.9249' N 87° 53.2010' W	48.5
8	14:14	14:27	43° 01.8893' N 87° 53.2286' W	47.9
9	14:27	14:41	43° 01.8893' N 87° 53.2286' W	47.0
10	14:41	14:54	43° 01.8893' N 87° 53.2286' W	49.0

2.2. Sample Preparation

In preparation for drying, metal trays intended for use in the Millrock Quanta Series Freeze Dryer located in NIST's Cryogenic Reference Material Production Facility were transported to the NIST Biosafety Level 2 (BSL2) lab at the Hollings Marine Laboratory, rinsed with acetone and hexane and wiped with Kimwipes in order to remove any debris. Trays were then laid out on the counter.

The next day, two collection vessels of marine sediment were removed from the 4° C walk-in cooler and sediment was spread out on the clean trays to begin the drying process. Each day sediment was stirred and re-spread to promote efficient drying. Once all trays appeared dry, a small aliquot (approximately 5 g) of sediment was taken from each of two trays, one that had been drying consistently quickly and another that had taken a longer time to dry and placed in a 15 mL conical vial (all assessments thus far were made only visually). These aliquots were analyzed in triplicate for moisture content using the CEM SMART Turbo Microwave moisture analyzer. Once the moisture content consistently reached approximately 2 % or below, the sediment was considered "dry" and was scooped into 40 cm x 61 cm plastic bags and stacked in the BSL2 lab.

This process was repeated over a two-month interval until all ten canisters of sediment were emptied, spread and dried. Once all sediment was dried and bagged, 21 plastic bags containing a total of 192 kg dried sediment were numbered, weighed, labeled and stacked in one of five coolers for shipment to the NIST Office of Reference Materials (ORM) in Gaithersburg, MD.

2.2.1. Moisture Evaluation

The CEM SMART Turbo Microwave was operated consistently with an established protocol. Briefly, one piece of balance paper was tared and sediment (0.3 to 0.7) g was added to the balance paper. The moisture content was determined by mass loss upon drying. The following

parameters were used: Power = 100%, Δ weight = 0.1 mg, Δ time = 5 s, Max time = 10 min, Bias = 0 %, and Max temp = 105°C.

2.3. Packaging

At ORM's Gaithersburg facility, the material was sieved to 61 μm and homogenized in a cone blender. This processed material was radiation-sterilized by Neutron Products Inc. (Dickerson MD) with an absorbed dose between 6 kGy and 15 kGy. The material was packaged at the ORM facility in screw-capped amber glass bottles. Each bottle contains approximately 50 g of the final material. A total of 2985 bottles were produced. A unit of SRM 1936 consists of one of these bottles.

3. Per- and polyfluoroalkyl substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) are persistent compounds found in a variety of matrices worldwide [1]. With the ever-increasing number of laboratories measuring PFAS in environmental media, measurement proficiency is important.

Quantitative measurements of PFAS in ten randomly stratified bottles of the SRM 1936 material were analyzed to determine homogeneity. Table 2 lists the codes and bottling sequence numbers for these samples.

Table 2. Sample Codes and Bottle Numbers

Sample	Bottle	Sample	Bottle
SRM 1936-1	1	SRM 1936-6	509
SRM 1936-2	147	SRM 1936-7	1686
SRM 1936-3	2861	SRM 1936-8	584
SRM 1936-4	498	SRM 1936-9	1029
SRM 1936-5	241	SRM 1936-10	2985

3.1. Materials

A seven-point calibration curve, ranging from 0.1 ng/g to 100 ng/g was prepared from three independent weighings of NIST RM 8446 Perfluorinated Carboxylic Acids and Perfluorooctane Sulfonamide in Methanol and RM 8447 Perfluorinated Sulfonic Acids in Methanol. The internal standard (IS) solution was prepared by diluting a solution containing eleven isotopically-labeled PFAS in methanol. Table 3 lists the IS used for the analytes considered in this report.

Table 3. PFAA Analytes, Acronyms, and Internal Standards

PFAA	Acronym	IS
Perfluorobutanoic acid	PFBA	$^{13}C_4$-PFBA
Perfluoropentanoic acid	PFPeA	$^{13}C_2$-PFHxA
Perfluorohexanoic acid	PFHxA	$^{13}C_8$-PFOA
Pentadecafluorooctanoic acid	PFOA	$^{13}C_8$-PFOA
Perfluorononanoic acid	PFNA	$^{13}C_9$-PFNA
Perfluorodecanoic acid	PFDA	$^{13}C_9$-PFDA
Perfluoroundecanoic acid	PFUnA	$^{13}C_2$-PFUnA
Perfluorododecanoic acid	PFDoA	$^{13}C_2$-PFDoA
Perfluorotridecanoic acid	PFTriA	$^{13}C_2$-PFDoA
Perfluorotetradecanoic acid	PFTA	$^{13}C_2$-PFDoA
Perfluorobutane sulfonate	PFBS	$^{18}O_2$-PFBS
Perfluorohexane sulfonate	PFHxS	$^{18}O_2$-PFHxS
Perfluorooctane sulfonate	PFOS	$^{13}C_4$-PFOS
Perfluorooctane sulfonamide	PFOSA	$^{18}O_2$-PFOSA

NIST SRMs 1941b Organics in Marine Sediment, 1944 New York/New Jersey Waterway Sediment, and 2585 Organic Contaminants in House Dust were used as control materials for this analysis. The PFAS measurements were compared to values previously measured to determine the consistency of the analysis method [1].

3.2. Sample Preparation
The calibrants, 1.0 g water (used as blank), 0.5 g SRM 2585 and 2 g of SRMs1941b, 1944, and 1936 were weighed into 50 mL polypropylene tubes and spiked with 600 μL of the IS mixture. Tubes were vortexed for 10 s and allowed to equilibrate for 1.5 h. Five mL of 0.1 mol/L potassium hydroxide in methanol was added to the samples and the samples were sonicated for 30 min. The samples were centrifuged (at room temperature) for 5 min at 262 rad/s (2500 rpm). The supernatant was transferred to a pre-cleaned 15 mL polypropylene tube using a glass pipet and evaporated under nitrogen to approximately 1 mL.

The resulting solutions were cleaned up further using established solid phase extraction (SPE) methods. In brief, the sample was loaded into a preconditioned Supelco Supelclean ENVI-Carb SPE column (3 mL, 250 mg, (120 to 400) mesh; Bellefonte, PA) using RapidTrace workstation modules. The SPE fractions were evaporated at 35 °C to 1 mL and the extracts transferred to autosampler vials for analysis via liquid chromatography coupled with a tandem mass spectrometer (LC-MS/MS).

3.3. Instrumental method
Samples (5 μL) were injected onto a Phenomenex Kinetex PFP analytical column, (3 mm × 50 mm × 2.6 μm). The solvent gradient flow started at 25:75 volume fraction (20 mmol/L ammonium acetate in methanol):(20 mmol/L ammonium acetate in water) at a flow rate of 150 μL/min. The proportion of the methanol solution increased to 28.5:71.5 by 4.2 min, 55:45 methanol by 55 min and was held for 5 min. The methanol proportion was then increased to 62.5:37.5 by 22 min, 87.5:12.5 by 52 min, and to 100 % methanol by 55 min and was held for 5 min. The gradient reverted back to the starting conditions of 25:75 methanol at 60 min with a 10 min hold time.

The autosampler held the samples at 18 °C prior to LC analysis (Agilent 1100 HPLC) interfaced to MS/MS (API 4000, Applied Biosystems-MDS Sciex). The Scheduled MRM feature of the Analyst 1.5.2 software was used to improve the reproducibility and quantitation.

3.4. Quantification

Levels of each PFAS in the SRMs and the samples were calculated using the linear equation of the calibration curve, not forcing the intercept through zero. The calibration curves for all of the analytes were linear with R^2 values ≥ 0.99. Compounds were quantified using a relative response ratio to an internal standard compound that most closely matched the compound (Table 3). The limits of quantitation (LOQ) were determined as the maximum value of either the average mass (in ng) measured in the extract plus three times the standard deviation of the blanks or the lowest calibrant detected, all divided by the mass (in g) of extracted sample. Final concentrations are totals including branched and linear isomers.

3.4.1. Comparison to Controls

Table 4 compares results for SRMs 1941b and 1944 from the current study to those from a preliminary study in 2012. PFAS levels in these materials are very low, mostly below the limits of quantification.

Table 4. Comparison of Current Results to 2012 Analyses for SRMs 1941b and 1944
All values are in units of ng/g. "<" values are the mean of individual LOD determinations.

| Analyte | SRM 1941b | | | SRM 1944 | | | |
| | Current, n=3 | | 2012, n=6 | Current, n=3 | | 2012, n=6 | |
	Mean	SD	Mean	Mean	SD	Mean	SD
PFBA	<0.6		<1.1	<0.3		<1.2	
PFPeA	<0.8		<0.3	<0.5		<0.3	
PFHxA	<0.9		<0.9	<0.5		<1.0	
PFOA	0.022	0.012	<0.3	0.949	0.073	<0.3	
PFNA	<0.01		<0.3	<0.005		<0.3	
PFDA	<0.01		<0.3	<0.005		<0.3	
PFUnA	0.108	0.011	<1.0	0.473	0.020	<1.2	
PFDoA	<0.01		<1.0	<0.005		<1.1	
PFTriA	0.129	0.033	<0.3	0.856	0.070	3.8	1.0
PFTA	<0.01		<0.3	0.203	0.020	<0.3	
PFBS	3.53	0.74	<0.3	1.26	0.49	<0.4	
PFHxS	<0.1		<0.3	0.273	0.041	<0.3	
PFOS	0.424	0.022	<0.5	1.113	0.038	0.96	0.25
PFOSA	<0.01		<0.3	<0.04		<0.4	

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Table 5 compares results for SRM 2585 from the current study to those from analyses performed in 2011 and 2012. The results for the much higher PFAS levels in this material are similar across the studies.

Table 5. Comparison of Current Results to 2011 and 2012 Analyses for SRM 2585
All values are in units of ng/g

Analyte	Current Results					2012, n=6		2011, n=6	
	Rep$_1$	Rep$_2$	Rep$_3$	Mean	SD	Mean	SD	Mean	SD
PFBA	222	207	221	216.7	8.4	265	38	218	17
PFPeA	207	215	208	210.0	4.4	195	15	179	13
PFHxA	404	375	378	386	16	251	20	236	18
PFOA	693	699	722	705	15	626	30	430	25
PFNA	82	81.6	82.7	82.10	0.56	95.9	5.1	103	8
PFDA	60.2	63	67	63.4	3.4	47.6	4.8	23.9	1.3
PFUnA	43.5	44.3	46.7	44.8	1.7	55.8	13.7	45.2	4
PFDoA	34.4	33.9	35.4	34.57	0.76	40.6	5.8	34.3	4.2
PFTriA	28.7	29.2	31.4	29.8	1.4	27.9	5.4	29.3	1.5
PFTA	22.8	23	25.3	23.7	1.4	22.4	6	10.7	1.2
PFBS	18.5	16.3	16.2	17.0	1.3	130	12	21.1	1.0
PFHxS	1777	1736	1663	1725	58	1343	106	1166	71
PFOS	2584	2471	2448	2501	73	2412	510	2025	107
PFOSA	16.2	15.3	15.6	15.70	0.46	11.6	0.8	7.78	0.48

3.4.2. Evaluation of SRM 1936

Table 6 lists the mean LOQs for nine PFAS in SRM 1936 that are present at or below current detection limits in all or the majority of the ten samples.

Table 6. Limits of Quantification (LOQ) for Selected PFAS in SRM 1936
All values are in units of ng/g. "<" values are the mean of ten individual LOQ determinations.

Analyte	Mean LOQ
PFBA	<0.3
PFPeA	<0.4
PFHxA	<0.4
PFOA	<0.008
PFNA	<0.005
PFDA	<0.004
PFDoA	<0.004
PFBS	<0.02
PFOSA	<0.005

Table 7 lists the quantitative results for the five PFAS present above LOQ in all SRM 1936 samples.

Table 7. Quantitative Results for PFAS in SRM 1936, Wet-Mass Basis
Measurement results are in units of ng/g

Sample	PFUnA	PFTriA	PFTA	PFHxS	PFOS
SRM1936-1	0.077	0.124	0.106	0.107	0.788
SRM1936-2	0.059	0.121	0.085	0.111	0.834
SRM1936-3	0.072	0.126	0.095	0.081	0.757
SRM1936-4	0.069	0.124	0.100	0.098	0.768
SRM1936-5	0.075	0.133	0.093	0.101	0.794
SRM1936-6	0.068	0.116	0.091	0.096	0.767
SRM1936-7	0.077	0.121	0.083	0.080	0.715
SRM1936-8	0.069	0.119	0.091	0.084	0.774
SRM1936-9	0.077	0.117	0.094	0.106	0.742
SRM1936-10	0.073	0.106	0.087	0.078	0.710
Mean	0.072	0.121	0.093	0.094	0.765
SD	0.006	0.007	0.007	0.012	0.037
%CV	7.9	5.9	7.5	13	4.8

3.4.3. Conversion from a Wet- to a Dry-Mass Basis

The quantitative results listed in Table 7 are calculated on a wet-mass basis. After they were run, a dry-mass conversion factor was obtained by weighing out six samples of approximately 1 g sample into weigh boats that had been cleaned with hexane and dried. The samples were dried in a drying oven at 105 °C for 24 hours and then reweighed. The mass loss was calculated and the results were adjusted to the dry weight for all calculations. The mean percentage loss for the six SRM 1936 samples was 1.82 % with a standard deviation (SD) of 0.059 %. Table 8 summarizes the conversion.

Table 8. Conversion of PFAAs Results to a Dry-Mass Basis
Measurement results are in units of ng/g

Analyte	Wet Mass		Dry Mass	
	Mean	SD	Mean	SD
PFUnA	0.072	0.006	0.073	0.006
PFTriA	0.121	0.007	0.123	0.007
PFTA	0.093	0.007	0.095	0.007
PFHxS	0.094	0.012	0.096	0.012
PFOS	0.765	0.037	0.779	0.038

3.5. Homogeneity Evaluation

Figure 3 displays the quantitative results for these five PFAS (Tables 7 and 8) in bottling sequence. The panel to the left indicates that the level of PFOS, the most abundant PFAS in SRM 1936, may have declined slightly with production. The panel to the right suggests that the levels PFTriA, PFTA and PFHxS similarly declined while the level of PFUnA is essentially constant across the samples. Given the relatively small changes in the fractional ng/g levels of these analytes, the SRM 1936 material appears to be fit-for-purpose homogeneous with regard to PFAS content.
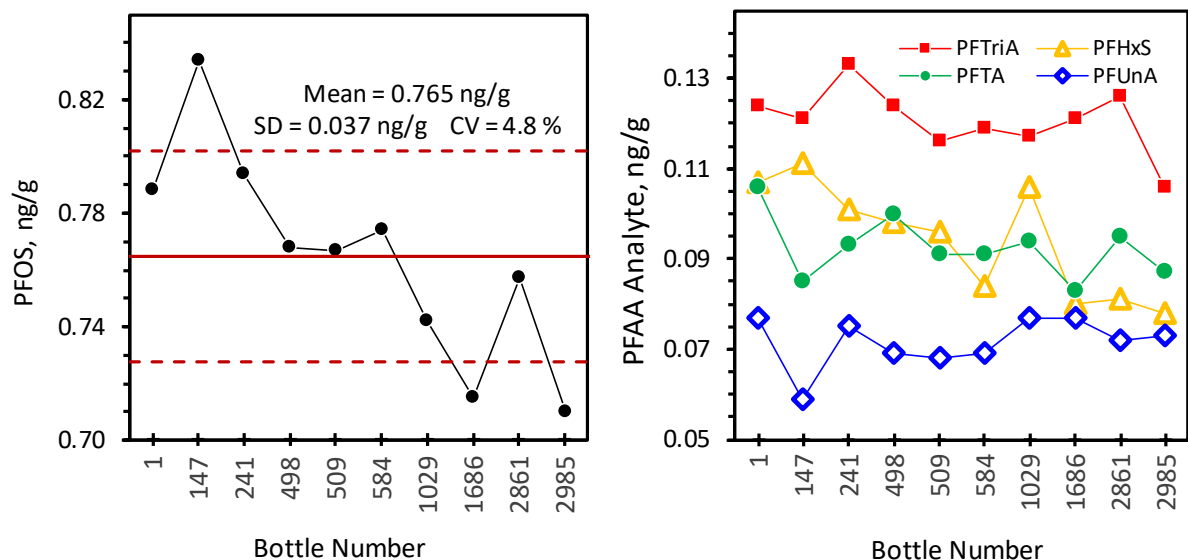
Figure 3. Quantitative Results for Selected PFAAs in SRM 1936

The solid line in the left-hand panel for PFOS represents the mean of the ten measurements; the dashed lines bracket the interval [Mean – SD, Mean + SD].

4. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) contain only carbon and hydrogen and are composed of multiple aromatic rings. They are generated during the incomplete combustion of coal, oil, wood, and other organic fuels. PAHs are highly lipid soluble and accumulate in body fat. PAHs are ubiquitous environmental contaminants that pose significant risk to the health of marine species [2].

The analysis of PAHs in SRM 1936 is based on extractions using two solvent systems and analysis using two gas chromatography with mass spectrometric detection (GC-MS) methods.

4.1. Materials

Calibration solutions were prepared from SRM 2260a Aromatic Hydrocarbons in Toluene and SRM 1491a Methyl-Substituted Polycyclic Aromatic Hydrocarbons in Toluene. These solutions contained both unalkylated and alkylated PAHs. Three solutions with the highest concentrations of compounds (called Cals A-C) were prepared independently by gravimetrically combining aliquots of SRM 2260a and SRM 1491a. A portion of Cal A was gravimetrically diluted to make Cal D, Cal B was gravimetrically diluted to make Cal E, and Cal C was gravimetrically diluted to make Cal F. These calibration solutions provided a six-point calibration curve with PAH concentrations ranging from approximately (2 to 5000) ng prior to extraction.

A mixed internal standard (IS) solution was prepared from SRM 2269 Perdeuterated PAH-I Solution in Hexane/Toluene and SRM 2270 Perdeuterated PAH-II Solution in Hexane/Toluene. This IS contained biphenyl-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, benz[a]anthracene-d_{12}, dibenz[a,h]anthracene-d_{14}, naphthalene-d_8, acenaphthene-d_{10}, pyrene-d_{10}, perylene-d_{12}, benzo[a]pyrene-d_{12}, and benzo[ghi]perylene-d_{12}. The IS was added to each sample, calibrant, and blank by weighing to the nearest 0.1 mg (approximately 0.25 mL of the solution), resulting in the addition of a range from approximately (130 to 1200) ng of each of the perdeuterated compounds.

SRM 1944 New York/New Jersey Waterway Sediment was used as the control material.

4.2. Sample Preparation

Calibrants, blanks and SRMs 1944 and 1936 were extracted using a Pressurized Fluid Extractor (PFE) (ASE; Dionex, Salt Lake City, UT) using two extraction solvents, depending on sample preparation method employed. Sample preparation Method One used dichloromethane (DCM); Method Two used a 50% hexane and 50% acetone mixture. The extraction conditions for both methods were: cell temperature = 100 °C, equilibration = 5 min, static time = 5 min, cell pressure = 13.8 MPa. There were three cycles, each using one-third of the solvent. All samples (calibrants, sediment extracts and blanks) were evaporated by nitrogen blow-down (Turbovap, Biotage, Uppsala, Sweden) to approximately 0.5 mL.

Deactivated alumina (5%) clean-ups were performed on both extraction methods with automated SPE workstations (RapidTrace, Caliper Life Sciences, Hopkinton, MA, USA). Extracts were evaporated to 0.5 mL. Three mL cartridges were packed with approximately 3.0 g of alumina 5 % deactivated. Samples were eluted with 10 mL of DCM and hexane.

Samples were then evaporated and solvent exchanged with iso-octane and transferred to autosampler vials with a final volume of approximately 0.5 mL.

4.3. Instrumental Methods
Calibration solutions, blanks, SRM 1944, and SRM 1936 were placed randomly in the injection sequence. Following the injection of the highly concentrated calibrants A, B, and C, a hexane and then an instrument blank was injected to avoid potential carry over to the next sample.

4.3.1. Method One: Restek Rxi-17Sil Column
Method One used an Agilent 6890 gas chromatograph coupled to a 5973 mass spectrometer (Palo Alto, CA) with an electron impact (EI) source. An autosampler injected 2 µL of each extract into a cool on-column inlet and onto a 5 m × 0.25 mm Restek Siltek guard column (Bellefonte, PA) connected to a 0.250 mm × 60 m Restek Rxi-17sil MS capillary column with a film thickness of 25 µm. The GC oven was held at 90 °C for 1.0 min, ramped at 45 °C/min to 150 °C, ramped to 310 °C at 2 °C/min, and held isothermally for 57.67 min. Total run time for each sample was 140 min. Helium was the carrier gas set at a constant flow rate of 1.3 mL/min. Quadrupole, source, and transfer line temperatures were maintained at (150, 230, and 300) °C, respectively.

Table 9 lists the elution order and monitored ions for the PAH analytes using method One. The selective ion monitoring (SIM) ions, windows, and method parameters are displayed in Figure 4.

Table 9. Elution Order and Ions Used to Quantifying and Qualifying PAHs Using Method One

PAH Analyte	Retention Time, min	Quantifier Ion, m/z	Qualifier Ions, m/z
naphthalene-d_8	8.762	136	134
naphthalene	8.833	128	126
2-methylnaphthalene	10.775	142	141
1-methylnaphthalene	11.451	142	141
biphenyl-d_{10}	13.009	164	166
biphenyl	13.152	154	152
1,6-dimethylnaphthalene	13.377	155	141
2,6-dimethylnaphthalene	14.217	156	141
1,2-dimethylnaphthalene	15.693	141	156
acenaphthylene	16.799	152	150
acenaphthene-d_{10}	17.414	164	163
acenaphthene	17.701	154	153
fluorene	21.635	166	164
dibenzothiophene	30.862	184	139
phenanthrene-d_{10}	31.911	188	184
phenanthrene	32.202	178	176
anthracene	32.537	178	176
3-methylphenanthrene	36.596	192	190
2-methylphenanthrene	37.118	192	190
2-methylanthracene	37.355	192	191

PAH Analyte	Retention Time, min	Quantifier Ion, *m/z*	Qualifier Ions, *m/z*
9-methylphenanthrene	38.448	192	191
1-methylphenanthrene	38.744	192	191,189
4-H-cyclopenta[*def*]phenanthrene	38.881	190	192
1,7-dimethylphenanthrene	43.679	206	191,190
pyrene-d_{10}	45.895	212	213,210
pyrene	46.151	202	200
fluoranthene-d_{10}	49.254	212	213,210
retene	49.303	219	234
fluoranthene	49.510	202	200
1-methylpyrene + 4-methylpyrene	52.536	216	215,189,213
3-methylfluoranthene	55.493	216	215
1-methylfluoranthene	55.843	216	215
cyclopenta[*cd*]pyrene	61.713	226	224
benzo[*c*]phenanthrene	61.828	228	227,226,113
benz[*a*]anthracene-d_{12}	63.684	240	242
benzo[*a*]anthracene	63.992	228	226
benzo[*ghi*]fluoranthene	64.991	226	224,113
chrysene + triphenylene	68.682	228	226
3-methylchrysene	69.837	242	240
6-methylchrysene	76.867	242	240
benzo[*k*]fluoranthene	77.124	252	250
benzo[*b*]fluoranthene	77.466	252	250
benzo[*a*]fluoranthene	78.301	252	250
benzo[*j*]fluoranthene	80.811	252	250
benzo[*e*]pyrene	81.053	252	250
benzo[*a*]pyrene-d_{12}	81.360	264	262
benzo[*a*]pyrene	82.351	252	250
perylene-d_{12}	82.664	264	262
perylene	92.378	252	150
dibenz[*a,j*]anthracene	94.141	278	276
dibenz[*a,c*]anthracene	94.163	278	276
dibenzo[*a,h*]anthracene-d_{14}	94.702	292	288
indeno[1,2,3-*cd*]pyrene	96.713	276	277,139
dibenz[*a,h*]anthracene	97.768	278	279,278,139
picene	97.768	278	276
benzo[*b*]chrysene	99.475	278	276
benzo[*ghi*]perylene-d_{12}	100.026	288	292,290
benzo[*ghi*]perylene	102.597	276	278
anthanthrene	122.420	276	274
dibenzo[*a,h*]pyrene	134.560	302	300
dibenzo[*a,e*]pyrene	136.087	302	300
Coronene	132.469	300	150,298,301

OVEN
Initial temp: 90 'C (On)   Maximum temp: 350 'C
Initial time: 1.00 min   Equilibration time: 1.00 min
Ramps:
   # Rate Final temp Final time
   1 45.00   150   0.00
   2 2.00   310   57.67
   3 0.0(Off)
Post temp: 90 'C
Post time: 0.00 min
Run time: 140.00 min

FRONT INLET (SPLIT/SPLITLESS)   BACK INLET (COOL ON COLUMN)
   Mode: Split   Mode: Oven track
   Initial temp: 50 'C (Off)   Pressure: 23.48 psi (On)
   Pressure: 0.00 psi (Off)   Gas type: Helium
                      Total flow: 45.0 mL/min
                    Gas saver: Off
                    Gas type: Helium

COLUMN 1
   Model Number: Restek Rxi-17SilMS
   60m x 0.25 x 0.25
   Max temperature: 340 'C
   Nominal length: 60.0 m
   Nominal diameter: 250.00 um
   Nominal film thickness: 0.25 um
   Mode: constant flow
   Initial flow: 1.2 mL/min
   Nominal init pressure: 23.49 psi
   Average velocity: 29 cm/sec
   Inlet: Back Inlet
   Outlet: MSD
   Outlet pressure: vacuum

THERMAL AUX 2
   Use: MSD Transfer Line Heater
   Initial temp: 300 'C (On)

   GC Injector
     Back Injector:
       Sample Washes   0
       Sample Pumps   6
       Injection Volume   2.00 microliters
       Syringe Size   5.0 microliters
       PreInj Solvent A Washes   3
       PreInj Solvent B Washes   3

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   Plunger Speed   Fast

   MS ACQUISITION PARAMETERS:

Tune File   : atune.u
Acquistion Mode   : SIM
Solvent Delay   : 6.00 min
EMV Mode   : Absolute
Resulting EM Voltage   : 1906

GROUP 1
Group ID   : 1
Resolution   : Low
Plot 1 Ion   : 156.00
Ions/Dwell in Group   (Mass, Dwell) (126.00, 40) (128.00, 40) (134.00, 40)
                (136.00, 40) (138.00, 40) (140.00, 40) (141.00, 40)
                (142.00, 40) (156.00, 40)
GROUP 2
Group ID   : 2
Resolution   : Low
Group Start Time   : 10.40
Plot 1 Ion   : 170.00
Ions/Dwell in Group   (Mass, Dwell) (141.00, 100) (142.00, 100) (150.00, 100)
                (152.00, 100) (153.00, 100) (154.00, 100) (155.00, 100)
                (156.00, 100) (163.00, 100)(164.00, 100) (166.00, 100)
                (170.00, 100)
GROUP 3
Group ID   : 3
Resolution   : Low
Group Start Time   : 25.60
Plot 1 Ion   : 188.00
Ions/Dwell in Group   (Mass, Dwell) (139.00, 40) (176.00, 40) (178.00, 40)
                (184.00, 40) (186.00, 40) (188.00, 40)
GROUP 4
Group ID   : 4
Resolution   : Low
Group Start Time   : 31.50
Plot 1 Ion   : 234.00

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Ions/Dwell In Group   (Mass, Dwell) (187.00, 40) (190.00, 40) (191.00, 40)
                (192.00, 40) (200.00, 40) (202.00, 40) (206.00, 40) (210.00, 40)
                (212.00, 40) (213.00, 40) (214.00, 40) (216.00, 40)
                (219.00,,40) (234.00, 40)
GROUP 5
Group ID   : 5
Resolution   : Low
Group Start Time   : 50.50
Plot 1 Ion   : 242.00
Ions/Dwell In Group   (Mass, Dwell) (113.00, 40) (213.00, 40) (216.00, 40)
                (224.00, 40) (226.00, 40) (227.00, 40) (228.00, 40)
                (239.00, 40) (240.00, 40) (242.00, 40)
GROUP 6
Group ID   : 6
Resolution   : Low
Group Start Time   : 67.50
Plot 1 Ion   : 264.00
Ions/Dwell In Group   (Mass, Dwell) (213.00, 40) (216.00, 40) (226.00, 40)
                (228.00, 40) (240.00, 40) (242.00, 40) (250.00, 40)
                (252.00, 40) (262.00, 40) (264.00, 40)
GROUP 7
Group ID   : 7
Resolution   : Low
Group Start Time   : 85.00
Plot 1 Ion   : 302.00
Ions/Dwell in Group   (Mass, Dwell)(125.00, 40) (138.00, 40) (139.00, 40)
                (150.00, 40) (274.00, 40) (276.00, 40) (277.00, 40)
                (278.00, 40) (279.00, 40) (288.00, 40) (290.00, 40)
                (292.00, 40) (298.00, 40) (300.00, 40) (301.00, 40) (302.00, 40)
[MSZones]
MS Source   : 230 C   maximum 300 C
MS Quad   : 150 C   maximum 200 C

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Figure 4. GC/MS-EI Parameters for Analysis on Restek Rxi-17Sil Column

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4.3.2. Method Two: Sigma SLB_ILPAH 20 m Column

Method Two also used an Agilent 6890 gas chromatograph coupled to a 5973 mass spectrometer with an EI source. An autosampler injected 0.5 µL of each extract into a cool on-column inlet and onto a 5 m × 0.25 mm Restek Siltek guard column connected to a 0.180 mm × 20 m Supelco SLB_ILPAH capillary column (St. Louis, MO) with a 0.05 µm film thickness. The GC oven was held at 110 °C for 0.5 min, ramped at 5 °C/min to 175 °C held for 5 min, ramped at 6 °C/min to 250 °C held for 3 min, ramped at 45 °C/min to 275 °C held for 10 min, ramped at 45 °C/min to 290 °C held for 10 min, and ramped at 45 °C/min to 300 °C held for 10 min. Total run time for each sample was 65.11 min. Helium was the carrier gas set at a constant flow rate of 1.3 mL/min. Quadrupole, source, and transfer line temperatures were maintained at (150, 230, and 300) °C respectively.

Table 10 lists the elution order and monitored ions for the PAH analytes using method Two. The selective ion monitoring (SIM) ions, windows, and method parameters are displayed in Elution order and monitored ions are listed in Table 3. The SIM ions, windows, and method parameters are displayed in Figure 5.

Table 10. Elution Order and Ions Used to Quantify and Qualify PAHs Using Method Two

PAH Analyte	Retention Time, min	Quantifier Ion, m/z	Qualifier Ions, m/z
naphthalene	2.833	128	126,127
naphthalene- d_8	2.856	136	134
2-methylnaphthalene	3.702	142	141
1-methylnaphthalene	3.782	142	141
biphenyl	4.257	154	153,152
biphenyl-d_{10}	4.310	164	162
1,6-dimethylnaphthalene	4.891	156	141,155
1,2-dimethylnaphthalene	4.961	156	141,155
2,6-dimethylnaphthalene	5.525	141	156,139
acenaphthene	5.851	153	154
acenaphthene-d_{10}	5.868	164	162
acenaphthylene	7.269	152	153
fluorene	8.299	166	164
dibenzothiophene	12.487	184	139,185
phenanthrene	14.042	178	176
phenanthrene-d_{10}	14.126	188	184
anthracene	14.189	178	176
4-H-cyclopenta[*def*]phenanthrene	16.027	190	189
3-methylphenanthrene	16.457	192	191,189
1-methylphenanthrene	16.647	192	191,189
2+9-methylphenanthrene + 2-methylanthracene	16.983	192	191
1,7-dimethylphenanthrene	20.522	206	191,189
retene	22.460	216	219,234
pyrene	23.489	202	200
pyrene-d_{10}	23.612	212	213,210
fluoranthene	24.422	202	200
fluoranthene-d_{10}	24.536	212	213,210

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PAH Analyte	Retention Time, min	Quantifier Ion, m/z	Qualifier Ions, m/z
3-methylfluoranthene	25.715	216	215,213
1-methylfluoranthene	25.988	216	215,213
1-methylpyrene	26.666	216	215,189,213
4-methylpyrene	26.780	216	215,189,213
benzo[c]phenanthrene	28.432	228	227,113
benzo[ghi]fluoranthene	29.705	226.1	224.1,113
benz[a]anthracene	30.476	228	226,113
benz[a]anthracene-d_{12}	30.570	240	242
chrysene	30.601	228	226,113
triphenylene	30.714	228	226,113
cyclopenta[cd]pyrene	31.072	226	113,224,227
3-methylchrysene	31.993	242	240
6-methylchrysene	32.213	242	240
benzo[b]fluoranthene	35.952	252	250
benzo[k]fluoranthene	36.071	252	250
benzo[j]fluoranthene	36.195	252	250
benzo[a]fluoranthene	36.419	252	250
benzo[a]pyrene + benzo[e]pyrene	37.096	252	250
benzo[a]pyrene-d_{12}	37.188	264	260,132
perylene	37.774	252	150
perylene-d_{12}	37.883	264	260,132
picene	43.102	278	276
dibenz[a,c]anthracene + dibenz[a,h]anthracene + dibenz[a,j]anthracene	44.395	278	276
dibenzo[a,h]anthracene-d_{14}	44.595	292	288
anthanthrene + indeno[1,2,3-cd]pyrene	44.952	276	274,278
benzo[b]chrysene	45.089	278	276
benzo[ghi]perylene	46.234	276	277,278
benzo[ghi]perylene-d_{12}	46.392	288.2	292
dibenzo[a.e]pyrene	55.953	302	300
coronene	58.160	300.1	150,301,298
dibenzo[b,k]fluoranthene	58.398	302	300

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```
OVEN
Initial temp:  110 'C (On)          Maximum temp:  350 'C
Initial time:  0.50 min            Equilibration time:  0.50 min
Ramps:
   # Rate Final temp  Final time   CRYO (N2)
   1  5.00    175       5.00      Cryo:  Off
   2  6.00    250       3.00      Cryo fault:  Off
   3 45.00    275      10.00      Cryo timeout:  120.00 min (Off)
   4 45.00    290      10.00      Quick cryo cool:  Off
   5 45.00    300      10.00      Ambient temp:  25 'C
   6  0.0(Off)
Post temp:  110 'C
Post time:  0.00 min
Run time:  65.11 min

FRONT INLET (HP PTV)         BACK INLET (COOL ON COLUMN)
Mode:  Split                Mode:  Oven track
Initial temp:  50 'C (Off)       Pressure:  34.80 psi (On)
Cryo:  Off                 Gas type:  Helium
Cryo use temp:  25 'C
Cryo Timeout:  30.00 min (On)
Cryo Fault:  On
Pressure:  0.00 psi (Off)
Total flow:  45.0 mL/min
Gas saver:  Off
Gas type:  Helium


COLUMN 1              COLUMN 2
Capillary Column            (not installed)
Model Number:  supelco SLB_ILPAH
Fused Silica
Max temperature:  300 'C
Nominal length:  20.0 m
Nominal diameter:  180.00 um
Nominal film thickness:  0.05 um
Mode:  constant flow
Initial flow:  1.3 mL/min
```

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```
Nominal init pressure: 34.82 psi
Average velocity:  49 cm/sec
Inlet:  Back Inlet
Outlet:  MSD
Outlet pressure:  vacuum

THERMAL AUX 2
  Use:  MSD Transfer Line Heate
  Initial temp:  300 'C (On)


                 GC Injector
   Back Injector:
       Sample Washes          0
       Sample Pumps           3
       Injection Volume        0.50 microliters
       Syringe Size          5.0 microliters
       PreInj Solvent A Washes    3
       PreInj Solvent B Washes    3
       PostInj Solvent A Washes   3
       PostInj Solvent B Washes   3
       Viscosity Delay         0 seconds
       Plunger Speed          Slow
       PreInjection Dwell       0.00 minutes
       PostInjection Dwell      0.00 minutes

              MS ACQUISITION PARAMETERS

Tune File        : atune.u
Acquistion Mode     : SIM
Solvent Delay      : 2.50 min
EMV Mode         : Relative
Relative Voltage     : 0
Resulting EM Voltage   : 1918
GROUP 1
Group ID         : 1
Resolution        : Low
Plot 1 Ion        : 126.00
Plot 2 Ion        : 136.0
Ions/Dwell In Group      (Mass, Dwell) (126.00, 50) (127.00, 50) (128.00, 50)
                  (134.00, 50) (136.00, 50)
```

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```
GROUP 2
Group ID          : 2
Resolution         : Low
Group Start Time      : 3.25
Plot 1 Ion         : 142.00
Plot 2 Ion         : 154.0
Ions/Dwell In Group    (Mass, Dwell) (76.00, 50) (115.00, 50) (141.00, 50) (142.00, 50)
                  (152.00, 50) (153.00, 50) (154.00, 50) (156.00, 50) (162.00, 50)
                  (164.00, 50)
GROUP 3
Group ID          : 3
Resolution         : Low
Group Start Time      : 6.60
Plot 1 Ion         : 152.00
Plot 2 Ion         : 164.0
Ions/Dwell In Group    (Mass, Dwell) (152.00, 50) (153.00, 50) (154.00, 50)
                  (164.00, 50) (166.00, 50)
GROUP 4
Group ID          : 4
Resolution         : Low
Group Start Time      : 12.00
Plot 1 Ion         : 184.00
Plot 2 Ion         : 178.0
Ions/Dwell In Group    (Mass, Dwell) ( 89.00, 50) ( 95.00, 50) (139.00, 50)
                  (176.00, 50) (178.00, 50) (184.00, 50) (188.00, 50) (189.00, 50)
                  (190.00, 50) (191.00, 50) (192.00, 50) (206.00, 50)
GROUP 5
Group ID          : 5
Resolution         : Low
Group Start Time      : 21.50
Plot 1 Ion         : 219.00
Plot 2 Ion         : 213.0
Ions/Dwell In Group    (Mass, Dwell)(189.00, 50) (200.00, 50) (202.00, 50)
                  (210.00, 50) (212.00, 50) (213.00, 50) 215.00, 50) (216.00, 50)
                  (219.00, 50) (234.00, 50)
```

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```
GROUP 6
Group ID          : 6
Resolution         : Low
Group Start Time      : 27.50
Plot 1 Ion         : 228.00
Plot 2 Ion         : 227.0
Ions/Dwell In Group    (Mass, Dwell)(113.00, 50) (224.00, 50) (226.00, 50)
                  (227.00, 50) (228.00, 50) (240.00, 50) (242.00, 50)
GROUP 7
Group ID          : 7
Resolution         : Low
Group Start Time      : 34.00
Plot 1 Ion         : 252.00
Plot 2 Ion         : 264.0
Ions/Dwell In Group    (Mass, Dwell) (132.00, 50) (250.00, 50) (252.00, 50)
                  (260.00, 50) (264.00, 50)
GROUP 8
Group ID          : 8
Resolution         : Low
Group Start Time      : 40.00
Plot 1 Ion         : 279.00
Plot 2 Ion         : 277.0
Ions/Dwell In Group    (Mass, Dwell)(138.00, 50) (139.00, 50) (150.00, 50)
                  (274.00, 50) (276.00, 50) (277.00, 50) (278.00, 50) (279.00, 50)
                  (288.00, 50) (292.00, 50) (300.00, 50) (302.00, 50)

GROUP 9
Group ID          : 9
Resolution         : Low
Group Start Time      : 51.00
Plot 1 Ion         : 300.00
Plot 2 Ion         : 298.0
Ions/Dwell In Group    (Mass, Dwell)(150.00, 50) (298.00, 50) (300.00, 50)
                  (301.00, 50) (302.00, 50)


[MSZones]
MS Source        : 230 C   maximum 300 C
MS Quad          : 150 C   maximum 200
```

Figure 5. GC/MS-EI Parameters for Analysis on Sigma SLB_ILPAH 20 m Column

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4.3.3. Conversion from a Wet- to a Dry-Mass Basis

Results were initially calculated on a wet-mass basis. After they were run, a dry-mass conversion factor was obtained by weighing out six samples of approximately 1 g sample into weigh boats that had been cleaned with hexane and dried. The samples were dried in a drying oven at 105 °C for 24 hours and then reweighed. The mass loss was calculated and the results were adjusted to the dry weight for all calculations. The mean percentage loss for the six SRM 1936 samples was 1.642 % with a standard deviation (SD) of 0.056 %.

4.4. Quantitation

Using NIST's Environmental Metrology Measurement Assistant (EMMA) [3], amounts of each analyte were calculated using the slope and floating *y*-intercept of at least a three-point calibration curve that bracketed the peak area ratios observed in the extracts. Mass fractions were determined by dividing the calculated mass of each analyte by the extracted sample mass. LOQs were determined as the maximum value of either the average mass (in ng) measured in the extract plus three times the standard deviation of the blanks or the lowest calibrant detected, all divided by the mass (in g) of the extracted sample.

4.4.1. Comparison to Control

Table 11 lists values derived from the certified and "reference" (non-certified) values provided in the of SRM 1944 Certificate of Analysis (COA) and the summary results for the triplicate analyses of SRM 1944 using methods One and Two.

Figure 6 compares the method One and Two results with those derived from the COA. Due to different number of analytes determined in each method, there are 42 comparisons for method One but 34 for method Two. The median ratio between the COA values and the measurement results for both methods is 1.2; that is, half of the measurement results for both methods are within a factor of 1.2 smaller and 1.2 larger than the values derived from the SRM 1944 COA. All of the method Two results are within a factor-of-two of the COA values. However, two of the method One results are less than one-half of the COA values and seven are more than twice the COA values. The values outside this factor-of-two window shown in Figure 6 are labeled with the code given in Table 11.

Given that the majority of the measurement results for the SRM 1944 control agree with values stated on the COA, the two methods can be used to value-assign PAH analytes when the results are in good agreement (the values determined were within the expanded uncertainty).

Table 11. SRM 1944 Values from Certificate and Method One and Two Results
All values are in units of ng/g

Code[a]	PAH Analyte	SRM 1944 Value	SRM 1944 U_{95}	Method One, n=3 Mean	Method One, n=3 SD	Method Two, n=3 Mean	Method Two, n=3 SD
C01	dibenz[*a,c*]anthracene	335	13	444	29		
C02	dibenz[*a,h*]anthracene	424	69	997	55		
C03	dibenz[*a,j*]anthracene	500	44	4122	369		
C04	picene	518	93	835	27	385	47
C05	benzo[*b*]chrysene	630	100	1036	32	650	80
C06	benzo[*c*]phenanthrene	760	100	804	19	727	16
C07	benzo[*a*]fluoranthene	780	120	605	34	798	88
C08	triphenylene	1040	270			1565	14
C09	perylene	1170	240	1014	60	959	76
C10	dibenz[*a,c*]anthracene + dibenz[*a,h*]anthracene + dibenz[*a,j*]anthracene	1259	126	5563	374	1325	154
C11	benzo[*j*]fluoranthene	2090	440	1956	95	1948	332
C12	benzo[*k*]fluoranthene	2300	200	2369	117	2047	376
C13	indeno[1,2,3-*cd*]pyrene	2780	100	647	39		
C14	benzo[*ghi*]perylene	2840	100	3020	150	2768	334
C15	benzo[*e*]pyrene	3280	110	1869	93		
C16	benzo[*b*]fluoranthene	3870	420	3618	173	3450	632
C17	benzo[*a*]pyrene	4300	130	2238	161		
C18	benzo[*a*]anthracene	4720	110	6873	193	6678	48
C19	chrysene	4860	100			6330	83
C20	phenanthrene	5270	220	5355	207	5306	217
C21	chrysene + triphenylene	5900	260	19669	395	7289	112
C22	fluoranthene	8920	320	8406	277	8987	162
C23	pyrene	9700	420	9502	394	9826	204
N01	dibenzo[*a,h*]pyrene	110	10	351	33		
N02	biphenyl	250	20	235	9	155	13
N03	1-methylfluoranthene	390	10	788	22	297	2
N04	acenaphthene	390	30	317	9	282	13
N05	1-methylnaphthalene	470	20	411	49	320	16
N06	fluorene	480	40	426	20	254	20
N07	dibenzothiophene	500	30	505	24	541	13
N08	coronene	530	40	559	40	260	2
N09	3-methylfluoranthene	560	20	1431	50	527	13
N10	2-methylanthracene	580	40	629	9		
N11	1,7-dimethylphenanthrene	620	20	1234	35	954	49
N12	dibenzo[*a,e*]pyrene	670	50	423	38	1329	137
N13	2-methylnaphthalene	740	60	929	75	431	34
N14	anthanthrene	900	100	5599	469		
N15	anthracene	1130	70	1116	45	843	115
N16	naphthalene	1280	40	1358	25	858	32
N17	1-methylpyrene	1290	30			1341	52
N18	4-methylpyrene	1440	30			845	10
N19	9-methylphenanthrene	1600	200	1373	7		
N20	1-methylphenanthrene	1700	100	1502	4	1514	81
N21	2-methylphenanthrene	1900	60	1960	43		
N22	3-methylphenanthrene	2100	100	2103	5	2032	62
N23	4-methylpyrene + 1-methylpyrene	2730	60	1173	45		

a SRM 1944 values for PAHs C01 to C23 are derived from certified values, those for PAHs N01 to N23 are derived from "reference" (non-certified) values. Within each group PAHs are ordered by increasing SRM 1944 value.
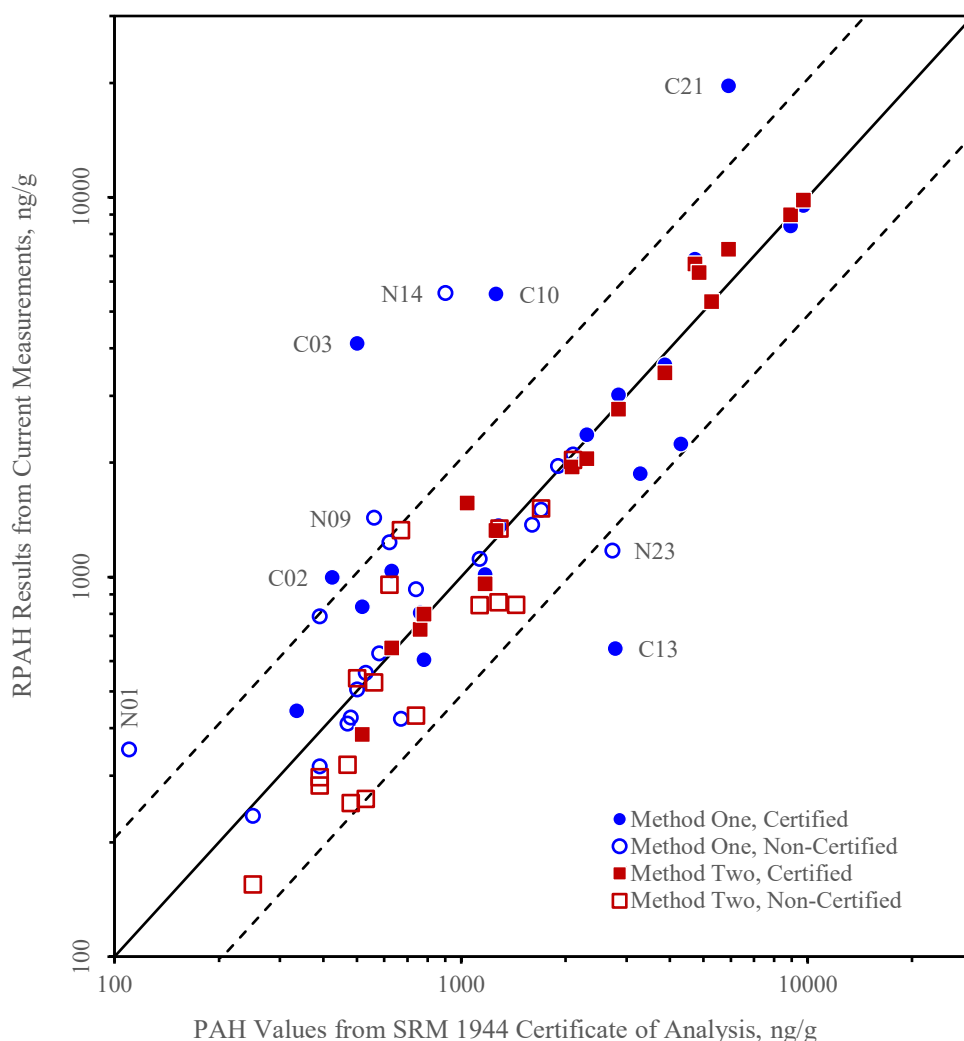
Figure 6. Comparison of SRM 1944 Values with Method One and Two Results

The solid diagonal line represents equality between the measurement results and the values derived from the SRM 1944 Certificate of Analysis (COA). The bracketing dashed lines represent the factor-of-two window about equality (i.e., results between half and twice the COA values). PAH results that are outside this window are labelled with the code provided in Table 11.

4.4.2. Measurement Results

Table 12 lists the method One results for six SRM 1936 bottles and the mean and standard deviation summary. It also lists the mean LOQ for each of the PAH analytes as determined from the analysis of three blanks. Table 13 likewise lists the Method Two results.

Table 14 compares the summary results for the 31 PAH analytes in-common between methods One and Two. The variability among the results for each set of six samples is characterized as the standard uncertainty of the mean, u(Mean), rather than the standard deviation (SD): u(Mean) = SD/$\sqrt{6}$. The analytes are ordered by the ratio between the result from method One divided by that from method Two.

Table 12. Measurement Results for SRM 1936 (Dry-Mass Basis) from Method One
All values are in units of ng/g

PAH Analyte	Mean LOD	241	498	593	710	2419	2861	Mean	SD
		SRM 1936 Bottle Numbers							
naphthalene	<25	133	114	152	128	126	102	126	17
2-methylnaphthalene	<4	74	63	90	71	72	56	71	11
1-methylnaphthalene	<4	44	38	47	43	41	34	41	5
biphenyl	<12	20	18	25	20	24	18	21	3
1,6-dimethylnaphthalene	<81	<74	<79	<81	<77	<80	<82		
2,6-dimethylnaphthalene	<3	51	45	55	50	48	40	48	5
1,2-dimethylnaphthalene	<4	<4	<4	16	18	<4	<4	17	2
acenaphthylene	<14	24	19	28	22	22	19	23	3
acenaphthene	<12	76	<12	<12	<11	<12	<12		
fluorene	<10	103	91	103	98	93	82	95	8
dibenzothiophene	<9	56	50	55	55	50	47	52	4
phenanthrene	<27	1233	1142	1135	1213	1135	1023	1147	74
anthracene	<8	218	198	202	213	199	175	201	15
3-methylphenanthrene	<5	167	152	152	162	154	134	154	11
2-methylphenanthrene	<5	221	199	200	214	202	176	202	15
2-methylanthracene	<3	92	82	82	87	81	72	83	7
9-methylphenanthrene	<5	119	105	107	115	108	92	108	9
1-methylphenanthrene	<5	138	124	126	134	125	107	126	11
4-H-cyclopenta[*def*]phenanthrene	<6	219	203	198	216	207	180	204	14
1,7-dimethylphenanthrene	<4	99	90	96	97	90	81	92	6
pyrene	<26	3912	3781	3872	3984	3732	3343	3771	228
retene	<4	74	76	81	75	73	89	78	6
fluoranthene	<61	2857	2770	2834	2893	2738	2442	2756	164
4-methylpyrene + 1-methylpyrene	<6	213	202	213	209	201	179	203	13
3-methylfluoranthene	<3	212	201	212	211	201	179	203	13
1-methylfluoranthene	<2	110	106	107	109	104	93	105	6
cyclopenta[*cd*]pyrene	<4	341	323	375	345	333	289	334	28
benzo[*c*]phenanthrene	<10	216	216	236	218	220	188	216	16
benzo[*a*]anthracene	<16	2142	2068	2394	2167	2141	1857	2128	173
chrysene + triphenylene	<38	7467	7230	6974	6061	6346	5287	6561	820
3-methylchrysene	<2	204	203	240	213	187	182	205	21
6-methylchrysene	<3	93	85	105	80	100	78	90	11
benzo[*b*]fluoranthene	<57	2314	1994	2360	2120	2195	1771	2126	218
benzo[*k*]fluoranthene	<7	1376	1185	1423	1268	1316	1047	1269	137
benzo[*a*]fluoranthene	<5	308	316	335	329	316	260	311	27
benzo[j]fluoranthene	<9	626	540	624	566	571	476	567	56
benzo[*e*]pyrene	<10	946	988	996	997	967	814	951	70
benzo[*a*]pyrene	<10	1060	1141	1099	1153	1079	921	1076	84
perylene	<10	760	534	628	588	606	472	598	97
dibenz[*a,j*]anthracene	<31	1494	1401	1604	1493	1395	1228	1436	127
dibenz[*a,c*]anthracene	<6	313	220	256	233	248	195	244	40
indeno[1,2,3-*cd*]pyrene	<63	321	290	329	306	313	258	303	26
dibenz[*a,h*]anthracene	<14	291	283	312	300	277	243	284	24
benzo[*b*]chrysene	<11	473	457	520	487	460	394	465	42
picene	<7	381	368	419	393	370	317	375	34
benzo[*ghi*]perylene	<12	1769	1684	1887	1788	1674	1455	1710	147
anthanthrene	<50	2582	2627	2518	2828	2051	2208	2469	287
dibenzo[*a,h*]pyrene	<3	239	255	238	255	246	200	239	20
dibenzo[*a,e*]pyrene	<20	259	279	263	276	259	217	259	22
Coronene	<19	620	435	527	462	491	383	486	82

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Table 13. Measurement Results for SRM 1936 (Dry-Mass Basis) from Method Two
All values are in units of ng/g

PAH Analyte	Mean LOD	SRM 1936 Bottle Numbers						Mean	SD
		241	498	593	710	2419	2861		
naphthalene	<28	74.4	84.4	103	88.3	91.1	75.7	89	10
2-methylnaphthalene	<5	45.4	51.6	56.9	54.9	54.7	45.6	53	4
1-methylnaphthalene	<4	28.1	28.3	29.1	31.4	27.1	28.8	29	2
biphenyl	<14	13.9	14.1	18.4	16.8	15.1	<13.3	16	2
1,6-dimethylnaphthalene	<15	38.1	40.7	43.7	40.9	42.2	38.5	41	2
1,2-dimethylnaphthalene	<13	67.6	78.7	78.9	76.3	77.9	71.1	77	3
2,6-dimethylnaphthalene	<15	28.3	29.5	35.7	30.3	32.3	27.2	31	3
acenaphthene	<14	60.7	63.9	73.3	65.4	78.3	68.4	70	6
acenaphthylene	<16	<15	<14	<15	<15	<16	<15		
fluorene	<12	68.5	82.6	96.7	78.4	97.7	82.6	88	9
dibenzothiophene	<11	51.8	54.9	65.1	58.7	66.2	58.7	61	5
phenanthrene	<29	993	1107	1302	1158	1315	1196	1216	91
anthracene	<9	131	174	236	179	236	155	196	38
4-H-cyclopenta[*def*]phenanthrene	<6	154	178	212	179	217	192	196	18
3-methylphenanthrene	<5	122	147	171	152	177	153	160	13
1-methylphenanthrene	<6	136	158	186	162	189	168	173	14
2+9-methylphenanthrene + 2-methylanthracene	<17	57.7	63.7	76.4	70	78.7	70.5	72	6
1,7-dimethylphenanthrene	<5	49.7	58.2	74.9	65.3	71.6	59.9	66	7
retene	<5	<5	<4	<5	<5	<5	<5		
pyrene	<35	2815	3247	3711	3286	3797	3412	3491	250
fluoranthene	<21	3080	3526	4034	3603	4145	3730	3808	270
3-methylfluoranthene	<3	80.6	91.5	107.4	94.2	72.9	96	92	12
1-methylfluoranthene	<4	43.3	50	55.5	51.5	58.1	52	53	3
1-methylpyrene	<13	161	189	213	196	216	193	201	12
4-methylpyrene	<6	105.5	122.4	140	125.9	143	126.2	132	9
benzo[*c*]phenanthrene	<11	163	186	210	189	219	191	199	15
benzo[*ghi*]fluoranthene	<32	384	418	473	432	511	448	456	37
benz[*a*]anthracene	<15	1839	2078	2331	2122	2480	2187	2240	165
chrysene	<53	2025	2214	2491	2256	2692	2380	2407	193
triphenylene	<10	581	627	736	668	796	645	694	70
cyclopenta[*cd*]pyrene	<15	36	26.7	48.1	27.7	46	44	39	10
3-methylchrysene	<15	219	237	270	274	292	248	264	22
6-methylchrysene	<14	128	147	157	150	176	157	157	11
benzo[*b*]fluoranthene	<76	1694	1714	2008	1731	2659	2230	2068	393
benzo[*k*]fluoranthene	<30	899	912	1069	923	1422	1188	1103	212
benzo[*j*]fluoranthene	<38	765	787	993	770	1335	1011	979	228
benzo[*a*]fluoranthene	<8	282	265	362	274	409	315	325	61
benzo[*a*]pyrene + benzo[*e*]pyrene	<100	2493	2649	3082	2674	4055	3326	3157	577
perylene	<11	518	533	605	537	1021	818	703	212
picene	<8	160	157	202	163	191	187	180	19
dibenz[*a,c*]anthracene + dibenz[*a,h*]anthracene + dibenz[*a,j*]anthracene	<30	538	532	685	559	645	629	610	63
anthanthrene + indeno[1,2,3-*c*d]pyrene	<55	1598	1688	1952	1746	1878	1888	1830	109
benzo[*b*]chrysene	<24	292	282	347	300	333	338	320	28
benzo[*ghi*]perylene	<14	1502	1475	1878	1547	1795	1759	1691	172
dibenzo[*a.e*]pyrene	<29	770	766	977	802	941	902	878	90
Coronene	<6	117	156	172	166	177	141	162	14
dibenzo[*b,k*]fluoranthene	<23	328	343	435	352	409	389	386	39

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Table 14. Comparison of Measurement Results from Methods One and Two
Measurement results are in units of ng/g

PAH Analyte	Method One		Method Two		Method One/Two	
	Mean	u(Mean)	Mean	u(Mean)	Ratio	u(Ratio)
cyclopenta[cd]pyrene	39	10	334	28	0.12	0.01
coronene	162	14	486	82	0.33	0.03
3-methylfluoranthene	92	12	203	13	0.46	0.03
picene	180	19	375	34	0.48	0.03
1-methylfluoranthene	53	3	105	6	0.51	0.02
2,6-dimethylnaphthalene	31	3	48	5	0.64	0.04
benzo[b]chrysene	320	28	465	42	0.69	0.03
naphthalene	89	10	126	17	0.70	0.05
1-methylnaphthalene	29	2	41	5	0.70	0.04
1,7-dimethylphenanthrene	66	7	92	6	0.72	0.04
2-methylnaphthalene	53	4	71	11	0.74	0.05
biphenyl	16	2	21	3	0.77	0.06
benzo[k]fluoranthene	1103	212	1269	137	0.87	0.08
benzo[c]phenanthrene	199	15	216	16	0.92	0.04
fluorene	88	9	95	8	0.92	0.05
pyrene	3491	250	3771	228	0.93	0.04
4-H-cyclopenta[def]phenanthrene	196	18	204	14	0.96	0.05
benzo[b]fluoranthene	2068	393	2126	218	0.97	0.09
anthracene	196	38	201	15	0.98	0.08
benzo[ghi]perylene	1691	172	1710	147	0.99	0.05
3-methylphenanthrene	160	13	154	11	1.04	0.05
benzo[a]fluoranthene	325	61	311	27	1.05	0.09
phenanthrene	1216	91	1147	74	1.06	0.04
dibenzothiophene	61	5	52	4	1.16	0.05
perylene	703	212	598	97	1.18	0.16
3-methylchrysene	264	22	205	21	1.29	0.07
1-methylphenanthrene	173	14	126	11	1.37	0.07
fluoranthene	3808	270	2756	164	1.38	0.05
benzo[j]fluoranthene	979	228	567	56	1.73	0.18
6-methylchrysene	157	11	90	11	1.75	0.10
1,2-dimethylnaphthalene	77	3	17	2	4.59	0.19

4.4.3. Homogeneity

Figure 7 displays the quantitative results from both methods for ten selected PAHs plotted as a function of bottle number. While the correlation among the analytes within each method suggests sample-specific differences in extraction completeness, there is little to no evidence for a bottling-related systematic decline in PAH levels. The SRM 1936 material appears to be fit-for-purpose homogeneous with regard to PAH content.
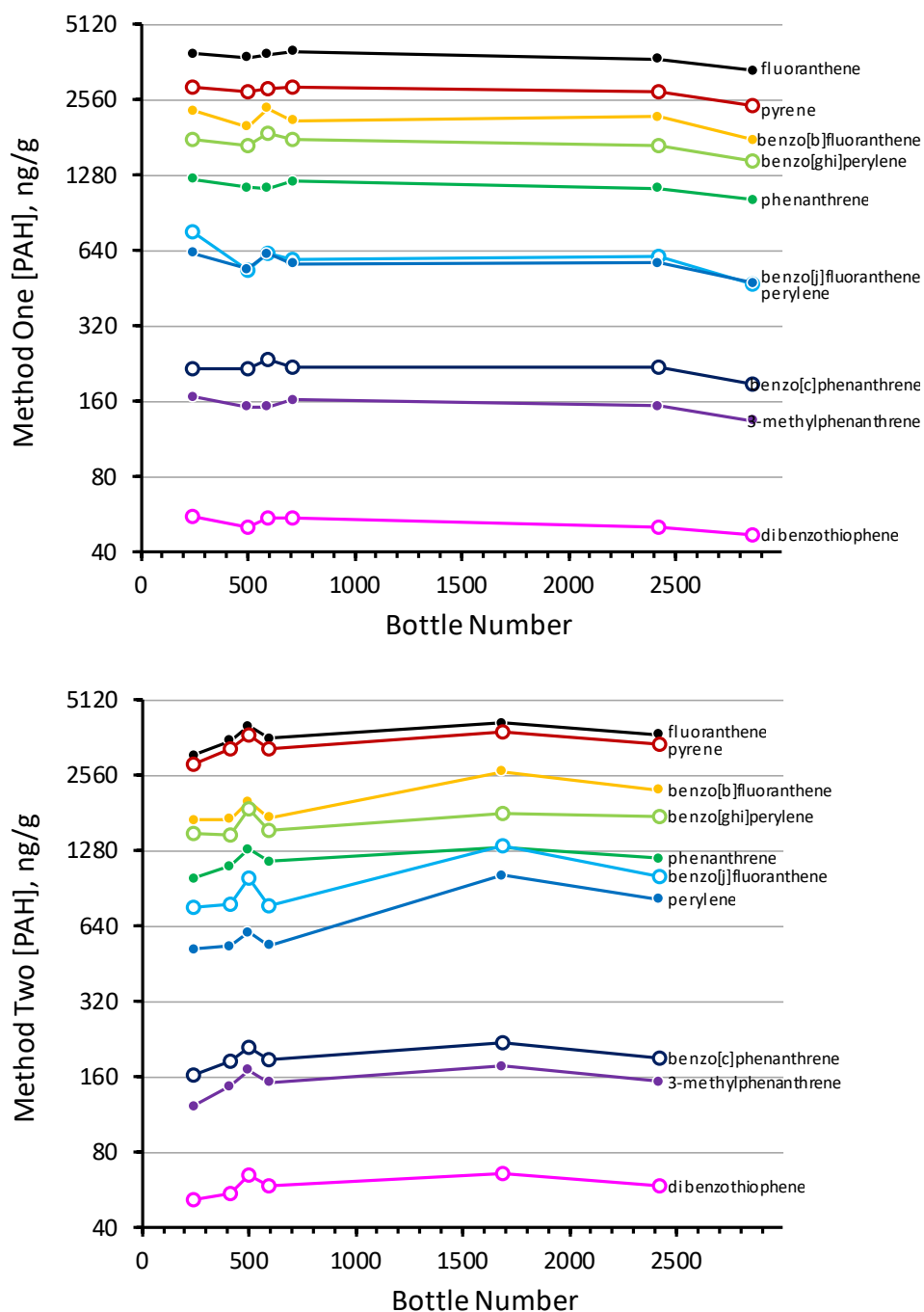
Figure 7. Method One and Two Results for Selected PAHs in SRM 1936

5. Interlaboratory Studies

The Northern Contaminants Program (NCP) Quality Assurance/Quality Control Program started in 2005 to support laboratories in maintaining and developing capabilities for high-quality environmental analyses (https://science.gc.ca/eic/site/063.nsf/eng/h_7A463DBA.html). In 2017, NIST provided SRM 1944 and SRM 1936 for NCP's Phase 11 assessment.

5.1. Trace Metals

Table 15. Trace Metals in SRMs 1944 and 1936
Values in units of µg/g on a dry-mass basis

| | SRM 1944 | | | | SRM 1936 | |
| | NCP Laboratory | | COA | | NCP Laboratory | |
Element	1613	1615	Mean	U_{95}	1613	1615
Al	na	17200			na	10300
Sb	na	2.61	4.6	0.9	na	0.563
As	18.1	17.9	18.9	2.8	5.68	4.73
Cd	6.99	9.77	8.8	1.4	1.08	1.28
Cr	108	244	266	24	50.1	80.1
Co	na	10.2			na	5.51
Cu	208	358	380	40	31.3	38.8
Fe	14700	29600			11300	16400
Pb	286	337	330	48	42.7	47.7
Mn	173	391	505	25	364	560
Mo	na	3.63			na	1.5
Ni	57.4	67.9	76.1	5.6	16.6	17.6
Rb	na	23.4			na	14
Se	<2.0	1.68	1.4	0.2	<2.0	0.863
Ag	na	6.5	6.4	1.7	na	0.518
Sr	na	62.8			na	75.9
Tl	na	0.356	0.59	0.1	na	0.194
Sn	na	45.6	42	6	na	5.1
V	na	49.7			na	20.2
Zn	555	737	656	75	162	192

NCP = Northern Contaminants Program
COA = Certificate of Analysis
na = not available
"<" value is the limit of detections

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5.2. Mercury and Methyl Mercury

Table 16. Mercury and Methyl Mercury in SRMs 1944 and 1936
Values in units of µg/g on a dry-mass basis

NCP Laboratory	SRM 1944		SRM 1936	
	Hg	MeHg	Hg	MeHg
1610	3.30	0.00475	0.143	0.00076
1613	3.15	0.00600	0.142	0.00090
1615	3.79		0.151	
1617	3.70		0.154	
1624	3.67	0.00241	0.145	0.00049
1642	3.92		0.147	
n	6	3	6	3
Mean	3.59	0.00439	0.147	0.00072
COA Value	3.45			

5.3. Polychlorinated Biphenyls (PCBs)

Table 17. Polychlorinated Biphenyls (PCBs) in SRMs 1944 and 1936
Values in units of ng/g on a dry-mass basis

	SRM 1944					SRM 1936		
	NCP Laboratory			COA		NCP Laboratory		
Analyte	1614	1621	1629	Mean	U_{95}	1614	1621	1629
PCB-1	1.42	3.01	4.12			0.143	0.196	0.317
PCB-3	1.6	3.88	5.65			0.157	0.225	0.349
PCB-4	co	11.6	13.2			co	2.08	2.91
PCB-8	17.1	15	22.5	**22.3**	**2.3**	4.63	3.78	6.09
PCB-10	co	0.634	0.548			co	0.0807	0.102
PCB-11	na	9.51	12.4			na	0.525	0.623
PCB-12	na	4.85	co			na	1.95	co
PCB-15	11.8	26	34.3			5.04	7.26	9.71
PCB-18	51.8	41.1	co	**51.0**	**2.6**	17.2	13.9	co
PCB-19	3.86	4.61	5.34			1.29	1.38	1.71
PCB-28	63.2	84.4	co	**80.8**	**2.7**	26.7	31.7	co
PCB-31	56.7	65	65.2	**78.7**	**1.6**	21.6	22.7	24.8
PCB-32	na	14.4	11			na	5.55	5.31
PCB-33	28.6	27.3	co			7.53	5.34	co
PCB-35	na	2.47	3.31			na	0.347	0.48
PCB-37	22.5	28.4	31.5			8.77	8.33	9.58
PCB-38	na	0.0773	na			na	0.019	nd
PCB-44	51.6	69.6	co	**60.2**	**2**	22.6	32.6	co
PCB-45	na	13.5	12.4	*10.8*	*1.4*	na	6.19	5.35
PCB-47	na	69.6	co			na	32.6	co
PCB-49	49.8	50	co	**53.0**	**1.7**	21.9	24.2	co
PCB-52	69.8	74.4	64.6	**79.4**	**2.0**	25.7	33.7	27.7
PCB-54	0.192	0.215	0.209			0.0684	0.0734	0.0894
PCB-57	na	0.4	0.36			na	0.21	0.24
PCB-66	52.1	64.5	54.1	**71.9**	**4.3**	20.4	21.8	22.6

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| | SRM 1944 | | | | | SRM 1936 | | |
| | NCP Laboratory | | | COA | | NCP Laboratory | | |
Analyte	1614	1621	1629	Mean	U_{95}	1614	1621	1629
PCB-70	60.2	113	co			19.4	33.3	co
PCB-74	29.3	113	co			10.4	33.3	co
PCB-77	6.27	8.71	11.6			2.54	2.76	3.23
PCB-78	na	0.0253	nd			na	<0.0150	na
PCB-79	na	0.7	0.638			na	0.187	0.227
PCB-81	0.24	0.275	0.288			0.0434	0.038	0.0613
PCB-87	26.7	44	co	**29.9**	**4.3**	7.6	11.9	co
PCB-95	41	46.7	co	**65.0**	**8.9**	12.8	18.3	16.9
PCB-97	18.9	44	co			5.74	11.9	co
PCB-99	25.9	41	co	**37.5**	**2.4**	7.87	12.5	co
PCB-101	na	65.8	co	**73.4**	**2.5**	na	21.3	co
PCB-104	0.0341	<0.0536	0.0356			0.0151	0.013	0.0179
PCB-105	19.9	25.3	26	**24.5**	**1.1**	5.42	6.28	6.81
PCB-110	55.1	76.1	co	**63.5**	**4.7**	17.5	24.1	co
PCB-114	1.27	1.41	1.56			0.347	0.367	0.435
PCB-118	46.4	57.8	58.5	**58.0**	**4.3**	12.6	15.2	16.6
PCB-123	0.893	0.734	1.04			0.272	0.147	0.309
PCB-126	0.225	0.304	0.276			0.0536	<0.0677	0.066
PCB-128	7.65	10.5	co	**8.47**	**0.28**	2.49	3.14	co
PCB-137	2.29	2.81	2.47			0.532	0.543	0.517
PCB-138	58.2	82.7	co	**62.1**	**3.0**	25	32.9	co
PCB-141	9.5	15.2	12.1			4.76	7.34	6.13
PCB-146	na	10.9	9.07	*10.1*	*1.9*	na	4.98	4.3
PCB-149	59.1	68.3	co	**49.7**	**1.2**	29.4	34.8	co
PCB-151	18.5	27.3	co	**16.9**	**0.36**	10.5	15.3	co
PCB-153	57.1	69.4	co	**74.0**	**2.9**	27	30.5	co
PCB-155	0.186	0.195	0.197			0.0038	<0.00600	0.0036
PCB-156	5.46	7.88	na	**6.52**	**0.67**	1.96	2.43	na
PCB-157	1.13	7.88	na			0.279	2.43	na
PCB-158	5.55	7.5	6.16			2.12	2.72	2.46
PCB-162	na	<0.340	0.348			na	0.0495	0.0414
PCB-163	na	82.7	na	*14.4*	*2.0*	na	32.9	co
PCB-167	2.65	2.73	2.63			0.812	0.84	0.842
PCB-169	0.013	0.116	0.045			0.0024	<0.0198	0.0033
PCB-170	18.3	16.6	15.8	**22.6**	**1.4**	12.3	10.1	10.3
PCB-172	na	2.91	2.78			na	1.57	1.68
PCB-174	15.2	19.3	17	*16.0*	*0.6*	9.41	13	10.4
PCB-177	8.92	10.9	9.93			5.62	6.71	5.88
PCB-178	4.06	4.12	3.9			2.43	2.44	2.25
PCB-180	34.3	41.7	co	**44.3**	**1.2**	20.7	24.4	co
PCB-183	11.1	12.9	co	**12.2**	**0.57**	6.44	8.34	co
PCB-187	25.1	28.5	24.2	**25.1**	**1.0**	13.2	14.2	12.6
PCB-188	0.094	0.102	0.1			0.0155	0.0169	0.0174
PCB-189	0.584	0.697	0.763			0.342	0.375	0.419
PCB-194	9.13	9.7	9.45	**11.2**	**1.4**	4.42	4.66	5.46
PCB-195	na	3.57	3.77	**3.75**	**0.39**	na	2.12	2.36
PCB-196	na	4.87	5.3			na	2.6	2.52

| | SRM 1944 | | | | | SRM 1936 | | |
| | NCP Laboratory | | | COA | | NCP Laboratory | | |
Analyte	1614	1621	1629	Mean	U_{95}	1614	1621	1629
PCB-199	12.2	12.1	co			5.34	4.71	co
PCB-202	2.71	3.11	3.6			0.817	0.847	1.08
PCB-203	11.7	7.53	7.89			5.61	3.03	3.24
PCB-205	0.46	0.515	0.523			0.25	0.277	0.28
PCB-206	7.15	7.96	5.25	**9.21**	**0.51**	1.24	1.33	1.45
PCB-208	2.5	3.2	3.45			0.274	0.315	0.379
PCB-209	5.96	7.57	6.52	**6.81**	**0.33**	0.313	0.387	0.354

na = not available, nd = not detected, co = coeluted, value not reported, "<" value is the limit of detections
Values from the SRM 1944 Certificate of Analysis in **bold** are certified, in *italic* are "reference" (non-certified)

5.4. Organochlorine Pesticides

Table 18. Organochlorine Pesticides in SRMs 1944 and 1936
Values in units of ng/g on a dry-mass basis

| | SRM 1944 | | | | SRM 1936 | |
| | NCP Laboratory | | COA | | NCP Laboratory | |
Analyte	1614	1629	Mean	U_{95}	1614	1629
Aldrin	na	0.206			na	0.135
α-Chlordane	18.5	20.7	**16.51**	**0.83**	1.31	1.59
γ-Chlordane	21.4	24.7	*19.0*	*1.7*	1.21	1.54
α-BHC	0.111	0.309			<0.0191	nd
β-BHC	0.161	0.427			<0.0232	nd
γ-BHC	1.53	0.428			1.72	nd
δ-BHC	na	0.078			na	nd
2,4'-DDD	41.7	28.9	*38*	*8*	2.02	2.19
2,4'-DDE	13.2	17.8	*19*	*3*	0.31	0.392
2,4'-DDT	3.26	4.35			0.926	1.08
4,4'-DDD	101	114	*108*	*16*	8.89	10.9
4,4'-DDE	66	88.1	*86*	*12*	13.3	17.2
4,4'-DDT	103	274	*170*	*32*	4.3	6.75
Dieldrin	na	7.88			na	0.403
Heptachlor	inf	0.118			<0.00857	nd
Heptachlor epoxide (Isomer B)	0.224	0.293			0.0515	nd
Methoxychlor	na	7.25			na	nd
Mirex	0.976	1.02			0.0382	0.046
cis-Nonachlor	4.17	5.71	*3.7*	*0.7*	0.361	0.431
trans-Nonachlor	13.6	12.6	**8.2**	**0.51**	0.69	0.906
Octachlorostyrene	na	0.175			na	nd
Oxychlordane	<0.00678	nd			inf	nd
Hexachlorobenzene	5.01	6.54	**6.03**	**0.35**	1.00	1.24

na = not available, nd = not detected, co = coeluted, inf = interference, "<" value is the limit of detections
Values from the SRM 1944 Certificate of Analysis in **bold** are certified, in *italic* are "reference" (non-certified)

5.5. Polybrominated Diphenyl Ethers (PBDEs)

Table 19. Polybrominated Diphenyl Ethers (PBDEs) in SRMs 1944 and 1936
Values in units of ng/g on a dry-mass basis

| | SRM 1944 | | | | SRM 1936 | |
| | NCP Laboratory | | COA | | NCP Laboratory | |
Analyte	1614	1629	Mean	U_{95}	1614	1629
BDE-3	<0.0579	na			<0.0262	na
BDE-7	1.04	0.350			0.0951	0.0451
BDE-15	0.591	0.996			0.0198	0.024.6
BDE-17	0.481	co			0.199	co
BDE-28	0.201	co			0.105	co
BDE-47	1.25	1.55	*1.72*	0.28	3.10	3.91
BDE-49	0.635	0.945			0.642	0.662
BDE-66	0.0505	0.088			0.108	0.173
BDE-71	<0.00857	0.17			<0.00318	0.110
BDE-77	<0.00619	0.00437			<0.00230	nd
BDE-85	inf	0.0772			0.188	0.156
BDE-99	1.58	1.68	*1.98*	0.26	3.53	4.32
BDE-100	0.407	0.457	*0.447*	0.27	0.855	0.964
BDE-119	<0.00987	co			<0.00485	co
BDE-126	<0.00653	nd			<0.00463	nd
BDE-138	0.538	co			0.0274	co
BDE-153	5.62	11.3	*6.44*	0.37	0.529	0.605
BDE-154	1.02	1.25			0.359	0.485
BDE-155	na	0.0751			na	0.034
BDE-156	<0.0422	na			<0.0171	na
BDE-183	32.6	44.9	*31.8*	0.1	0.149	0.214
BDE-184	<0.0125	na			<0.00891	na
BDE-191	<0.0238	na			<0.0171	na
BDE-196	23.2	na			0.147	na
BDE-197	15.7	co			inf	co
BDE-203	na	17.8			na	0.275
BDE-206	7.99	12.1	*6.2*	1	0.980	2.64
BDE-207	18	68.7			0.635	4.18
BDE-209	148	117	*93.5*	*4.4*	28.6	46.2

na = not available, nd = not detected, co = coeluted, inf = interference, "<" value is the limit of detections
Values from the SRM 1944 Certificate of Analysis in *italic* are "reference" (non-certified)

5.6. Dioxins and Furans

Table 20. Dioxins and Furans in SRMs 1944 and 1936
Values in units of ng/g on a dry-mass basis

Analyte	SRM 1944					SRM 1936		
	NCP Laboratory			COA		NCP Laboratory		
	1614	1621	1629	Mean	U_{95}	1614	1621	1629
2,3,7,8-T4CDD	0.0976	0.123	0.117	*0.133*	*0.009*	0.00169	0.00291	nd
1,2,3,7,8-P5CDD	0.0118	0.0142	0.0172	*0.019*	*0.002*	0.00378	0.00345	nd
1,2,3,4,7,8-H6CDD	0.0159	0.0208	0.0266	*0.026*	*0.003*	0.00313	0.00362	0.00397
1,2,3,6,7,8-H6CDD	0.0312	0.042	0.0456	*0.056*	*0.006*	0.0112	0.011	0.0135
1,2,3,7,8,9-H6CDD	0.0239	0.0577	0.0429	*0.053*	*0.007*	0.00804	0.0128	0.0107
1,2,3,4,6,7,8-H7CDD	0.534	0.691	0.774	*0.80*	*0.07*	0.212	0.234	0.261
OCDD	4.13	5.3	5.87	*5.8*	*0.7*	1.94	2.40	2.42
2,3,7,8-T4CDF	0.0245	0.0462	0.0282	*0.039*	*0.015*	0.00293	0.00519	0.00403
1,2,3,7,8-P5CDF	0.0358	0.0401	0.0428	*0.045*	*0.007*	0.00207	0.00169	nd
2,3,4,7,8-P5CDF	0.0313	0.03	0.039	*0.045*	*0.004*	0.0028	0.00249	nd
1,2,3,4,7,8-H6CDF	0.191	0.225	0.184	*0.22*	*0.03*	0.00698	0.00781	0.00516
1,2,3,6,7,8-H6CDF	0.0665	0.0829	0.09	*0.09*	*0.01*	0.00423	0.00423	0.00542
1,2,3,7,8,9-H6CDF	0.0011	0.0018	0.0031			0.00016	<0.0028	nd
2,3,4,6,7,8-H6CDF	0.0397	0.0363	0.0453	*0.054*	*0.006*	0.00503	0.0033	nd
1,2,3,4,6,7,8-H7CDF	0.735	0.985	1.13	*1.0*	*0.1*	0.0602	0.0769	0.0852
1,2,3,4,7,8,9-H7CDF	0.032	0.0344	0.0421	*0.040*	*0.006*	0.00352	0.00406	nd
OCDF	0.868	1.2	1.15	*1.0*	*0.1*	0.162	0.175	0.203

nd = not detected, "<" value is the limit of detections
Values from the SRM 1944 Certificate of Analysis in *italic* are "reference" (non-certified)

5.7. Perfluoroalkyl Substances (PFAS)

Table 21. Perfluoroalkyl Substances (PFAS) in SRMs 1944 and 1936
Values in units of ng/g on a dry-mass basis

Analyte	SRM 1944				SRM 1936			
	1615	1621	1629	1631	1615	1621	1629	1631
PFNA	<0.100	<1.00	ND	<0.290	<0.100	<1.00	ND	2.97
PFPeA	<0.100	1.88	ND	na	0.120	<1.00	0.157	na
PFHxA	0.213	<1.00	0.213	0.486	0.219	<1.00	0.219	1.53
PFHpA	0.253	<1.00	0.208	na	0.105	<1.00	0.0859	na
PFOA	0.828	<1.00	0.851	1.17	0.236	<1.00	0.187	0.415
PFNA	<0.100	<1.00	0.122	<0.190	<0.100	<1.00	0.0738	<0.190
PFDA	<0.100	<1.00	0.155	<0.270	<0.100	<1.00	0.0967	<0.270
PFUdA	0.298	<1.00	0.367	0.339	<0.100	<1.00	0.103	<0.220
PFDoA	0.287	<1.00	0.261	0.260	0.171	<1.00	0.178	<0.250
PFTrDA	0.524	<1.00	0.933	na	<0.100	<1.00	0.366	na
PFTeDA	<0.200	<1.00	0.205	na	<0.200	<1.00	0.211	na
PFHxDA	<0.500	na	na	na	<0.500	<1.00	na	na
PFODA	<0.500	na	na	na	<0.500	<1.00	na	na
L-PFBS[a]	<0.100	<1.00	ND	na	<0.100	<1.00	ND	na
L-PFHxS[a]	<0.100	9.07	ND	na	<0.100	<1.00	ND	na
P6MHpS	na	na	na	na	na	<1.00	na	na
L-PFHpS[a]	<0.100	na	na	na	<0.100	na	na	na
L-PFOS[a]	1.26	7.62	1.04	1.67	0.696	<1.00	0.719	0.870
L-PFDS[a]	1.28	na	na	na	0.130	na	na	na
FOSA	0.279	<1.00	0.358	na	<0.100	<1.00	0.0736	na
N-MeFOSA	na	<1.00	ND	na	na	<1.00	ND	na
N-EtFOSA	0.437	<1.00	0.430	na	<0.300	<1.00	ND	na
N-MeFOSE	na	1.92	2.39	na	na	<1.00	ND	na
N-Et-FOSE	na	2.15	3.24	na	na	<1.00	ND	na
6:2 FTS	<0.100	na	na	na	1.05	na	na	na
8:2 FTS	0.145	na	na	na	0.776	na	na	na

na = not available, nd = not detected, "<" value is the limit of detections
[a] The analyte measured is only inclusive of the linear isomer (L)

6. Statistical Evaluation

For PFOS, measurements were made at NIST using LC-MS/MS and another set of measurements are consensus values from an interlaboratory study. For all other analytes, measurements were made using two different methods at NIST. Method One used GC-MS with a Restek Rsi-17sil capillary column. Method Two used GC-MS with a Supelco SLB ILPAH capillary column. Table 22 lists the summary values for the selected analytes.

Table 22. Summary Results for Value-Assignable Analytes in SRM 1936
Values in units of ng/g on a dry-mass basis

Analyte	Method 1			Method 2		
	n	Mean	SD	n	Mean	SD
PFOS	10	0.779	0.038	3	0.762	0.095
3-methylphenanthrene	6	154	11	6	154	19
benzo[b]fluoranthene	6	2126	218	6	2006	383
benzo[c]phenanthrene	6	216	16	6	193	20
benzo[ghi]perylene	6	1710	147	6	1659	172
benzo[j]fluoranthene	6	567	56	6	944	222
dibenzothiophene	6	52.3	3.5	6	59.2	5.6
fluoranthene	6	2756	164	6	3686	383
perylene	6	598	97	6	672	204
phenanthrene	6	1147	74	6	1179	122
pyrene	6	3771	228	6	3378	355

6.1. Description of Analysis

The values and uncertainties below are calculated by combining the results from both measurement methods using the following model:

$$y_{ij} = \mu + m_i + \varepsilon_{ij}; i = 1, 2\ldots, n_{mm}; j = 1, 2\ldots, n_i$$

where i indexes measurement methods, j indexes replication within measurement method, n_{mm} represents the number of measurement methods, n_i represents the number of replications within measurement method, $m_i \sim \mathrm{N}(0,\sigma_m^2)$, and $\varepsilon_{ij} \sim \mathrm{N}(0, \sigma_i^2)$ independently of m_i. The values are estimates of μ, say $\hat{\mu}$, in the above equation, and the estimator employed is the DerSimonian-Laird (DSL) described in [4]. The uncertainties were determined using the Horn-Horn-Duncan (HHD) method for variances described in [5] and also with the bootstrap method [6].

6.2. Results

Table 23 lists the DSL consensus mean values, standard uncertainties (u) and expanded uncertainties (U) for the HHD method, and the u and U for the bootstrap method. This table also lists the maximum of HHD and bootstrap expanded uncertainty estimates; it is recommended that these conservative estimates be used for the Certificate of Analysis.

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Table 23. Multiple Method Consensus Values and Uncertainties for SRM 1936
Values in units of ng/g on a dry-mass basis

	DSL	DSL-HHD		DSL-Bootstrap		Max
Analyte	Mean	u	U	u	U	U
PFOS	0.778	0.004	0.007	0.021	0.046	0.046
3-methylphenanthrene	154.00	0	0	4.24	8.36	8.36
benzo[b]fluoranthene	2096.6	51.6	103.2	84.7	166.9	167
benzo[c]phenanthrene	205.0	11.5	23.0	11.6	22.7	23.0
benzo[ghi]perylene	1688.5	25.2	50.4	47.1	92.8	92.8
benzo[j]fluoranthene	745	188	376	190	371	376
dibenzothiophene	55.52	3.44	6.89	3.45	6.78	6.89
fluoranthene	3210	465	930	464	910	930
perylene	611.6	28.7	57.4	41.0	81.6	81.6
phenanthrene	1155.6	14.2	28.4	27.8	54.7	54.7
pyrene	3590	196	392	197	386	392

References

[1] Reiner JL, Blaine AC, Higgins CP, Huset C, Jenkins TM, Kwadijk CJAF, Lange CC, Muir DCG, Reagen WK, Rich C, Small JM, Strynar MJ, Washington JW, Yoo H, Keller JM. Polyfluorinated substances in abiotic standard reference materials. Anal Bioanal Chem. 2015;407:2975-2983.

[2] Baali A, Yahyaoui.A. Polycyclic Aromatic Hydrocarbons (PAHs) and Their Influence to Some Aquatic Species. In: Biochemical Toxicology – Heavy Metals and Nanomaterials, Ince M, ed. IntechOpen, London (2020). https://doi.org/10.5772/intechopen.86213 (Accessed 3/18/2021)

[3] NIST. Environmental Metrology Measurement Assistant (EMMA), Version 1 (2014) https://www.nist.gov/programs-projects/environmental-metrology-measurement-assistant-emma (Accessed 3/18/2021)

[4] DerSimonian R Laird N. Meta-Analysis in Clinical Trials. Control Clin Trials 1986:7:177-188. https://doi.org/10.1016/0197-2456(86)90046-2

[5] Horn RA, Horn SA, Duncan DB. Estimating Heteroscedastic Variance in Linear Models. J Am Stat Assoc 1975;70(350):380-385. https://doi.org/10.2307/2285827

[6] Efron B, Tibshirani RJ. An Introduction to the Bootstrap, Chapman & Hall/CRC Monographs on Statistics and Applied Probability (1993)