Supporting Information

Development and validation of a multi-residue method for the simultaneous analysis of brominated and organophosphate flame retardants, organochlorine pesticides, and polycyclic aromatic compounds in household dust

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This supporting information consists of five sections:

1. GC-NCI-MS for the analysis of PBDEs

2. LC-ESI-MS/MS for the analysis of HBCDs

3. Elution behavior of six classes of compounds (Fig.S1)

4. Spiking experiments (Table S1, Fig.S2, and Fig.S3)

5. Comparisons of concentrations of six classes of compounds in SRM 2585 (Table S2)

1. GC-NCI-MS for the analysis of PBDEs

PBDEs in sample extracts were determined using an Agilent 7890A series gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC-MS). Selected ion monitoring (SIM) in negative chemical ionization (NCI) mode was used for quantification. A non-polar DB-5HT column (15 m × 0.25 mm, i.d.; 0.10 μm film thickness; J&W Scientific, Folsom, CA, USA) was used to determine PBDE congeners. The GC injection port was held at 280 °C. Methane was used as the chemical ionization reagent gas and helium as the carrier gas at a flow rate of 1.2 mL/min. The ion source and interface temperatures were set at 250 °C and 290 °C, respectively. The GC oven temperature program was set as follows: held at 110 °C for 5 min, 20 °C/min to 200 °C, held for 4.5 min, and then 7.5 °C/min to 300 °C, held for 16 min. The following ions were monitored: m/z 79 and 81 for tri- to nona-BDEs, m/z 486.7 and 488.7 for BDE-209, and m/z 494.7 for ^{13}C-BDE-209, respectively.

2. LC-ESI-MS/MS for the analysis of HBCDs

HBCDs were analyzed using an Agilent 1100 series liquid chromatograph (Agilent Technologies, Palo Alto, CA) coupled to an Applied Biosystems/Sciex API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA). A Zorbax SB-C18 reversed-phase column (4.6 × 250 mm, 5 μm, Agilent) was used for separating HBCD diastereomers. Injection of a 10 μL sample was conducted with an automatic sampler. The nozzle voltage was set at 500 V for negative ESI modes, and the capillary voltage was set at 3500 V. The mobile phase were water (A), MeOH (B) and acetonitrile (C). The flow rate was 0.5 mL/min. The gradient elution program was initialized with 10:80:10 A/B/C (V/V), ramped to 10:50:40 A/B/C within 18 min, then to 30:70 B/C at 23 min and hold on 7 min, then returned to 10:80:10 A/B/C over 8 min, finally allowed column equilibrium in 6 min for the next run. The MS/MS transitions of m/z 640.6>79 and 652.6>79 were monitored for the three native and $^{13}C_{12}$-labeled HBCD isomers, respectively.

3. Elution behavior of the six compound classes

To identify appropriate elution solvents, we evaluated the elution behavior of six classes of compounds on Florisil-1 g/6 mL. Recovery experiments were performed with six mixtures of standards and four eluents: A-3×4 mL of Hex; B-3×4 mL of Hex/DCM (1:1, v/v); C-3×4 mL of DCM, and D-3×4 mL of EtAc. The resulting fractions were concentrated to approximately 500 μL and then transferred to cell bottles. The washing solvents for each tube were also transferred to the corresponding cell bottles. After this solvent combination, each eluate was evaporated and reconstituted in 200 μL Hex for determination of PBDEs, PAHs, OCPs and Musks. The fractions were then evaporated to dryness under a gentle stream of nitrogen and resolubilized in MeOH for determination of HBCDs and OPEs by LC-MS/MS. Fig.S1 shows that the recovery of compounds from the Florisil-1 g/6 mL SPE cartridge increased with the solvent polarity.

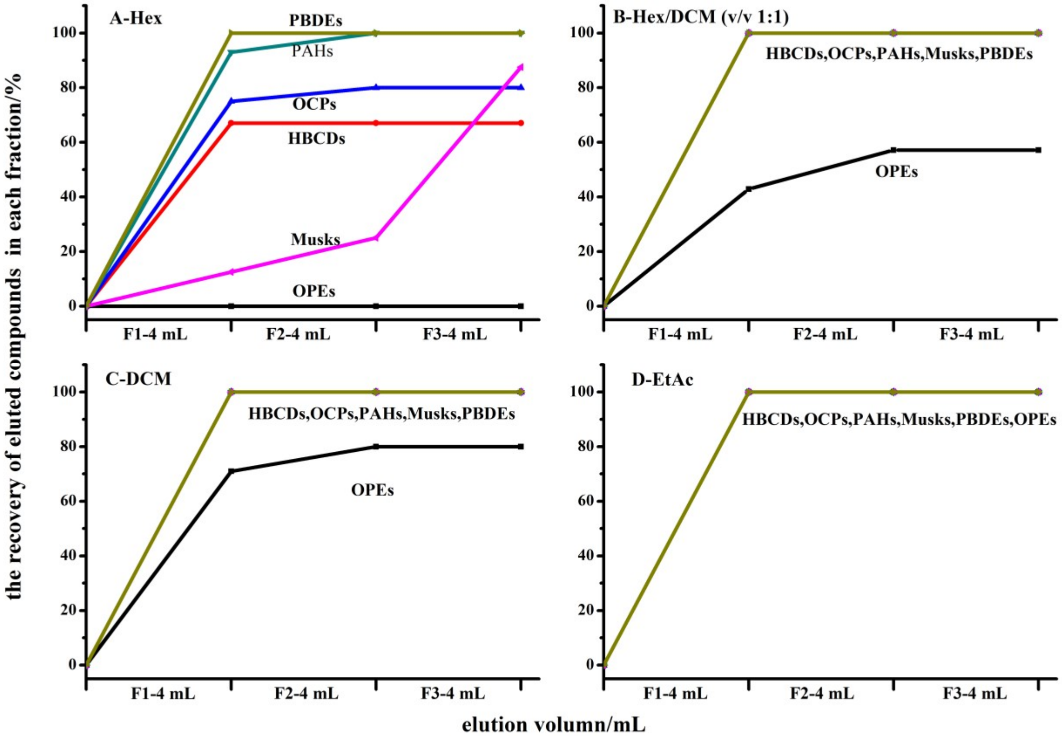

Fig.S1. The elution behavior of six compound mixtures on Florisil-1 g/6 mL SPE: A-3×4 mL Hex (F1-F3); B-3×4 mL Hex/DCM (v/v 1:1) (F1-F3); C-3×4 mL DCM (F1-F3); D-3×4 mL EtAc (F1-F3)

4. Spiking experiments

The final method was validated by performing spiking experiments based on pre-extracted matrix blank on Florisil SPE cartridges at three concentration levels (Q_{low}, Q_{middle} and Q_{high}) with three replicates per level. Recoveries were calculated by dividing by the calculated concentration of a mixed solution of standards (in which the overall concentration of the standard solution was equal to the concentration level chosen for the spiking experiment). For PAHs, Musks and OPEs, the low, middle, and high concentration levels were 50, 500, and 2500 ng/g respectively. For OCPs, they were 10, 100, and 500 ng/g. For HBCDs, the spiking levels were 5, 50, and 100 ng/g. For PBDEs, the spiking levels were 5, 20, and 100 ng/g. The average recoveries and relative standard deviations (RSD) for six compound classes at three different concentration levels are presented in Table S1. The target analytes were in both solvent and matrix blank were below the detection limited. A typical chromatogram was added in SI (Fig. S2).

Table S1 Average recoveries and relative standard deviations (RSD) for six classes of analytes at three different concentration levels (ng/g)

Name		Average recovery ± RSD, % (n = 3)		
		High level:100	Middle level: 20	Low level:5
PBDEs	BDE-28	105 ± 2%	108 ± 0%	103 ± 3%
	BDE-47	103 ± 3%	106 ± 1%	109 ± 3%
	BDE-100	107 ± 1%	112 ± 2%	106 ± 2%
	BDE-99	111 ± 2%	109 ± 2%	108 ± 4%
	BDE-154	107 ± 2%	107 ± 5%	104 ± 4%
	BDE-153	111 ± 3%	105 ± 9%	107 ± 1%
	BDE-183	113 ± 5%	105 ± 5%	99 ± 3%
	BDE-209	111 ± 12%	100 ± 14%	112 ± 10%
		High level:100	Middle level:50	Low level:5
HBCDs	α-HBCD	94 ± 4%	95 ± 2%	99 ± 5%
	β-HBCD	89 ± 4%	105 ± 1%	96 ± 3%
	γ-HBCD	95 ± 5%	97 ± 1%	98 ± 6%
		High level:2500	Middle level:500	Low level:50
PAHs	Ace	83 ± 6%	74 ± 4%	71 ± 6%
	Dih	85 ± 7%	74 ± 4%	74 ± 7%
	Flu	88 ± 5%	76 ± 3%	105 ± 12%
	Phen	93 ± 5%	76 ± 1%	87 ± 4%
	Ant	93 ± 4%	77 ± 2%	76 ± 8%
	Flua	98 ± 5%	90 ± 2%	83 ± 5%
	Pyr	101 ± 6%	92 ± 3%	85 ± 9%
	BaA	113 ± 6%	106 ± 3%	92 ± 8%
	Chry	108 ± 7%	114 ± 2%	97 ± 10%
	BaF	107 ± 5%	99 ± 5%	93 ± 11%
	BkF	81 ± 3%	109 ± 7%	95 ± 12%
	BaP	93 ± 3%	110 ± 2%	113 ± 12%
	IcdP	111 ± 9%	97 ± 2%	116 ± 17%
	BghiP	110 ± 9%	106 ± 10%	115 ± 10%
	DahA	120 ± 9%	102 ± 10%	113 ± 16%
		High level:2500	Middle level:500	Low level:50
Musks	DPMI	120 ± 11%	90 ± 9%	98 ± 8%
	ADBI	89 ± 6%	79 ± 5%	79 ± 6%
	AHMI	93 ± 5%	80 ±4 %	77 ± 8%
	ATII	102 ± 8%	113 ±4%	92 ± 12%
	HHCB	95 ± 6%	84 ± 4%	89 ± 7%
	musk xylene	88 ± 7%	82 ± 2%	66 ± 13%
	AHTN	95 ± 7%	83 ± 4%	80 ± 9%
	musk ketone	102 ± 7%	83 ± 2%	77 ± 12%

Table S1 (continued)

Name		Average recovery ± RSD, % (n = 3)		
		High level:500	Middle level:100	Low level:10
OCPs	α-BHC	86 ± 8%	77 ± 8%	71 ± 3%
	β-BHC	97 ± 7%	87 ± 9%	74 ± 6%
	γ-BHC	86 ± 7%	78 ± 8%	72 ± 4%
	δ-BHC	90 ± 6%	85 ± 12%	75 ± 4%
	Heptachlor	93 ± 4%	75 ± 10%	78 ± 8%
	Aldrin	92 ± 7%	84 ± 9%	75 ± 17%
	Heptachlor epoxide	100 ± 7%	95 ± 8%	87 ± 6%
	γ-Chlordane	100 ± 8%	94 ± 9%	76 ± 7%
	α-Chlordane	101± 7%	97 ± 10%	82 ± 2%
	Endosulfan I	100 ± 6%	91 ± 9%	85 ± 7%
	p,p'-DDE	112 ± 5%	95 ± 10%	87 ± 6%

	Dieldrin	102 ± 5%	105 ± 6%	86 ± 13%
	Endrin	107 ± 4%	107 ± 13%	90 ± 17%
	Endosulfan II	108 ± 10%	104 ± 8%	82 ± 3%
	p,p’-DDD	106 ± 7%	100 ± 8%	77 ± 8%
	Endrin aldehyde	92 ± 5%	97 ± 7%	66 ± 12%
	Endosulfan sulfate	108 ± 7%	97 ± 7%	82 ± 9%
	p,p’-DDT	122 ± 8%	116 ± 14%	107 ± 12%
	Endrin ketone	106 ± 7%	107 ± 8%	79 ± 10%
	Methoxychlor	116 ± 9%	116 ± 8%	102 ± 14%
		High level:2500	Middle level:500	Low level:50
OPEs	TBP	86 ± 3%	87 ± 4%	79 ± 3%
	TCEP	87 ± 3%	83 ± 14%	119 ± 6%
	TCPP	85 ± 3%	85 ± 6%	127 ± 5%
	TDCPP	80 ± 1%	94 ± 4%	120 ± 10%
	TPhP	92 ± 5%	95 ± 2%	92 ± 9%
	TBEP	97 ± 3%	99 ± 6%	82 ± 4%
	TCP	100 ± 2%	90 ± 9%	120 ± 8%

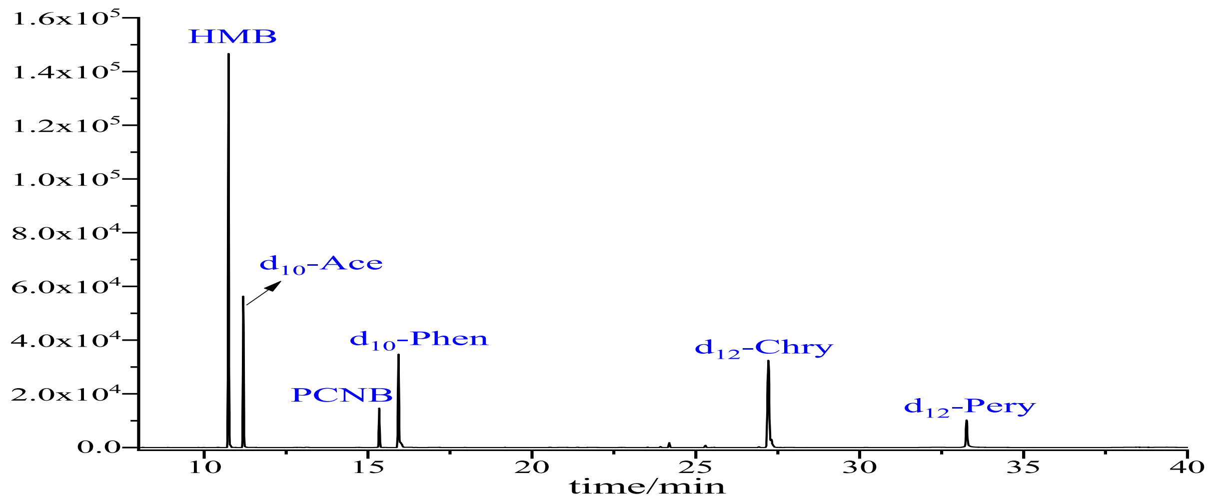

Fig. S2 Total ion chromatogram (TIC) of a pre-extracted matrix blank for PAHs analysis by GC-EI-MS/MS.

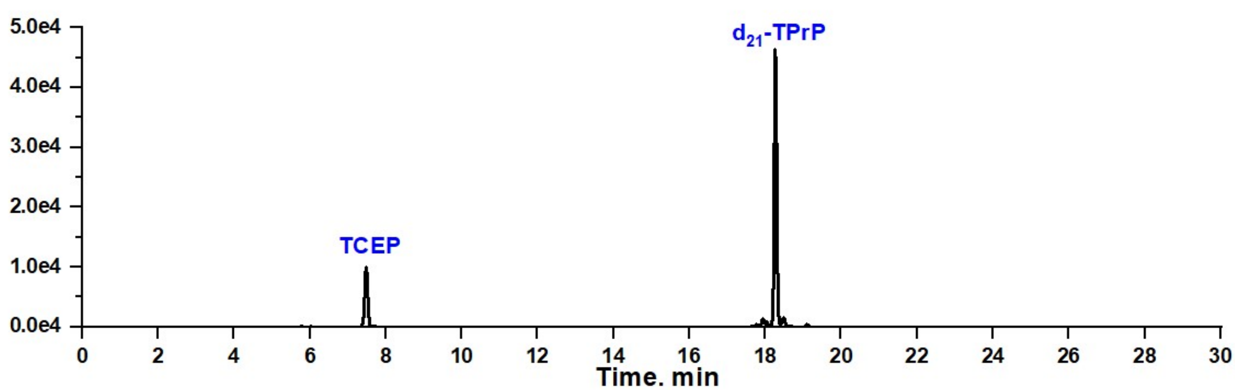

Fig. S3 Total ion chromatogram (TIC) of a method blank sample for OPEs analysis by LC-MS/MS.

5. Comparisons of concentrations of six classes of compounds in SRM 2585

The dust used to prepare the Standard Reference Material (SRM) 2585 was collected in 1993-1994 from US homes, cleaning services, motels and hotels. There are two important advantages of using this reference material: (1) its matrix effects closely resemble those of real dust samples, and (2) its concentrations of several target FRs (PBDEs) are certified. It is therefore widely used to evaluate the performance of analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, chlorinated pesticides, and polybrominated diphenyl ether (PBDE) congeners in household dust and similar matrices. The analyte concentrations range from approximately 10 to 4,500 ng/g for PAHs, 4 to 300 ng/g for chlorinated pesticides, and 4 to 2,500 ng/g for BDE congeners. No certified or reference concentrations exist for Musks and OPEs, but indicative values have been reported in the literature for some of these compounds. The concentrations determined using our new method are compared to previously reported concentrations and certified/indicative concentrations for SRM 2585 in Table S2.

Table S2 Concentrations (all in ng/g dust) of six classes of compounds previously reported in literature together with the results of the present study in SRM2585 compared to the certified/indicative Values

		Reference [1]	Reference [2]	Reference [3]	This study	Certified values [4]
PBDEs	BDE-28	45.8±3.1	35±2	32.8±1.1	50.9 ± 2.6	46.9 ± 4.4
	BDE-47	506 ±54	390±36	409±11	499 ± 46	497 ± 46
	BDE-100	154±29	110±14	116±3	151 ± 4	145 ± 11
	BDE-99	873±58	680±86	742±33	937 ± 39	892 ± 53
	BDE-154	76.2±10.5	70±6	77.2±2.7	90.6 ± 3.5	83.5 ± 2.0
	BDE-153	137±24	90±12	97±2	121 ± 9	119 ± 1
	BDE-183	38±4	25±2	32.3±4.8	41.9 ± 1.6	43.0 ± 3.5
	BDE-209	2149±1205	2480±500	2150±231	2682 ± 163	2510 ± 190
		Reference [5]	Reference [3]		This study	Indicative values [6]
HBCDs	α-HBCD	19.0±3.6	19.0±9.0		20.4 ± 2.2	19.0 ± 3.7
	β-HBCD	4.4±0.4	4.2±1.4		4.8 ± 0.3	4.3 ± 1.1
	γ-HBCD	125±18	119±42		115 ± 9.6	120 ± 22
		Reference [1]	Reference [7]	Reference [8]	This study	Certified values [4]
PAHs	Phen	1514±206	1670±84	1818±145	1795± 148	1920 ± 20
	Ant	106±31	182±15	267±5.3	93.2 ± 3.8	96.0 ± 5.2
	Fluo	3477±93	4280±428	3110±280	3805 ±218	4380 ± 100
	Pyr	2723±116	3330±466	2154±237	2864 ±272	3290 ± 30
	BaA	1001±443	/	/	1145 ± 60	1160 ± 54
	Chry	2929±1356	/	/	2357 ±139	2260 ± 60
	BbF	1402±268	/	/	2765 ±234	2700 ± 90
	BkF	582±231	/	/	1289 ±38	1330 ± 70

	BaP	674±41	906±54	879±62	1333 ±30	1140 ± 10
	IcdP	2167±634	/	/	2064 ±118	2080 ± 100
	BghiP	1948±995	/	/	2159 ±109	2280 ± 40
	DahA	832±450	/	/	336 ±29	301 ± 50
		Reference [9]	Reference [10]	Reference [11]	This study	Indicative values [12]
Musks	ADBI	105±9	162±8	/	122.8± 9.4	150.0±15.7
	AHMI	152±26	196±12	/	239.2±18.9	202.0±25.2
	ATII	100±14	142±9	/	147.3± 8.4	139.0±5.81
	HHCB	1220±143	1410±80	/	1461± 6	1460 ± 67
	musk xylene	705±60	/	946±14	910.1± 6.9	895.0±57.2
	AHTN	1420±169	1680±90	/	1702± 11	1650 ± 88
	musk ketone	436±61	/	491±8	544.5± 9.2	477.0±29.7

Table S2 (continued)

		Reference [7]	Reference [13]	This study	Certified Values [4]
OCPs	δ-BHC	<65.8	/	3.87±13.35	4.06± 0.55
	Heptachlor	113±21	/	113 ± 6	166 ± 34
	Heptachlor epoxide	/	/	10.2 ± 11.3	11.3 ± 0.6
	γ-Chlordane	170±17	/	171 ± 6	174 ± 45
	α-Chlordane	322±35	165±4	303 ± 9	277 ± 96
	p,p'-DDE	191±17	213±6	283 ± 6	261 ± 2
	Dieldrin	93±19	/	97 ± 7	88 ± 21
	p,p'-DDD	/	35.5±4.1	26.4 ± 7.6	27.3 ± 0.8
	p,p'-DDT	123±28	84±2.3	129 ± 5	111 ± 23
		Reference [3]	Reference [14]	This study	Indicative values [15]
OPEs	TBP	190±10	190±20	187±9	180 ± 20
	TCEP	680±60	840±60	743±98	700 ± 170
	TCPP	860±70	880±140	846±65	820 ± 100
	TDCPP	3180±70	2300±280	2225±136	2020 ± 260
	TBEP	63000±2000	82000±6500	49216±3966	49000 ± 9600
	TCP	1140±30	1100±100	1166±112	1070 ± 110

"/"- no values for this compound

Reference:

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