



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1939a

Polychlorinated Biphenyls Congeners in River Sediment A

This Standard Reference Material (SRM) is an air-dried river sediment. It is intended primarily for use in validating analytical methods used in determining selected polychlorinated biphenyl (PCB) congeners in sediments. All of the constituents for which certified and reference values are provided in SRM 1939a are naturally present in the sediment material. SRM 1939a is the same sediment material that was issued previously in 1990 as SRM 1939 [1]. This material has been reanalyzed to provide updated certified values as well as certified and reference values for additional constituents. A unit of SRM 1939a consists of a bottle containing approximately 50 g of sediment.

Certified Concentration Values: Certified values, expressed as mass fractions, are provided for 34 PCB congeners in Table 1. The certified values for the PCB congeners are based on the agreement of results obtained from two or more independent analytical techniques [2]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST. The measurand is the total concentration of each of the analytes in Table 1. The certified value is traceable to the SI units for mass, expressed as mass fraction.

Reference Concentration Values: Reference values, also expressed as mass fractions, for 30 additional PCB congeners plus total PCBs, 5 chlorinated pesticides, and 7 polycyclic aromatic hydrocarbons (PAHs) are provided in Tables 2, 3, and 4, respectively. Reference values are noncertified values that are the best estimates of the true values. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods. The measurand is the concentration of each of the analytes in 2-4 as determined by the methods indicated in the text. The certified value is traceable to the SI units for mass, expressed as mass fraction.

Expiration of Certification: The certification of **SRM 1939a** is valid, within the measurement uncertainty specified, until **31 October 2017**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Preparation of the original SRM 939 material was performed by R.M. Parris and R.E. Rebbert of the NIST Chemical Sciences Division, and optical microscopy for the original certification was performed by J.A. Small of the NIST Materials Measurement Science Division. The analyses for the update of the certificate were performed by A. Guichard, J.R. Kucklick, B.J. Porter, D.L. Poster, and M.M. Schantz of the NIST Chemical Sciences Division.

Coordination of the technical measurements leading to the recertification was under the direction of M.M. Schantz and S.A. Wise.

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Certificate Issue Date: 16 June 2017
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Consultation on the statistical design of the experimental work and evaluation of the data was provided by S.D Leigh of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

NOTICE AND WARNING TO USERS

CAUTION: This material is a naturally occurring river sediment and may contain constituents of unknown toxicities; therefore, caution and care should be exercised during its handling and use.

INSTRUCTIONS FOR USE

Prior to removal of subsamples for analysis, the bottle should be shaken. Subsamples for analysis of this SRM should be withdrawn from the bottle immediately after opening and used without delay for the certified values to be valid within the stated uncertainties. The bottle should be tightly closed immediately after removal of the subsamples and the remaining material stored for later analyses. The concentrations of constituents in SRM 1939a are reported on a dry-mass basis. The SRM, as received, contains approximately 2.6 % moisture. A separate subsample of the SRM should be removed from the bottle at the time of analysis and dried to determine the concentration based on dry mass. When not in use, the sediment should be stored in the dark at a temperature of 25 °C or below.

SOURCE AND PREPARATION⁽¹⁾

Source of Material: The sediment material from which this SRM was prepared was donated by the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Sample Collection and Preparation: The sediment material was collected from the Hudson River in New York State. It was dried, passed through a 325 mesh (45 µm) size sieve, and homogenized in a V-blender. The material was then radiation sterilized (⁶⁰Co) at an estimated minimum dose of 3.2 megarads. Approximate 50 g quantities were then transferred to amber bottles fitted with Teflon[®] lined screw caps.

Conversion to Dry Mass Basis: The values for the constituents in SRM 1939a are reported on a dry-mass basis; however, the material “as received” contains residual moisture. The amount of moisture in SRM 1939a was determined by measuring the mass loss after freeze-drying subsamples of 3 g for five days at 1 Pa with a -10 °C shelf temperature and a -50 °C condenser temperature. The moisture content in SRM 1939a at the time of the recertification analyses was 2.56 % ± 0.16 % (95 % confidence).

ANALYTICAL METHODS USED FOR THE ANALYTES OF INTEREST

SRM 1939a was analyzed for selected analytes of interest by up to three methods using gas chromatography/mass spectrometry (GC/MS) on two columns with different selectivity. For all of the methods described below, multipoint calibration response curves for the compounds of interest relative to the internal standards were determined by processing gravimetrically-diluted solutions of appropriate SRMs (SRM 2259, SRM 2260a, SRM 2261, SRM 2262, SRM 2274, and/or SRM 2275) with the internal standards added.

GC/MS (I): For the GC/MS (I) analyses, duplicate subsamples of approximately 2 g from each of three bottles were extracted using pressurized fluid extraction (PFE) with dichloromethane (DCM). The analytes of interest were isolated using a silica solid-phase extraction (SPE) column. GC/MS analysis was performed on a 0.25 mm × 30 m fused-silica capillary column containing a 5 % (mole fraction) phenyl methyl-substituted polysiloxane phase (0.25 µm film thickness) (HP-5MS, Agilent Technologies, Wilmington, DE). SRM 2269, SRM 2270, PCB 103, PCB 198, and carbon-13 labeled 4,4'-DDE, 4,4'-DDT, lindane, and *trans*-nonachlor were added to the sediment prior to extraction for quantification purposes.

GC/MS (II): For the GC/MS (II) analyses, duplicated subsamples of approximately 1 g from each of three bottles were extracted using pressurized fluid extraction (PFE) with dichloromethane (DCM). Size exclusion

⁽¹⁾ Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify 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.

chromatography (SEC) with two columns in series (the first a 600 mm × 21.2 mm i.d. column with 10 µm particle diameter pores) was used to remove the higher molecular mass interferences, as well as sulfur. The concentrated extracts were then cleaned-up using alumina SPE columns. GC/MS analysis was performed on a 0.25 mm × 60 m fused silica capillary column containing a 5 % phenyl methyl-substituted polysiloxane phase (0.25 µm film thickness) (DB-5MS, Agilent Technologies). Carbon-13 labeled PCB 28, PCB 52, PCB 77, PCB 118, PCB 126, PCB 153, PCB 169, PCB 180, PCB 194, and PCB 206 were added to the sediment prior to extraction for quantification purposes.

GC/MS (III): For the GC/MS (III) analyses, duplicate subsamples of approximately 1 g from each of three bottles were Soxhlet extracted using DCM for 18 h. Finely divided copper powder that had been acid-washed and solvent-rinsed was added to the round-bottom flasks to remove elemental sulfur. The concentrated extracts were then processed through a precleaned amino SPE column. GC/MS analysis for the PCBs was performed on a 0.25 mm × 60 m fused silica capillary column containing a nonpolar proprietary polysiloxane phase (0.25 µm film thickness) (DB-XLB, Agilent Technologies) while GC/MS analysis for the pesticides and PAHs was performed on a 25 mm × 60 m fused silica capillary column containing a 50% phenyl methyl-substituted polysiloxane phase (0.25 µm film thickness) (DB-17, Agilent Technologies). SRM 2269, SRM 2270, PCB 30, PCB 103, PCB 198, PCB 204, carbon-13 labeled lindane, 4,4'-DDE and *cis*-nonachlor were added to the sediment prior to extraction for quantification purposes.

GC/MS (IV): For the GC/MS (IV) analyses, duplicate subsamples of approximately 1.5 g from each of three bottles were extracted using PFE with DCM. Finely divided copper powder that had been acid-washed and solvent-rinsed was added to the round bottom flasks to remove elemental sulfur. The concentrated extracts were then processed through a precleaned amino SPE column. GC/MS analysis was performed on a 25 mm × 60 m fused silica capillary column containing a 50% phenyl methyl-substituted polysiloxane phase (0.25 µm film thickness) (DB-17, Agilent Technologies). SRM 2269 and SRM 2270 were added to the sediment prior to extraction for quantification purposes.

Total PCBs: The data for total PCBs was combined from three methods: GC/MS (I) where the total PCB value was determined by summing the PCBs by chlorine group, GC/MS (II) where the total PCB value was a sum of the congener concentrations, and GC/MS (III) where the total PCB value was also the sum of the congener concentrations.

Particle Size: SRM 1939a was examined by optical microscopy and found to be homogenous with respect to the distribution of particle size both within and between SRM units.

Table 1. Certified Concentrations (Mass Fractions) for Selected PCB Congeners^(a) in SRM 1939a^(b,c)

			$\mu\text{g/kg}$		
PCB	8	(2,4'-Dichlorobiphenyl) ^(d,e,f)	5049	±	294
PCB	18	(2,2',5-Trichlorobiphenyl) ^(d,e,f)	2126	±	264
PCB	28	(2,4,4'-Trichlorobiphenyl) ^(d,f)	1676	±	91
PCB	31	(2,4',5-Trichlorobiphenyl) ^(d,f)	5698	±	135
PCB	44	(2,2',3,5'-Tetrachlorobiphenyl) ^(d,e,f)	766	±	53
PCB	49	(2,2',4,5'-Tetrachlorobiphenyl) ^(d,e,f)	3314	±	317
PCB	52	(2,2',5,5'-Tetrachlorobiphenyl) ^(d,e,f)	3691	±	68
PCB	56	(2,3,3',4'-Tetrachlorobiphenyl) ^(d,e)	355	±	14
PCB	66	(2,3',4,4'-Tetrachlorobiphenyl) ^(d,e,f)	556	±	25
PCB	87	(2,2',3,4,5'-Pentachlorobiphenyl) ^(d,f)	166	±	21
PCB	92	(2,2',3,5,5'-Pentachlorobiphenyl) ^(d,f)	386	±	27
PCB	95	(2,2',3,5',6-Pentachlorobiphenyl) ^(d,f)	859	±	29
PCB	101	(2,2',4,5,5'-Pentachlorobiphenyl) ^(d,e,f)	476	±	42
PCB	110	(2,3,3',4',6-Pentachlorobiphenyl) ^(d,e,f)	1008	±	118
PCB	112	(2,3,3',5,6-Pentachlorobiphenyl) ^(e,f)	33.5	±	3.1
PCB	153	(2,2',4,4',5,5'-Hexachlorobiphenyl) ^(d,e,f)	357	±	92
	132	(2,2',3,3',4,6'-Hexachlorobiphenyl)			
PCB	156	(2,3,3',4,4',5-Hexachlorobiphenyl) ^(d,e,f)	40.7	±	4.4
PCB	167	(2,3',4,4',5,5'-Hexachlorobiphenyl) ^(e,f)	17.9	±	2.0
PCB	172	(2,2',3,3',4,5,5'-Heptachlorobiphenyl) ^(e,f)	16.7	±	1.5
PCB	175	(2,2',3,3',4,5,6-Heptachlorobiphenyl) ^(e,f)	6.47	±	0.23
PCB	177	(2,2',3,3',4',5,6-Heptachlorobiphenyl) ^(e,f)	73.3	±	6.8
PCB	180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl) ^(d,e)	167	±	11
	193	(2,3,3',4',5,5',6-Heptachlorobiphenyl)			
PCB	189	(2,3,3',4,4',5,5'-Heptachlorobiphenyl) ^(e,f)	3.40	±	0.47
PCB	191	(2,3,3',4,4',5',6-Heptachlorobiphenyl) ^(e,f)	2.92	±	0.15
PCB	194	(2,2',3,3',4,4',5,5'-Octachlorobiphenyl) ^(d,e,f)	41.1	±	5.7
PCB	199 ^a	(2,2',3,3',4,5,5',6'-Octachlorobiphenyl) ^(e,f)	7.61	±	0.92
PCB	201 ^a	(2,2',3,3',4,5,5',6'-Octachlorobiphenyl) ^(d,e)	18.9	±	1.0
PCB	202	(2,2',3,3',5,5',6,6'-Octachlorobiphenyl) ^(e,f)	18.9	±	2.8
PCB	206	(2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl) ^(d,e,f)	33.4	±	2.4
PCB	207	(2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) ^(e,f)	3.96	±	0.22
PCB	208	(2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl) ^(e,f)	13.1	±	0.78
PCB	209	(2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl) ^(d,e,f)	8.32	±	0.60

^(a) PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [4] and later revised by Schulte and Malisch [5] to conform with IUPAC rules. For the congeners listed, the differences are PCB 201 (BZ#) is PCB 199 in the IUPAC nomenclature and PCB 199 (BZ#) is PCB 200 in the IUPAC nomenclature. When two or more congeners are known to coelute under the conditions used, the PCB congener listed first is the major component and the additional congeners may be present as minor components. The quantitative results are based on the response of the congener listed first.

^(b) Concentrations reported on dry mass basis; material as received contains approximately 2.6 % moisture.

^(c) Certified values are unweighted means of the results for two or three data sets. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [6] with a pooled, within-method variance following the ISO/JCGM and NIST Guides [3].

^(d) GC/MS (I)

^(e) GC/MS (II)

^(f) GC/MS (III)

Table 2. Reference Concentrations (Mass Fractions) for Selected PCB Congeners ^(a) and Total PCBs in SRM 1939a ^(b,c)

			µg/kg		
PCB	45	(2,2',3,6-Tetrachlorobiphenyl) ^(d,e,f)	619	±	94
PCB	63	(2,3,4',5-Tetrachlorobiphenyl) ^(d,e,f)	342	±	61
PCB	70	(2,3',4',5-Tetrachlorobiphenyl) ^(d,e,f)	482	±	85
PCB	74	(2,4,4',5-Tetrachlorobiphenyl) ^(d,e,f)	591	±	119
PCB	82	(2,2',3,3',4-Pentachlorobiphenyl) ^(d,e)	116	±	19
PCB	99	(2,2',4,4',5-Pentachlorobiphenyl) ^(d,e,f)	386	±	81
PCB	105	(2,3,3',4',5-Pentachlorobiphenyl) ^(d,e,f)	173	±	47
PCB	107 ^a	(2,3,3',4',5-Pentachlorobiphenyl) ^(d,e,f)	55.8	±	8.9
PCB	114	(2,3,4,4',5-Pentachlorobiphenyl) ^(e,f)	18.3	±	4.2
PCB	118	(2,3',4,4',5-Pentachlorobiphenyl) ^(d,e,f)	385	±	103
PCB	119	(2,3',4,4',6-Pentachlorobiphenyl) ^(e,f)	58	±	15
PCB	128	(2,2',3,3',4,4'-Hexachlorobiphenyl) ^(d,e,f)	76	±	24
PCB	130	(2,2',3,3',4,5'-Hexachlorobiphenyl) ^(e,f)	42	±	11
PCB	137	(2,2',3,4,4',5-Hexachlorobiphenyl) ^(e,f)	21.7	±	4.1
PCB	138	(2,2',3,4,4',5'-Hexachlorobiphenyl) ^(e,f)	190	±	52
PCB	146	(2,2',3,4,5,5'-Hexachlorobiphenyl) ^(e,f)	91	±	23
PCB	149	(2,2',3,4,5',6-Hexachlorobiphenyl) ^(d,e,f)	402	±	105
PCB	151	(2,2',3,5,5',6-Hexachlorobiphenyl) ^(d,e,f)	181	±	49
PCB	154	(2,2',4,4',5,6'-Hexachlorobiphenyl) ^(e,f)	29	±	11
PCB	157	(2,3,3',4,4',5'-Hexachlorobiphenyl) ^(d,e,f)	10.0	±	2.0
PCB	158	(2,3,3',4,4',6-Hexachlorobiphenyl) ^(d,e,f)	33.4	±	7.0
PCB	163	(2,3,3',4',5,6-Hexachlorobiphenyl) ^(e,f)	170	±	48
PCB	170	(2,2',3,3',4,4',5-Heptachlorobiphenyl) ^(d,e,f)	97	±	27
PCB	174	(2,2',3,3',4,5,6'-Heptachlorobiphenyl) ^(d,e,f)	57	±	21
PCB	176	(2,2',3,3',4,6,6'-Heptachlorobiphenyl) ^(e,f)	12.6	±	4.2
PCB	178	(2,2',3,3',5,5',6-Heptachlorobiphenyl) ^(e,f)	31.8	±	6.8
PCB	183	(2,2',3,4,4',5',6-Heptachlorobiphenyl) ^(d,e,f)	38	±	11
PCB	185	(2,2',3,4,5,5',6-Heptachlorobiphenyl) ^(e,f)	6.8	±	2.0
PCB	187	(2,2',3,4',5,5',6-Heptachlorobiphenyl) ^(d,e,f)	139	±	47
PCB	195	(2,2',3,3',4,4',5,6-Octachlorobiphenyl) ^(d,e,f)	17.8	±	3.0
Total PCBs			46900	±	8600

^(a) PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [4] and later revised by Schulte and Malisch [5] to conform with IUPAC rules. For the congeners listed, the only difference is PCB 107 (BZ#) is PCB 109 in the IUPAC nomenclature.

^(b) Concentrations reported on dry mass basis; material as received contains approximately 2.6 % moisture.

^(c) Reference values are unweighted means of the results for two or three data sets. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [6] with a pooled, within-method variance following the ISO/JCGM and NIST Guides [3].

^(d) GC/MS (I)

^(e) GC/MS (II)

^(f) GC/MS (III)

Table 3. Reference Concentrations (Mass Fractions) for Selected Chlorinated Pesticides in SRM 1939a ^(a,b)

	µg/kg	
2,4'-DDE ^(c,d)	1.64 ± 0.41	
4,4'-DDE ^(c,d)	5.46 ± 0.83	
<i>trans</i> -Chlordane ^(c,d)	1.81 ± 0.33	
<i>cis</i> -Chlordane ^(c,d)	1.70 ± 0.61	
<i>trans</i> -Nonachlor ^(c,d)	0.91 ± 0.31	

^(a) Concentrations reported on dry-mass basis; material as received contains approximately 2.6 % moisture.

^(b) Reference values are unweighted means of the results for two or three data sets. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [6] with a pooled, within-method variance following the ISO/JCGM and NIST Guides [3].

^(c) GC/MS (I)

^(d) GC/MS (III)

Table 4. Reference Concentrations (Mass Fractions) for Selected PAHs in SRM 1939a ^(a,b,c)

	µg/kg	
Benzo[<i>b</i>]fluoranthene ^(c,d,e)	165 ± 27	
Benzo[<i>j</i>]fluoranthene ^(c,d,e)	85 ± 15	
Benzo[<i>k</i>]fluoranthene ^(c,d,e)	94 ± 17	
Benzo[<i>a</i>]fluoranthene ^(c,d,e)	32 ± 4	
Benzo[<i>e</i>]pyrene ^(c,d,e)	160 ± 42	
Benzo[<i>a</i>]pyrene ^(c,d,e)	178 ± 21	
Perylene ^(c,d,e)	99 ± 19	

^(a) Concentrations reported on dry-mass basis; material as received contains approximately 2.6 % moisture.

^(b) Reference values are unweighted means of the results for two or three data sets. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [6] with a pooled, within-method variance following the ISO/JCGM and NIST Guides [3].

^(c) GC/MS (I)

^(d) GC/MS (III)

^(e) GC/MS (IV)

REFERENCES

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Certificate Revision History: 16 June 2017 (Title updated, editorial changes); 30 September 2008 (Updated to include revised and additional values for the PCB congeners and chlorinated pesticides, new values for PAHs, and editorial changes); 29 May 1998 (Original certificate date)

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.