Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

Milk and serum standard reference materials for monitoring organic contaminants in human samples

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Supporting Information

Included in the supporting information are the method details for NIST, CDC, and the interlaboratory study as well as a list of compounds used in the spiking solution added to SRM 1954 Organic Contaminants in Fortified Human Milk and SRM 1958 Organic Contaminants in Fortified Human Serum. (Table S1). Tables S2 through S5 summarize the data from each of the methods used in the certification of SRMs 1953, 1954, 1957, and 1958, respectively. Figure S1 is a flow chart of the methods used. Figure S2 shows a comparison of the mass fractions of selected PCBs, pesticides, and PBDEs in the milk and serum while Figure S3 illustrates the relative levels of selected PCB and BDE congeners in the non-fortified milk and serum.

METHOD DETAILS

Analytical Methods Used at NIST: Control materials and calibration solutions, SRM 1588b Organics in Cod Liver Oil; SRM 1589a PCBs, Pesticides, PBDEs, and Dioxins and Furans in Human Serum; SRM 2261 Chlorinated Pesticides in Hexane; SRM 2262 PCB Congeners in 2,2,4-Trimethylpentane, SRM 2274 PCB Congeners in 2,2,4-Trimethylpentane II, and SRM 2275 Chlorinated Pesticides in Hexane II, were obtained from the Standard Reference Material Program, NIST (Gaithersburg, MD). The ^{13}C-labeled compounds used as internal standards were obtained from Cambridge Isotope Labs (Andover, MA), while the fluorinated PBDE compounds were obtained from Chiron (Trondheim, Norway). All solvents were HPLC-grade.

For NIST Method 1, the freeze-dried serum in each of ten bottles was reconstituted by adding 10.7 mL (mass known) of HPLC-grade water, and the frozen milk in each of ten bottles was thawed. A known amount of internal standard solution (containing selected ^{13}C-labeled PCB congeners, selected ^{13}C-labeled pesticides, ^{13}C-labeled PBDE 209, fluorinated PBDE 47, PCB 103, and PCB 198) was added to each bottle, sonicated for 15 min and allowed to equilibrate overnight under refrigeration. After samples were removed from refrigeration and allowed to reach ambient temperature, 10 mL of formic acid, was added as a denaturation agent followed immediately by 10 mL of a 1:1 (volume fraction) mixture of *n*-hexane:methyl-*tert*-butyl ether for extraction. The samples were vortexed and left to stand for 0.5 h with occasional stirring. After centrifugation to obtain a sharp phase boundary, the upper organic phase was transferred to a concentration vessel. The extraction was repeated two more times with 10 mL of *n*-hexane each time. The combined hexane layers were concentrated to approximately 4 mL using an automated evaporation system. Approximately 2 mL of concentrated sulfuric acid was added to the concentration vessel with swirling. Following phase separation, the hexane phase was removed, and the sulfuric acid phase was washed twice using 4 mL portions of *n*-hexane each time. The combined hexane phases were concentrated to approximately 0.5 mL for silica solid-phase extraction (SPE) clean-up. The fraction of interest was eluted with 15 mL of 10 % (volume fraction) dichloromethane in hexane. The concentrated samples were analyzed using gas chromatography/mass spectrometry (GC/MS) operated in both the electron ionization (EI) and negative ion chemical ionization (NICI) mode. A 0.25 mm x 60 m fused silica capillary column containing a non-polar proprietary phase (DB-XLB, Agilent Technologies, Wilmington, DE) 0.25 μm film thickness was used for the EI analysis (NIST Method 1a) while a 0.25 mm x 60 m fused silica capillary column containing a 50 % (mole fraction) phenyl-substituted methylpolysiloxane phase (DB-17MS, Agilent Technologies, Wilmington, DE) was used for the NICI analysis (NIST Method 1b). All injections were 1 μL using an on-column inlet.

For NIST Method 2, the freeze-dried serum in each of six bottles was reconstituted by adding 10.7 mL (mass known) of HPLC grade water, and the frozen milk in each of six bottles was thawed. A known amount of internal standard solution (containing selected ^{13}C-labeled PCB congeners, selected ^{13}C- labeled pesticides, ^{13}C-labeled PBDE 209, and selected fluorinated PBDE congeners) was added to a 2 g serum or

2.5 g milk subsample from each bottle, vortexed, and allowed to equilibrate overnight under refrigeration. After samples were removed from refrigeration and allowed to reach ambient temperature, 2 mL of formic acid was added followed by 3 mL of 20 % (volume fraction) dichloromethane in hexane. Samples were extracted using focused microwave extraction. Following extraction, samples were centrifuged, the organic phase was removed, and another 3 mL of 20 % (volume fraction) dichloromethane in hexane was added. The extraction was repeated, and the organic phases were combined. Following concentration with a solvent exchange to *iso*-octane, acidified silica column clean-up followed by alumina column (5 % deactivated) clean-up was used. The eluant from the clean-up columns was concentrated to 0.2 mL with a solvent change to *iso*-octane for analysis. The concentrated samples were analyzed using GC/MS in the EI mode (NIST Method 2a) with a 0.18 mm × 30 m fused silica capillary column containing a 5 % (mole fraction) phenyl-substituted methylpolysiloxane phase (DB-5MS, Agilent Technologies, Wilmington, DE) 0.18 µm film thickness. All injections were 20 µL using a programmable temperature vaporization (PTV) inlet. The mass fractions for the higher chlorinated PCBs (PCB 196/203, PCB 199, and PCB 206) in the non-fortified milk sample, SRM 1953, (Supplemental Table 2) were generally higher when determined using this method possibly a result of matrix interferences. For NIST Method 2b, the same extracts, same column, and PTV inlet were used with the GC/MS in the NICI mode. For NIST Method 2c, the same extracts were analyzed by GC/MS in the NICI mode using on-column injection into a 0.18 mm x 10 m fused silica capillary column containing a 5 % (mole fraction) phenyl-substituted methylpolysiloxane phase (DB-5MS, Agilent Technologies, Wilmington, DE), 0.18 µm film thickness.

For NIST Method 3, the freeze-dried serum in each of six bottles was reconstituted by adding 10.7 mL (mass known) of HPLC grade water. A known amount of internal standard solution (containing selected ^{13}C-labeled hydroxylated compounds) was added to each bottle, vortexed, and allowed to equilibrate overnight under refrigerated conditions. After samples were removed from refrigeration and allowed to reach ambient temperature, 2 mL of formic acid and 0.5 mL of 6 mol/L hydrochloric acid (HCl) were added to the serum sample followed by 2 mL of 20 % (volume fraction) dichloromethane in hexane. Samples were extracted using open-focused microwave extraction. Following extraction, samples were centrifuged, the organic phase was removed, and another 3 mL of 20 % (volume fraction) dichloromethane in hexane was added. The extraction was repeated, and the organic phases were combined. Potassium hydroxide (KOH) was then added to the organic phase. The samples were shaker-extracted for 15 min, centrifuged, and the KOH was removed. This step was repeated two times with the KOH phases combined. HCl (6 mol/L) was added to the KOH phases, followed by 2 mL 20 % (volume fraction) dichloromethane in hexane. The hexane phase was removed, and this step was repeated two times combining the hexane phases. A silica column was used for clean-up followed by analysis using liquid chromatography coupled to a triple quadrupole mass spectrometer (LC/MS/MS) using a C-18 column (Agilent Eclipse Plus C18 3.0 mm × 150 mm × 3.5 µm, Agilent Technologies, Wilmington, DE) with a methanol-water gradient.

For NIST Method 4, the freeze-dried serum in each of five bottles was reconstituted by adding 10.7 mL (mass known) of HPLC grade water. A known amount of internal standard solution (containing selected ^{13}C-labeled PFCs) was added to a serum subsample (from 0.15 g to 0.5 g) from each bottle, vortexed, and allowed to equilibrate overnight under refrigerated conditions. After samples were removed from refrigeration and allowed to reach ambient temperature, 0.6 mL of 50 % (volume fraction) formic acid in water was added, and the samples were loaded onto 60 mg Oasis WAX SPE columns (Waters, Milford, MA). Compounds of interest were eluted off the columns using methanol followed by 2 mL of 1 % (volume fraction) ammonium hydroxide in methanol. Following concentration, samples were analyzed using LC/MS/MS with a C-8 column (Thermo Betasil C8, 100 mm × 2.1 mm × 5 μm, Thermo Fisher Scientific, Waltham, MA) and methanol-ammonium acetate in water gradient.

For all of the NIST methods, multi-point calibration response curves for the compounds of interest relative to the internal standards were determined by processing gravimetrically diluted solutions of SRM 2261, SRM 2262, SRM 2274, and SRM 2275 plus gravimetrically prepared solutions of the additional analytes of interest with the internal standards added. SRM 1589a PCBs, Pesticides, PBDEs, and Dioxins/Furans in Human Serum was analyzed with each set of samples as the control material for the serum analysis, and cow's milk (whole milk purchased from a grocery store) with SRM 1588b Organics in Cod Liver Oil added gravimetrically was analyzed with each set of samples as the control material for the milk analysis.

Analytical Methods Used at CDC: Details for the analytical methods used at CDC for the analytes other than the PFCs can be found in Patterson and Turner [1] and Sjödin et al [2,3]. In summary, the freeze-dried serum was reconstituted by adding 10.7 mL of HPLC-grade water and mixing; and the frozen milk was thawed and mixed. Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F) sample preparation was done using a C_{18} SPE method. After addition of the internal standard solution and formic acid, the sample was eluted through an SPE column using appropriate solvents. The eluant was then cleaned-up using a Universal Prep system (Fluid Management Systems, Waltham, MA) containing an acid/neutral/base silica column, an alumina column, and a carbon column. Corresponding ^{13}C-labeled compounds were used as internal standards for the majority of the analytes.

The sample preparation for other persistent organic pollutants in serum [2] included fortification of the samples with internal standards, addition of formic acid and water for denaturation of serum proteins and dilution of the sample using the Gilson 215 liquid handler (Gilson Inc, Middleton, WI) for automation. The samples were than extracted using SPE using the Rapid Trace (Caliper Life Sciences; Hopkinton, MA) for automation. Removal of co-extracted lipids was performed on a silica/sulfuric acid column using the Rapid Trace for automation.

Milk samples were extracted using solid-phase dispersion [3] and a lipid removal procedure that was identical to the serum method [2].

Serum lipids were determined using enzymatic methods [5] while milk lipids were determined gravimetrically [3].

Gas chromatography/high resolution mass spectrometry (GC/HRMS) with mass resolution of 10,000 was used for the determination of the PCBs, chlorinated pesticides, PBDEs, PCDDs, and PCDFs. The GC column used for PCDD/F and PCBs and pesticides was a DB-5MS column (30m x 0.25 mm ID x 0.25 μm film thickness, J&W Scientific, Folsom, CA) while a DB-5HT column (15m x 0.25mm ID x 0.10 μm film thickness, J&W Scientific, Folsom, CA) was used for brominated flame retardants. All injections were splitless with helium as the carrier gas.

Interlaboratory Study: The laboratories participating in the interlaboratory study used the methods commonly used in their laboratories for these analyses. The methods used by University of Liege are described in more detail in Focant et al. [4]. Not every laboratory reported data for every analyte. When more than one laboratory did report data for a particular analyte, the mean of the concentrations was used for combination with other data to assign the certified and reference mass fraction values.

SUPPLEMENTAL REFERENCES

[1] Patterson DG Jr, Turner WE (1997) CLIA Document, Environmental Health Laboratory, Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, GA

[2] Sjödin A, Jones RS, Lapeza CR, Focant J-F, McGahee EE III, Patterson DG Jr (2004) Anal Chem 76: 1921-1927

[3] Sjödin A, McGahee EE III, Focant J-F, Jones RS, Lapeza CR, Zhang Y, Patterson DG Jr (2004) Anal Chem 76: 4508-4514

[4] Focant J-F, Eppe G, Massart A-C, Scholl G, Pirard C, De Pauw E (2006) J Chromatogr A 1130: 97-107

[5] Bernert JT, Turner WE, Patterson DG Jr, Needham LL (2007) Chemosphere 68: 824-831

Table S1. List of compounds in spiking solution used for SRM 1954 and SRM 1958.

These compounds were chosen based on current and anticipated future interest in human monitoring studies.

PCDDs/PCDFs/cPCBs
2,3,7,8-Tetrachlorodienzo- *p* -dioxin (TCDD)
1,2,3,7,8-Pentachlorodibenzo- *p* -dioxin (PnCDD)
1,2,3,4,7,8-Hexachlorodibenzo- *p* -dioxin (HxCDD)
1,2,3,6,7,8-Hexachlorodibenzo- *p* -dioxin (HxCDD)
1,2,3,7,8,9-Hexachlorodibenzo- *p* -dioxin (HxCDD)
1,2,3,4,6,7,8-Heptachlororodibenzo- *p* -dioxin (HpCDD)
1,2,3,4,6,7,8,9-Octachlorodibenzo- *p* -dioxin (OCDD)
2,3,7,8,-Tetrachlorodibenzofuran (TCDF)
1,2,3,7,8-Pentachlorodibenzofuran (PnCDF)
2,3,4,7,8-Pentachlorodibenzofuran (PnCDF)
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)
2,3,4,6,7,8,-Hexchlorodibenzofuran (HxCDF)
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)
1,2,3,4,6,7,8,9-Octachlorodibenzofuran (OCDF)
PCB 77 3,3',4,4'-Tetrachlorobiphenyl (TCB)
PCB 81 3,4,4',5-Tetrachlorobiphenyl (TCB)
PCB 126 3,3',4,4',5-Pentachlorobiphenyl (PnCB)
PCB 169 3,3',4,4',5,5'-hexachlorobiphenyl (HxCB)
ORGANOCHLORINE PESTICIDES
Hexachlorobenzene
Beta-hexachloro-cyclohexane
Gamma-hexachloro-cyclohexane
Aldrin
Heptachlor epoxide
Oxychlordane
trans-nonachlor
p,p'-DDE
Dieldrin
Endrin
o,p'-DDT
p,p'-DDT
Mirex
alpha-Hexachlorocyclohexane (HCCH)
cis-Chlordane (or alpha)
trans-Chlordane (or gamma)
cis-Nonachlor
o,p'-DDE
p,p'-DDD
o,p'-DDD
p,p'-Methoxychlor
Isodrin
Other PERSISTENT ORGANOHALOGEN COMPOUNDS
Pentachloronitrobenzene
Hexachlorocyclopentadiene
Hexachloro-1,3-butadiene
1,2,3,4-Tetrachlorobenzene
1,2,4,5-Tetachlorobenzene
1,2,3,5-Tetrachlorobenzene
1,2,3,4,5-Pentachlorobenzene
Octachlorosytrene

Table S1 (cont). List of compounds in spiking solution used for SRM 1954 and SRM 1958.

Non- and Mono-*ortho* CLORINATED BIPHENYLS
PCB 18 2,2',5-Trichloro biphenyl
PCB 28 2,4,4'-Trichloro biphenyl
PCB 52 2,2',5,5'-Tetrachloro biphenyl
PCB 49 2,2',4,5'-Tetrachloro biphenyl
PCB 44 2,2'3,5'-Tetrachloro biphenyl
PCB 74 2,4,4',5-Tetrachloro biphenyl
PCB 66 2,3',4,4'-Tetrachloro biphenyl
PCB 101 2,2',4,5,5'-Pentachloro biphenyl
PCB 99 2,2',4,4',5-Pentachloro biphenyl
PCB 87 2,2',3,4,5'-Pentachloro biphenyl
PCB 110 2,3,3',4',6-Pentachlorobiphenyl
PCB 118 2,3',4,4',5-Pentachloro biphenyl
PCB 105 2,3,3',4,4'-Pentachloro biphenyl
PCB 151 2,2',3,5,5',6-Hexachloro biphenyl
PCB 149 2,2',3,4',5',6-Hexachloro biphenyl
PCB 146 2,2',3,4',5,5-Hexachloro biphenyl
PCB 153 2,2',4,4',5,5'-Hexachloro biphenyl
PCB 138 & 158 2,2',3,4,4',5' and 2,3,3',4,4',6-Hexachloro biphenyl
PCB 128 2,2',3,3',4,4' Hexachloro biphenyl
PCB 167 2,3',4,4',5,5'-Hexachloro biphenyl
PCB 156 2,3,3',4,4',5-Hexachloro biphenyl
PCB 157 2,3,3',4,4',5'-Hexachloro biphenyl
PCB 178 2,2,3,3',5',5',6-Heptachloro biphenyl
PCB 187 2,2',3,4',5,5',6-Heptachloro biphenyl
PCB 183 2,2',3,4,4',5',6-Heptachloro biphenyl
PCB 177 2,2',3,3',4',5,6-Heptachloro biphenyl
PCB 172 2,2',3,3',4,5,5'-Heptachloro biphenyl
PCB 180 2,2',3,4,4',5,5'-Heptachloro biphenyl
PCB 170 2,2',3,3',4,4',5-Heptachloro biphenyl
PCB 189 2,3,3',4,4',5,5' -Heptachloro biphenyl
PCB 201 2,2',3,3',4,5,5',6'-Octachloro biphenyl
PCB 196 & 203 2,2',3,3,4,4',5,6'- and 2,2',3,4,4',5,5'6-Octachloro biphenyl
PCB 195 2,2'3,3',4,4',5,6-Octchloro biphenyl
PCB 194 2,2',3,3',4,4',5,5'-Octachloro biphenyl
PCB 206 2,2',3,3',4,4',5,5,6'-Nonachloro biphenyl
PCB 209 2,2',3,3',4,4',5,5',6,6'-Decachloro biphenyl
PCB 114 2,3,3',4,4'-Pentachloro biphenyl
PCB 123 2',3,4,4',5-Pentachloro biphenyl
POLYBROMINATED DIPHENYL ETHERS
PBDE 17 2,2',4'-Tribromodiphenyl ether
PBDE 28 2,4,4'-Tribromodiphenyl ether
PBDE 47 2,2',4,4'-Tetrabromodiphenyl ether
PBDE 66 2,3',4,4'-Tetrabromodiphenyl ether
PBDE 100 2,2',4,4',6-Pentabromodiphenyl ether
PBDE 99 2,2',4,4',5-Pentabromodiphenyl ether
PBDE 85 2,2',3,4,4'-Pentabromodiphenyl ether
PBB 153 2,2',4,4',5,5'-Hexabromobiphenyl
PBDE 154 2,2',4,4',5,6'-Hexabromodiphenyl ether
PBDE 153 2,2',4,4',5,5'-Hexabromodiphenyl ether
Hexabromocyclododecane (HBCDD)
PBDE 183 2,2',3,4,4',5',6-Heptabromodiphenyl ether
PBDE 203 2,2',3,4,4',5,5',6-Octabromodiphenyl ether
PBDE 209 Decabromodiphenyl ether
PBDE 196 2,2',3,3',4,4',5,6'-Octabromodiphenyl ether
PBDE 197 2,2',3,3',4,4',6,6'-Octabromodiphenyl ether
PBDE 206 2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether
PBDE 207 2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl ether
PBDE 208 2,2',3,3',4,5,5',6,6'-Nonabromodiphenyl ether
1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE)
Hexabromobenzene (HBB)
Decabromodiphenyl ethane (DBDEthane)

Table S1 (cont). List of compounds in spiking solution used for SRM 1954 and SRM 1958.

POLYCHLORINATED NAPHTHALENES
PCN 27 1,2,3,4-Tetra-CN
PCN 52 1,2,3,5,7-Penta-CN
PCN 60 1,2,4,6,7-Penta-CN
PCN 66 1,2,3,4,6,7-Hexa-CN
PCN 67 1,2,3,5,6,7-Hexa-CN
PCN 64 1,2,3,4,5,7-Hexa-CN
PCN 68 1,2,3,5,6,8-Hexa-CN
PCN 69 1,2,3,5,7,8-Hexa-CN
PCN 73 1,2,3,4,5,6,7-Hepta-CN
HALOGENATED PHENOLIC COMPOUNDS
2,4,6-Trichlorophenol
2,6-Dibromophenol
2,4-Dibromophenol
2,4,6-Tricbromophenol
Pentachlorophenol
Pentachloroanisole
4-Hydroxyheptachlorostyrene
5-Chloro-2-(2,4-dichlorophenoxy)-phenol
Hexachlorophene
Pentabromphenol
Tetrachlorobisphenol A
Tetrabromobisphenol A
HYDROXYLATED POLYCHLORINATED BIPHENLYS
4-HO-CB107
3'-HO-CB138
3-HO-CB153
4-HO-CB146
4-HO-CB187
POLYBROMINATED DIBENZODIOXINS
2,3,7,8-Tetrabromorodienzo-*p* -dioxin (TBDD)
1,2,3,7,8-Pentabromodibenzo-*p* -dioxin (PnBDD)
1,2,3,4,7,8-Hexabromorodibenzo-*p* -dioxin (HxBDD)
1,2,3,6,7,8-Hexabromodibenzo-*p* -dioxin (HxBDD)
1,2,3,7,8,9-Hexabromodibenzo-*p* -dioxin (HxBDD)
1,2,3,4,6,7,8-Heptabromoodibenzo-*p* -dioxin (HpBDD)
1,2,3,4,6,7,8,9-Octabromodibenzo-*p* -dioxin (OBDD)
POLYBROMINATED DIBENZOFURANS
2,3,7,8,-Tetrabromodibenzofuran (TBDF)
1,2,3,7,8-Pentabromodibenzofuran (PnBDF)
2,3,4,7,8-Pentabromodibenzofuran (PnBDF)
1,2,3,4,7,8-Hexabromodibenzofuran (HxBDFf)
1,2,3,6,7,8-Hexabromodibenzofuran (HxBDFf)
1,2,3,7,8,9-Hexabromodibenzofuran (HxBDFf)
2,3,4,6,7,8,-Hexabromodibenzofuran (HxBDF)
1,2,3,4,6,7,8-Heptabromodibenzofuran (HpBDFf)
1,2,3,4,7,8,9-Heptabromodibenzofuran (HpBDF)
1,2,3,4,6,7,8,9-Octabromodibenzofuran (OBDFf)
MIXED CHLORO-BROMO DIBENZODIOXNS
2,Bromo-3,7,8-Trichlorodibenzo-*p* -dioxin
2,3-Dibromo-7,8-Dichlorodibenzo-*p* -dioxin
1-Bromo-2,3,7,8-Tetrachlorodibenzo-*p* -dioxin
2-Bromo-3,6,7,8,9-Pentachlorodibenzo-*p* -dioxin
1-Bromo-2,3,6,7,8,9-Hexachlorodibenzo*p* -dioxin
1-Bromo-2,3,4,6,7,8,9-Hepatachlorodibenzo-*p* -dioxin
MIXED CHLORO-BROMO DIBENZOFURANS
3-Bromo-2,7,8-Trichlorodibenzofuran
1-Bromo-2,3,7,8-Tetrachlorodibenozofuran

Table S2. Data used for the Certification of SRM 1953 Organic Contaminants in Non-Fortified Human Milk						
mean (std dev) for each method in mass fraction, ng/kg milk						
Analyte	Method 1a	Method 1b	Method 2a	Method 2b	CDC	Interlab
PCB 28	63.3 (1.8)				63.9 (3.8)	62.0 (1.0)
PCB 66	33.3 (1.4)				32.2 (1.4)	
PCB 74	148 (5)				150 (3)	
PCB 99	143 (9)	138 (80	145 (18)		135 (5)	
PCB 105	45.0 (2.8)	45.2 (2.9)	39.0 (4.0)		51.9 (3.1)	87.6 (17.2)
PCB 110		12.3 (0.6)			12.5 (1.8)	
PCB 118	216 (7)	210 (5)	208 (17)		215 (9)	255 (43)
PCB 126					0.770 (0.065)	1.10 (0.54)
PCB 138	338 (17)		301 (24)			312 (66)
PCB 146	55.2 (1.8)	55.9 (1.9)	55.0 (9.0)		56.6 (4.3)	
PCB 153	478 (11)				479 (27)	483 (35)
PCB 153/132		555 (16)	605 (66)			
PCB 156	61.2 (1.3)	58.6 (2.7)	55.0 (3.0)		61.7 (3.5)	70.2 (4.4)
PCB 157	15.2 (0.6)				14.4 (1.4)	14.3 (0.3)
PCB 167	15.1 (0.6)				14.4 (1.9)	18.0 (0.7)
PCB 169					0.205 (0.021)	0.225 (0.007)
PCB 170		109 (5)	112 (11)		106 (4)	73.6 (5)
PCB 172		14.7 (1.5)			14.8 (1.2)	
PCB 177		23.8 (1.5)	27.0 (5.0)		22.8 (2.0)	
PCB 178		22.2 (0.9)			22.2 (1.2)	
PCB 180	230 (11)				238 (9)	239 (62)
PCB 180/193		267 (9)	241 (23)			
PCB 183		34.1 (2.0)	47.0 (8.0)		35.9 (2.3)	
PCB 187		98.1 (3.4)	145 (32)		91.7 (5.0)	78.2 (4.5)
PCB 194		36.9 (2.5)	57 (15)		36.8 (4.1)	68.6 (2.5)
PCB 196/203			92 (22)		43.8 (4.0)	
PCB 199			111 (29)		39.8 (2.0)	
PCB 206		15.1 (2.1)	60 (13)		12.1 (0.3)	
hexachlorobenzene	254 (17)		221 (23)		290 (29)	279 (14)
?-HCH	610 (7)				613 (29)	607 (46)
oxychlordane		598 (13)	596 (32)		706 (21)	547 (10)
cis -nonachlor		129 (6)				123 (5)
trans -nonachlor		1249 (24)			1305 (93)	1164 (73)
mirex		54.5 (1.7)	94 (7)		55.5 (3.8)	
4,4'-DDE	7354 (89)	7980 (230)			7031 (202)	7364 (425)
4,4'-DDT	230 (8)		214 (12)		242 (11)	
PBDE 17		16.8 (1.2)			17.2 (8.5)	
PBDE 28					145 (7)	127 (11)
PBDE 28/33		151 (7)		152 (10)		
PBDE 47		2242 (54)	2230 (70)		2232 (79)	2076 (227)
PBDE 66					17.9 (0.6)	14.5 (0.8)
PBDE 85		46.0 (2.3)	62 (5)		45.7 (4.0)	43.9 (3.8)

Table S2 (cont). Data used for the Certification of SRM 1953 Organic Contaminants in Non-Fortified Human Milk
mean (std dev) for each method in mass fraction, ng/kg milk

Analyte	Method 1a	Method 1b	Method 2a	Method 2b	CDC	Interlab
PBDE 99		342 (12)	320 (25)	343 (25)	348 (17)	342 (41)
PBDE 100		816 (10)	819 (34)	917 (79)	813 (25)	832 (112)
PBDE 153		978 (14)	936 (42)	955 (55)	996 (50)	1056 (136)
PBDE 154		43.6 (1.5)	44 (11)		40.9 (3.8)	
PBB 153			36.5 (2.1)		36.6 (3.4)	
PBDE 183					7.17 (0.11)	3.88 (0.53)
2,3,7,8-TCDD					0.0568 (0.0075)	0.052 (0.006)
1,2,3,7,8-PCDD					0.118 (0.013)	0.129 (0.008)
1,2,3,4,7,8-HxCD					0074 (0.012)	0.083 (0.009)
1,2,3,6,7,8-HxCD					0.458 (0.028)	0.549 (0.035)
1,2,3,7,8,9-HxCD					0.0953 (0.0071)	0.106 (0.006)
1,2,3,4,6,7,8-HpCD					0.400 (0.037)	0.560 (0.048)
OCDD					2.06 (0.21)	2.42 (0.15)
2,3,7,8-TCDF					0.016 (0.002)	0.019 (0.008)
2,3,4,7,8-PCDF					0.123 (0.006)	0.134 (0.009)
1,2,3,4,7,8-HxCF					0.067 (0.005)	0.077 (0.002)
1,2,3,6,7,8-HxCF					0.066 (0.005)	0.067 (0.004)
2,3,4,6,7,8-HxCF					0.032 (0.005)	0.033 (0.008)
1,2,3,4,6,7,8-HpCF					0.102 (0.007)	0.084 (0.027)

Table S3. Data used for the Certification of SRM 1954 Organic Contaminants in Fortified Human Milk						
mean (std dev) for each method in mass fraction, ng/kg milk						
Analyte	Method 1a	Method 1b	Method 2a	Method 2b	CDC	Interlab
PCB 18	393 (13)		317 (23)			
PCB 28	507 (14)				541 (29)	510 (43)
PCB 44	411 (9)		389 (33)		446 (25)	
PCB 49	425 (14)		435 (47)		428 (24)	
PCB 52	430 (14)		365 (31)		450 (24)	499 (134)
PCB 66	442 (13)		387 (29)		454 (29)	
PCB 74	561 (14)		553 (44)		574 (36)	
PCB 87	464 (16)		406 (34)		501 (61)	
PCB 99	554 (16)	548 (17)	535 (49)		562 (53)	593 (73)
PCB 101	452 (17)	449 (16)	388 (27)		456 (43)	485 (102)
PCB 105	480 (12)	475 (17)	465 (43)		484 (42)	504 (128)
PCB 110	475 (14)	475 (8)	396 (33)		482 (60)	
PCB 118	582 (16)	577 (17)			668 (61)	573 (86)
PCB 126					9.12 (1.00)	11.6 (0.5)
PCB 128	421 (10)	414 (10)	344 (76)		428 (41)	362 (12)
PCB 138	648 (12)		609 (51)			661 (24)
PCB 146	501 (8)	506 (9)	437 (35)		526 (69)	
PCB 149	410 (7)	407 (9)	406 (33)		407 (54)	
PCB 151	414 (14)	426 (15)	398 (32)		430 (57)	
PCB 153	980 (9)				981 (119)	971 (163)
PCB 153/132		1079 (22)	1073 (123)			
PCB 156	503 (10)	509 (9)	470 (47)		512 (67)	559 (87)
PCB 157	455 (18)	462 (13)	412 (34)		473 (56)	529 (17)
PCB 158	414 (10)	407 (7)	384 (36)			
PCB 167	444 (11)	443 (13)	415 (42)		450 (49)	584 (21)
PCB 169					8.25 (0.62)	10.3 (0.3)
PCB 170	516 (11)	517 (16)	511 (51)		616 (83)	389 (20)
PCB 172	449 (24)	462 (21)	388 (38)		470 (61)	
PCB 177	450 (13)	453 (12)	422 (36)		463 (69)	
PCB 178	461 (16)	441 (13)	430 (43)		457 (63)	
PCB 180	653 (17)				718 (101)	717 (221)
PCB 180/193		673 (16)	626 (77)			
PCB 183	455 (17)	452 (15)	448 (46)		480 (68)	41 (14)
PCB 187	522 (12)	541 (17)	515 (61)		545 (83)	474 (17)
PCB 189	414 (10)	412 (9)	392 (40)		439 (59)	506 (20)
PCB 194		484 (10)	472 (53)		491 (93)	
PCB 195		464 (15)	431 (49)		487 (89)	
PCB 196/203			856 (96)		887 (129)	
PCB 199			460 (60)		477 (71)	
PCB 206		463 (20)	452 (56)		479 (93)	
PCB 209		450 (16)	409 (55)		448 (99)	
hexachlorobenzene	703 (9)		607 (53)		733 (134)	662 (24)

Table S3 (cont). Data used for the Certification of SRM 1954 Organic Contaminants in Fortified Human Milk						
mean (std dev) for each method in mass fraction, ng/kg milk						
Analyte	Method 1a	Method 1b	Method 2a	Method 2b	CDC	Interlab
?-HCH	820 (10)		865 (89)		810 (47)	822 (17)
?-HCH	561 (21)				615 (35)	
oxychlordane		1142 (50)	1033 (97)		1217 (261)	867 (40)
cis -chlordane		372 (14)				363 (11)
trans -chlordane		378 (12)				376 (15)
cis -nonachlor		500 (9)				492 (18)
trans -nonachlor		1724 (41)			1792 (324)	1596 (80)
mirex		511 (11)	506 (50)		526 (97)	517 (22)
2,4'-DDE	403 (9)		397 (32)			
4,4'-DDE	8049 (65)		8175 (815)		7955 (1365)	8293 (144)
2,4'-DDD	420 (12)		433 (32)			
4,4'-DDD	421 (13)					428 (27)
2,4'-DDT	443 (14)				445 (63)	
4,4'-DDT	688 (19)		654 (67)		767 (134)	
PBDE 17		434 (8)		431 (48)	411 (31)	325 (29)
PBDE 28					553 (41)	498 (37)
PBDE 28/33		576 (12)		581 (50)		
PBDE 47		2602 (70)		2540 (250)	2719 (266)	2433 (192)
PBDE 66		419 (9)	383 (35)	420 (40)	416 (32)	415 (26)
PBDE 85		471 (21)	442 (33)	485 (53)	519 (58)	476 (26)
PBDE 99		771 (18)	688 (64)	682 (65)	791 (98)	763 (98)
PBDE 100		1282 (27)	1200 (110)	1340 (130)	1262 (160)	1313 (87)
PBDE 153		1503 (41)	1310 (140)	1310 (190)	1523 (283)	1534 (111)
PBDE 154		473 (49)	443 (49)		477 (79)	
PBDE 154/PBB 153				963 (129)		953 (59)
PBB 153		476 (15)			471 (72)	
PBDE 183		534 (13)		534 (58)	506 (100)	448 (42)
PBDE 206				674 (73)		958 (72)
PBDE 209		434 (19)	435 (35)			
2,3,7,8-TCDD					0.146 (0.018)	0.178 (0.008)
1,2,3,7,8-PCDD					0.226 (0.21)	0.253 (0.008)
1,2,3,4,7,8-HxCD					0.171 (0.015)	0.192 (0.016)
1,2,3,6,7,8-HxCD					0.767 (0.043)	1.009 (0.053)
1,2,3,7,8,9-HxCD					0.190 (0.012)	0.223 (0.007)
1,2,3,4,6,7,8-HpCD					0.877 (0.107)	1.287 (0.066)
OCDD					4.18 (0.48)	5.60 (0.29)
2,3,7,8-TCDF					0.118 (0.020)	0.131 (0.007)
1,2,3,7,8-PCDF					0.117 (0.018)	0.146 (0.006)
2,3,4,7,8-PCDF					0.330 (0.028)	0.363 (0.025)
1,2,3,4,7,8-HxCF					0.160 (0.017)	0.182 (0.009)
1,2,3,6,7,8-HxCF					0.175 (0.015)	0.196 (0.019)
1,2,3,7,8,9-HxCF					0.119 (0.008)	0.138 (0.017)
2,3,4,6,7,8-HxCF					1.006 (0.071)	1.165 (0.059)
1,2,3,4,6,7,8-HpCF					0.374 (0.046)	0.440 (0.034)
1,2,3,4,7,8,9-HpCF					0.096 (0.014)	0.231 (0.118)

Table S4. Data used for the Certification of SRM 1957 Organic Contaminants in Non-Fortified Human Serum								
mean (std dev) for each method in mass fraction, ng/kg reconstituted serum								
Analyte	Method 1a	Method 1b	Method 2a	Method 2b	Method 2c	Method 3	CDC	Interlab
PCB 74							13.8 (0.9)	13.7 (1.2)
PCB 99							11.9 (0.7)	11.3 (0.6)
PCB 105							6.0 (2.5)	1.6 (1.5)
PCB 114							4.7 (1.6)	0.7 (0.1)
PCB 118	19.5 (0.7)						18.6 (1.6)	16.0 (4.6)
PCB 138		41.4 (2.5)						32.4 (1.5)
PCB 153		58.3 (2.0)						56.1 (5.1)
PCB 153/132	59.5 (1.7)		37.8 (7.5)				57.4 (1.7)	63.0 (1.0)
PCB 156							8.8 (1.7)	8.1 (0.4)
PCB 157							6.6 (2.2)	1.37 (0.2)
PCB 167							4.4 (1.8)	2.1 (0.3)
PCB 170		15.5 (0.8)					18.1 (0.7)	15.0 (1.0)
PCB 180							44.5 (1.8)	50.9 (0.5)
PCB 180/193		54.6 (1.5)						54.2 (4.1)
PCB 187		15.7 (0.6)					15.2 (1.0)	15.0 (1.0)
PCB 194		12.0 (0.6)					11.4 (1.1)	11.7 (0.6)
pentachlorophenol						3150 (160)		2267 (115)
hexachlororbenzene	28.1 (0.9)		28.5 (2.6)		29.5 (3)		36.2 (1.0)	26.3 (1.2)
?-HCH		27.7 (1.4)					37.4 (2.2)	29 (1)
trans -nonaclor		59.7 (1.2)			61.4 (6.5)		56.6 (1.6)	57.3 (1.5)
4,4'-DDE	924 (32)		817 (25)				942 (25)	1000 (10)
PBDE 17							5.1 (1.5)	3.52 (0.16)
PBDE 28							21.2 (1.4)	18.8 (0.7)
PBDE 28/33		25.1 (0.9)		24.6 (6.2)				
PBDE 47		284 (7)	250 (7)	256 (7)			265 (5)	283 (13)
PBDE 66							7.06 (1.6)	6.69 (0.31)
PBDE 85							9.4 (2.3)	7.44 (0.34)
PBDE 99		79.6 (1.2)	76.8 (1.4)	70.8 (4.8)			72.04 (2.3)	81.4 (8.5)
PBDE 100		51.3 (1.5)	51.7 (2.8)	45.0 (2.3)			48.7 (2.0)	52.3 (5.6)
PBDE 153		60.7 (1.0)		58.1 (2.1)			59.6 (3.1)	65.8 (3.5)
PBB 153		15.5 (0.7)					15.3 (1.9)	15.3 (1.2)
PBDE 183							4.8 (2.5)	1.7 (0.7)
1,2,3,7,8-PCDD							0.0191 (0.0055)	0.0161 (0.0017)
1,2,3,4,7,8-HxCD							0.0109 (0.0017)	0.0126 (0.0008)
1,2,3,6,7,8-HxCD							0.0729 (0.0050)	0.0910 (0.0056)
1,2,3,7,8,9-HxCD							0.0181 (0.0041)	0.0187 (0.0006)
1,2,3,4,6,7,8-HpCD							0.0871 (0.0050)	0.1234 (0.0146)
OCDD							0.676 (0.051)	0.757 (0.027)
2,3,4,7,8-PCDF							0.0176 (0.0032)	0.0151 (0.0019)
1,2,3,4,7,8-HxCF							0.0153 (0.0026)	0.0184 (0.0004)
1,2,3,6,7,8-HxCF							0.0153 (0.0013)	0.0128 (0.0014)
1,2,3,4,6,7,8-HpCF							0.0371 (0.0032)	0.0434 (0.0046)
OCDF							0.0148 (0.0013)	0.0057 (0.0023)

Table S4 (cont). Data used for the Certification of SRM 1957 Organic Contaminants in Non-Fortified Human Serum

mean (std dev) for each method in mg/dL reconstituted serum

Analyte	Method 1a	Method 1b	Method 2a	Method 2b	Method 2c	Method 3	CDC	Interlab
Total Cholesterol							155 91)	150 (1)
"Free" Cholesterol							34.2 (0.6)	34.7 (0.6)
Phospholipids							183 (2)	180 (1)
Triglycerides							118 (1)	120 (1)

Table S5. Data used for the Certification of SRM 1958 Organic Contaminants in Fortified Human Serum								
mean (std dev) for each method in mass fraction, ng/kg reconstituted serum								
Analyte	Method 1a	Method 1b	Method 2a	Method 2b	Method 2c	Method 3	CDC	Interlab
PCB 18	409 (13)	335 (28)					388 (50)	
PCB 28	408 (10)						394 (7)	413 (58)
PCB 44	405 (9)		388 (23)				427 (11)	
PCB 49	408 (7)		435 (19)				405 (11)	
PCB 52	413 (8)		392 (43)				392 (12)	403 (66)
PCB 66	417 (13)		412 (50)				411 (13)	
PCB 74	403 (13)		363 (22)				414 (13)	477 (12)
PCB 87	396 (10)		376 (6)				416 (6)	
PCB 99	382 (21)	391 (11)	335 (19)				387 (7)	427 (12)
PCB 101	429 (12)	431 (12)	363 (13)				393 (7)	428 (19)
PCB 105	416 (14)	424 (12)	387 (7)				394 (5)	477 (19)
PCB 110	400 (11)	410 (14)	360 (6)				418 (6)	
PCB 114	50.4 (3.2)	49.0 (2.6)	34.5 (2.8)				40.2 (1.5)	58.7 (0.9)
PCB 188	436 (13)	437 (11)	348 (7)				405 (7)	436 (24)
PCB 123							50.1 (1.4)	54.9 (0.4)
PCB 128	428 (9)	426 (12)					394 (15)	430 (10)
PCB 138	453 (10)		438 (43)					530 (63)
PCB 146	392 (9)	393 (9)	326 (5)				391 (8)	387 (12)
PCB 149	391 (9)	389 (10)	365 (9)				345 (10)	
PCB 151	396 (13)	397 (9)	363 (7)				367 (9)	
PCB 153	487 (9)						425 (10)	460 (8)
PCB 153/132		484 (13)	473 (16)					513(22)
PCB 156	426 (8)	424 (9)	403 (22)				391 (10)	449 (27)
PCB 157	436 (11)	435 (12)	351 (25)				394 (9)	481 (38)
PCB 158	388 (10)	388 (13)	311 (26)					
PCB 167	415 (12)	411 (21)	358 (9)				397 (17)	435 (17)
PCB 170	432 (13)	430 (8)	384 (11)				412 (7)	461 (39)
PCB 172	406 (13)	411 (11)	375 (14)				379 (5)	403 (6)
PCB 177	397 (11)	396 (12)	375 (14)				388 (10)	403 (6)
PCB 178	391 (11)	397 (13)	358 (18)				375 (9)	403 (6)
PCB 180	478 (11)						411 (7)	489 (2)
PCB 180/193		495 (11)	349 (12)					496 (15)
PCB 183	418 (10)	435 (7)	355 (12)				379 (13)	462 (77)
PCB 187	433 (9)	435 (7)	350 (16)				384 (10)	459 (50)
PCB 189	408 (7)	408 (11)	359 (18)				380 (7)	464 (37)
PCB 194		397 (9)	370 (6)				370 (14)	410 (10)
PCB 195		399 (11)	352 (12)				379 (11)	412 (15)
PCB 196		397 (10)						403 (21)
PCB 196/203			681 (23)				707 (16)	
PCB 203		402 (8)						423 (15)
PCB 199			353 (18)				368 (7)	
PCB 201		400 (9)						393 (6)

Table S5 (cont). Data used for the Certification of SRM 1958 Organic Contaminants in Fortified Human Serum								
mean (std dev) for each method in mass fraction, ng/kg reconstituted serum								
Analyte	Method 1a	Method 1b	Method 2a	Method 2b	Method 2c	Method 3	CDC	Interlab
PCB 206		373 (11)	357 (6)				369 (5)	363 (12)
PCB 209		344 (18)	346 (12)				347 (9)	307 (15)
pentachlorobenzene			346 (61)					537 (31)
pentachlorophenol						3050 (140)		2500 (100)
pentabromophenol						490 (20)		397 (31)
hexachlorobenzene	439 (11)		390 (10)		416 (11)		440 (12)	537 (21)
?-HCH	241 (13)				225 (5)		324 (9)	250 (10)
?-HCH	282 (13)				212 (20)		326 (12)	290 (17)
?-HCH	292 (9)				286 (12)		378 (15)	303 (15)
oxychlordane		210 (8)	237 (18)		214 (9)		299 (7)	167 (15)
cis-chlordane		411 (12)			378 (13)		419 (10)	440 (10)
trans-chlordane		413 (12)			409 (8)		414 (12)	
cis-nonachlor		423 (11)			383 (29)		452 (30)	433 (6)
trans-nonachlor		468 (8)			463 (27)		464 (10)	480 (10)
mirex		376 (11)	287 (37)		479 (11)		380 (6)	390 (10)
octachlorostyrene			374 (20)				343 (17)	363 (15)
2,4'-DDE	447 (9)		478 (30)				435 (23)	
4,4'-DDE	1389 (32)		1109 (48)				1185 (21)	1333 (58)
2,4'-DDD	367 (17)		321 (40)					
4,4'-DDD	408 (8)		425 (8)					
2,4'-DDT	302 (11)		281 (26)				354 (15)	
4,4'-DDT	303 (15)		274 (36)				290 (7)	
PBDE 17		453 (10)		521 (28)			437 (7)	440 (11)
PBDE 28			439 (34)				459 (13)	478 (14)
PBDE 28/31		476 (8)		494 (18)				
PBDE 47		682 (12)	608 (23)	629(10)			647 (8)	686 (21)
PBDE 66		445 (9)	368 (15)	426 (13)			484 (13)	477 (11)
PBDE 85		495 (8)	468 (50)	413 (13)			472 (39)	525 (8)
PBDE 99		498 (8)	494 (26)	484 (9)			473 (11)	537 (57)
PBDE 100		497 (7)	460 (18)	444 (11)			459 (7)	521 (44)
PBDE 153		498 (8)	343 (61)	426 (7)			462 (9)	518 (25)
PBDE 154		476 (14)	425 (55)				419 (14)	
PBB 153		431 (9)					411 (8)	420 (17)
PBDE 183		463 (12)		418 (19)			423 (23)	508 (14)
PBDE 206		426 (9)		422 (29)				
PBDE 209		418 (13)		411 (22)				
Parlar 26					295 (15)		446 (12)	290 (10)
Parlar 50					152 (14)		372 (33)	163 (6)
Parlar 62					174 (21)		470 (63)	
PCB 126							7.21 (0.23)	8.35 (0.04)
PCB 169							7.93 (0.21)	8.26 (0.12)

Table S5 (cont). Data used for the Certification of SRM 1958 Organic Contaminants in Fortified Human Serum

mean (std dev) for each method in mass fraction, pg/kg reconstituted serum

Analyte	CDC	Liege	AXYS	Interlab
2,3,7,8-TCDD	87.9 (6.4)	100 (2)	94.5 (6.7)	
1,2,3,7,8-PCDD	105 (8)	115 (5)	93.2 (8.6)	
1,2,3,4,7,8-HxCD	88.0 (6.5)	102 (4)	96.3 (11.0)	
1,2,3,6,7,8-HxCD	303 (8)	400 (6)	317 (8)	
1,2,3,7,8,9-HxCD	94.3 (3.5)	105 (4)	100 (8)	
1,2,3,4,6,7,8-HpCD	502 (20)	650 (19)	541 (33)	
OCDD	2450 (100)	2860 (71)	2410 (14)	
2,3,7,8-TCDF	102 (5)	105 (4)	115 (11)	
1,2,3,7,8-PCDF	96.3 (4.6)	111 (1)	81.2 (11.0)	
2,3,4,7,8-PCDF	206 (6)	220 (1)	169 (6)	
1,2,3,4,7,8-HxCF	93.5 (7.5)	104 (3)	88.3 (6.6)	
1,2,3,6,7,8-HxCF	100 (7)	112 (5)	92.2 (5.5)	
1,2,3,7,8,9-HxCF	87.7 (6.6)	105 (3)	89.5 (7.6)	
2,3,4,6,7,8-HxCF	843 (30)	1010 (22)	838 (33)	
1,2,3,4,6,7,8-HpCF	282 (11)	317 (26)	290 (1)	
1,2,3,4,7,8,9-HpCF	73.0 (5.0)	93.8 (5.4)	86.7 (5.2)	
OCDF	83.2 (5.5)	87.6 (12.5)	78.3 (4.7)	
The following are mean (std dev) for each method in mg/dL reconstituted serum				
Total Cholesterol	128.3 (1.4)			130 (1)
"Free" Cholesterol	31.0 (0.5)			31.7 (0.6)
Phospholipids	149.8 (0.9)			150 (1)
Triglycerides	92.9 (0.9)			98.3 (0.6)

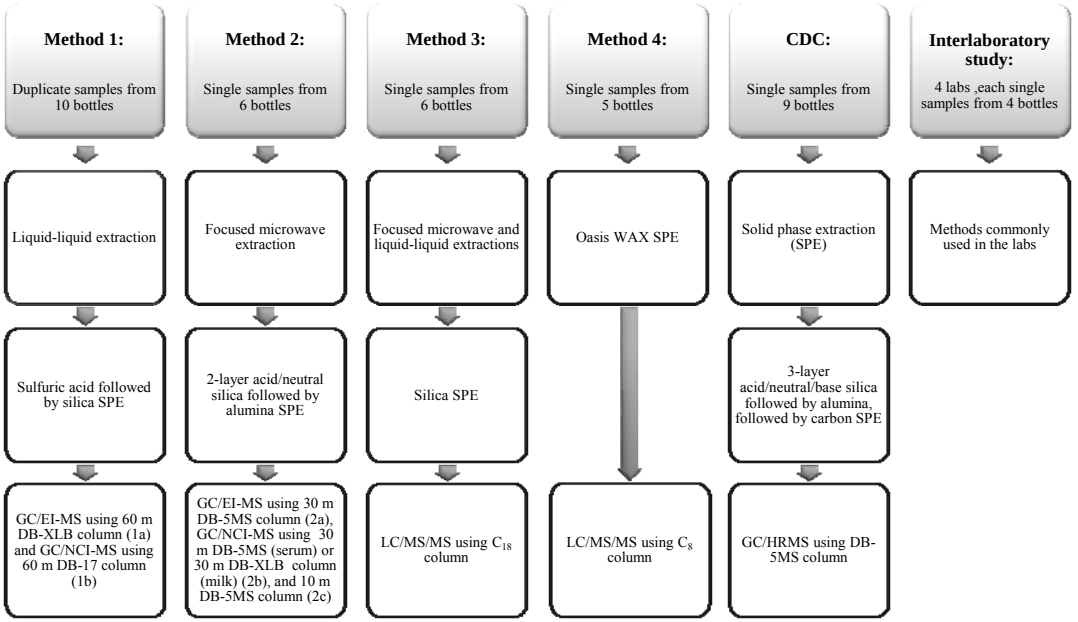

Figure S1 Analytical Methods Used.

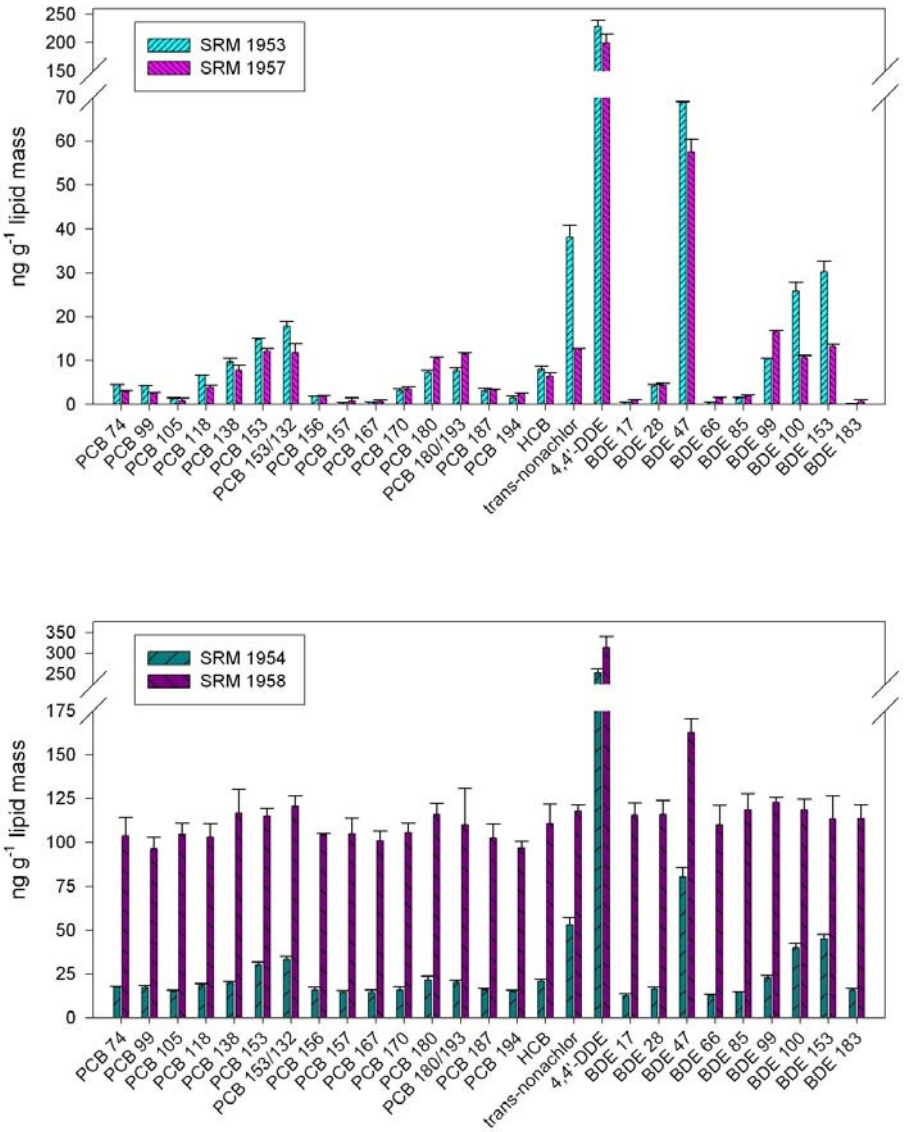

Figure S2. Comparison of mass fractions of selected compounds on a lipid-mass basis in the non-fortified milk (SRM 1953) and serum (SRM 1957) and in the fortified milk (SRM 1954) and serum (SRM 1958). Error bars represent the expanded uncertainty.

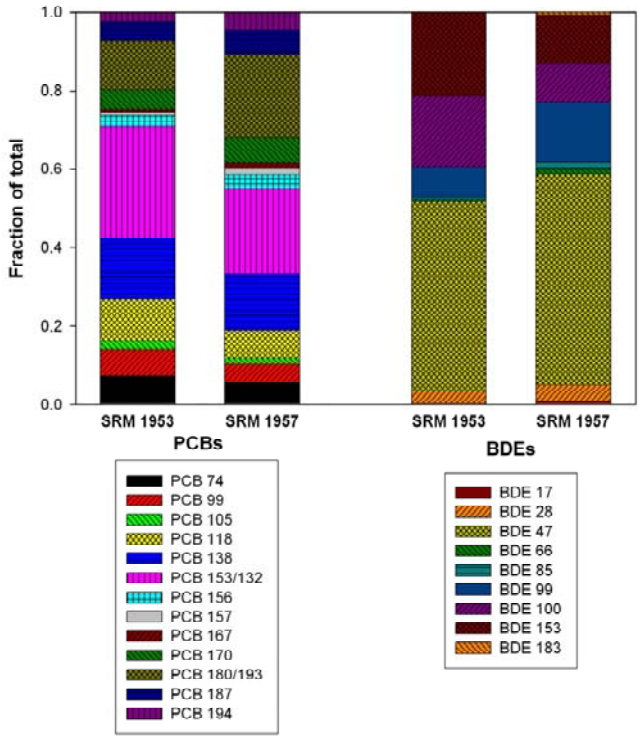

Figure S3. Relative proportions of PCB and PBDE congeners in the non-fortified milk (SRM 1953) and serum (SRM 1957) samples.