Supplemental Materials

Analytical method for measuring brominated dioxins and furans in air and wipe extracts

Prior to analysis, the extracts were reduced in volume to ~500 µL and spiked with 800 ng of decachlorodiphenylether (DCDE) (AccuStandard, Inc., New Haven, CT. USA) to serve as the internal standard. Each extract (2 µL) was introduced into a pressure pulse split/splitless injector, equipped with a glass liner (1 mm, ID) and analytes were separated from the carrier solvent and co-extractables with a 30 m gas chromatograph capillary retention column (Agilent Tech., DB-5MS, 30 m x 0.25 mm, 0.1 µm stationary phase). The injector temperature was 250 °C, carrier gas (helium) with an initial head pressure of 50 psi. The split vent was opened and pressure reduced to 19.5 psi, 4 minutes following sample injection. Thereafter, column flow rate (1.2 mL/min) was kept constant throughout the remaining portion of the run. The initial column oven temperature of 120 °C, was held for 2 min, increased to 180 °C at 30 °C/min, then to 190 °C at 1.5 °C/min, followed by 240 °C at 5 °C/min and finally to 320 °C at 20 °C/min and held for 10 min completing the analysis.

Operating values for the quadrupole mass spectrometer were: electron energy 70 eV, filament 35 µA, source temperature 230 °C, quadrupole temperature 150 °C and interface temperature 280 °C. EI mass spectra were collected in low resolution selected ion monitoring (SIM) mode with 3.09 or 3.75 scan cycle/sec.

Surrogate standards added during initial extraction and cleanup steps were at concentrations below the detection limit (12 ng/sample). Therefore, results were not corrected for surrogate recoveries and should be considered qualitative.

Tables

Table S1. Flame retardant analyte abbreviations

Abbreviation	Compound Name
PBDEs	
BDE-28	2,4,4'-tribromodiphenyl ether
BDE-47	2,2',4,4'-tetrabromodiphenyl ether
BDE-66	2,3',4,4'-tetrabromodiphenyl ether
BDE-85	2,2',3,4,4'-pentabromodiphenyl ether
BDE-99	2,2',4,4',5-pentabromodiphenyl ether
BDE-100	2,2',4,4',6-pentabromodiphenyl ether
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether
BDE-166	2,3,4,4',5,6-hexabromodiphenyl ether
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether
BDE-206	2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether
BDE-209	decabromodiphenyl ether
NPBFRs	
TBBPA	tetrabromobisphenol-A
TBB or EH-TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate
TBPH or BEH-TEBP	Di(2-ethylhexyl) tetrabromophthalate
BTBPE	1,2-bis (2,4,6-tribromophenoxy) ethane
DBDPE	decabromodiphenyl ethane
OPFRs	
a-HBCD	a-hexabromocyclododecane
b-HBCD	b-hexabromocyclododecane
g-HBCD	g-hexabromocyclododecane
TCEP	tris (2-chlororethyl) phosphate
TCPP or TCIPP	tris (1-chloro-2-propyl) phosphate
TDCPP or TDCIPP	tris (1,3-dichloro-2-propyl) phosphate
TPP or TPhP	triphenyl phosphate
TCP or TMPP	tricresyl phosphate

Table S2. Brominated dioxin and furan abbreviations

Abbreviation	Compound Name
2,3,7,8-TBDD	2,3,7,8-tetrabromodibenzodioxin
1,2,3,7,8-PeBDD	1,2,3,7,8-pentabromodibenzodioxin
1,2,3,4,7,8-HxBDD	1,2,3,4,7,8-hexabromodibenzodioxin
1,2,3,6,7,8-HxBDD	1,2,3,6,7,8-hexabromodibenzodioxin
1,2,3,7,8,9-HxBDD	1,2,3,7,8,9-hexabromodibenzodioxin
OBDD	Octabromodibenzodioxin
2,3,7,8-TBDF	2,3,7,8-tetrabromodibenzofuran
1,2,3,7,8-PeBDF	1,2,3,7,8-pentabromodibenzofuran
2,3,4,7,8-PeBDF	2,3,4,7,8-pentabromodibenzofuran
1,2,3,4,7,8-HxBDF	1,2,3,4,7,8-hexabromodibenzofuran
1,2,3,4,6,7,8-HpBDF	1,2,3,4,6,7,8-heptabromodibenzofuran

Table S3. Chlorinated dioxin and furan abbreviations

Abbreviation	Compound Name
2,3,7,8-Tetra CDD	2,3,7,8-Tetrachlorodibenzodioxin
1,2,3,7,8-Penta CDD	1,2,3,7,8-Pentachlorodibenzodioxin
1,2,3,4,7,8-Hexa CDD	1,2,3,4,7,8-Hexachlorodibenzodioxin
1,2,3,6,7,8-Hexa CDD	1,2,3,6,7,8-Hexachlorodibenzodioxin
1,2,3,7,8,9-Hexa CDD	1,2,3,7,8,9-Hexachlorodibenzodioxin
Hepta CDD	Heptachlorodibenzodioxin
Octa CDD	Octachlorodibenzodioxin
2,3,7,8-Tetra CDF	2,3,7,8-Tetrachlorodibenzofuran
1,2,3,7,8-Penta CDF	1,2,3,7,8-Pentachlorodibenzofuran
2,3,4,7,8-Penta CDF	2,3,4,7,8-Pentachlorodibenzofuran
1,2,3,4,7,8-Hexa CDF	1,2,3,4,7,8-Hexachlorodibenzofuran
1,2,3,6,7,8-Hexa CDF	1,2,3,6,7,8-Hexachlorodibenzofuran
2,3,4,6,7,8-Hexa CDF	2,3,4,6,7,8-Hexachlorodibenzofuran
1,2,3,7,8,9-Hexa CDF	1,2,3,7,8,9-Hexachlorodibenzofuran
1,2,3,4,6,7,8-Hepta CDF	1,2,3,4,6,7,8-Heptachlorodibenzofuran
1,2,3,4,7,8,9-Hepta CDF	1,2,3,4,7,8,9-Heptachlorodibenzofuran
1,2,3,4,6,7,8,9-Octa CDF	Octachlorodibenzofuran

Table S4. Concentrations of FRs (μg/g) in bulk samples of the burn room furnishings

Compound Measured	Carpet Padding (N=3)	Curtain Liner (N=1)	Inner Spring Mattress Foam (N=2)	Foam Topper for Bed (N=2)	Head-board Padding (N=1)	Chair Cushion (N=2)	Chair Cushion Liner (N=1)	Flat Screen TV Plastic (N=1)
Labelling	None	None	California TB-603	None	None	California TB-117 (1975)	None	None
Polybrominated diphenyl ethers (PBDEs)								
BDE-47	<0.1 - 0.41	0.19	<0.1	<0.1 - 0.74	5,600	<0.1 - 4.1	<0.1	<0.1
BDE-85	<0.1	<0.1	<0.1	<0.1	840	<0.1 - 1.6	<0.1	<0.1
BDE-99	0.11 - 0.56	0.25	<0.1 - 0.44	<0.1 - 2.9	15,000	<0.1 - 25	<0.1	<0.1
BDE-100	<0.1	<0.1	<0.1	<0.1 - 0.6	2,500	<0.1 - 3.8	<0.1	<0.1
BDE-153	<0.1 - 5.6	<0.1	<0.1	<0.1 - 2.0	2,000	<0.1 - 13	<0.1	<0.1
BDE-154	<0.1	<0.1	<0.1	<0.1 - 0.69	1,400	<0.1 - 5.0	<0.1	<0.1
BDE-183	<0.1 - 1.1	<0.1	<0.1	<0.1 - 2.0	67	<0.1	<0.1	<0.1
BDE-206	<0.1 - 14	2.8	<0.1 - 6.3	<0.1	<0.1	<0.1	<0.1	<0.1
BDE-209	0.41 - 102	440	<0.1 - 61	<0.1	<0.1	<0.1 - 0.68	<0.1	<0.1
Non-PBDE brominated FRs (NPBFRs)								
TBBPA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TBB	0.38 - 3.2	910	<0.1 - 0.5	<0.1 - 7.5	<0.1	18,500 - 26750	68.5	<0.1
TBPH	0.22 - 5.7	340	<0.1 - 1.2	<0.1 - 3.7	<0.1	5,800 - 6,380	19.6	<0.1
DBDPE	<0.1 - 0.53	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Organophosphate FRs (OPFRs)								
TCEP	<0.1	1.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TCPP	59 - 630	5.4	<0.1	<0.1	8.4	<0.1 - 1.3	<0.1	<0.1
TDCPP	240 - 9,100	1.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TPP	0.43 - 3.8	4.0	0.16 - 0.23	<0.1 - 1.3	1,690	1,400 - 7,380	22.6	19
TCP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table S5. Air concentrations of FRs (µg/m^3) by solid and gas phase partitioning. ND values were replaced by LOD/2 (divided by air volume).

	Gas (N=3)[4]				Particulate (N=3)[4]			
Analyte	**Median[3]**	**Range**	**N of samples detected**	**LOD/2 Range**	**Median[3]**	**Range**	**N of samples detected**	**LOD/2 Range**
PBDEs[1]								
BDE-47	0.16	0.10-0.66	1	0.10-0.16	1.27	0.05-9.89	2	0.05
BDE-99	0.83	0.31-4.45	3	-	4.76	2.02-9.37	3	-
BDE-206	0.16	0.16-0.30	1	0.16	0.08	0.08-4.20	1	0.08
BDE-209	12.8	9.65-16.5	3	-	5.55	2.42-35.9	3	-
NPBFRs								
TBBPA	-	-	-	-	0.08	0.08-9.10	1	0.08
TBB	0.93	0.78-3.65	3	-	7.44	6.28-19.4	3	-
TBPH	0.16	0.10-0.64	1	0.10-0.16	1.23	0.08-3.00	2	0.08
DBDPE	0.26	0.16-2.10	2	0.16	0.08	0.08-0.24	1	0.08
OPFRs[2]								
TCPP	-	-	-	-	0.12	0.12-3.90	1	0.12
TDCPP	-	-	-	-	0.12	0.12-8.63	1	0.12
TPP	72.7	29.2-126	3	-	223	135-394	3	-

1. BDE-100, BDE-153, BDE-154, and BDE-183 were not detected for solid phase and gas phase.
2. TCEP and TCP were not detected for solid phase and gas phase.
3. All non-detects were replaced with LOD/2. Reported medians for analytes with less than 67% detection rate are heavily influenced by the imputed levels. Caution should be exercised in interpreting these results.
4. Due to extreme conditions, air samples ran for 6-10 min of the fire period (which lasted 14-16 min).

Table S6. Brominated dioxin and furan concentrations (ng/cm^2) measured from left-handed gloves without any decontamination after completion of 4 scenarios involving a combination of the following fireground tasks: fire attack, search, outside vent, overhaul. ND values were replaced by LOD/2. Although numbers are provided, results should be considered qualitative.

	Attack, Search, Outside Vent, and Overhaul (N=7)			
Analyte	**Median[2]**	**Range**	**N of samples detected**	**LOD/2**
Brominated dioxins[1]				
Brominated furans				
2,3,7,8-TBDF	0.14	0.06-0.35	4	0.06
Unk_TBDF-1	8.04	0.17-23.7	7	-
Unk_TBDF-2	1.28	0.06-2.99	5	0.06

1,2,3,7,8-PeBDF	0.06	0.06-0.13	2	0.06
Unk_PeBDF-1	4.87	0.06-14.6	6	0.06
Unk_PeBDF-2	0.78	0.06-7.43	6	0.06
Unk_PeBDF-3	0.73	0.06-4.32	5	0.06
2,3,4,7,8-PeBDF	0.12	0.06-0.31	4	0.06
1,2,3,4,7,8-HxBDF	0.41	0.06-2.19	6	0.06
Unk_HxBDF-1	3.57	0.06-16.40	6	0.06
Unk_HxBDF-2	1.57	0.06-14.80	6	0.06
1,2,3,4,6,7,8-HpBDF	0.74	0.06-13.30	6	0.06
Unk_HpBDF-1	1.60	0.43-26.50	7	-
Unk_HpBDF-2	0.06	0.06-4.84	3	0.06
Unk_HpBDF-3	0.06	0.06-1.12	1	0.06

1. 2,3,7,8-TBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, and OBDD analytes were not detected for all samples.
2. Reported medians for analytes with less than 50% detection rate are heavily influenced by the imputed levels. Caution should be exercised in interpreting these results.

Abbreviations: TBDF = tetrabromodibenzofuran, UNK = Unknown dioxin or furan mixture, PeBDF = pentabromodibenzofuran, HxBDF = hexabromodibenzofuran, HpBDF = heptabromodibenzofuran

Table S7. Chlorinated dioxin and furan concentrations (ng/cm^2) measured from left-handed gloves without any decontamination after completion of 4 scenarios involving a combination of the following fireground tasks: fire attack, search, outside vent, overhaul. ND values were replaced by LOD/2.

	Attack, Search, Outside Vent, and Overhaul (N=7)			
Analyte	**Median**	**Range**	**N of samples detected**	**LOD/2 Range**
Chlorinated dioxins[1,2]				
Hepta CDD	0.00014	0.00002-0.00024	6	0.00002
Octa CDD	0.00072	0.00008-0.00229	5	0.00008-0.00029
Chlorinated furans[3]				
2,3,7,8-Tetra CDF	0.00006	0.00003-0.00008	6	0.00003

1. Hepta_CDD and Octa_CDD were detected in field blanks at levels <0.00008 and < 0.00021 ng/cm^2, respectively.
2. 2,3,7,8-Tetra CDD, 1,2,3,7,8-Penta CDD, 1,2,3,4,7,8-Hexa CDD, 1,2,3,6,7,8-Hexa CDD, and 1,2,3,7,8,9- Hexa CDD analytes were not detected for all samples.
3. 1,2,3,7,8-Penta CDF, 2,3,4,7,8-Penta CDF, 1,2,3,4,7,8-Hexa CDF, 1,2,3,6,7,8-Hexa CDF, 2,3,4,6,7,8-Hexa CDF, 1,2,3,7,8,9-Hexa CDF, 1,2,3,4,6,7,8-Hepta CDF, 1,2,3,4,7,8,9-Hepta CDF, and Octa CDF analytes were not detected for all samples.

Abbreviations: CDD = Chloro Dibenzo-p-Dioxin, CDF = Chloro Dibenzo-p-Furan.

Figures

Fig. S1. Overhead view and floorplan of the residential structure used for the controlled fires.

Fig. S2. Box-and-whisker plot showing air concentrations (µg/m^3) of brominated furans (brominated dioxins were not detected). ND values were replaced by LOD/2 (divided by air volume) ranging from 0.3 µg/m^3 to 0.6 µg/m^3. Boxes were created only if 50% or more of the data were detectable. Results should be considered qualitative.

Fig. S3. Box-and-whisker plot showing air concentrations (µg/m^3) of chlorinated dioxins and furans. ND values were replaced by LOD/2 (divided by air volume) ranging from 0.00006 µg/m^3 to 0.00035 µg/m^3. Boxes were created only if 50% or more of the data were detectable. Note that Octa CDD and 1,2,3,4,6,7,8-Hepta CDF were detected in field blanks, suggesting either environmental FR contamination or matrix interference.

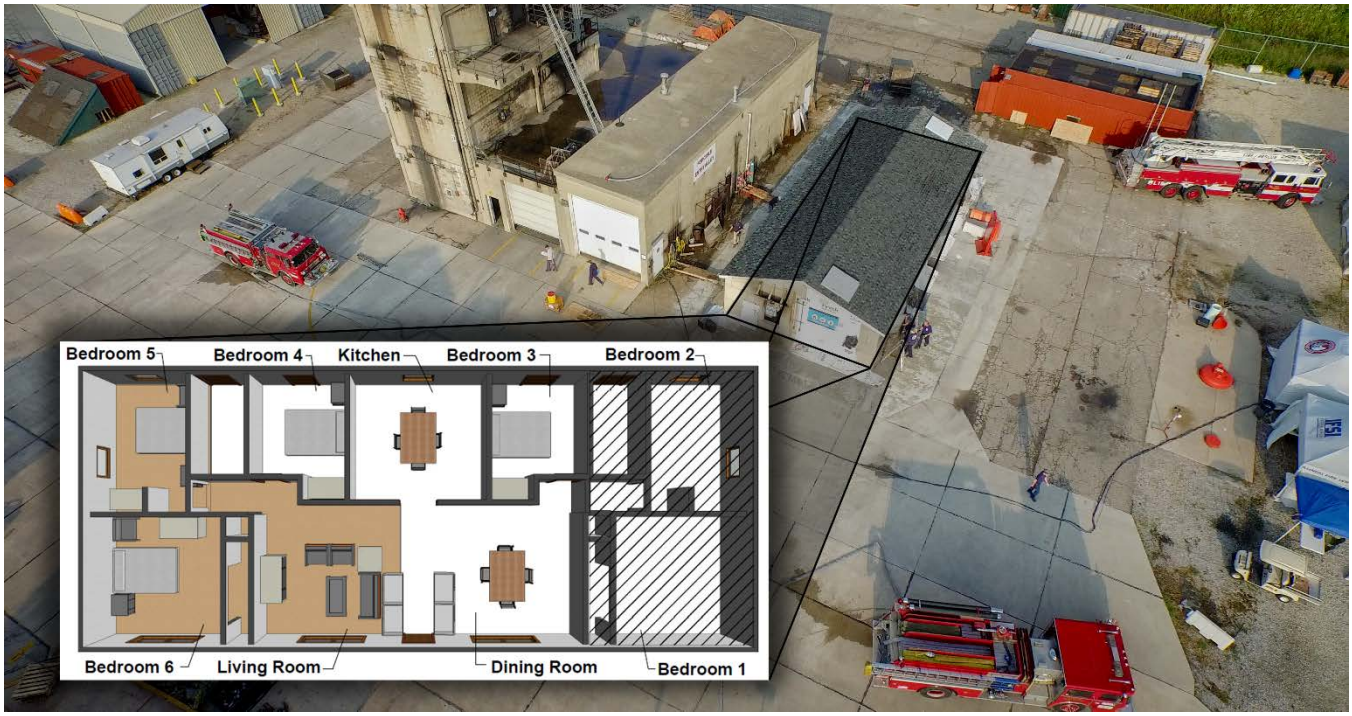

Fig. S1.

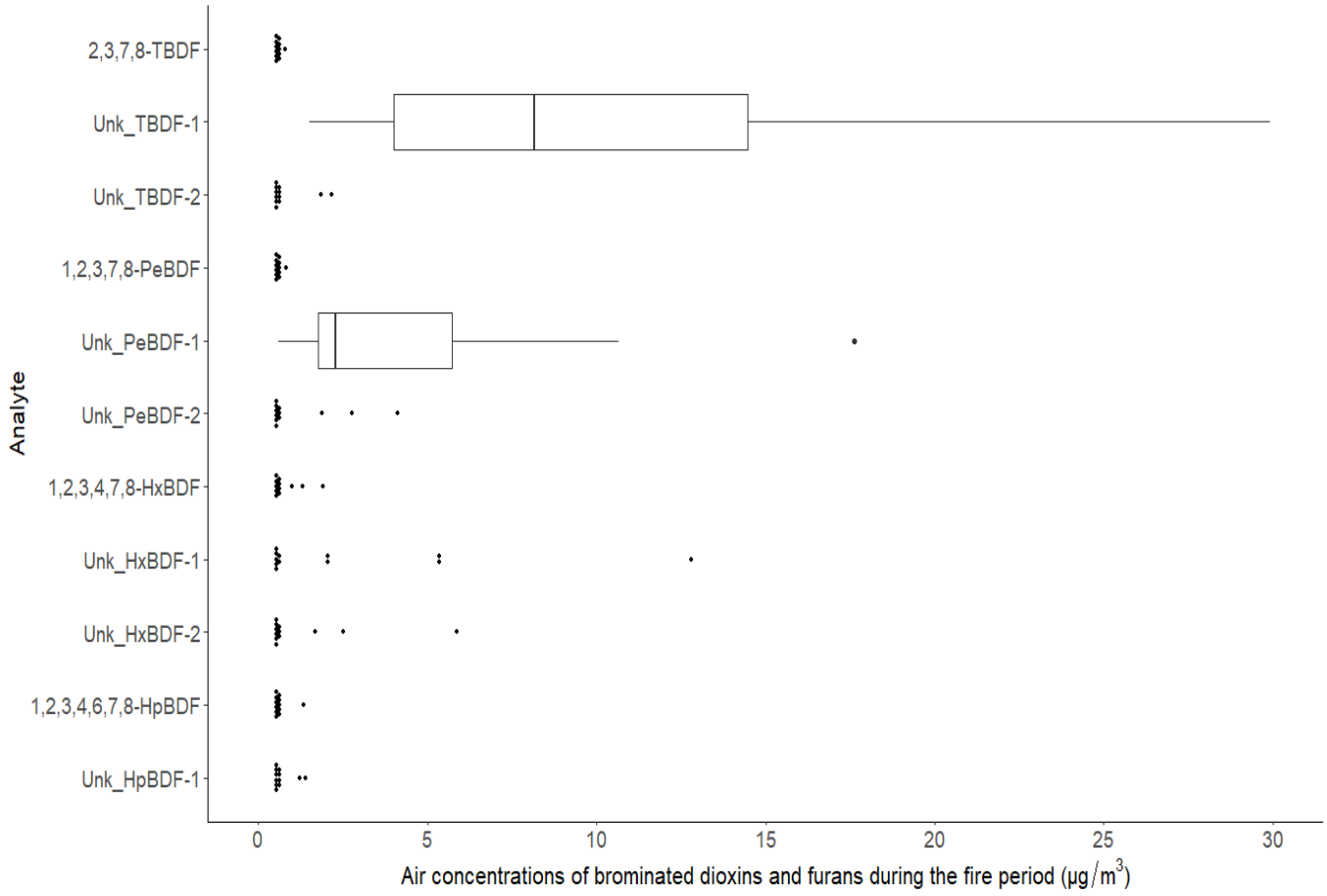
2,3,7,8-TBDF
Unk_TBDF-1
Unk_TBDF-2
1,2,3,7,8-PeBDF
Unk_PeBDF-1
Unk_PeBDF-2
1,2,3,4,7,8-HxBDF
Unk_HxBDF-1
Unk_HxBDF-2
1,2,3,4,6,7,8-HpBDF
Unk_HpBDF-1
Analyte
0
5
10
15
20
25
30
Air concentrations of brominated dioxins and furans during the fire period (μg/m3)

Fig. S2.

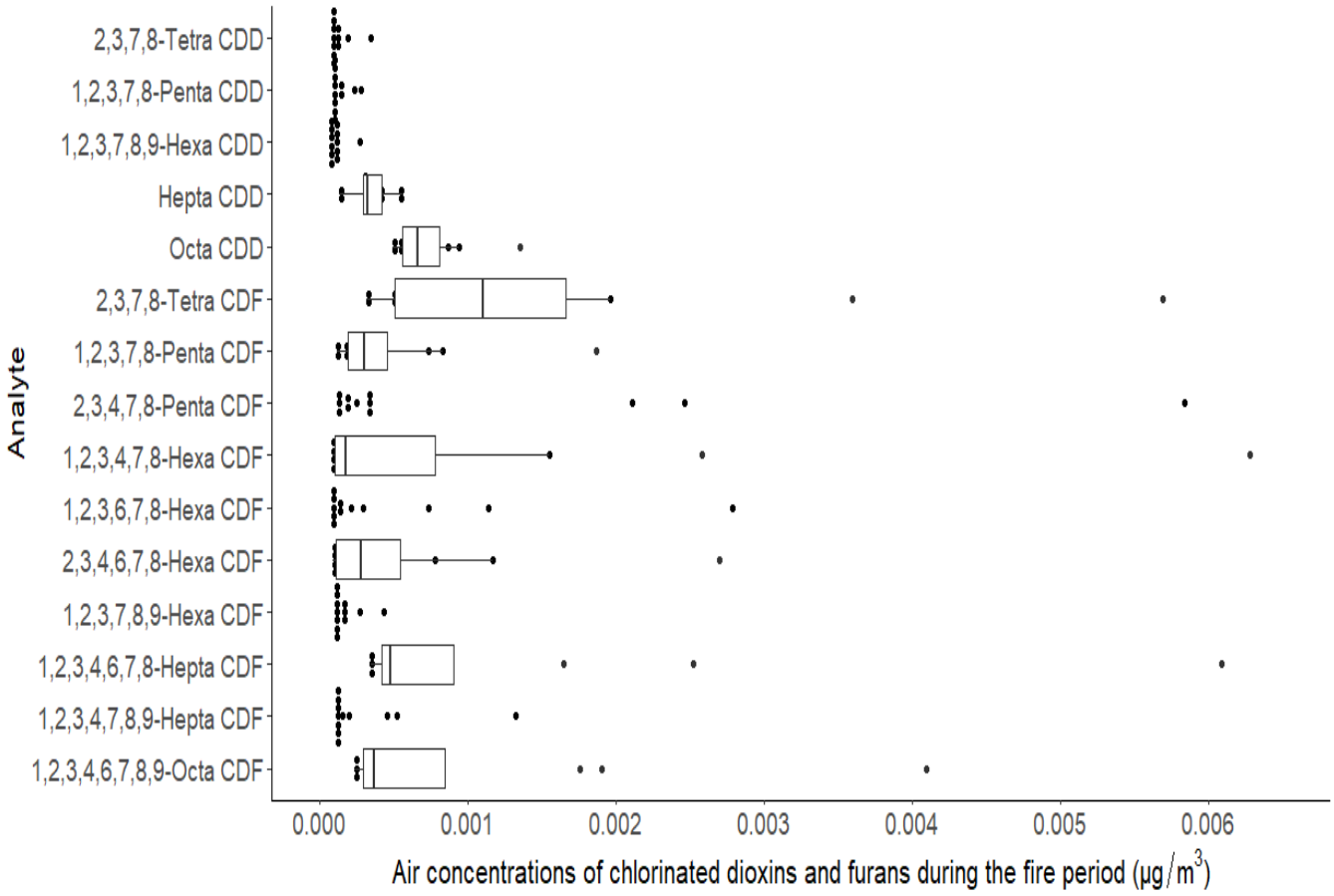
Analyte
2,3,7,8-Tetra CDD
1,2,3,7,8-Penta CDD
1,2,3,7,8,9-Hexa CDD
Hepta CDD
Octa CDD
2,3,7,8-Tetra CDF
1,2,3,7,8-Penta CDF
2,3,4,7,8-Penta CDF
1,2,3,4,7,8-Hexa CDF
1,2,3,6,7,8-Hexa CDF
2,3,4,6,7,8-Hexa CDF
1,2,3,7,8,9-Hexa CDF
1,2,3,4,6,7,8-Hepta CDF
1,2,3,4,7,8,9-Hepta CDF
1,2,3,4,6,7,8,9-Octa CDF
0.000
0.001
0.002
0.003
0.004
0.005
0.006
Air concentrations of chlorinated dioxins and furans during the fire period (µg/m3)

Fig. S3.