SEASONAL VARIATION OF PCDD/PCDF AND dl-PCB CONCENTRATIONS IN AMBIENT AIR USING PASSIVE SAMPLERS

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1. INTRODUCTION

Monitoring of PCDDs/PCDFs and dl-PCBs in ambient air using passive air sampler (PAS) with polyurethane foam (PUF) disk at sampling intervals of approximately three months was conducted in Hanoi and Danang, Vietnam[1-4]. The ^{13}C-labeled PCDD/PCDF standards were spiked on the PUF disks as surrogates at the beginning of each sampling interval. The seasonal variation of PCDD/PCDF and dl-PCB concentrations was studied by Spring, Summer, Autumn and Winter in 7 continuous years from 2012 to 2018 in Hanoi. This paper presents the results of seasonal monitoring and the temporal trends of PCDDs/PCDFs and dl-PCBs in ambient air between Winter 2015 - Autumn 2018 and in comparision with our previous study between Spring 2012 - Autumn 2015[5].

2. MATERIALS AND METHODS

2.1. Passive air sampler

The TE-200 PAS sampler of Tisch Environmental Inc (Ohio, USA) with the PUF disk was hanged outdoor[6]. The PUF disks were pre-cleaned by Soxhlet extraction with acetone, then with toluene and were dried in a vacuum oven, then stored in an air-tight container before use.

2.2. Standards of PCDDs/PCDFs and dl-PCBs

The surrogate standards consisted of 15 isotopes of ^{13}C-labeled PCDDs/PCDFs diluted from the stock solution EDF-8999 of Cambridge Isotope Laboratories (Massachusetts, USA). The native PCDD/PCDF standards, and other ^{13}C-labeled recovery and ^{37}Cl-labeled clean-up standards were used as described in the US EPA method 1613B[7]. The native and ^{13}C-labeled dl-PCB standards were used according to the US EPA method 1668B[8].

2.3. Experiments

The experiments were conducted seasonally at an urban area in Hanoi and were described as in the previous study[5]. The PAS sample IDs and sampling intervals are shown in Table 1. The sample IDs with the additional suffix (-D) were the field duplicate PAS samples. Their UTM coordinates were 582988E-2327289N and 582984E-2327299N, respectively.

Table 1: PAS sample IDs and sampling intervals

Season	Spring	Summer	Autumn	Winter
2015				HNP33, HNP34-D (03 Nov - 03 Feb 2016)
2016	HNP35, HNP36-D (03 Feb - 04 May)	HNP37, HNP38-D (04 May - 03 Aug)	HNP39, HNP40-D (03 Aug - 02 Nov)	HNP41, HNP42-D (02 Nov - 07 Feb 2017)
2017	HNP43, HNP44-D (07 Feb - 05 May)	HNP45, HNP46-D (05 May - 14 Aug)	HNP48 (14 Aug - 09 Nov)	HNP50 (14 Nov - 26 Feb 2018)
2018	HNP53 (26 Feb -18 May)	HNP56 (18 May - 15 Aug)	HNP59 (15 Aug - 14 Nov)	

2.4. Analysis of PCDDs/PCDFs and dl-PCBs

The recovery standards of ^{13}C-1234-TCDD and ^{13}C-123789-HxCDD were added before PAS sample extraction to determine the efficiency of surrogate retention on the passive PUF disks. Then PAS samples were prepared and analyzed as described in the US EPA method 1613B[7] and method 1668B[8].

PCDDs/PCDFs and dl-PCBs were analyzed by high resolution gas chromatography (HRGC Aligent 7890A) and high resolution mass spectrometry (HRMS AutoSpec Premier, Water). Temperature program: 150ºC for 2 minutes, increasing from 150ºC to 220ºC at 20ºC/min, 220ºC for 16 minutes, from 220ºC to 320ºC at 5ºC/min and keeping at 320ºC until finish. Temperature of the injector: 280ºC, interface: 290ºC. Helium: 1.0 ml/min. DB-5MS column: 60 m length, 0.25 mm id., 0.25 µm film thickness The MS was operated at resolution ⩾ 10,000 at 10% valley under positive electron ionization.

LODs of method are 0.2 pg/sample for TetraCDDs/CDFs, 0.5 pg/sample for Pen- through Hepta-CDDs/CDFs, and 1.0 pg/sample for OCDD/OCDF and dl-PCBs.

3. RESULTS AND DISCUSSION

The concentrations of PCDDs/PCDFs and dl-PCBs (pg/disk/day) in ambient air were adsorbed on PUF disks in each season and their temporal trends from Winter 2015 to Autumn 2018 are presented in figures 1,2,3 and 4. The seasonal variations of concentrations of Total PCDDs, Total PCDFs, Total dl-PCBs and their Total TEQ (pg/disk/day) are summarised in tables 2,3.

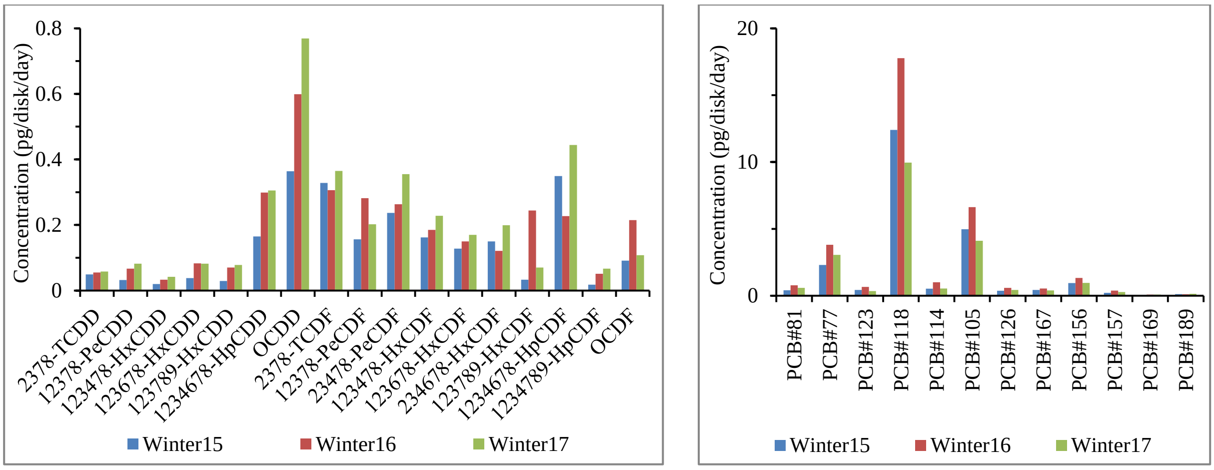

Figure 1: Concentration of PCDDs/PCDFs, dl-PCBs and their temporal trend in Winter

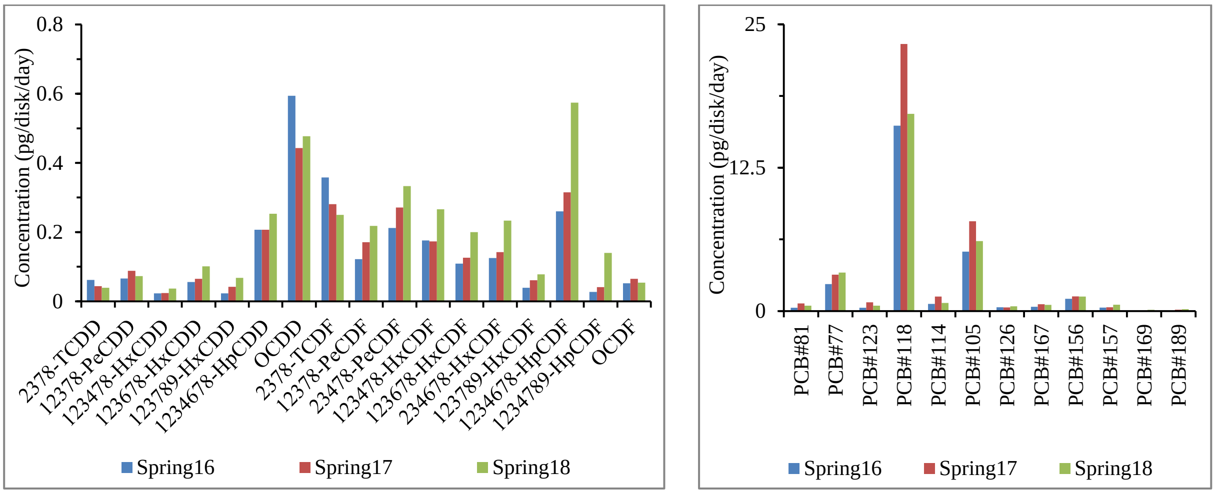

Figure 2: Concentration of PCDDs/PCDFs, dl-PCBs and their temporal trend in Spring

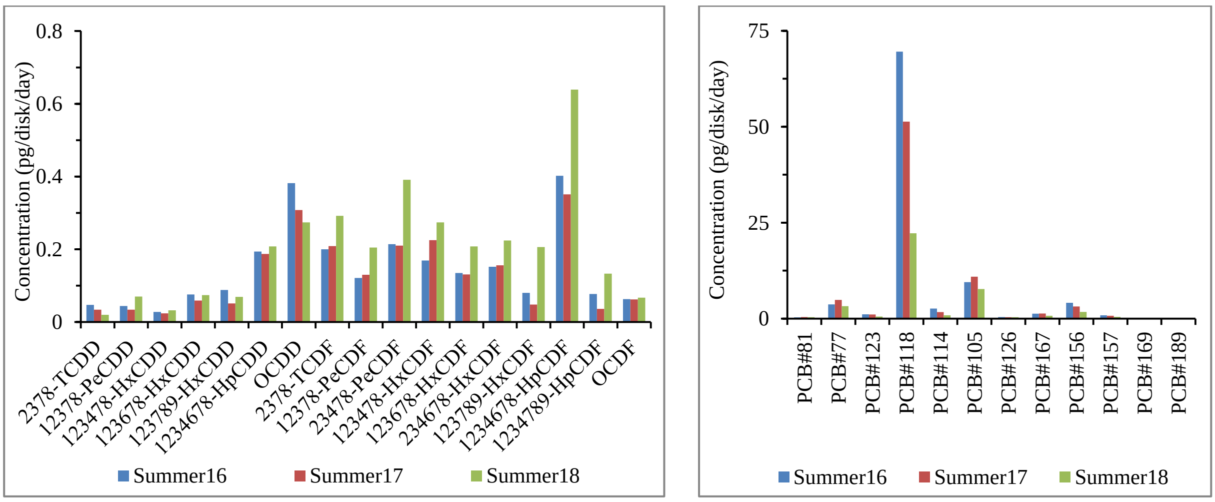

Figure 3: Concentration of PCDDs/PCDFs, dl-PCBs and their temporal trend in Summer

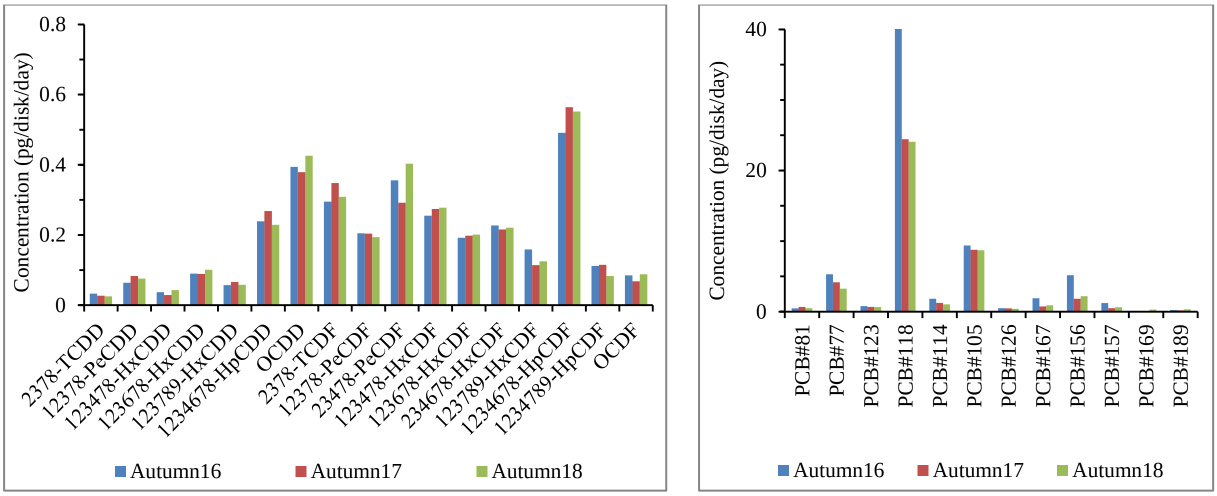

Figure 4: Concentration of PCDDs/PCDFs, dl-PCBs and their temporal trend in Autumn

The figures 1,2,3,4 and tables 2,3 show that the concentration of PCDDs/PCDFs and Total $TEQ_{D/F}$ between Winter 2015 and Autumn 2018 were lowest in summers and highest in autumns. The variation of total $TEQ_{D/F}$ (pg/disk/day) was from 0.196 to 0.351 (average 0.255) in summer; 0.334-0.371 (average 0.351) in autumn; 0.241-0.378 (0.309) in winter; and 0.282-0.352 (0.302) in spring. The concentrations of total PCDDs/PCDFs (pg/disk/day) were in the range as follows: 2.12-3.39 (2.56) in summer; 3.18-3.41 (3.33) in autumn; 2.34-3.62 (2.96) in winter; and 2.45-3.39 (2.70) in spring. In all seasons, almost PCDF congeners were predominant. The concentrations of total PCDFs in ambient air were always 1.7- to 2.6-fold higher than total PCDDs. The principal PCDD congeners were 1234678-HpCDD and OCDD, in there the concentrations of OCDD were 1.6- to 2.4-times greater than 1234678-HpCDD. The average concentration of the most toxic congener 2378-TCDD contributed from 8.3% to 17.2% to the total $TEQ_{D/F}$ and from 7.2% to 14.9% to the total $TEQ_{D/F\&dl\text{-}PCB}$.

The concentrations of Total dl-PCBs between Winter 2015 and Autumn 2018 were lowest in winters and highest in summers (Table 2). The major dl-PCB congeners in all seasons were PCB#118, then PCB#105 and PCB#77 (Figures 1,2,3 and 4). PCB#118 was always predominant in profiles of dl-PCB congeners. The average seasonal concentration of PCB#118 contributed from 52.1% to 69.9% to Total dl-PCBs. The variation of Total dl-PCB concentrations (pg/disk/day) was in the range of 20.9-36.9 (average 27.0) in winters; 24.5-48.4 (average 33.0) in springs; 38.5-104 (average 75.6) in summers; and 43.0-80.0 (average 55.6) in autumns. The seasonal average of Total $TEQ_{dl\text{-}PCB}$ was only in the range of 0.034-0.053 pg/disk/day (Table 3) and insignificantly contributed from 10.1% to 14.1% to the total $TEQ_{D/F\&dl\text{-}PCB}$.

Table 2: Seasonal variation of PCDD/PCDF and dl-PCB concentrations (pg/disk/day) in the ambient air between 2015 and 2018

Season	Total PCDDs			Total PCDFs			Total dl-PCBs		
	Min	Average	Max	Min	Average	Max	Min	Average	Max
Winter	0.648	1.04	1.42	1.59	1.92	2.21	20.9	27.0	36.9
Spring	0.876	0.985	1.06	1.48	1.72	2.35	24.5	33.0	48.4
Summer	0.658	0.771	0.875	1.47	1.79	2.64	38.5	75.6	104
Autumn	0.909	0.931	0.958	2.27	2.40	2.48	43.0	55.6	80.0

Table 3: Seasonal variation of Total $TEQ_{D/F}$, Total $TEQ_{dl\text{-}PCB}$ and their Total TEQ (pg/disk/day) in the ambient air between 2015 and 2018

Season	Total $TEQ_{D/F}$			Total $TEQ_{dl\text{-}PCB}$			Total $TEQ_{D/F\&dl\text{-}PCB}$		
	Min	Average	Max	Min	Average	Max	Min	Average	Max
Winter	0.241	0.309	0.378	0.037	0.051	0.063	0.285	0.360	0.424
Spring	0.282	0.302	0.352	0.025	0.034	0.038	0.320	0.336	0.377
Summer	0.196	0.255	0.351	0.021	0.038	0.048	0.239	0.293	0.372
Autumn	0.334	0.351	0.371	0.050	0.053	0.061	0.384	0.404	0.421

The assessment of variations and temporal trends of PCDD/PCDF concentrations in ambient air through two phases from 2012 to 2018 are illustrated in Figure 5. The concentrations of PCDDs/PCDFs in four seasons between Spring 2012 and Autumn 2015 were presented in our previous study[5].

Generally, the concentrations of Total PCDDs in all seasons between Winter 2015 and Autumn 2018 were 1.03- to 1.5-fold lower than that in comparision with our previous study between Spring 2012 and Autumn 2015[5]. The seasonal concentrations of Total PCDFs and Total $TEQ_{D/F}$ between Winter 2015 and Autumn 2018 were also 1.04- to 1.5-fold lower in winters and autumns, however, were approximately 1.1-fold higher in spring and summer between Spring 2012 and Autumn 2015. Especially, the variation of PCDD/PCDF concentrations in ambient air between Winter 2015 and Autumn 2018 was shown in a narrower range compared to the period of Spring 2012 and Autumn 2015 (Figure 5).

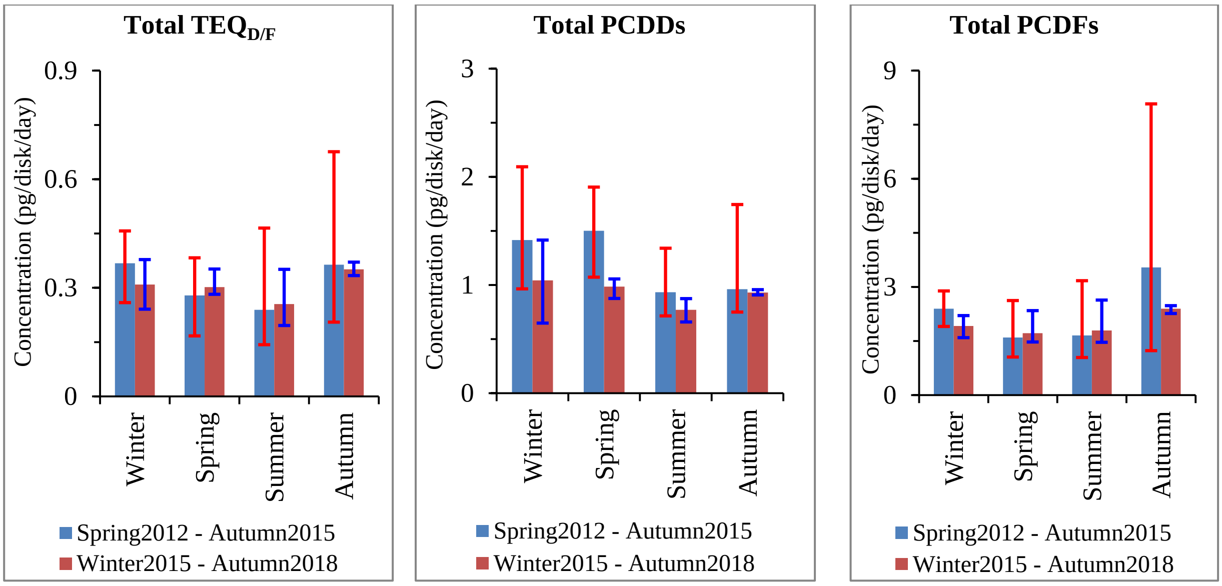

Figure 5: Seasonal variation of PCDD/PCDF concentrations (pg/disk/day) in the ambient air between 2012-2015 and 2015-2018

The relative percent difference (RPD) between PCDD/PCDF and dl-PCB concentrations of the field duplicate PAS samples was calculated as follows: RPD% = [(C1–C2)/(C1+C2)/2]*100% [9]. In which: C1 represents the PCDD/PCDF concentration on the PUF disk with spiking ^{13}C-labeled PCDD/PCDF surrogates; and C2 represents the PCDD/PCDF concentration on the PUF disk without spiking surrogates. Approximately 87% of PCDD/PCDF concentrations and 79% of dl-PCB concentrations had the RPD < 40%. This agreement of PCDD/PCDF and dl-PCB concentrations from the field duplicate PAS samples in this study shows that the seasonal monitoring of PCDDs/PCDFs and dl-PCBs using PAS is reliable and suitable in the monsoon tropical climatic conditions in Northern Vietnam.

Acknowledgements

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