Supplementary Material

Each sample was spiked with 1 ng of $^{13}C_{12}$ mass-labelled internal standards, and then was Soxhlet extracted by 250 mL toluene (solid sample for PCDD/Fs in gas and solid phases) or liquid-liquid extracted (liquid sample for PCDD/Fs in liquid phase) for 24 hours. Next, a rotary evaporator concentrated the Soxhlet extract into 1-2 mL. Subsequently, $^{37}Cl_4$-labelled clean-up standard was added to the extract, followed by the process in which sulphuric acid washed the concentrated extract several times until the solution colour turned visible. The washed extract was further cleaned with a multilayer silica gel column and a basic-alumina column. After the clean-up procedures, the extract was concentrated to 20 μL with nitrogen and then spiked with 1 ng of $^{13}C_{12}$-labelled recovery standards before analysis. The index of recovery standards was presented in Table S4. All solvents for pre-treatment were purchased from Mallinckrodt Baker Inc., USA, and were pesticide residue analysis grade.

After the pre-treatment procedures, the PCDD/Fs in the samples were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (GC/MS, JMS-800D, JEOL, Japan) with a DB-5MS column. Table S5 illustrated detailed instrumental parameters and procedures of GC/MS. The target compounds were 136 tetra- to octa-chlorinated dibenzo-p-dioxins and dibenzofuran congeners (Table S3), including the 17 kinds of toxic PCDD/Fs and as far as separated individually-all congeners from homologue classed TCDD through OCDF. Concentrations of 136 PCDD/Fs were estimated based on the recovery standards, as each chlorinated homologue group had at least one set of standards. The PCDD/Fs recovery rates were based on $^{13}C_{12}$-PCDD/F surrogates. The recovery rates of $^{13}C_{12}$-labelled recovery standards were calculated as the following equation:

$$R = \frac{A_{es}}{A_{rs}} \times \frac{Q_{rs}}{RRF_{rs}} \times \frac{100\%}{Q_{es}}$$

where: R – Recovery rates of internal standard, %;

where: A_{es} – Summed area of monitoring ion peak of extract internal standard;

where: A_{rs} – Summed area of monitoring ion peak of recovery internal standard;

where: Q_{rs} – Quantity of recovery internal standards, ng;

where: RRF_{rs} – Relative response factor of internal extract standard to recovery internal standard;

where: Q_{es} – Quantity of extract internal standards, ng;

The recovery rates of the PCDD/Fs were estimated by $^{13}C_{12}$-PCDD/F surrogates and range from 50.8% to 112.0%, meeting the requirement of HJ 77.2-2008 and HJ 77.3-2008. Following this, NATO/CCMS factors were utilized to calculate international toxic equivalents. All calculated concentrations of PCDD/Fs and major air pollutants were also normalized to 11% O_2, 273.15K, and 100 kPa (GB 18485-2014).

Table S1. Information of 2,3,7,8-PCDD/Fs and corresponding I-TEF.

PCDDs & PCDFs	I-TEF
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.001
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.001

Table S2. Full titles of PCDD/F homologues.

Abbreviations	Full titles
TCDD	Tetrachlorinated dibenzo-*p*-dioxins
PeCDD	Pentachlorinated dibenzo-*p*-dioxins
HxCDD	Hexachlorinated dibenzo-*p*-dioxins
HpCDD	Heptachlorinated dibenzo-*p*-dioxins
OCDD	Octachlorinated dibenzo-*p*-dioxin
TCDF	Tetrachlorinated dibenzofurans
PeCDF	Pentachlorinated dibenzofurans
HxCDF	Hexachlorinated dibenzofurans
HpCDF	Heptachlorinated dibenzofurans
OCDF	Octachlorinated dibenzofuran

Table S3. Information of 136 kinds of tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofuran congeners (136 PCDD/Fs).

Terms	
1,3,7,9-TCDD	1,2,3,6,8-PeCDD
1,3,6,9-TCDD	1,2,4,7,8-PeCDD
1,2,4,7/1,2,4,8/1,2,4,6/1,2,4,9-TCDD	1,2,3,7,9-PeCDD
1,3,7,8-TCDD	1,2,3,6,9/1,2,4,6,7/1,2,4,8,9-PeCDD
1,4,6,9-TCDD	1,2,34,7/1,2,3,4,6-PeCDD
1,2,6,8-TCDD	1,2,3,7,8-PeCDD
1,4,7,8-TCDD	1,2,3,6,7-PeCDD
1,2,7,9-TCDD	1,2,3,8,9-PeCDD
1,2,3,4/1,2,6,9-TCDD	1,2,4,6,7,9/1,2,4,6,8,9-HxCDD
1,2,3,6-TCDD	1,2,3,4,6,8-HxCDD
1,2,3,7/1,2,3,8-TCDD	1,2,3,6,7,9/1,2,3,6,8,9-HxCDD
2,3,7,8-TCDD	1,2,3,4,6,9-HxCDD
1,2,3,9-TCDD	1,2,3,4,7,8-HxCDD
1,2,7,8-TCDD	1,2,3,6,7,8-HxCDD
1,2,6,7-TCDD	1,2,3,4,6,7-HxCDD
1,2,8,9-TCDD	1,2,3,7,8,9-HxCDD
1,3,6,8-TCDD	1,2,3,4,6,7,9-HpCDD
1,2,4,7,9/1,2,4,6,8-PeCDD	1,2,3,4,6,7,8-HpCDD
1,2,4,6,9-PeCDD	1,2,3,4,6,7,8,9-OCDD
1,3,6,8-TCDF	1,2,3,4,6-PeCDF
1,4,6,8-TCDF	1,2,3,4,8-PeCDF
2,4,6,8-TCDF	1,2,3,7,8-PeCDF
1,2,4,7/1,3,4,7/1,3,7,8/1,3,4,6/1,2,4,6-TCDF	1,2,3,6,7/1,2,6,7,8-PeCDF
1,3,6,7/1,3,4,8/1,3,7,9/1,2,4,8-TCDF	1,2,3,7,9-PeCDF
1,2,6,8-TCDF	2,3,4,7,8/1,2,4,8,9-PeCDF
1,4,6,7-TCDF	1,2,6,7,9-PeCDF
1,4,7,8-TCDF	1,2,3,6,9/2,3,4,6,7-PeCDF
1,3,6,9/1,2,3,7-TCDF	1,2,3,4,9-PeCDF
2,4,6,7-TCDF	1,2,3,8,9-PeCDF
1,2,3,8/1,2,3,6/1,4,6,9/1,6,7,8/1,2,3,4 /2,3,6,8-TCDF	1,2,3,4,6,8-HxCDF
1,2,7,8/1,3,4,9-TCDF	1,3,4,6,7,8/1,2,4,6,7,8-HxCDF
1,2,6,7-TCDF	1,3,4,6,7,9-HxCDF
2,3,4,8-TCDF	1,2,4,6,7,9-HxCDF
2,3,7,8-TCDF	1,2,4,6,8,9-HxCDF
2,3,4,7/1,2,7,9-TCDF	1,2,3,4,6,7-HxCDF
2,3,4,6/1,2,4,9-TCDF	1,2,3,4,7,8-HxCDF
2,3,6,7/3,4,6,7-TCDF	1,2,3,6,7,8-HxCDF

Terms	
1,2,6,9-TCDF	1,2,3,4,7,9-HxCDF
1,2,3,9-TCDF	1,2,3,4,6,9-HxCDF
1,2,8,9-TCDF	1,2,3,6,7,9-HxCDF
1,3,4,6,8-PeCDF	2,3,4,6,7,8/1,2,3,6,8,9-HxCDF
1,3,6,7,8/1,3,4,6,7/1,2,4,6,7-PeCDF	1,2,3,7,8,9/1,2,3,4,8,9-HxCDF
1,2,3,6,8/1,3,4,7,8/1,2,4,7,8-PeCDF	1,2,3,4,6,7,8-HpCDF
1,3,4,7,9-PeCDF	1,2,3,4,6,7,9-HpCDF
1,4,6,7,8-PeCDF	1,2,3,4,6,8,9-HpCDF
1,2,4,7,9/1,3,4,6,9-PeCDF	1,2,3,4,7,8,9-HpCDF
2,3,4,6,8/1,2,4,6,9/1,2,3,4,7-PeCDF	1,2,3,4,6,7,8,9-OCDF

Table S4. Information of recovery standards added during pre-treatment of PCDD/Fs.

Terms	Composition
Extract standards (LCS)	1)$^{13}C_{12}$-2,3,7,8-TCDD, 2)$^{13}C_{12}$-1,2,3,7,8-PeCDD, 3)$^{13}C_{12}$-1,2,3,4,7,8-HxCDD, 4)$^{13}C_{12}$-1,2,3,6,7,8-HxCDD, 5)$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD, 6)$^{13}C_{12}$-OCDD, 7)$^{13}C_{12}$-2,3,7,8-TCDF, 8)$^{13}C_{12}$-1,2,3,7,8-PeCDF, 9)$^{13}C_{12}$-2,3,4,7,8-PeCDD, 10)$^{13}C_{12}$-1,2,3,4,7,8-HxCDF, 11)$^{13}C_{12}$-1,2,3,6,7,8-HxCDF, 12)$^{13}C_{12}$-1,2,3,7,8,9-HxCDF, 13)$^{13}C_{12}$-2,3,4,6,7,8-HxCDF, 14)$^{13}C_{12}$-1,2,3,4,6,7,8-HxCDF, 15)$^{13}C_{12}$-1,2,3,4,7,8,9-HxCDF,
Clean-up standard (CUS)	$^{37}Cl_4$-2,3,7,8-TCDD
Recovery standards (ISS)	1)$^{13}C_{12}$-1,2,3,4-TCDD, 2) $^{13}C_{12}$-1,2,3,7,8,9-HxCDD

Table S5. Instrumental parameters of PCDD/Fs analysis of gas chromatography/high-resolution mass spectrometry (GC/MS).

Terms	Operational parameters
Type	High Resolution, JMS800D, JEOL, Japan
Mass Analyzer	Double-focusing magnetic mass analyzer
Chromatographic parameter	Column: DB-5s, 60m×0.25mm×0.25μm
	Sample inlet temperature: 270℃
	Carrier gas: He (99.9995%)
	Volumatic flow rate: 1.2ml/min
	Splitless inlet, 1μl
	Column oven temperature program: 150℃ (1min)-(25℃/min)190℃-(3℃/min)280℃ (20min)
Mass spectrometry parameter	Ionization mode: electrons bombarded the ionization source
	Ionization energy: 38ev
	Selected ion monitoring

Terms	Operational parameters
	Resolution: >10000
	Pertetrafluorokerosene (PFK) is used as a quality correction substance
Quantitative method	Isotopic dilution method
	^{13}C labelled standard for U.S. EPA Method 1613