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EVALUATION OF SEASONAL VARIATION OF PCDDS/PCDFS' CONCENTRATION IN THE AMBIENT AIR BY USING PASSIVE MONITORING METHOD

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Introduction

Monitoring of PCDDs/PCDFs in the ambient air by using passive air sampler with the polyurethane foam (PUF) disk have been conducted at two typical cities of Vietnam1-3. This paper presents the results of seasonal monitoring of PCDDs/PCDFs in the ambient air at a central city in the North in four consecutive years (2012-2015). The efficiency of PCDD/PCDF retention on the PUF disks have been evaluated by using the 13C-labeled PCDD/PCDF surrogate standards. Congener profile of PCDDs/PCDFs in the ambient air, the variation of their concentration and temporal trend have been determined.

Materials and method

Passive air sampler:

The passive air sampler TE-200 PAS of Tisch Environmental Inc. (USA) was used with PUF disk3. The sampler and disk have been cleaned before monitoring.

Standards of PCDDs/PCDFs:

The surrogate standards with sign of CLDF consists of 15 isotopes 13C-labeled PCDDs/PCDFs diluted from the stock solution EDF-8999 of Cambridge Isotope Laboratories. The concentration of CLDF is 2000 pg/mL for each 13C-labeled PCDD/PCDF and 4000 pg/mL for 13C-OCDD. The native and other labeled standards are used as described in the method US.EPA1613B4.

Experiments:

The experiments have been conducted at the central city in the North of Vietnam dominated by tropical climate in four seasons: spring, summer, autumn and winter. In each season, two passive air samplers have been used with clean PUF disks. 1 ml CLDF has been added on the disk from the start of sampling. The samplers were hanged outdoor at a high of 2.5 m and a distance of 10 m. Sample code and interval of experiment are shown in Table 1. The code with suffix -D is the sample of duplicate monitoring.

The purposes of experiment are: (1) Assessing the stability of 13C-labeled PCDD/PCDF surrogate standards and their retention which is similar to the retention of native PCDDs/PCDFs on the disk during the whole sampling period; (2) Determining the amount of PCDDs/PCDFs in the ambient air adsorbed on the disk, then assessing the variation of their concentration in the ambient air; (3) Assessing the replication of the monitoring method.

Analysis of PCDDs/PCDFs:

Before extraction only 13C-labeled PCDD recovery standards were added in sample. PCDDs/PCDFs were analyzed by high resolution gas chromatography coupled with high resolution mass spectrometry (AutoSpec Premier, Waters)1.

Results and discussion

Depending on annual weather conditions, the monitoring interval in each season was adjusted suitably as in Table 1. Average efficiency of 13C-labeled PCDD/PCDF retention on the PUF disks during different seasons in 4 years (2012-2015) is shown in Table 2.

Table 2 shows that the average efficiency of surrogates retention on the PUF disks is relatively high, between 38.4% and 125.9% with the relative standard deviation (RSD) in the range of 5.3% to 62.6%, of which most of data (83.3%) has RSD less than 40%. And the efficiency of retention of each surrogate in all seasons with 3-month monitoring period reaching 26.9% to 174.8% has satisfied with requirements of method US.EPA1613B (between 17% and 185%)4. Therefore, 13C-labeled PCDDs/PCDFs are sustainable, stable and well maintained on PUF disks. For this reason, the use of 13C-labeled PCDDs/PCDFs as associated quantitative and surrogate standards at the beginning of monitoring is completely reasonable.

Amount of PCDDs/PCDFs (pg/disk/day) was adsorbed on PUF disks in different seasons and temporal trend during 2012 to 2015 and total WHO-TEQ2005(ND=½DL) illustrated in figures 1,2,3,4. Variation of concentration of toxic PCDDs/PCDFs in the ambient air, total TEQ in seasons and their temporal trend and also average contribution rate of 2378-TCDD to total TEQ are summarized in table 3 and illustrated in figure 5.

The figures 1,2,3,4 show variation of concentration and congener profile of toxic PCDDs/PCDFs in the ambient air in four seasons. Method of PCDD/PCDF monitoring using passive air sampler with PUF

disk can detect most (97.9%) of congeners. Concentration of PCDDs/PCDFs and total TEQ found on the PUF disks during 2012 to 2015 are lowest in the summer and highest in the autumn and the winter. Specifically, in summer average concentration of total PCDDs is 0.93 pg/disk/day; total PCDFs: 1.66; total TEQ: 0.239 and total TEQ are varied from 0.143 to 0.465 (table 3). In autumn, average concentration of total PCDDs is 0.96; total PCDFs: 3.55; total TEQ: 0.364 with variation from 0.205-0.676. In every season due to various variations in concentration of each congener, so average concentration of total PCDDs, total PCDFs and total TEQ is different, therefore the percentage of 2378-TCDD compared to total TEQ has also the various changes.

Generally, in all seasons 1234678-HpCDD, OCDD have high concentration than other PCDDs. And 123789-HxCDF, 1234789-HpCDF, OCDF have lower concentration than other PCDFs. Total concentration of PCDFs is always higher than the PCDDs. Three congeners frequently have the highest concentration in descending order as follows: OCDD > 1234678-HpCDF > 1234678-HpCDD.

Figure 5 illustrates a general evaluation of variation and temporal trend of the concentration of toxic PCDDs/PCDFs in the ambient air and their total TEQ in each season during 2012 to 2015. The result shows that the concentration of PCDDs/PCDFs and total TEQ in the autumn 2013 is the highest: 8.83 and 0.676 pg/disk/day (PAS15), and in the summer 2013 is the lowest: 2.01 and 0.143 respectively (PAS14).

Quality assurance and quality control have been implemented. The analytical result of blank samples indicates that there is no any cross-contamination of PCDDs/PCDFs from PUF and during sample preparation. The concentration of PCDDs/PCDFs found in the monitoring samples is several times higher than their detection limit. 95% samples of duplicate monitoring have a low coefficient of variance (CV) from 0.06% to 26.6%, average of 11.6%. Only one sample (PAS22) of 20 duplicate samples has CV of 44.6%. This confirms the sampler operates in stable manner, monitoring results ensure reliability and sampling method is perfectly suitable to tropical climates in the Northern Vietnam.

Acknowledgements

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References:

1. Sau T.K, Thu N.T, Dung N.T (2013) Organohalogen Compounds 75: 418-421.
2. Sau T.K, Truong N.X (2013) Organohalogen Compounds 75: 422-425.
3. Sau T.K, Truong N.X, Hung L.B, Tuan N.T (2014) Organohalogen Compounds 76: 98-101.
4. US. Environmental Protection Agency (1994) Method 1613B.

Table 1: Sample code and interval of passive air sampling

Year	Spring	Summer	Autumn	Winter
2012	PAS03 (15 Feb - 11 Apr)	PAS05 (11 Apr - 28 May)	PAS07 (22 Aug - 14 Nov)	PAS9 (14 Nov 2012 - 04 Feb 2013)
2013	PAS11 (04 Feb - 03 May)	PAS13, PAS14-D (03 May - 26 Jul)	PAS15, PAS16-D (26 Jul -17 Oct)	PAS17, PAS18-D (17 Oct 2013 - 09 Jan 2014)
2014	PAS19, PAS20-D (09 Jan - 01 Apr)	PAS21, PAS22-D (01 Apr - 02 Jul)	PAS23, PAS24-D (02 Jul - 06 Oct)	PAS25, PAS26-D (06 Oct 2014 - 12 Jan 2015)
2015	PAS27, PAS28-D (12 Jan - 14 Apr)	PAS29, PAS30-D (14 Apr - 15 Jul)	PAS31, PAS32-D (03 Aug - 03)	PAS33, PAS34-D (03 Nov 2015 - 03 Feb 2016)

Table 2: Efficiency of ^{13}C-labeled PCDDs/PCDFs retention on the PUF disks

Surrogate standards	Spring (n=6)		Summer (n=7)		Autumn (n=7)		Winter (n=5)	
	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD
^{13}C-2378-TCDD	84.1	48.8	97.6	7.5	79.4	30.4	97.5	13.8
^{13}C-12378-PeCDD	107.0	55.0	123.2	11.9	116.2	32.4	101.7	17.9
^{13}C-123478-HxCDD	79.3	32.0	97.1	13.4	85.7	32.4	95.6	12.8
^{13}C-123678-HxCDD	68.3	33.1	87.4	5.3	69.2	33.7	83.0	7.8
^{13}C-1234678-HpCDD	88.1	38.9	101.0	7.7	81.4	33.5	96.0	9.7
^{13}C-OCDD	96.5	10.8	97.5	23.0	74.7	39.5	109.6	15.9
^{13}C-2378-TCDF	85.8	56.9	90.4	12.4	66.2	49.8	86.4	16.1
^{13}C-12378-PeCDF	100.4	42.5	125.9	12.9	98.7	54.4	107.2	21.3
^{13}C-23478-PeCDF	83.3	39.0	108.1	11.5	74.3	62.6	87.9	19.5
^{13}C-123478-HxCDF	72.7	29.9	72.2	23.7	69.9	34.9	80.0	11.3
^{13}C-123678-HxCDF	82.3	33.1	89.4	14.6	81.8	35.3	94.4	11.7
^{13}C-234678-HxCDF	73.1	37.7	77.9	15.0	69.7	35.7	83.3	9.8
^{13}C-123789-HxCDF	45.6	33.4	39.7	27.7	56.0	53.0	53.1	17.9
^{13}C-1234678-HpCDF	75.0	23.9	66.3	15.2	62.2	41.9	75.0	10.7
^{13}C-1234789-HpCDF	53.4	28.8	38.4	25.8	49.3	48.9	59.3	17.9

Table 3: Variation of PCDD/PCDF concentration (pg/disk/day) in the ambient air (2012-2015)

Season	Total TEQ			Average concentration of toxic congeners		% 2378-TCDD/ Total TEQ
	Min	Average	Max	PCDDs	PCDFs	
Spring	0.167	0.279	0.383	1.50	1.60	20.0
Summer	0.143	0.239	0.465	0.93	1.66	12.7
Autumn	0.205	0.364	0.676	0.96	3.55	8.0
Winter	0.259	0.368	0.457	1.42	2.40	21.0

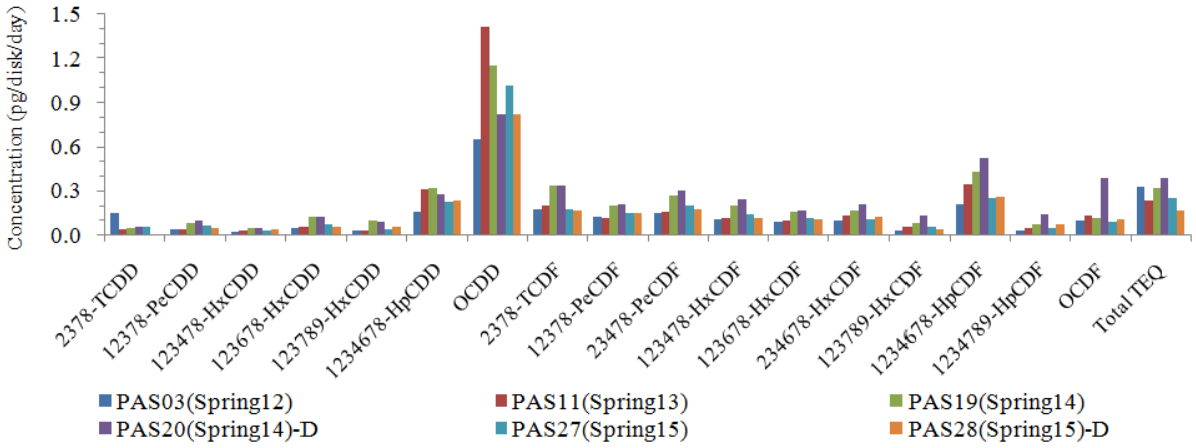

Figure 1: Concentration of PCDDs/PCDFs and their congener profile in Spring

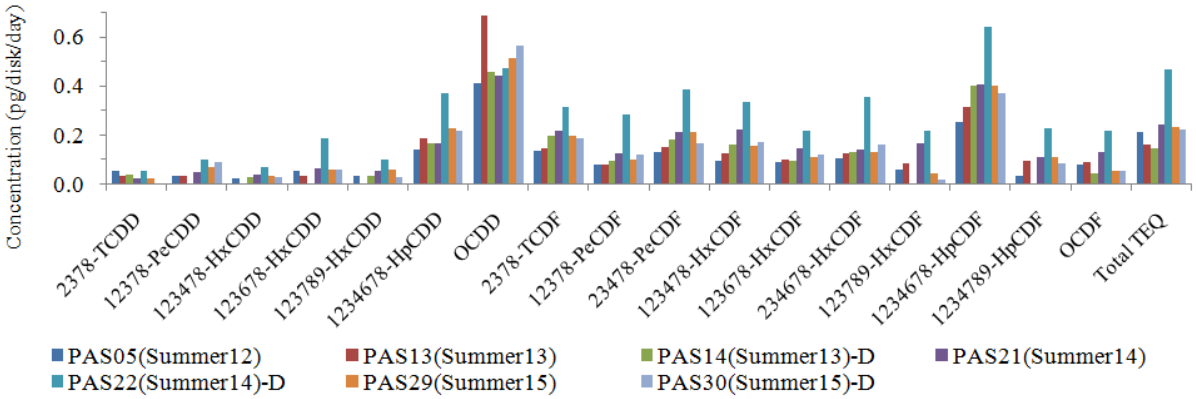

Figure 2: Concentration of PCDDs/PCDFs and their congener profile in Summer

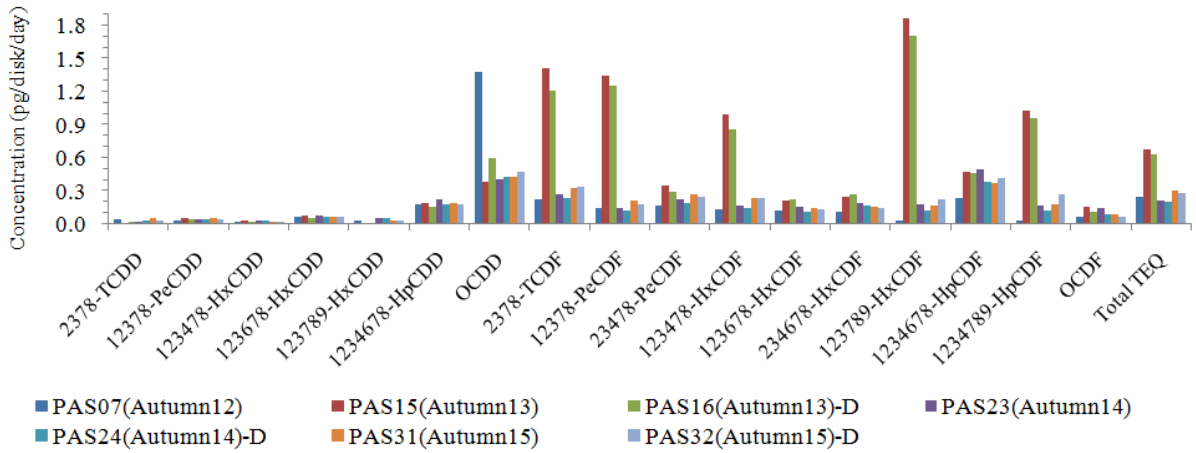

Figure 3: Concentration of PCDDs/PCDFs and their congener profile in Autumn

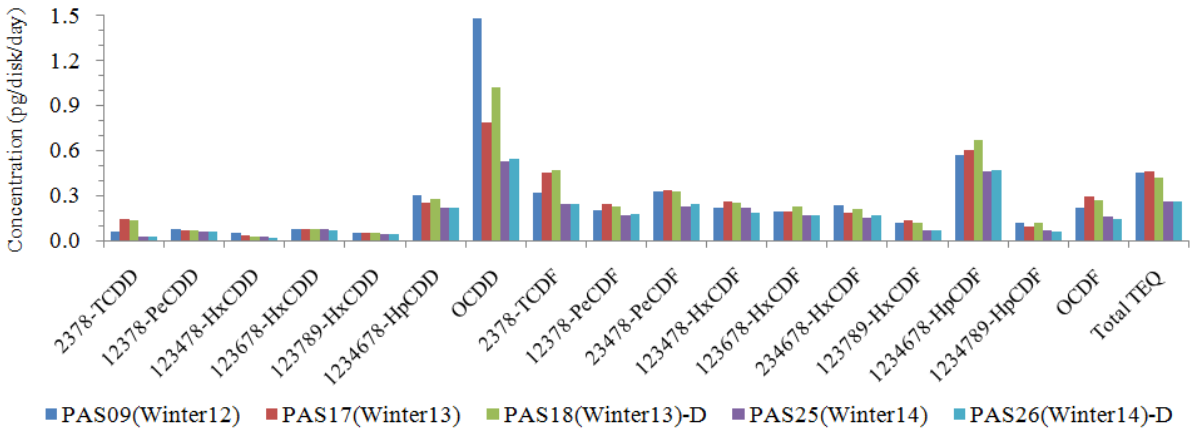

Figure 4: Concentration of PCDDs/PCDFs and their congener profile in Winter

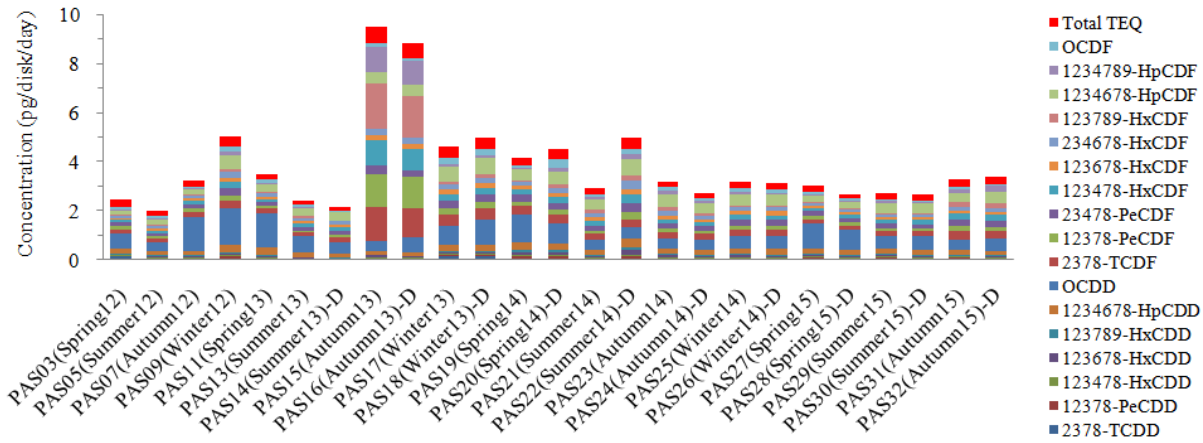

Figure 5: Variation of PCDD/PCDF concentration in the ambient air and their temporal trend