Supporting Information for

After the PBDE phase-out: A broad suite of flame retardants in repeat house dust samples from California

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Analytical Methods

Materials and reagents

Solvents used during analysis were all of pesticide grade. *n*-hexane (Hex) was purchased from Acros Organics (Geel, Belgium). Acetone (Ac), dichloromethane (DCM), ethyl acetate (EA), *iso*-octane and methanol (MeOH) were purchased from Merck (Darmstadt, Germany).

Standards of BDE 28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203 and 209, α-HBCYD, β-HBCYD, γ-HBCYD, BTBPE, DBDPE, HCDBCO, EH-TBB (or TBB), BEH-TEBP (or TBPH), HBB, TBBPA-BDBPE, TBBPA, DBE-DBCH (or TBECH) isomers, TBP-AE (or ATE), TBP-BAE (or BATE), TBP-DBPE (or DPTE), TBCO isomers, OBTMPI (or OBIND), dechlorane plus (DP) isomers, and labeled internal standards (IS) ^{13}C-BDE 209, ^{13}C-α-HBCD, ^{13}C-β-HBCD, ^{13}C-γ-HBCD, and ^{13}C-TBBPA were purchased from Wellington Laboratories (Guelph, ON, Canada). Standards of PCBs, PBBs and OCPs were purchased from Dr. Ehrenstorfer (Augsburg, Germany). BDE 77 and 128 (IS) were obtained from AccuStandard Inc. (New Haven, CT, USA). See Table 1 (main manuscript) for abbreviations and acronyms.

Standards of TEP, tri-*n*-propyl phosphate (T*n*PP), tri-*iso*butyl phosphate (TIBP), tri-*n*-butyl phosphate (TNBP), triphenyl phosphate (TPHP), tris(2-chloroethyl) phosphate (TCEP), tri-2-ethyl-hexyl phosphate (TEHP), ethyl-hexyl-diphenyl phosphate (EHDPP), tricresyl phosphate (TMPP or TCP, mixture of 4 isomers), tris(1,3-dibromopropyl) phosphate (TDBPP) and tris(1,3-dichloro-isopropyl) phosphate (TDCIPP, mixture of 2 isomers) were purchased from Chiron AS (Trondheim, Norway). Triamyl phosphate (TAP; IS) was purchased from TCI Europe (Zwijndrecht, Belgium). Labeled TPHP-d15 (IS) and tris(2-butoxyethyl) phosphate (TBOEP) were purchased from Sigma Aldrich. Tris(1-chloro-2-propyl) phosphate (TCIPP, mixture of 3 isomers) was purchased from Pfaltz & Bauer (Waterbury, CT, USA). Purity of analytical standards was >98%, except for TBOEP (>94%). Standard stock solutions were prepared in *iso*-octane, except for NBFRs which were prepared in a mixture of *iso*-octane:toluene (8:2, *v/v*).

Indoor dust SRM 2585 was purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Silica SPE cartridges (500 mg/3 mL, Bond Elut) were purchased from Agilent, while empty polypropylene filtration tubes (3 mL) SPE cartridges and 500 mg/3 mL Supelclean ENVI- Florisil cartridges were purchased from Supelco (Bellefonte, PA, USA). Silica gel, anhydrous sodium sulfate (Na_2SO_4), and concentrated sulfuric acid (H_2SO_4, 98%) were purchased from Merck. The preparation of acid impregnated silica (44%, *w/w*) was carried out as described elsewhere.[1] Glass test tubes were cleaned by soaking for at least 12 h in an alkali solution (diluted RBS 35, pH 11–12). After washing, the tubes were rinsed with water and dried at 100 °C for at least 12 h. The tubes were rinsed with Hex before use.

Sample Preparation

Due to the very comprehensive list of targeted flame retardants and the large differences in their physico-chemical properties, we have decided to use two separate sample preparation methods which have led to four extracts per sample (two fractions obtained per analytical method). These extracts were injected in various instruments, according to the expected presence of the FR groups.

<u>Method I (Florisil fractionation)</u>

The fractionation on Florisil was employed to measure the bulk of BFRs and OCs which elute in the first fraction (Fraction 1 – F1) and OPFRs which elute in the 2nd fraction (Fraction 2

– F2). The method is largely based on the recent method described by Van den Eede et al.[2] In detail, a sample aliquot (around 50 mg) was accurately weighed and spiked with IS (^{13}C-BDE 209, BDE 77, BDE 128, CB 143, TCEP-d12, TBOEP-d6, TDCIPP-d15, TAP, and TPHP-d15). Samples were extracted using 2 mL Hex-Ac (3:1 v/v) by a combination of vortexing and ultrasonic extraction (2 × 1 min vortex and 5 min ultrasonic extraction) which was repeated three times. After each extraction cycle, dust extracts were centrifuged at 3500 rpm for 2 min and supernatants were collected and transferred into clean glass tubes. The pooled supernatants were evaporated until dryness under a gentle nitrogen flow and redissolved in 1 mL Hex.

Prior to fractionation, Florisil® cartridges were prewashed with 6 mL of Hex. The extracts were quantitatively transferred and fractionation was achieved by eluting with 8 mL of Hex (F1) and 10 mL of EA (F2). The 1st fraction (F1) was evaporated until 1 mL and quantitatively transferred onto acidified silica 44% cartridges (prewashed with 6 mL Hex) for a second clean-up. The target analytes were eluted with 10 mL of Hex/DCM (1:1 v/v), and afterwards evaporated until dryness under gentle nitrogen flow and reconstituted in 100 µL of iso-octane.

In the 2nd fraction (F2), IS BDE 128 was added for the quantification of TBPH, followed by evaporation until dryness and resolubilized in 100 µL of iso-octane.

Fraction F1, contained PBDEs, most NBFRs, OCs and PBBs, was subjected to analysis by GC-ECNI/MS (different acquisition methods) and GC-EI/MS (confirmation of OCs and PBBs). The 2nd fraction (F2), containing OPFRs and BEH-TBEP was subjected to analysis by GC-EI/MS (for OPFRs) and GC-ECNI/MS (for BEH-TBEP and TDBPP).

Method II (Silica fractionation)

The fractionation on Silica was in first instance employed to measure HBCYDs and TBBPA which eluted in the 2nd fraction (Fraction B – FB) and confirmation of PBDEs which eluted in the first fraction (Fraction A – FA). The extraction was similar to that described above[2] while the fractionation on silica was similar to the procedure described by Roosens et al.[3]

In detail, a sample aliquot (typically 50 mg) was accurately weighed and spiked with a mixture containing IS (^{13}C-α-, β-, γ-HBCYD, ^{13}C-TBBPA, ^{13}C-BDE 209, BDE 77, and BDE 128). Samples were extracted using 2 mL Hex-Ac (3:1 v/v) by a combination of vortexing and ultrasonic extraction (2 × 1 min vortex and 5 min ultrasonic extraction) which was repeated three times. After each extraction cycle, dust extracts were centrifuged at 3500 rpm for 2 min and supernatants were collected and transferred into clean glass tubes. The pooled supernatants were evaporated until dryness under a gentle nitrogen flow and redissolved in 1 mL Hex.

Prior to fractionation, silica cartridges were topped with 100 mg acid silica (44%) and prewashed with 6 mL of Hex. The extracts were quantitatively transferred and fractionation was achieved by eluting with 8 mL of Hex (Fraction A – FA) and 10 mL of DCM (Fraction B – FB).

Both fractions were afterwards evaporated until dryness under gentle nitrogen flow. Fraction FA, containing PBDEs, was reconstituted in 100 µL of iso-octane and was subjected to GC-ECNI/MS. The 2nd fraction (FB), containing HBCYDs, was resolubilized in 100 µL of methanol and further subjected to LC-MS/MS analysis.

Chemical Analysis

GC/ECNI-MS Analysis

The analysis of F1, containing PBDEs, most NBFRs, and OCs, and the analysis of F2, containing BEH-TBEP, was performed with an Agilent 6890 GC coupled to an Agilent 5973 MS operated in electrochemical negative ionization (ECNI) mode. The GC system was equipped

with electronic pressure control and a programmable-temperature vaporizer (PTV). A volume of 2 μL of cleaned extract was injected on a DB-5 column (15 m × 0.25 mm × 0.10 μm) using solvent vent injection. The injection temperature was set at 90 °C, hold 0.04 min, ramp 700 °C/min to 295 °C. Vent time was 0.02 min and vent flow 75 mL/min. Injection was performed under a pressure of 10 psi until 1.25 min and purge flow to split vent of 50 mL/min after 1.25 min. The GC temperature program was 90 °C, hold 1.50 min, ramp 10 °C/min to 300 °C, hold 3 min, ramp 40 °C/min to 310 °C, hold 5 min. Helium was used as a carrier gas with a ramped flow rate of 1.0 mL/min until 20 min and then raised to 2.0 mL/min. The mass spectrometer was employed in selected ion monitoring (SIM) mode, with ions 79 and 81 monitored the whole run time. For BDE 209, ions 487 and 485 were used, while ^{13}C-BDE 209 was monitored using ions 495 and 497. Dwell times were set on 35 ms. The ion source, quadrupole and interface temperatures were set at 250, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V. Methane was used as moderating gas. An overview of analytes containing detailed nomenclature and applied abbreviation, together with ions acquired for identification and quantification purposes on the GC-EI-MS and GC-ECNI-MS are presented in Table SI1.

GC/EI-MS Analysis

Analysis of OPFRs in F2 was performed with an Agilent 6890 GC coupled to an Agilent 5973 MS operated in electron impact ionization (EI) mode. The GC system was equipped with electronic pressure control and a programmable-temperature vaporizer (PTV). One μL of purified extract was injected on a HT-8 column (25 m × 0.22 mm × 0.25 μm) using cold splitless injection. The injection temperature was set at 90 °C, hold 0.03 min, ramp 700 °C/min to 290 °C. Injection was performed using a pressure of1 bar until 1.25 min and purge flow to split vent of 50 mL/min after 1.25 min. The GC temperature program was 90 °C, hold 1.25 min, ramp 10 °C/min to 240 °C, ramp 20 °C/min to 310 °C, hold 16 min. Helium was used as a carrier gas with a flow rate of 1.0 mL/min. The mass spectrometer was run in selected ion monitoring (SIM) mode. Dwell times ranged between 20 and 30 ms in different acquisition windows. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively, and the electron multiplier voltage was at 2200 V.

LC-MS/MS

The determination of individual HBCYD isomers and TBBPA in the Fraction B (silica fractionation) was achieved using a dual pump Agilent 1100 Series liquid chromatograph equipped with autosampler and vacuum degasser. A Luna C18(2) reversed phase (RP) analytical column (150 mm × 2 mm i.d., 3 μm particle size, Phenomenex) was used for the separation of α-, β-, and γ-HBCYD. A mobile phase of (A) ammonium acetate 2mM in water/methanol (1:1 v/v) and (B) methanol at a flow rate of 0.250 mL/min was applied for elution of HBCYD isomers; starting at 75% (B) held for 2 min, then increased linearly to 100% (b) until 9 min; held until 12 min followed by a linear decrease to 70% (B) over 0.5 min and held for 7.5 min.

The target analytes were baseline separated on the RP column with retention times of 4.0, 6.0, 6.8 and 7.4 min for TBBPA, α-, β- and γ-HBCYD, respectively. MS analysis was performed using an Agilent 6410 triple quadrupole MS system operated in the electrospray negative ionization mode. N2 was used as drying gas at a flow of 10 L/min and heated to 300 °C. Nebulizer pressure was 35 psi and capillary voltage 4000 V. HBCYD isomers were quantified by isotope dilution. MS/MS detection operated in the MRM mode was used for quantitative determination of the HBCYD isomers based on m/z 640.6 to 81 and m/z 652.6 to 81 for the native and ^{13}C-labeled diastereomers, respectively. Fragmentor voltage and collision energy were

set as 80 and 15 V, respectively. For quantitative determination of TBBPA, the following MRMs were used: m/z 5 to 81 and m/z 652.6 to 81 for the native and 13C-labeled diastereomers, respectively.

Quality Control

Six procedural blanks were analyzed in the same batches as the samples and results are blank corrected. This implies subtraction of mean blank values (in pg) from the raw FR values (in pg) in the samples. Blank values, when detected, were <0.5% of sample values. Compounds consistently detected (found in all blanks) in the procedural blanks at levels >1 ng (organophosphates) or >10 pg (all others) were: TIBP (mean=3.4ng), TNBP (13.1ng), TEHP (3.8ng), β-HBCYD (40pg), BDE 47 (19pg), BDE 85 (14pg), BDE 154 (40pg), BDE 196 (11pg), BTBPE (18pg), and BDE 209 (1330pg). See Table SI2 for summary of mass values in procedural blanks.

Method limits of quantification (LOQ) were calculated as three times the standard deviation of blank values and divided by the amount of dust used for analysis (typically 50 mg). For compounds not detected in the blanks, the LOQ was calculated based on the signal to noise ratio 10/1, taking into account also the chromatogram's characteristics for the respective retention time (co-elution, noisy baseline, etc). LOQs are compound-specific variables and therefore spanned a large range of concentrations (see Table 1 in manuscript).

The method has been recently validated as described by Van den Eede et al.[2] A series of optimization and spiking experiments were performed for BFRs and OPFRs at two concentration levels, Q_{low} and Q_{high}, and three replicates for each level. Precision between different days were assessed using the same concentration levels spiked on a low contaminated dust sample, using three replicates per level and executed on three different days. Precision was within 12% for each set of triplicates and all analytes. The recovery was calculated by subtracting the blank concentrations and divided by the calculated concentration of a mixed solution of standards (having the same concentrations). Further details can be found in Van den Eede et al.[2]

SRM 2585 (Organic Contaminants in House Dust), which has certified values for PBDEs and indicative values for EH-TBB, BEH-TBEP, HBCYDs, chlorinated OPFRs and TBOEP, was used to test the accuracy (Figure SI1). Concentrations of PBDEs range between 2 and 30% relative difference from the certified values. EH-TBB, BEH-TBEP and chlorinated OPFRs were within 0 and 56% relative difference; while analytes with lower concentration ranges (e.g. HBCYD) fared worse. Despite a few discrepancies, there does not appear to be a systematic bias to the samples and values were not adjusted.

Inter-laboratory comparisons were conducted using samples collected in 2006 and analyzed at two different time periods. In 2006, as part of the Northern California Household Exposure Study, Southwest Research Institute (SWRI) analyzed 50 dust for approximately 100 semivolatile organic compounds, including PBDEs and legacy compounds. The 16 homes in this study are a subset of the 50 homes studied in 2006. In 2011, for this study, University of Antwerp analyzed stored dust samples (splits of the original samples collected in 2006) for FRs and legacy compounds. Results from the 2006 and 2011 analysis are compared for the 9 overlapping analytes (Figure SI2). Results for all 9 are significantly correlated (Spearman ρ = 0.76-1, $p<0.05$). PBDE concentrations were similar, except for the one or two homes with the highest concentrations where SWRI reports higher concentrations (up to 2-fold) than University of Antwerp. However, University of Antwerp appears to report higher concentrations (up to 2-fold) for legacy analytes at the upper end of the concentration range.

Correlation and Cluster Analysis

Kendall's tau rank correlation estimates, adjusted for censored data, were calculated to investigate relationships between analytes within each sampling round and for each analyte across rounds, with p-values obtained from 1,000 bootstrap replications (Figure SI4). Kendall's tau correlation estimates, with adjustments for ties, are more accurate for censored data than Pearson or Spearman estimates with arbitrary substitutions (e.g. LOQ/2); although, in general, they tend to be lower than corresponding Pearson or Spearman estimates.[4]

Cluster analysis was performed to elucidate common mixtures and potential sources (Figure SI5). Distance matrices were constructed using Kendall's tau correlation estimates for all analytes with sufficient number of simultaneous detects (>3 pairs) within each sampling round. A simple approach of using one minus correlation to represent the dissimilarity matrix was used for ease of interpretability. Chemicals close together on the same long stem on the dendrogram have higher correlations. Sensitivity of clusters to bootstrapping for correlation estimates was evaluated by comparing results from multiple iterations. Hierarchical cluster analysis, using the complete agglomeration method, and subsequent graphing were performed using the 'hclust' package in R.

Daily Intake Calculation

Daily intake (DI) rate (μg/day) for FRs in house dust was calculated using the following equation:

$$C \times IR \times CF = DI$$

where, C is the concentration (ng/g), IR is the ingestion rate (mg_{dust}/day), and CF is the conversion factor (0.001 g/mg × 0.001 ug/ng) The cumulative FR concentration is 290,000 ng/g. We assume a dust ingestion rate of 100 mg/day.[5]

Table SI1. Full and abbreviated nomenclature, identification and quantification ions (bold values), their respective internal standards (IS) used for quantification of targeted analytes, together with instrumental technique employed for their analysis.

Compound	**Acronym**	Identification - **Quantification Ions**	**Internal Standard (IS)**	**Instrument For Analysis**
1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)-ethane	*p,p'*-DDD	248, **71**	CB 143	GC-ECNI/MS
1,1-bis-(4-chlorophenyl)-2,2-dichloroethene	*p,p'*-DDE	318, **316**	CB 143	GC-ECNI/MS
1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane	*p,p'*-DDT	248, **71**	CB 143	GC-ECNI/MS
trans-nonachlor	TN	**444**	CB 143	GC-ECNI/MS
trans-chlordane	TC	410, **408**	CB 143	GC-ECNI/MS
cis-chlordane	CC	410, **408**	CB 143	GC-ECNI/MS
2,2',4,4',5,5'-Hexachlorobiphenyl	CB 153	360, **362**	CB 143	GC-ECNI/MS
2,2',3,4,4',5,5'-Heptachlorobiphenyl	CB 180	396, **394**	CB 143	GC-ECNI/MS
2,2',3,4,5,6'-Hexachlorobiphenyl (IS)	*CB 143*	*360, **362***	n.a.	*GC-MS*
2,4,4'-Tribromodiphenyl ether	BDE 28	81, **79**	BDE 77	GC-ECNI/MS
2,2',4,4'-Tetrabromodiphenyl ether	BDE 47	81, **79**	BDE 77	GC-ECNI/MS
2,2',4,4',6-Pentabromodiphenyl ether	BDE 100	81, **79**	BDE 77	GC-ECNI/MS
2,2',4,4',5-Pentabromodiphenyl ether	BDE 99	81, **79**	BDE 77	GC-ECNI/MS
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE 154	81, **79**	BDE 77	GC-ECNI/MS
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE 153	81, **79**	BDE 77	GC-ECNI/MS
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE 183	81, **79**	BDE 128	GC-ECNI/MS
2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	BDE 197	81, **79**	BDE 128	GC-ECNI/MS
2,2',3,4,4',5,5',6-Octabromodiphenyl ether	BDE 203	81, **79**	BDE 128	GC-ECNI/MS
2,2',3,3',4,4',5,6'-Octabromodiphenyl ether	BDE 196	81, **79**	BDE 128	GC-ECNI/MS
Decabromodiphenyl ether	BDE 209	485, **487**	^{13}C-BDE 209	GC-ECNI/MS
3,3',4,4'-Tetrabromodiphenyl ether (IS)	*BDE 77*	*81, **79***	n.a.	*GC-ECNI/MS*
2,2',3,3',4,4'-Hexabromodiphenyl ether (IS)	*BDE 128*	*81, **79***	n.a.	*GC-ECNI/MS*
^{13}C-Decabromodiphenyl ether (IS)	*^{13}C-BDE 209*	*497, **495***	n.a.	*GC-ECNI/MS*
α-Hexabromocyclododecane	α-HBCYD**	640.6→78.9	^{13}C-α-HBCYD	LC/ESI-MS/MS
β-Hexabromocyclododecane	β-HBCYD**	640.6→78.9	^{13}C-β-HBCYD	LC/ESI-MS/MS
γ-Hexabromocyclododecane	γ-HBCYD**	640.6→78.9	^{13}C-γ-HBCYD	LC/ESI-MS/MS
^{13}C-Hexabromocyclododecanes (α-, β-, γ-)	*^{13}C-HBCYDs***	*652.8→78.9*	n.a.	*LC/ESI-MS/MS*
Tetrabromobisphenol-A	TBBPA	542.6→78.9	^{13}C-TBBPA	LC/ESI-MS/MS
^{13}C-Tetrabromobisphenol-A	*^{13}C-TBBPA*	*554.6→78.9*	n.a.	*LC/ESI-MS/MS*
Tri-ethyl-phosphate	TEP	**155**	TAP	GC-EI/MS
Tri-*n*-propyl-phosphate	TNPP	**183**	TAP	GC-EI/MS
Tri-*iso*-butyl-phosphate	TIBP	155, **211**	TAP	GC-EI/MS
Tri-*n*-butyl-phosphate	TNBP	155, **211**	TAP	GC-EI/MS
Tris-(2-chloroethyl)-phosphate	TCEP	251, **249**	TCEP-d12	GC-EI/MS
Tris-(1-chloro-2-propyl)-phosphate	TCIPP	279, **277**	TCEP-d12	GC-EI/MS
Tri-(2-butoxyethyl)-phosphate	TBOEP	199, **299**	TBEP-d6	GC-EI/MS

Compound	**Acronym**	Identification - **Quantification Ions**	**Internal Standard (IS)**	**Instrument For Analysis**
Tris-(1,3-dichloro-isopropyl)-phosphate	TDCIPP	379, **381**	TDCPP-d15	GC-EI/MS
Tri-phenyl-phosphate	TPHP	325, **326**	TPP-d15	GC-EI/MS
Tri-cresyl-phosphate	TMPP	367, **368**	TPP-d15	GC-EI/MS
tri-(2-ethylhexyl)-phosphate	TEHP	99, **211**	TBEP-d6	GC-EI/MS
ethylhexyl diphenyl phosphate	EHDPP	250, **251**	TPP-d15	GC-EI/MS
Tri-amyl-phosphate (IS)	TAP	169, **239**	n.a.	GC-EI/MS
Tri-phenyl-phosphate-d15 (IS)	*TPHP-d15*	*339, **341***	n.a.	*GC-EI/MS*
Tri-(2-chloro-ethyl)-phosphate-d12 (IS)	*TCEP-d12*	*263, **261***	n.a.	*GC-EI/MS*
Tri--(1,3-dichloro-isopropyl-*phosphate-d15 (IS)*	*TDCIPP-d15*	*394, **396***	n.a.	*GC-EI/MS*
Tri-(2-butoxyethyl)-*phosphate-d15 (IS)*	*TBOEP-d6*	*202, **303***	n.a.	*GC-EI/MS*
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	EH-TBB (TBB)	359, **357**	BDE 77	GC-ECNI/MS
bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate	BEH-TEBP (TBPH)	515, **384**	BDE 128	GC-ECNI/MS
1,2-*bis*(2,4,6-tribromophenoxy)ethane	BTBPE	81, **79**	BDE 128	GC-ECNI/MS
Decabromodiphenylethane	DBDPE	81, **79**	^{13}C-BDE 209	GC-ECNI/MS
Hexachlorocyclopentadienyl-Dibromocyclooctane	DBHCTD (HCDBCO)	79, **310**	BDE 77	GC-ECNI/MS
hexabromobenzene	HBB	81, **79**	BDE 77	GC-ECNI/MS
tetrabromobisphenol A - bis(2,3-dibromopropylether)	TBBPA-BDBPE	81, **79**	^{13}C-BDE 209	GC-ECNI/MS
alpha-1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	alpha-TBECH	81, **79**	BDE 77	GC-ECNI/MS
beta-1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	beta-TBECH	81, **79**	BDE 77	GC-ECNI/MS
gamma-1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	gamma-TBECH	81, **79**	BDE 77	GC-ECNI/MS
delta-1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	delta-TBECH	81, **79**	BDE 77	GC-ECNI/MS
2,4,6-tribromophenyl allyl ether	TBP-AE (ATE)	81, **79**	BDE 77	GC-ECNI/MS
2-bromoallyl-2,4,6-tribromophenyl ether	TBP-BAE (BATE)	81, **79**	BDE 77	GC-ECNI/MS
2,4,6-tribromophenyl 2,3-dibromopropyl ether	TBP-DBPE (DPTE)	81, **79**	BDE 77	GC-ECNI/MS
alpha-1,2,5,6-tetrabromocyclooctane	alpha-TBCO	81, **79**	BDE 77	GC-ECNI/MS
beta-1,2,5,6-tetrabromocyclooctane	beta-TBCO	81, **79**	BDE 77	GC-ECNI/MS
octabromo-1,3,3-trimethyl-1-phenylindane	OBTMPI (OBIND)	81, **79**	BDE 128	GC-ECNI/MS
tris(2,3-dibromopropyl) phosphate	TDBPP	81, **487**	BDE 128	GC-ECNI/MS
3,3',5,5'-tetrabromo biphenyl	BB 80	472, **470**	BDE 77	GC-EI/MS
2,2',4,5',6-pentabromo biphenyl	BB 103	548, **550**	BDE 77	GC-EI/MS
2,2',4,4',5,5'-hexabromo biphenyl	BB 153	625.5, **627.5**	BDE 77	GC-EI/MS
2,2',3,4,4',5,5'-heptabromo biphenyl	BB 180	548, **550**	BDE 77	GC-EI/MS
decabromo biphenyl	BB 209	81, **79**	^{13}C-BDE 209	GC-ECNI/MS
syn-Dechlorane plus	syn-DP	650, **652**	BDE 128	GC-ECNI/MS
anti-Dechlorane plus	anti-DP	650, **652**	BDE 128	GC-ECNI/MS

n.a. – not applicable

Table SI2. Summary of procedural blanks.

Compound	Units	Bl-01	Bl-02	Bl-03	Bl-04	Bl-05	Bl-06	Mean	SD	RSD (%)
TBBPA	pg	0	0	0	0	0	0	0	0.0	NA
α-HBCYD	pg	0	0	0	0	0	0	0	0.0	NA
β-HBCYD	pg	32	40	19	48	42	37	40	5.9	15
γ-HBCYD	pg	0	0	0	0	0	0	0	0.0	NA
pp-DDE	pg	0	0	0	0	0	0	0	0.0	NA
pp-DDD	pg	0	0	0	0	0	0	0	0.0	NA
pp-DDT	pg	0	0	0	0	0	0	0	0.0	NA
BB 80	pg	0	0	0	0	0	0	0	0.0	NA
BB 103	pg	0	0	0	0	0	0	0	0.0	NA
BB 153	pg	0	0	0	0	0	0	0	0.0	NA
BB 180	pg	0	0	0	0	0	0	0	0.0	NA
CB 153	pg	4	0	8	6	6	5	4	2.5	61
CB 180	pg	5	5	11	9	9	11	8	2.4	31
trans-chlordane (TC)	pg	0	0	0	0	0	0	0	0.0	NA
cis-chlordane (CC)	pg	0	0	0	0	0	0	0	0.0	NA
trans-Nonachlor (TN)	pg	0	0	0	0	0	0	0	0.0	NA
BDE 28	pg	0	0	7	0	0	0	0	0.0	NA
BDE 47	pg	12	17		21	23	23	19	4.8	25
BDE 66	pg	0	0		0	0	0	0	0.0	NA
BDE 100	pg	0	0		0	0	0	0	0.0	NA
BDE 99	pg	6	9		6	6	10	7	1.9	25
BDE 85	pg	9	9		18	17	19	14	4.9	35
BDE 154	pg	25	23	33	52	51	49	40	14.8	37
BDE 153	pg	5	8		13	12	11	10	3.4	36
HBB-ion79	pg	2	5	7	8	8	3	5	2.6	50
BDHCTD (HCDBCO)	pg	0	0	0	0	0	0	0	0.0	NA
EH-TBB (TBB)	pg	0	0	0	0	0	0	0	0.0	NA
BDE 183	pg	0	0	0	0	0	0	0	0.0	NA
BDE 197	pg	5	7	13	11	8	11	8	2.4	29
BDE 203	pg	5	6	11	13	10	10	9	3.1	35
BDE 196	pg	6	5	15	11	13	19	11	5.5	51
BTBPE	pg	18	20	29	19	14	17	18	2	12
BDE 209	pg	1540	920	2030	1490	1330	1370	1330	245	18
DBDPE	pg	0	0	0	0	0	0	0	0	NA
alpha-TBECH	pg		0	0	0	0	0	0	0	NA
beta-TBECH	pg	0	0	0	0	0	0	0	0	NA
gamma-TBECH	pg	0	0	0	0	0	0	0	0	NA
delta-TBECH	pg	0	0	0	0	0	0	0	0	NA
TBP-AE (ATE)	pg	0	0	0	0	0	0	0	0	NA
TBP-BAE (BATE)	pg	0	0	0	0	0	0	0	0	NA
TBP-DBPE (DPTE)	pg	0	0	0	0	0	0	0	0	NA
alpha-TBCO	pg	0	0	0	0	0	0	0	0	NA
beta-TBCO	pg	0	0	0	0	0	0	0	0	NA
OBTMPI (OBIND)	pg	0	0	0	0	0	0	0	0	NA
syn-DP	pg	5	7	0	0	8	0	3	4	112
anti-DP	pg	3	4	3	0	3	0	2	2	79

Compound	Units	BI-01	BI-02	BI-03	BI-04	BI-05	BI-06	Mean	SD	RSD (%)
TDBPP-ion79	pg	2	0	0	0	0	0	0	1	245
BEH-TEBP (TBPH) - ion515	pg	11	10	0	8	0	0	5	5	112
BEH-TEBP (TBPH) - ion384	pg	10	7	0	0	0	0	3	5	158
TBBPA-dbde	pg	0	0	0	0	0	0	0	0	NA
TEP	ng	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0	85
TnPP (propyl)	ng	0.2	0.0	0.0	0.2	0.1	0.0	0.1	0	116
TIBP (iso-butyl)	ng	4.2	4.7	3.2	2.1	2.2	4.1	3.4	1	32
TNBP (n-butyl)	ng	12.2	12.0	21.0	13.0	10.1	10.3	13.1	4	31
TCEP	ng	0.2	0.2	0.0	0.2	0.0	0.0	0.1	0	112
TCIPP 1	ng	1.3	1.3	0.8	0.7	0.5	0.9	0.9	0	36
TCIPP 2	ng	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0	245
TBOEP	ng	7.9	8.8	0.0	0.0	0.0	7.1	4.0	4	110
TEHP-ion 99	ng	5.7	2.6	3.3	4.5	4.3	2.5	3.8	1	33
TPHP	ng	0.3	0.3	0.3	0.2	0.2	0.1	0.2	0	44
EHDPP-ion 251	ng	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0	41
EHDPP-ion 250	ng	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0	34
TMPP 1	ng	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	NA
TMPP 2	ng	0.2	0.3	0.4	0.3	0.2	0.3	0.3	0	30
TCP 3	ng	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	NA
TCP 4	ng	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0	245
TDCIPP 1	ng	1.3	1.2	1.4	1.5	1.3	1.5	1.4	0	8
TDCIPP 2	ng	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	NA

NA – not applicable

Table SI3. Residential soil screening levels.[6]

Compound	SL (mg/kg)[a]
BDE 47	6.1
BDE 99	6.1
BDE 209	430
HBB	120
TCEP	24
TDCIPP	3.7[b]
TNBP	54
TEHP	150
CB 153	0.22
CB 180	0.22
BB 80	0.02
BB 103	0.02
BB 153	0.02
BB 180	0.02
BB 209	0.02
CC	1.6
TC	1.6
pp-DDT	1.7
pp-DDE	1.4
pp-DDD	2.0

[a] Screening levels include ingestion, inhalation and dermal pathways and are risk-based concentrations derived from standard exposure information and EPA toxicity values.

[b] Derived using standard assumptions and cancer slope factor published under California's Proposition 65 (0.13 $mg/kg\text{-}day^{--1}$)

Table SI4. Summary of flame retardant uses and health effects

Flame Retardant Class	Uses	Health Concerns[a]
Polybrominated diphenyl ethers (PBDEs)		
PentaBDE CAS 32534-81-9 *Includes congeners BDE 28, BDE 47, BDE 66, BDE 85, BDE 99, BDE 100, BDE 153, and BDE 154*	Additive flame retardant in polyurethane foams[7] Phased out in US in 2004 10-50 million pounds produced in 2002 in US	EPA Action Plan Chemical Dose-dependent decrease of T4, increased liver weight and P450 induction after 4 days of oral administration of DE-71 to 28 d.o. female rats. [8] Decrease of T4 and T3, increase of TSH, hypothyroid indicators, increased liver to body weight ratio, increased P450 induction, decrease in seminal vesicle and ventral prostate weights and delayed preputial separation in males, delayed vaginal opening in females; males more sensitive in this screening battery for EPA ED Screening Program using gavage of DE-71 on young Wistar rats[9] BDE-99: gestational exposure associated with hyperactivity and permanently impaired spermatogenesis in male rats[10] Decreased birth weight and birth length in humans associated with BDE 47, BDE 99, and BDE 100 levels in mothers' breast milk[11] Children with higher concentrations of BDE 47, BDE 99, and BDE 100 in cord blood scored lower on tests of mental and physical development at 12-48 and 72 months[12] In adult male sport fish consumers, serum levels of BDE 47, BDE 99, BDE 100, and BDE 153 were positively related to T4 and inversely related to T3 and TSH. Men over the 95th percentile of PBDE levels were more likely to have thyroglobulin antibodies[13] Serum concentrations of BDE 28, BDE 47, BDE 99, BDE 100, and BDE 153 in pregnant women were inversely associated with TSH levels; no relationship was found with T4.[14] Serum levels of BDE 47, BDE 99, and BDE 100 were positively associated with T4 in pregnant women in their third trimester[15] Endocrine disruption through androgen, progesterone, estrogen, T4 receptor agonism and antagonism in vitro[16] Decreased attention, motor skills, and IQ in children associated with mothers' PBDE blood serum concentrations during pregnancy; decreased attention and IQ in children (age 7) associated with PBDE serum concentrations[17]
OctaBDE CAS 32536-52-0 *Includes congeners BDE 183,*	Additive flame retardant in polymers for plastic housings and office equipment[7] Phased out in US in 2004	EPA Action Plan Chemical Dose-dependent decrease of T4, increased liver weight and P450 induction after 4 days of oral administration of DE-79 to 28 d.o. female rats[8]

Flame Retardant Class	Uses	Health Concerns[a]
BDE196, BDE 197, and BDE 203	1-10 million pounds produced in 2002 in US	Neonatal mice gavaged BDE 203 resulted in increased CaMKII and synaptophysin in the hippocampus[18]
DecaBDE CAS 1163-19-5 *Includes congener BDE 209*	Additive flame retardant in electrical and electronic equipment, textiles and fabric backings; accounts for 80% of total PBDE production[7] Volunteer phase-out in US by 2014 50-100 million pounds produced in 2006 in US	EPA Action Plan Chemical Impaired reproductive function to male mice exposed in utero[19] Neonatal exposure to mice effects neurobehavioral effects, including locomotion, rearing, and habituation activity; effects worsened with age.[20] Neonatal exposure to mice effects sensorimotor responses and locomotor activity, and reduction of thyroxine levels[21] Decreased birth weight and birth length in humans associated with BDE 209 levels in mothers' breast milk[11] Leukemia and liver, spleen, and thyroid tumors and cancers in oral high doses over 2 years to male rats[22]
Firemaster® 550 *2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB)* CAS 183658-27-7 *bis(2-ethyhexyl)-3,4,5,6-tetrabromophthalate (BEH-TBEP)* CAS 26040-51-7 *tri-phenyl phosphate (TPHP)* CAS 115-86-6	Replacement for PentaBDE in foams BEH-TBEP: 1-10 million pounds produced in 2006 in US TPHP: 10-50 million pounds produced in 2006 in US	FM® 550: DNA damage in liver tissue of fathead minnows after oral exposure.[23] Increased thyroxine, body weight in offspring, early puberty in female offspring, difficultly in glucose regulation in female offspring and thickened walls in the left ventricle in male offspring. [24] BEH-TBEP structurally similar to DEHP, a reproductive and developmental toxicant and listed carcinogen on CA's Proposition 65 List[25, 26] Hypothyroidism, decrease T3, hepatotoxicity in pregnant rats, and increased multinucleated germ cells in fetal testis following two days of oral dosing of TBMEHP, a metabolite of TBPH [27] TPHP: increased prolactin levels, reduced sperm concentration in men[28] *Lack of cancer, and 2 generation reproductive, and developmental studies*[29]
hexabromocyclododecanes (HBCYDs) CAS: 3194-55-6 *Includes alpha, beta, and gamma-hexabromocyclododecane*	Additive flame retardant in thermoplastic (moldable) polymers and styrene resins[7] Used in building insulation, upholstery textiles and electrical equipment housing[30] 10-50 million pounds produced in 2006 in US	EPA 2010 Action Plan to review potential reproductive, developmental and neurological effects[31] Listed as Substance of Very High Concern (SVHC) under REACH Hyperactive activity, reduced habituation, learning and memory impairment in neonatal mice with oral exposures[32] Non-monotonic dose response curve observed for TSH levels in adult mice and their offspring, decreased ovarian follicles in second generation female mice, decreases in the

Flame Retardant Class	Uses	Health Concerns[a]
		viability index of F2 pups[33] Thyroid hormone disruption in animals and in vitro models[34] Endocrine disruption through androgen, progesterone, estrogen, T4 receptor agonism and antagonism in vitro[16] Dopamine and GABA uptake inhibition due to effects on membrane potential in rat brain cells[35]
tetrabromobisphenol A (TBBPA) CAS: 79-94-7	Most widely used flame retardant; reactive in circuit boards; additive flame retardant in polymers[7] 100-500 million pounds produced in 2006 in US	Endocrine disruption through T3, T4 agonism and estradiol inhibition in vitro.[16] Strong T4 agonism.[36] CD25 inhibition in female mice.[37] Decreased T4, increased testis and pituitary weight in orally exposed rats, increased testis weight, testosterone, female gonadal weight in second generation[38] Dopamine and GABA uptake inhibition due to effects on membrane potential in rat brain cells[35] *Lack of health studies*
Other brominated flame retardants (BFRs)		
tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-BDBPE) CAS: 21850-44-2	Additive flame retardant in plastics, including pipes, water barriers, kitchen hoods and electronics[39] 1-10 million pounds produced in 2006 in US	Endocrine disruption through T4 agonism and estradiol inhibition in vitro[16] Mutagenic in salmonella; structural similarities to TDBPP, a classified carcinogen [40] *Lack of health studies*
hexabromobenzene (HBB) CAS: 87-82-1	Additive flame retardant in paper, wood, textiles, electronic and plastics; not used in Europe[39]	Disruption of heme formation in female rats following gavaged HBB over 28 days[41] Increased liver:body ratio and increased carboxylesterase in rats subchronically fed HBB[42] *Lack of health studies*
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) CAS: 37853-59-1	Replacement for OctaBDE[39] 1-10 million pounds produced in 2006 in US	Its metabolite is a endocrine disruptor through androgen, progesterone, estrogen, T4 receptor agonism and antagonism in vitro[16] Behavioral, gastrointestinal, and respiratory changes, and dermatitis following high dose inhalation in rats. Dermal exposure to rabbits led to metabolic changes[43]

Flame Retardant Class	Uses	Health Concerns[a]
		No chronic animal studies[43]
decabromodiphenylethane (DBDPE) CAS: 84852-53-9	Alternative to DecaBDE[39] 10-50 million pounds produced in 2006 in US	Reduced EROD activity in fish hepatocytes; acutely toxic to water fleas; reduced hatching rates of zebra fish eggs and increased mortality of hatched larvae[44] Structurally similar to BDE 209[39] *Lack of health studies*
Halogenated organophosphate flame retardants (OPFRs)		
tris(2-chloroethyl)phosphate (TCEP) CAS: 115-96-8	Used in polyurethane foams, plastics, polyester resins, and textiles[45, 46] Banned from children's products in NY in 2011[47] Up to 1 million pounds produced in 2006 in US	Listed as carcinogen on CA's Proposition 65 List in 1992 Listed as Substance of Very High Concern (SVHC) and persistent, bioaccumulative, and toxic (PBT) as a reproductive toxicant under REACH[48] Impaired memory in rats, cholinesterase inhibition in hen brains.[49] Neurotoxicity due to altered cellular neurodifferentiation in vitro.[50] Decreased cognitive function correlated with TCEP in house dust in boys and girls age 5-9[48]
tris(1-chloro-2-propyl)phosphate (TCIPP) CAS: 13674-84-5	Used in polyurethane foams[45] 10-50 million pounds produced in 2006 in US	Structurally similar to TCEP[51] *Lack of health studies*
tris(1,3-dichloro-isopropyl)phosphate (TDCIPP) CAS: 13674-87-8	Used in polyurethane foams, plastics, and textiles[45, 46] Removed from children's clothing in the late 1970s in the US[52] 10-50 million pounds produced in 2006 in US	Listed as carcinogen on CA's Proposition 65 List in 2011 Increased liver carcinomas and kidney, testicular, and brain tumors in male and female rats[49] Associated with Sick Building Syndrome in men and women[53] Endocrine disruption through decrease in thyroxine, increase in prolactin, and decrease in androgens in men[28] Neurotoxicity due to altered cellular neurodifferentiation and inhibited DNA synthesis in vitro[50]
tris-(2,3-dibromopropyl)phosphate (TDBPP)	Used in polyurethane foams[45] Banned in 1977 for use in children's clothing[54]	Listed as carcinogen on CA's Proposition 65 List in 1988; classified as IARC 2A carcinogen

Flame Retardant Class	Uses	Health Concerns[a]
CAS: 126-72-7		
Non-halogenated OPFRs		
tri-ethyl-phosphate (TEP) CAS: 78-40-0	Used for plasticizing properties and in antifoam agents and lacquers[45, 46] 1-10 million pounds produced in 2006 in US	Brain colinesterase inhibition and reduced righting reflex in rats following injection of TEP[55] *Lack of health studies*
tri-iso-butyl-phosphate (TIBP) CAS: 126-71-6	Used for plasticizing properties and in antifoam agents and lacquers[45, 46]	*Lack of health studies*
Tri-n-butyl-phosphate (TNBP) CAS: 126-73-8	Used for plasticizing properties and as lubricants in hydraulic fluids[45] 1-10 million pounds produced in 2006 in US	A dose-related increase in the incidence and severity of urinary bladder tumors was found in male and female rats receiving TnBP in the diet for 2 years[56] Associated with Sick Building Syndrome in men and women[53] *Lack of health studies*
tri-(2-butoxyethyl)-phosphate (TBOEP) CAS: 78-51-3	Also used in floor wax, lacquers, and rubber and plastic stoppers[45, 46] 1-10 million pounds produced in 2006 in US	Decreased red cell acetylcholinesterase, ataxia, tremors, and increased liver weight in rats gavaged TBEP for 18 weeks[57] *Lack of health studies*
tri-(2-ethylhexyl)-phosphate (TEHP) CAS: 78-42-2	Used in clothing, as a plasticizer, and as a solvent [58]	Increase in lymphomas, liver, pituitary tumors in mice orally exposed to high doses of TEHP in diet for 2 years[59] *Lack of health studies*
tri-cresyl-phosphate (TMPP) CAS: 1330-78-5	Used as flame retardant plasticizers and as lubricants in hydraulic fluid [45] 1-10 million pounds produced in 2006 in US	Reproductive and developmental toxicity due to dose-dependent increase in abnormal sperm morphology in male rats and increased pup mortality following in utero exposure[60] Toxicity to central nervous system due to neuropathy of the sciatic nerve[60] *Lack of health studies*
Dechlorane-plus (DDC-CO) CAS: 13560-89-9	• Flame retardant in electronics[61] 1-10 million pounds produced in 2006 in US	Increased liver weight, increased lung weight and macrophages in alveoli in rats, decreased liver and ovarian weight in rabbits[62] Shares structural similarities with dieldrin, chlordane, heptachlor, endrin, and endosulfan[63]

Flame Retardant Class	Uses	Health Concerns[a]
		Lack of health studies

[a] From laboratory or animal studies unless otherwise indicated

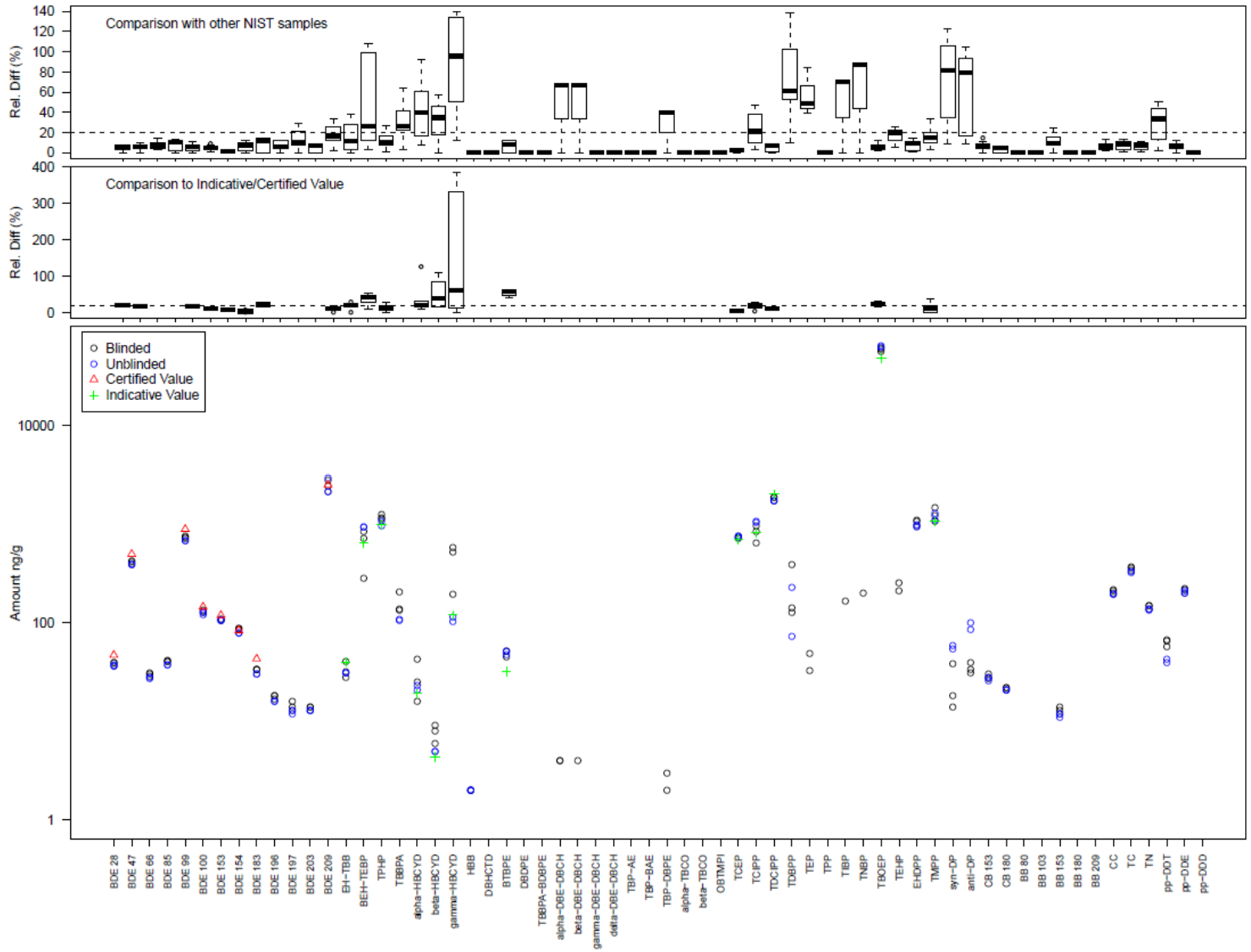

Figure SI1. Distributions of the absolute relative difference (%) among the 5 NIST samples (10 possible comparisons), dashed line represents 20% absolute difference (top); distributions of absolute relative differences (%) between 5 NIST samples and available Certified or Indicative values (middle); and measured concentrations (ng/g) of the 3 blinded and 2 unblinded NIST samples with available Certified or Indicative values (bottom).

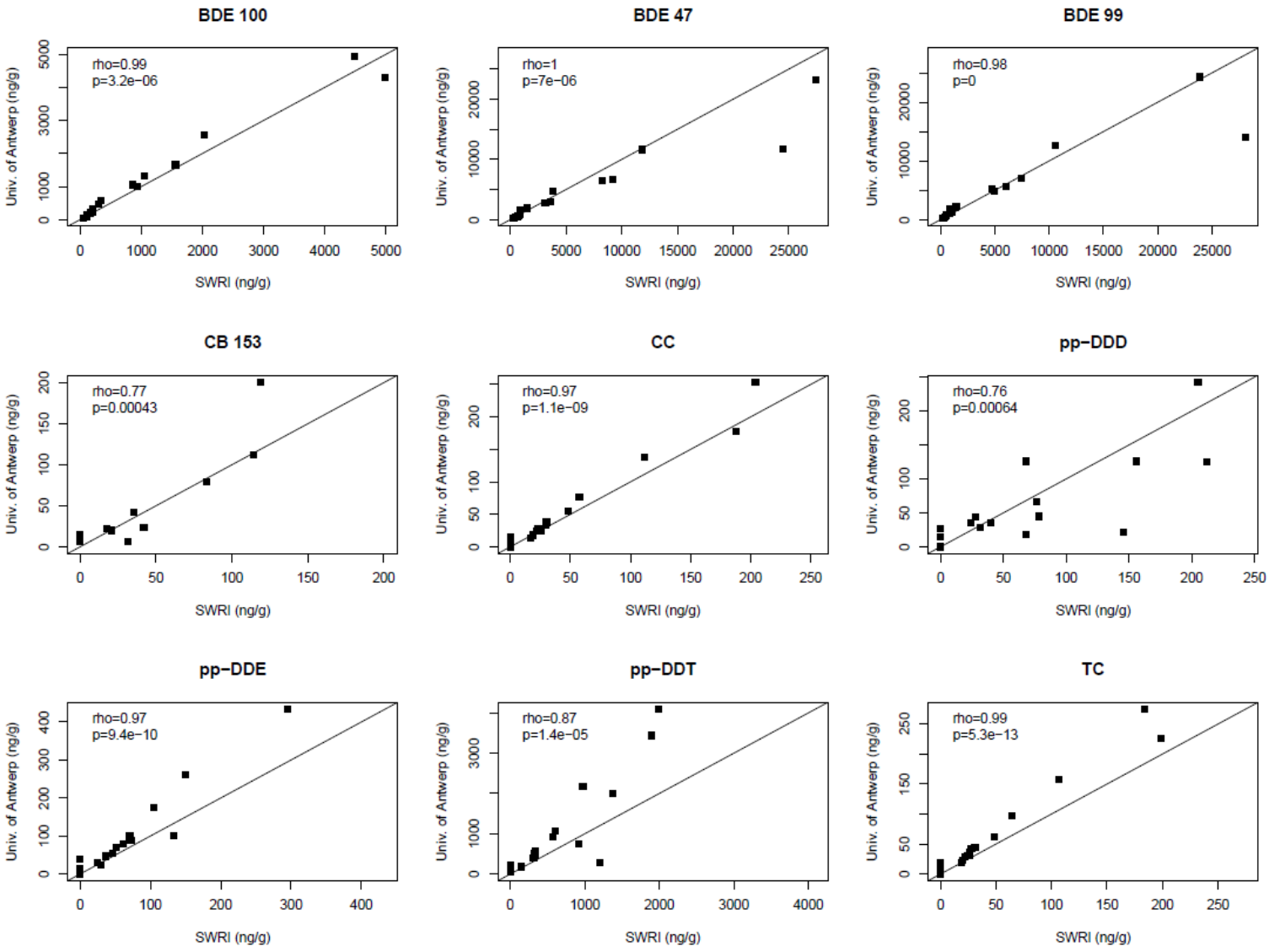

Figure SI2. Comparing analytical results for samples collected in 16 California homes in 2006. Southwest Research Institute (SWRI) analyzed samples in 2006 and University of Antwerp analyzed samples in 2011. Spearman correlation coefficients and associated p-values presented for each analyte.

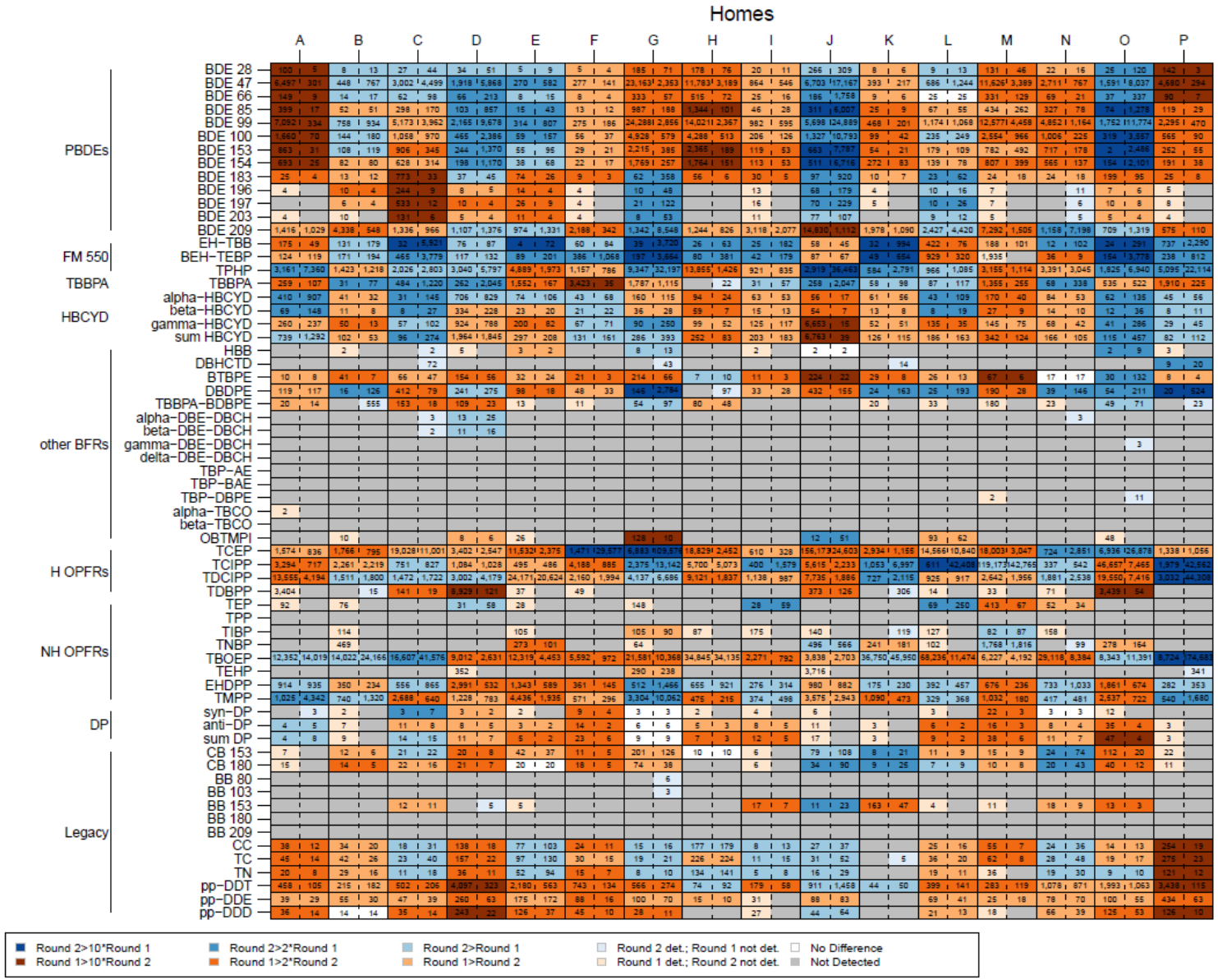

Figure SI3. Concentrations (ng/g) measured in individual samples collected in 2006 and 2011. Each home represented across the top margin with 2006 results in left column and 2011 results in right column.

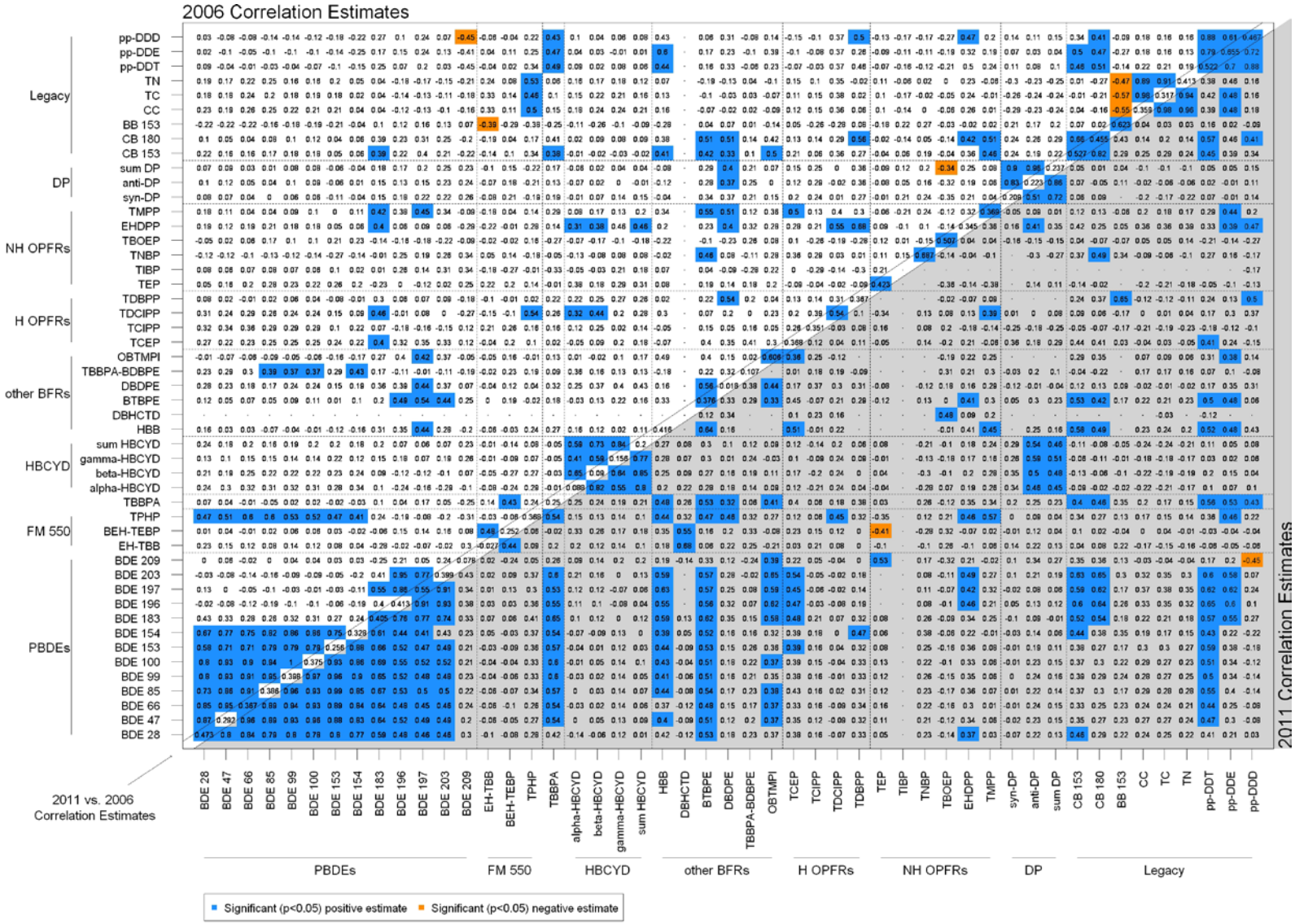

Figure SI4. Kendall's tau correlation estimates for analytes within each sampling round (2006 samples in top left corner and 2011 samples in bottom right corner) as well as correlations for each analyte across sampling rounds (diagonal). Significant ($p<0.05$) positive correlation estimates shaded blue; significant negative correlations estimates shaded orange. '·' indicates insufficient number (≤ 3) of simultaneous detects to estimate correlation. Correlated analytes suggest they are used in combination; correlation across sampling rounds indicates temporal stability.

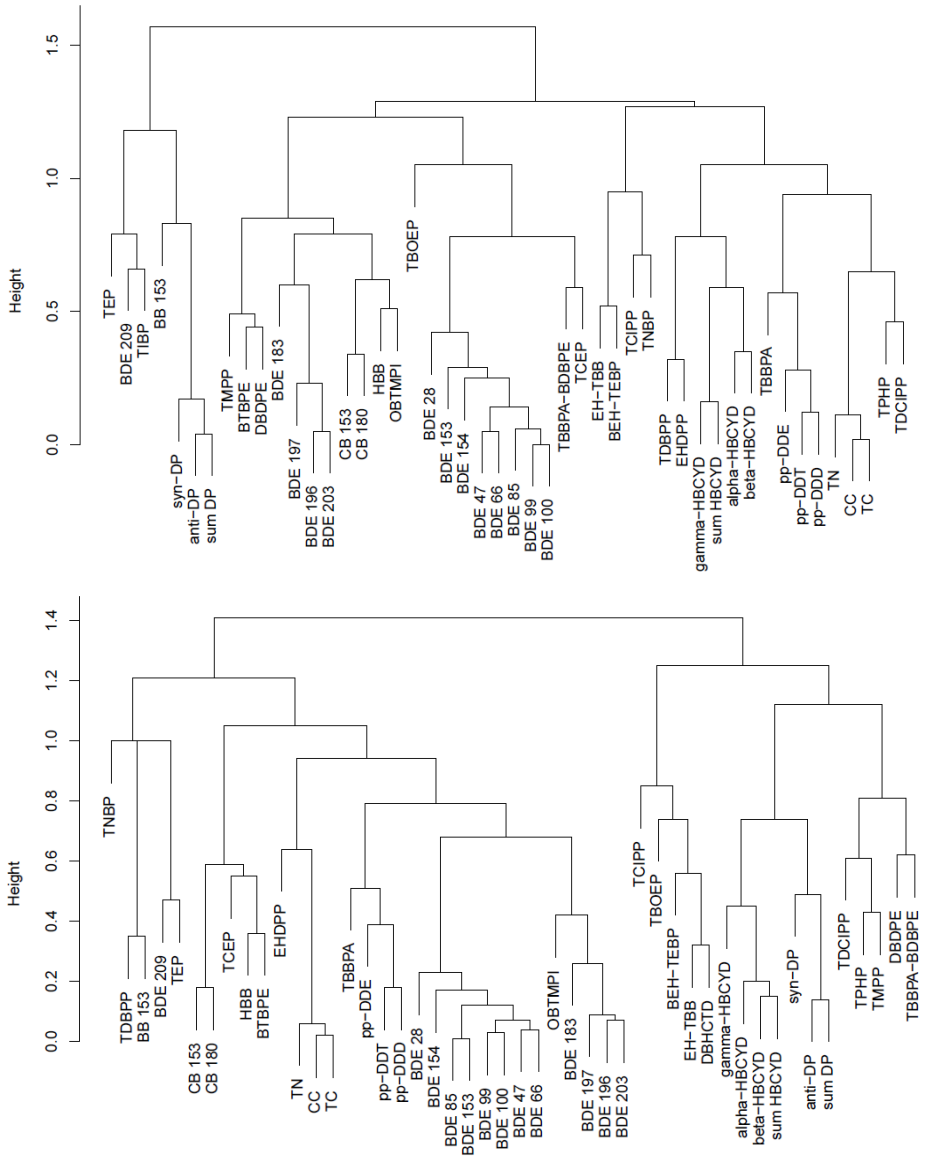

Figure SI5. Dendrograms from cluster analysis for each sampling round: 2006 samples (top) and 2011 samples (bottom). Dendrogram heights are 1 minus Kendall's tau correlation estimates. Chemicals never detected are removed. If insufficient number of simultaneous detects ($n \leq 3$) and correlation estimate could not be calculated, estimate replaced with 1.

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