Supporting Information for

Simultaneous determination of chlorinated aromatic hydrocarbons in fly ashes discharged from the industrial thermal processes

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Table S1 List of CAH standards used in this experiment

	Native Standards	Internal Standards	Recovery Standards
Tetra- to octa-CDD/Fs	2,3,7,8-TCDF 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF OCDF 2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD OCDD	$^{13}C_{12}$-2,3,7,8-TCDF $^{13}C_{12}$-1,2,3,7,8-PeCDF $^{13}C_{12}$-2,3,4,7,8-PeCDF $^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,7,8,9-HxCDF $^{13}C_{12}$-2,3,4,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF $^{13}C_{12}$-2,3,7,8-TCDD $^{13}C_{12}$-1,2,3,7,8-PeCDD $^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,6,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD $^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,4-TCDD $^{13}C_{12}$-1,2,3,7,8,9-HxCDD
Tri- to hepta-CBs	IUPAC numbers 28, 52, 101, 138, 153, 180, 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189	$^{13}C_{12}$- PCB 28, 52, 101, 138, 153, 180, 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189	$^{13}C_{12}$-PCB 70, 111, 170
Mono- to octa-CNs	IUPAC numbers 2, 6, 13, 28, 52, 66, 73, 75, 27, 36, 46, 48, 50, 53, 69, 72	$^{13}C_{12}$- PCN 27, 42, 52, 67, 73, 75	$^{13}C_{12}$- PCB 70, 111
Mono- and di-ClPAHs	9-chfluorene 9-chlorophenanthrene 2-chloroanthracene 9-chloroanthracene 9,10-dichloroanthracene 3-chlorofluoranthene 1,3-dichlorofluoranthene 1-chloropyrene 6-chlorobenzo[a]pyrene	Phenanthrene-d_{10}	Pyrene-d_{10}

Table S2 Masses and m/z types of monitored PCDD/Fs

Mass/Charge ratio	m/z type	PCDD/F	Mass/Charge ratio	m/z type	PCDD/F
319.8965	M	TCDD	331.9368	M	^{13}C TCDD
321.8936	M+2	TCDD	333.9339	M+2	^{13}C TCDD
355.8546	M+2	PeCDD	367.8949	M+2	^{13}C PeCDD
357.8516	M+4	PeCDD	369.8919	M+4	^{13}C PeCDD
389.8157	M+2	HxCDD	401.8559	M+2	^{13}C HxCDD
391.8128	M+4	HxCDD	403.8529	M+4	^{13}C HxCDD
423.7766	M+2	HpCDD	435.8169	M+2	^{13}C HpCDD
425.7737	M+4	HpCDD	437.8140	M+4	^{13}C HpCDD
457.7377	M+2	OCDD	469.7779	M+2	^{13}C OCDD
459.7348	M+4	OCDD	471.7750	M+4	^{13}C OCDD
303.9016	M	TCDF	315.9419	M	^{13}C TCDF
305.8987	M+2	TCDF	317.9389	M+2	^{13}C TCDF
339.8597	M+2	PeCDF	351.9000	M+2	^{13}C PeCDF
341.8567	M+4	PeCDF	353.8970	M+4	^{13}C PeCDF
373.8208	M+2	HxCDF	385.8610	M+2	^{13}C HxCDF
375.8179	M+4	HxCDF	387.8580	M+4	^{13}C HxCDF
407.7848	M+2	HpCDF	419.8220	M+2	^{13}C HpCDF
409.7789	M+4	HpCDF	421.8190	M+4	^{13}C HpCDF
441.7428	M+2	OCDF			
443.7399	M+4	OCDF			

Table S3 Masses and m/z types of monitored PCBs

Mass/Charge ratio	m/z type	PCB	Mass/Charge ratio	m/z type	PCB
255.9613	M	Cl-3 PCB	268.0016	M	^{13}C Cl-3 PCB
257.9584	M+2	Cl-3 PCB	269.9986	M+2	^{13}C Cl-3 PCB
289.9224	M	Cl-4 PCB	301.9626	M	^{13}C Cl-4 PCB
291.9194	M+2	Cl-4 PCB	303.9597	M+2	^{13}C Cl-4 PCB
325.8804	M+2	Cl-5 PCB	337.9207	M+2	^{13}C Cl-5 PCB
327.8775	M+4	Cl-5 PCB	339.9178	M+4	^{13}C Cl-5 PCB
359.8415	M+2	Cl-6 PCB	371.8817	M+2	^{13}C Cl-6 PCB
361.8385	M+4	Cl-6 PCB	373.8788	M+4	^{13}C Cl-6 PCB
393.8025	M+2	Cl-7 PCB	405.8428	M+2	^{13}C Cl-7 PCB
395.7995	M+4	Cl-7 PCB	407.8498	M+4	^{13}C Cl-7 PCB
427.7635	M+2	Cl-8 PCB	439.8038	M+2	^{13}C Cl-8 PCB
429.7606	M+4	Cl-8 PCB	441.8008	M+4	^{13}C Cl-8 PCB
461.7246	M+2	Cl-9 PCB			
463.7216	M+4	Cl-9 PCB			
495.6856	M+2	Cl-10 PCB			
497.6826	M+4	Cl-10 PCB			

Table S4 Masses and m/z types of monitored PCNs

Mass/Charge ratio	m/z type	PCN	Mass/Charge ratio	m/z type	PCN
162.0236	M	Cl-1 PCN			
164.0208	M+2	Cl-1 PCN			
195.9847	M	Cl-2 PCN			
197.9818	M+2	Cl-2 PCN			
229.9457	M	Cl-3 PCN			
231.9428	M+2	Cl-3 PCN			
263.9067	M	Cl-4 PCN	275.9469	M	^{13}C Cl-4 PCN
265.9038	M+2	Cl-4 PCN	277.9440	M+2	^{13}C Cl-4 PCN
299.8648	M	Cl-5 PCN	311.9050	M	^{13}C Cl-5 PCN
301.8619	M+2	Cl-5 PCN	313.9021	M+2	^{13}C Cl-5 PCN
333.8258	M	Cl-6 PCN	345.8661	M	^{13}C Cl-6 PCN
335.8229	M+2	Cl-6 PCN	347.8632	M+2	^{13}C Cl-6 PCN
367.7869	M	Cl-7 PCN	379.8271	M	^{13}C Cl-7 PCN
369.7839	M+2	Cl-7 PCN	381.8242	M+2	^{13}C Cl-7 PCN
401.7479	M	Cl-8 PCN	413.7881	M	^{13}C Cl-8 PCN
403.7450	M+2	Cl-8 PCN	415.7852	M+2	^{13}C Cl-8 PCN

Table S5 Masses and m/z types of monitored ClPAHs

Mass/Charge ratio	m/z type	ClPAH
200.0393	M	ClFLU
212.0393	M	ClPHE + ClANT
246.0003	M	Cl_2PHE +Cl_2ANT
236.0393	M	ClFLA + ClPYR
270.0003	M	Cl_2FLA + Cl_2PYR
262.0549	M	ClBaA + ClCHR
296.0160	M	Cl_2BaA + Cl_2CHR
286.0549	M	ClBAP
188.1410	M	d_{10}-PHE
212.1410	M	d_{10}-PYR

Table S6 HRGC/HRMS instrumental analysis conditions for PCDD/Fs, PCBs, PCNs and ClPAHs

Parameters	PCDD/F	PCB	PCN	ClPAH
Injector Temperature	280 °C	280 °C	280 °C	280 °C
GC Column	HP-5 ms (60 m × 250 μm mm ID × 0.25μm df)	HP-5 ms (60 m × 250 μm mm ID × 0.25μm df)	HP-5 ms (60 m × 250 μm mm ID × 0.25μm df)	HP-5 ms (60 m × 250 μm mm ID × 0.25μm df)
Temperature Program	120 °C (1 min) ,43 °C min^{-1} to 220 °C (15min), 2.3 °C min^{-1} to 250 °C, 0.9 °C min^{-1} to 260 °C, 20 °C min^{-1} to 310 °C (20 min)	90 °C (2 min), 20 °C min^{-1} to 180 °C (15 min), 3 °C min^{-1} to 300 °C, 30 °C min^{-1} to 320 °C (10 min)	90 °C (2 min), 20 °C min^{-1} to 200 °C, 3 °C min^{-1} to 280 °C (5 min), 20 °C min^{-1} to 320 °C (15 min)	100 °C (2 min), 5 °C min^{-1} to 300 °C (20 min)
Injection mode	Splitless	Splitless	Splitless	Splitless
Carrier gas	He	He	He	He
Ion source Temperature	250 °C	250 °C	250 °C	250 °C
Detection Ions	SIM	SIM	SIM	SIM
Ionization mode	EI	EI	EI	EI
Ionization Energy	37 eV	37 eV	37 eV	37 eV
Resolution	≥ 10 000	≥ 10 000	≥ 10 000	≥ 10 000

Table S7 Detailed results of method validation for the analysis of target CAHs congeners

	Linear range (pg)	MDL (pg g^{-1})	Spiking level (pg g^{-1})	Recovery (n = 7) %	Precision (n = 7) %
PCDD/F					
2,3,7,8-TCDF	0.5–200	6.8	100	81.5	2.8
2,3,4,7,8-PeCDF	2.5–1000	7.4	100	105.2	4.4
1,2,3,7,8-PeCDF	2.5–1000	6.3	100	97.4	6.1
1,2,3,4,7,8-HxCDF	2.5–1000	13.4	100	81.3	4.4
1,2,3,6,7,8-HxCDF	2.5–1000	2.9	100	84.6	3.6
2,3,4,6,7,8-HxCDF	2.5–1000	3.7	100	78.4	9.4
1,2,3,7,8,9-HxCDF	2.5–1000	0.1	100	80.9	4.4
1,2,3,4,6,7,8-HpCDF	2.5–1000	1.7	100	94.3	10.2
1,2,3,4,7,8,9-HpCDF	2.5–1000	1.0	100	92.8	8.2
OCDF	5.0–2000	1.6	200	83.3	13.0
2,3,7,8-TCDD	0.5–200	0.2	100	96.1	8.4
1,2,3,7,8-PeCDD	2.5–1000	0.5	100	116.0	1.6
1,2,3,6,7,8-HxCDD	2.5–1000	0.4	100	97.0	7.6
1,2,3,4,7,8-HxCDD	2.5–1000	0.2	100	90.2	6.2
1,2,3,7,8,9-HxCDD	2.5–1000	0.4	100	97.0	7.6
1,2,3,4,6,7,8-HpCDD	2.5–1000	0.8	100	107.7	3.4
OCDD	5.0–2000	1.6	200	83.3	13.0
PCB					
PCB-77	0.1–200	0.5	100	95.6	4.6
PCB-81	0.1–200	0.2	100	89.0	5. 5
PCB-105	0.1–200	0.6	100	73.2	7.7
PCB-114	0.1–200	0.1	100	96.3	6.3
PCB-118	0.6–1200	0.9	100	83.5	5.4
PCB-123	0.1–200	0.6	100	94.2	6.7
PCB-126	0.1–200	0.04	100	89.8	6.4
PCB-156	0.1–200	0.2	100	82.9	7.9
PCB-157	0.1–200	0.07	100	88.0	3.9
PCB-167	0.1–200	0.5	100	105.2	5.8
PCB-169	0.1–200	0.05	100	93.5	5.4
PCB-189	0.1–200	0.2	100	95.8	6.6
PCB-28	0.1–5000	11.1	100	87.9	5.7
PCB-52	0.1–5000	5.9	100	106.1	5.3
PCB-101	0.1–5000	2.4	100	99.7	7.1
PCB-138	0.1–5000	1.4	100	95.5	4.9

PCB-153	0.1–5000	3.1	100	90.8	6.0
PCB-180	0.1–5000	2.5	100	76.6	4.4
PCN					
PCN-27	2–100	1.2	100	96.6	4.1
PCN-36	2–100	0.7	100	101.3	2.9
PCN-46	2–100	0.3	100	115.8	6.7
PCN-48	2–100	0.6	100	109.4	5.2
PCN-50	2–100	0.7	100	100.6	5.5
PCN-53	2–100	0.7	100	121.2	4.1
PCN-69	2–100	0.3	100	125.8	3.4
PCN-72	2–100	0.2	100	126.4	6.0
PCN-2	2–100	19.4	100	25.7	14.9
PCN-6	2–100	48.5	100	31.6	9.1
PCN-13	2–100	7.0	100	70.8	7.5
PCN-28	2–100	2.3	100	124.5	4.1
PCN-52	2–100	0.5	100	102.9	6.1
PCN-66	2–100	1.5	100	122.3	4.8
PCN-73	2–100	1.1	100	135.6	0.9
PCN-75	2–100	9.7	100	132.8	3.1
ClPAH					
9-ClFLU	1–500	9.5	100	69.8	6.9
9-ClPHE	0.1–500	3.5	100	90.1	1.7
2-ClANT	0.1–500	5.4	100	61.7	7.6
9-ClANT	0.1–500	4.1	100	108.5	9.5
3-ClFLA	0.1–500	5.2	100	106.1	4.7
1-ClPYR	0.1–500	3.7	100	70.8	2.4
9,10-Cl_2ANT	1–500	3.5	100	63.4	4.3
1,3-Cl_2FlA	1–500	4.1	100	105.2	2.4
6-ClBaP	1–500	4.7	100	69.2	9.7

Table S8 Concentrations and WHO-TEQs of CAHs in fly ash from the industrial thermal processes

Compounds (ng kg^{-1})	Fly ash 1	Fly ash 2	Fly ash 3	Fly ash 4
PCDD/Fs				
2,3,7,8-TCDD	8.2	20.7	24.0	682.0
1,2,3,7,8-PeCDD	12.5	77.3	9.8	262.7
1,2,3,4,7,8-HxCDD	16.5	69.3	11.9	527.5
1,2,3,6,7,8-HxCDD	9.0	89.7	23.1	665.3
1,2,3,7,8,9-HxCDD/(1,2,3,4,6,7- HxCDD)	12.0	118.8	15.9	1331
1,2,3,4,6,7,8-HpCDD	46.4	522.2	316.1	8715
OCDD	30.5	732.6	832.9	10644
2,3,7,8-TCDF	400.6	2058	214.5	2992
1,2,3,7,8-PeCDF	79.4	458.2	32.3	372.4
2,3,4,7,8-PeCDF/(1,2,4,8,9-,1,2,6,7,9-, 1,2,3,6,9-PeCDF)	125.3	1089	69.8	1608
1,2,3,4,7,8-HxCDF/(1,2,3,4,6,7- HxCDF)	175.5	1928	82.3	2243
1,2,3,6,7,8-HxCDF	68.9	655.3	39.4	792.0
1,2,3,7,8,9-HxCDF	6.7	61.9	3.1	97.4
2,3,4,6,7,8-HxCDF	50.4	640.2	28.0	1360
1,2,3,4,6,7,8-HpCDF	141.9	1855	92.4	3043
1,2,3,4,7,8,9-HpCDF	19.8	250.8	13.4	511.7
OCDF	52.3	606.2	43.1	1117
WHO_{2005}-TEQ	153.6	1196	110.8	2754
PCDDs	559.0	3686	5060	102610
PCDFs	4431	26384	2424	38390
PCDF/PCDD	7.9	7.2	0.5	0.4
Total PCDD/Fs	4990	30070	7484	141000
Dl-PCBs				
PCB-77	475.0	224.1	50.5	134.3
PCB-81	46.7	38.9	22.4	35.2
PCB-105	746.4	324.7	72.0	125.2
PCB-114	16.9	6.5	7.6	6.9
PCB-118	713.1	148.1	49.5	54.4
PCB-123	107.6	92.6	23.3	58.4
PCB-126	32.4	230.8	31.0	179.4
PCB-156	232.8	213.8	26.8	73.3
PCB-157	24.9	91.3	21.3	56.9
PCB-167/ PCB-128	245.2	83.0	20.6	49.5
PCB-169	7.3	82.3	15.9	57.6
PCB-189	68.9	140.2	25.4	64.6

WHO_{2005}-TEQ	3.6	25.6	3.6	19.7
Indicator PCBs				
PCB-28	7610	463.3	1452	466.7
PCB-52	1329	149.7	342.9	188.5
PCB-101	722.1	96.9	83.8	67.8
PCB-138	2809	225.0	48.9	74.2
PCB-153	2215	87.0	25.6	38.9
PCB-180	2252	104.0	16.9	29.1
Total PCBs	58428	8027	9669	6252
PCNs				
PCN-2	99.3	35.0	533.0	129.7
PCN-1	79.2	55.4	1210	189.2
PCN-4	51.2	58.1	248.9	205.4
PCN-5/7	105.5	132.0	484.9	29.2
PCN-10	171.7	79.4	552.8	1004
PCN-48	18.0	24.7	76.3	116.3
PCN-38/40	30.9	48.9	77.5	86.8
PCN-50	31.3	126.2	71.9	132.1
PCN-35	30.4	48.0	108.5	114.6
PCN-54	19.4	1.5	29.0	9.9
PCN-57	42.0	43.67	136.24	135.60
PCN-56	6.7	25.48	23.50	53.28
PCN-66/67	227.6	678.41	177.13	242.68
PCN-64/68	3.1	3.4	1.7	2.7
PCN-69	12.5	69.8	31.4	52.6
PCN-72	7.3	13.4	11.4	14.5
PCN-63	13.9	117.2	26.3	99.2
PCN-70	3.2	2.6	3.2	3.9
PCN-TEQ	172.8	297.6	34.2	100.1
Total PCN	3707	5303	10398	10935
ClPAHs				
9-ClFLU	75.2	266.2	49.9	nd
9-ClPHE	1638	1898	900.9	434.2
2-ClANT	644.1	718.1	461.8	110.9
9-ClANT	24.7	14.4	6.3	1.7
3-ClFLA	1040	1299	1041	318.9
1-ClPYR	2071	137.1	1023	64.8
9,10-Cl_2ANT	44.0	108.1	33.4	nd
1,3-Cl_2FlA	75.4	84.2	29.7	7.0
6-ClBaP	125.9	400.6	38694	9.0
Total ClPAHs	24450	25255	218524	2524

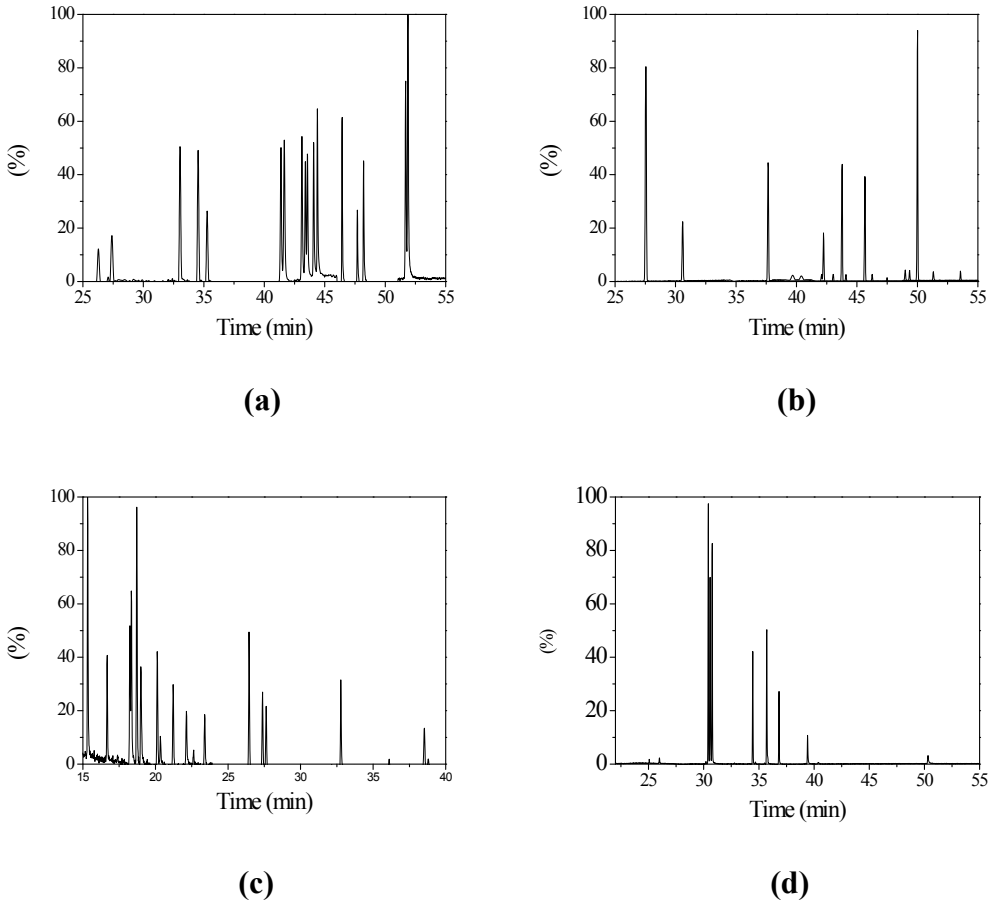

Fig. S1 Total ion current (TIC) chromatogram for a standard solution containing PCDD/Fs (a), PCBs (b), PCNs (c), and ClPAHs (d)