Published in final edited form as:

Environ Sci Technol. 2013 July 16; 47(14): 8015–8021. doi:10.1021/es401857v.

Temporal Trends of Polybrominated Diphenyl Ethers (PBDEs) in the Blood of Newborns from New York State during 1997 through 2011: Analysis of Dried Blood Spots from the Newborn Screening Program

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Abstract

Polybrominated diphenyl ethers (PBDEs) are ubiquitous environmental pollutants, and, on a global basis, North American populations are exposed to the highest doses of PBDEs. In response to the exponential increase in human exposure to PBDEs during the late 1990s, some PBDE formulations were phased out from production in the early 2000s. The effectiveness of the phase-out of commercial Penta-BDE and Octa-BDE mixtures in 2004 in the U.S. on human exposure levels is not known. Dried blood spots (DBSs), collected for the newborn screening program (NSP) in the U.S., are a valuable resource for the elucidation of trends in exposure to environmental pollutants in newborns. In this study, seven PBDE congeners were determined by gas chromatography-high resolution mass spectrometry (GC-HRMS) in archived DBS samples (in total, 51 blood spot composites from 1,224 newborns) collected from newborns in New York State (NYS) from 1997 to 2011. The most frequently detected PBDE congener was BDE-47, with a detection rate (DR) of 86%, followed by BDE-99 (DR: 45%) and BDE-100 (DR: 43%). The mean concentrations determined during 1997 through 2011 in the whole blood of newborns were 0.128, 0.040, and 0.012 ng/mL for BDEs -47, -99, and -100, respectively. A significant correlation was found among the concentrations of three major congeners ($p < 0.001$). PBDE concentrations were similar during 1997 through 2002 and, thereafter, decreased significantly, which was similar to the

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Supporting Information Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Conflict of interest/Disclaimer: None.

trends observed for perfluorinated compounds (PFCs) in DBS samples. Occurrence of PBDEs in the whole blood of newborns confirms that these compounds do cross the placental barrier.

Keywords

PBDEs; Dried blood spot; Human exposure; Temporal trend; Newborn

Introduction

On a worldwide basis, polybrominated diphenyl ethers (PBDEs) are commonly used flame retardants.¹ PBDEs have been used for over four decades in a wide variety of commercial and household products, such as polyurethane foams, plastics, textiles, and electronics.^{2–4} PBDEs have been marketed as three different commercial preparations: Penta-, Octa-, and Deca-BDE mixtures.⁵ PBDEs are now global environmental pollutants and have been detected in various environmental matrices and human tissues from around the world,^{6–10} including polar regions.^{11–13} Globally, PBDE levels were the highest in tissues of the North American general population and, in the 1990s, were increasing exponentially.^{3, 7, 14} Following reports of ubiquitous exposures and adverse health effects, the production of Penta- and Octa-BDE mixtures was phased out voluntarily by the manufacturers in the early 2000s and eventually ceased in the U.S. by the end of 2004.¹⁵

Diet, indoor air, and dust are the major sources of human exposure to PBDEs.⁵ As found by an exposure assessment, ingestion of indoor dust was reported as a predominant pathway of PBDE exposure for the U.S. general population.¹⁶ Human biomonitoring studies have shown that PBDE exposure in the U.S. is 10- to 100-fold higher than those in Europe and Asia.³ Although several studies have reported the occurrence of PBDEs in adults,^{2, 3} little is known about the exposure of newborns and infants to these chemicals. Further, the effectiveness of the phase-out of Penta- and Octa-BDE mixtures in 2004 in the U.S. on human exposures is not known. This study was conducted to address these knowledge gaps.

Newborn screening program (NSP), the practice of testing all newborns for certain disorders and conditions, has been conducted in the U.S. for over 40 years.¹⁷ The New York State (NYS) NSP receives dried blood spots (DBS) from approximately 250,000 newborns annually and began archiving unused residual blood spots from all newborns in 1997 for health-related follow-up testing and public health research.¹⁸ In our previous study, we documented the utility of NSP DBSs for tracking temporal trends in exposure to perfluorinated compounds (PFCs) in newborns.¹⁸ As the production of perfluorooctanesulfonate (PFOS) was phased out in 2002, we found a reduction in the exposure of newborns to this compound after 2002.¹⁸ No information is available on the trend for the exposure of newborns to PBDEs before and after the phase-out of Penta- and Octa-BDE mixtures in 2004 in the U.S.. In this study, archived DBS samples were collected at periodical intervals for over 15 years from 1997 to 2011. Concentrations of PBDEs were determined by gas chromatography-high resolution mass spectrometry (GC-HRMS) in pooled DBS samples collected from 1,224 newborns. The temporal trends of PBDE concentrations in newborns were compared with those reported for PFCs. To our knowledge, this is the first study to report the occurrence of PBDEs in DBS samples from newborns.

Methods and Materials

Chemicals and Reagents

Pesticide analysis-grade organic solvents (acetone, hexane, dichloromethane, and isooctane), ACS-grade formic acid (88%), and HPLC-grade water were purchased from J. T. Baker (Phillipsburg, NJ, USA). Target compounds, including seven PBDE congeners (BDEs -28, -47, -99, -100, -153, -154, and -183) and seven corresponding $^{13}\text{C}_{12}$ -labeled congeners were purchased from Wellington Laboratories (Guelph, ON, Canada). All $^{13}\text{C}_{12}$ -labeled congeners (5 ng/mL) were prepared in isooctane for use as internal standards (IS). Whatman 903 filter cards were purchased from Schleicher & Schuell Bioscience, Inc. (Keene, NH, USA) for use in method development and validation. The NSP uses the same type of filter card for the collection of DBS samples.

Two batches of working standard solutions were prepared for method validation and calibration curves. For method validation, standard solutions of 2 and 20 ng/mL each of PBDE congeners were prepared in acetone. The standards were used for spiking into adult whole blood for the preparation of in-house DBS samples with known concentrations. For calibration curves, both native and $^{13}\text{C}_{12}$ -labeled PBDE congeners were prepared at nine concentrations (0.02/0.02, 0.05/0.05, 0.1/0.1, 0.2/0.2, 0.5/0.5, 1/1, 2/2, 5/5, and 10/10 ng/mL) in isooctane.

Samples

In-house DBS samples were made to validate performance of the applied method. Briefly, 900 μL of whole blood was spiked with 100 μL of PBDE standards to yield final concentrations of 0.2 (low level) and 2 ng/mL (high level). After homogenization, the blood samples were allowed to equilibrate overnight, and 75 μL of the spiked blood was spotted on the filter card and allowed to air-dry overnight. All in-house DBS samples were stored at -20°C under desiccating conditions. This study was approved by the NYS Department of Health Institutional Review Board for the protection of human subjects.

Details in regard to the collection of NSP DBS samples from newborns are similar to those described in our previous study.¹⁸ Briefly, we selected 17 dates that spanned from 1997 to 2011. In some years, two dates were selected to represent winter and summer months. For each date, 24 1/4-in (~6.0 mm) diameter punches were collected from 24 individual DBS cards (i.e., from individual babies) and composited to represent one pooled DBS sample per time period (i.e., each sample represented blood from 24 newborns). Three pooled DBS samples were collected for each date. Overall, the samples originated from a total of 1,224 babies born in NYS between 1997 and 2011.

For the calculation of concentration of PBDEs in the pooled DBS samples, the whole blood volume represented by a 24 6 mm composite sample was estimated to be 322 μL . This estimation was based on a typical infant hematocrit level and the NYS NSP spot size and previous blood spot volume assessments.^{18, 19} Details on the blood volume estimation can be found in our previous study.¹⁸ Accordingly, for the method validation, four in-house DBS samples (75 μL each) were combined to prepare one pooled DBS sample for a collective volume of 300 μL whole blood.

Blanks

Adequate caution should be exercised in the analysis of trace levels of environmental chemicals present in DBS due to potential background contamination in filter cards and/or contamination that arises from sampling, transport, and storage of DBS.²⁰ For the characterization of levels of PBDE contamination, two types of blanks, procedural blanks

and field blanks, were analyzed. The procedural blanks were prepared by passage of all solvents and reagents through the entire analytical procedure. The field blanks were prepared by punching 24 6 mm spots from unspotted portions of 24 DBS cards archived by the NYS NSP. For each of the sampling years, a field blank (i.e., date-specific field blank) was collected. The blank spots were passed through the entire analytical procedure to discern contamination on the filter cards. All NSP DBS samples (including the field blanks) were stored at -20°C under desiccating conditions.

Extraction

The method for the extraction of DBS samples was similar to that reported earlier, with some modifications.⁴ Briefly, each pooled DBS sample was cut into small pieces with solvent-cleaned scissors and placed in a 10 mL glass tube. Then, 2 mL of formic acid-acetone mixture (2:3, v/v), 100 μL of IS solution (0.5 ng for each congener), and 2 mL of hexane-dichloromethane mixture (4:1, v/v) were added to each sample. Samples were sonicated in an ultrasonic bath (Branson Ultrasonics 3510R-DTH; Danbury, CT, USA) for 30 min and vortex mixed for 1 min. Then, the supernatant was separated by centrifugation (Eppendorf Centrifuge 5804; Hamburg, Germany) at $5000 \times g$ for 5 min and transferred into a new glass tube. The extraction was repeated with an additional 2 mL of hexane-dichloromethane mixture (4:1, v/v). The combined organic layer was washed with 1 mL of HPLC grade water and vortex mixed for 1 min. The organic layer was then separated by centrifugation and evaporated to ~ 0.2 mL under a gentle stream of nitrogen. The extract was further evaporated to 50 μL , vortex mixed, and stored at -20°C prior to analysis.

Instrumental Analysis

Identification and quantification of PBDE congeners were performed by a Thermo Scientific Ultra Trace gas chromatography-DFS high resolution mass spectrometry (GC-HRMS) (Thermo Electron Corporation; West Palm Beach, FL, USA). Two microliters of the sample were injected in the splitless mode by a TriPlus autosampler (Thermo Electron Corporation), and the injector temperature was maintained at 260°C . A ZB-5MSi Zebron® capillary column, with a 30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness, was used for the separation of PBDE congeners (Phenomenex; Torrance, CA, USA). The mass spectrometer was operated at a resolution of >10000 in selective ion monitoring (SIM) and at electron impact ionization energy of 40 eV. The MS transfer line temperature was 280°C , and the ion source temperature also was 280°C . Ultrapure helium was used as the carrier gas at a flow rate of 1 mL/min. Perfluorotributyl amine (PFTBA, FC43) was used as the calibrant. The GC oven temperature was programmed from 130°C (holding 1.5 min) to 216°C at $15^{\circ}\text{C}/\text{min}$ (holding 1 min), and then to 300°C at $5^{\circ}\text{C}/\text{min}$ with a final hold time of 4.1 min. The quantification and confirmation ions monitored for native and $^{13}\text{C}_{12}$ -labeled congeners and other MS parameters are shown in Table 1.

Figure S1 shows extracted ion chromatograms of PBDE congeners in standard solution at 0.05 ng/mL (2 μL injection) (Supporting Information, SI). The instrumental response was linear over a calibration range of 0.02–10 ng/mL ($n = 9$), with the regression coefficients (r) exceeding 0.99 for all congeners. The limit of quantification (LOQ) was set at a signal-to-noise ratio of 10. For the pooled DBS samples (i.e., whole blood volume equivalent of 322 μL), the LOQs were 0.003 ng/mL for BDEs -47, -153, and -154, 0.008 ng/mL for BDEs -28, -99, and -100, and 0.017 ng/mL for BDE-183. For statistical analysis, concentrations below the LOQs were assigned half the values of the LOQs. Method validation, quality assurance, and quality control details are presented below.

Results and Discussion

Method Validation

Totally, four procedural blanks were analyzed along with real DBS samples. Only BDEs -47 and -99 were detected in procedural blanks, with the mean concentrations of 0.09 ng/mL and 0.06 ng/mL, respectively. The source of these two congeners was thought to be from solvents and reagents used in the analysis.

For the in-house DBS samples, the recoveries were determined as the measured concentration divided by the spiked concentration and multiplied by 100. The respective mean recoveries ($n = 3$) of native and $^{13}\text{C}_{12}$ -labeled PBDE congeners ranged from 53.7% to 74.3% and 69.3% to 79.0% at the low level, and from 77% to 85.7% and 73.0% to 83.3% at the high level of fortification (Table 2). After the correction with the recoveries of IS (i.e., isotope dilution), the recoveries of target compounds were 77.0% to 95.8% and 102% to 107%, for low and high levels of fortification, respectively. Precision was expressed as a percentage of relative standard deviation (RSD) from triplicate analysis of samples at each level of fortification and measured on three different days (see details in Table 2). Except for BDE-28 at 0.2 ng/mL, all of the other congeners exhibited a RSD of <15% at both levels of fortification.

Field Blanks

In this study, 10 field blanks were analyzed. For 1997 and the period from 2008 to 2011, duplicate field blanks were collected, and an average concentration was used for these years below. Only BDEs -47, -99, and -100 were detected in field blanks, and their concentrations were similar during 1997 through 2002 and decreased thereafter (Fig. 1). Concentrations of PBDE congeners found in field blanks were much higher than those found in procedural blanks, which suggests the contamination in the filter cards and/or contamination during sampling, handling, and storage. An earlier study also found background levels of PBDEs in similar filter cards.⁴ Thus, monitoring of background levels of PBDE congeners present in DBS filter cards is crucial for accurate determination of these chemicals in DBS samples. The subtraction of background values from the concentrations determined in DBS sample is vital.

PBDE Concentrations in Dried Blood Spots

A typical extracted ion chromatogram (2 μL injection) of PBDE congeners in an actual DBS sample is presented in Fig. 2. In general, only less-brominated BDE congeners were frequently detected in NYS NSP DBS samples. Average recoveries of $^{13}\text{C}_{12}$ -BDE-28, -47, -99, -100, -153, -154, and -183 spiked into each DBS sample were 78%, 75%, 76%, 76%, 61%, 69%, and 61%, respectively. For each $^{13}\text{C}_{12}$ -labeled PBDE congener, RSD of recovery values was <25%. Reported concentrations of PBDEs in DBS samples were corrected for the recoveries of ISs. As discussed above, date-specific field blank concentrations were subtracted from all the measured concentrations of PBDEs in DBS samples. After field blank subtraction, the most frequently detected congeners in DBS were BDEs -47, -99 and -100, a pattern consistent with that reported in serum of pregnant women in the U.S.^{21, 22} Detection rates (DR%, concentration above the LOQ) for BDEs -47, -99, and -100 in DBS were 86%, 45%, and 43%, respectively.

The detection rates of the other four PBDE congeners (BDEs -28, -153, -154, and -183) were less than 30%, therefore, these congeners were not discussed individually in the following sections. The annual average concentrations of the three major congeners (BDEs -47, -99, and -100) and the sum of all PBDEs (ΣPBDEs) are summarized in Table 3. Whole blood concentrations ranged from <LOQ to 0.632 ng/mL for BDE-47, <LOQ to

0.398 ng/mL for BDE-99, and <LOQ to 0.072 ng/mL for BDE-100. The arithmetic (geometric) mean concentrations for BDEs -47, -99, and -100 and Σ PBDEs were 0.128 (0.074), 0.040 (0.017), 0.012 (0.008), and 0.197 (0.098) ng/mL, respectively. BDE-47 was the predominant congener, accounting for >60% of the total PBDE concentrations, followed by BDE-99 (16%) and BDE-100 (10%), which was consistent with the results reported in maternal blood (BDE-47 accounted for 53–64%, and BDE-99 for 15–19%).²³ Significant correlations were found between the concentrations of BDEs -47 and -99 (with a correlation coefficient (r) of 0.81, $p < 0.001$), BDEs -47 and -100 ($r = 0.86$, $p < 0.001$), BDEs -99, and -100 ($r = 0.91$, $p < 0.001$), which were expected because all the three congeners are the major constituents of the Penta-BDE mixture.²⁴

This is the first study to report the occurrence of PBDEs in DBS samples from newborns. In fact, no earlier study reported the occurrence of PBDEs in the blood of newborns. Nevertheless, several studies have reported the occurrence of PBDEs in cord blood and placenta from various countries.^{25–28} PBDEs were also reported to occur in liver tissues of fetuses and newborns in the U.S., which indicates maternal/trans-placental transfer of PBDEs to fetal tissues.²⁹ A significant correlation ($r^2 = 0.986$) was found between concentrations of PBDEs in maternal and cord blood.²³ All these findings provided the evidence for the exposure of fetuses (newborns) to PBDEs.^{25, 26}

Temporal Trends

The concentrations of PBDEs in DBS samples collected from 1997 to 2011 showed similar level between 1997 and 2002 and, thereafter, decreased sharply (Fig. 3). The sharp decrease in PBDE concentrations after 2004 reflects the phase-out in production of Penta- and Octa-BDE mixtures in the U.S. A statistically significant reduction in the concentrations was found for BDEs -47 and -100 and Σ PBDEs ($p < 0.003$) during 1997 through 2011. However, the reduction was not statistically significant for BDE-99 ($p > 0.1$) during 1997 through 2011 (Fig. 3). Although the production of Penta- and Octa-BDE mixtures has been ceased, products that contain PBDEs are expected to be sources of human exposures for years to come.³ Nevertheless, studies have shown that the concentrations of PBDEs in house dust collected from the U.S. have decreased since 2005.^{15, 30} For example, concentrations of PBDEs in house dust collected from California in 2011 were lower than those in the dust collected in 2006.³⁰ Because house dust is a major source of human exposure to PBDEs in the U.S.,¹⁶ a decline in the concentrations of PBDEs in dust suggests a reduction in human exposure to these compounds in recent years.

Earlier studies have shown that the concentrations of PBDEs increased in human serum collected from the U.S. during 1985 through 2002.³¹ After 2004, a declining trend for PBDEs in the whole blood of newborns was found, which is similar to the temporal trends of PBDEs reported for human breast milk from Sweden since the phase-out of the commercial PBDE mixtures in that country. For example, the concentrations of BDEs -47, -99, and -100 and Σ PBDE in mother's milk decreased during 1996 through 2010 in Sweden, following the phase-out of Penta-BDE in the late 1990s³².

The slopes of linear regression lines from 2006 through 2011 were used for the estimation of the disappearance half-lives of PBDE congeners in the blood of newborns in this study. The disappearance half-lives were 2.61, 2.56, and 5.52 years for BDE congeners -47, -99, and -100, respectively. The estimated half-lives of PBDEs in DBS samples were similar to those reported based on an experimental study in humans.³³ Further studies, however, are needed for a better understanding of the temporal trends in exposures of PBDEs in humans.

In our previous study, DBS samples collected from 1997 through 2007 were used for the assessment of temporal trends in exposure to PFCs in newborns.¹⁸ Concentrations of PFOS

exhibited a significant decline after the phase-out in production of this compound in the U.S., which is similar to that observed for PBDEs. A detailed comparison of temporal trends in the concentrations of PBDEs and PFCs in DBS is provided in the SI.

Limitations and Recommendations

This is the first study to evaluate temporal trends in PBDE exposures in newborns in the U.S. PBDE concentrations in DBS samples suggest a reduction in exposure of newborns after the phase-out of production in 2004. The archived samples of DBS collected from newborns offer an excellent resource for the study of fetal exposure of neonates to environmental chemicals. Further, the effectiveness of regulations on the production and use of environmental chemicals can be assessed through the analysis of temporally resolved DBS specimens. Nevertheless, it should be noted that this is a pilot study and that the number of samples analyzed is small. PBDEs are ubiquitous indoor pollutants, and, thus, PBDE contamination that arises during sampling, transport, and storage of DBS should be carefully assessed. Although field blanks were used in this study to account for the magnitude of PBDE contamination in archived filter cards, the extent of contamination in individual DBS cards is expected to vary. At least one field blank was collected and analyzed for each of the sampling years. Despite this, the relevance of the subtraction of concentrations found in field blanks with sample values is not known. Further, the volume of blood present in each punch was estimated from previously published hematocrit levels, and methods for the determination of accurate volume of blood present in each punch are needed. Nevertheless, the temporal trends reported in this study are independent of the absolute volume of blood contained in each pooled DBS sample.

In addition to the major findings of this study, some recommendations on the use of DBS for environmental chemical analysis can be presented. First, field blanks should be processed along with actual DBS samples; for trend studies, date-specific blank cards should be analyzed, and background levels should be subtracted from actual sample values. Second, for epidemiological studies, analysis of blood spots from individual cards (i.e., each newborn) would enable associations of health outcomes from environmental chemical exposures. Third, as the exact volume of blood present in each spot is still not known, quantification of the exact volume of blood in each spot should be a subject of future research.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This study was supported by the Intramural Research Program of the Eunice Kennedy Shriver National Institute of Child Health and Human Development (NICHD) contracts #HHSN275201200005C and #HHSN267200700019C to New York State Department of Health.

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Figure 1. Mean PBDE concentrations (ng/mL) found in field blanks collected from unspotted portions of archived dried blood spots (from 1997 to 2011) from New York State Newborn Screening Program

Figure 2.

Extracted ion chromatograms of PBDE congeners found in a pooled dried blood spot (DBS) sample and a date-specific field blank of the New York State Newborn Screening Program (Concentrations determined in the DBS sample are: BDE-47, 1.71 ng/mL; BDE-99, 1.03 ng/mL; BDE-100, 0.21 ng/mL; BDE-28, 0.11 ng/mL; other congeners, not detected)

Figure 3.
Temporal trends of PBDE concentrations in pooled dried blood spot samples from newborns, 1997 to 2011

Table 1

Quantification and Confirmation Ions Monitored for Native and $^{13}\text{C}_{12}$ -labeled PBDE Congeners for the Analysis of Dried Blood Spot Samples

Analyte	Quantification ion	Confirmation ion	Segment time	Lock Mass	Calibration Mass
BDE-28	405.8026	407.8006	10.5–14.2	401.97698	425.97698
BDE-47	485.7111	483.7131	14.2–17.4	463.97378	501.97059
BDE-99/100	405.7845	403.7865	17.4–21.0	401.97698	425.97698
BDE-153/154	483.6950	481.6970	21.0–24.9	463.97378	501.97059
BDE-183	561.6055	563.6035	24.9–29.0	501.97059	575.96740
$^{13}\text{C}_{12}$ -BDE-28	417.8429	419.8409	10.5–14.2	401.97698	425.97698
$^{13}\text{C}_{12}$ -BDE-47	497.7513	495.7533	14.2–17.4	463.97378	501.97059
$^{13}\text{C}_{12}$ -BDE-99/100	417.8247	415.8267	17.4–21.0	401.97698	425.97698
$^{13}\text{C}_{12}$ -BDE-153/154	495.7352	493.7372	21.0–24.9	463.97378	501.97059
$^{13}\text{C}_{12}$ -BDE-183	573.6457	575.6473	24.9–29.0	501.97059	575.96740

Table 2

Mean Recovery (% , mean) and Precision (RSD%) of the Analysis of PBDE Congeners in Dried Blood Spot Samples Prepared in the Laboratory at 0.2 ng/mL and 2 ng/mL Concentrations

Analyte	Native congeners		¹³ C ₁₂ -labeled congeners		Corrected by ISs	
	Recovery	RSD%	Recovery	RSD%	Recovery	RSD%
0.2 ng/mL						
BDE-28	65.3	15.5	79.0	15.8	82.8	3.3
BDE-47	71.0	11.0	75.0	8.0	94.6	5.1
BDE-99	74.3	18.3	77.3	5.2	95.8	14.3
BDE-100	65.3	12.8	74.7	5.4	87.3	8.1
BDE-153	62.7	13.0	69.3	5.1	90.2	8.9
BDE-154	62.3	12.1	76.0	3.5	82.0	10.4
BDE-183	53.7	13.5	69.7	5.8	77.0	11.0
2 ng/mL						
BDE-28	85.7	8.2	80.0	4.3	107	5.2
BDE-47	85.0	6.6	81.0	5.4	105	3.4
BDE-99	85.0	7.7	83.3	6.0	102	2.3
BDE-100	83.3	5.9	81.7	4.6	102	1.3
BDE-153	77.0	6.9	74.3	5.4	104	1.9
BDE-154	84.0	7.2	80.3	3.8	105	4.6
BDE-183	77.7	7.1	73.0	6.3	107	5.3

Table 3

Annual Mean Concentration^a (ng/mL) of BDEs –47, –99, –100, and ΣPBDEs in Pooled Dried Blood Spot Samples (322 µL Whole Blood) from the New York (after Subtraction of Date-specific Field Blank Concentrations)

Collection date	BDE-47	BDE-99	BDE-100	ΣPBDEs
1/2/1997	0.377	0.084	0.030	0.510
12/30/1997	0.296	0.031	0.026	0.367
12/29/1999	0.244	0.035	0.004	0.308
12/29/2001	0.351	0.165	0.042	0.598
12/30/2002	0.216	0.046	0.010	0.281
12/29/2004	0.051	0.036	0.009	0.110
6/26/2006	0.027	0.004	0.004	0.045
1/8/2007	0.072	0.011	0.007	0.095
6/1/2007	0.150	0.056	0.012	0.233
1/2/2008	0.098	0.025	0.010	0.142
5/31/2008 ^b	0.025	0.004	0.004	0.039
1/2/2009	0.031	0.013	0.006	0.056
6/1/2009	0.150	0.157	0.029	0.356
1/5/2010	0.008	0.004	0.004	0.022
6/1/2010	0.035	0.004	0.004	0.055
1/3/2011	0.023	0.004	0.004	0.036
6/1/2011	0.023	0.004	0.004	0.037
LOQ	0.003	0.008	0.008	-
DR (%)	86	45	43	-

^a Arithmetic mean. Concentrations below the LOQ were assigned half the values of the LOQ for analysis.

^b One extreme outlier was excluded, because more than two orders of magnitude concentration were found between concentrations for this sample and the other two samples on the date.