APPLYING THE PASSIVE AIR SAMPLER WITH POLYURETHANE FOAM FILTER FOR SEASONAL MONITORING PCDDs/PCDFs

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Introduction

Passive air sampler with polyurethane foam (PUF) has been used widely, from local to region, for monitoring, assessing the temporal and spatial distribution of persistent organic pollutants in ambient air[1-9], but its application to PCDDs/PCDFs has been inconsiderable. For advantages, the passive air samplers are of low cost, easy to use, no requiring electric power. Sampling period may be consecutive from a month to a season. Sampling method allows monitoring pollutants in ambient air, averaging analytical data at sampling intervals. To follow our previous study, we have conducted the experiments on passive air sampler with PUF filter for seasonal monitoring PCDDs/PCDFs in the tropical climate condition in Vietnam.

Materials and methods

Passive air sampler:

We used the passive air sampler of Tisch Environmental Inc. (USA), hanged outdoor and 2.5 m high from the ground level. The sampler consists of a stainless steel domed chamber in which is housed the PUF filter. The PUF filters are round shape with 5.5 inch diameter and 0.5 inch thick. The filter is pre-cleaned by soxhlet extraction with acetone, then with hexane for 24 h to remove the contaminated substances. Then is dried in vacuum oven at 50 ºC for 5 h and kept in tight condition before sampling.

^{13}C isotope labeled PCDDs/PCDFs:

We used the spiking solution, which includes 15 congeners of ^{13}C isotope labeled PCDDs/PCDFs from Cambridge Isotope Laboratories Inc. for adding to the samples before extraction as described in the US.EPA method 1613B[10]. The concentration of each ^{13}C-labeled PCDD/PCDF is 2000 pg/mL in acetone and of ^{13}C-labeled OCDD is 4000 pg/mL for the purpose of our experiment. This solution is marked C_L.

Native PCDDs/PCDFs:

Native PCDDs/PCDFs congeners are created from the dioxin-contaminated soil[11] after extracting, separating and clean-up as described in the US.EPA method 1613B. The solution to be spiked on the PUF filter is marked Control C_N in hexane. The concentration of the seventeen 2,3,7,8-substituted PCDDs/PCDFs congeners and total $TEQ_{PCDD/PCDF}$ in 50 µl of the Control C_N is shown in Table 1.

Experiments:

The native PCDDs/PCDFs (spiked C_N) and ^{13}C-labeled PCDDs/PCDFs (spiked C_L) were added to the PUF filters to evaluate the retaining of PCDDs/PCDFs. After experimental intervals of 8 or 12 weeks, the PUF filters are collected for evaluating the retention efficiency of spiked native PCDDs/PCDFs and the recovery of ^{13}C-labeled PCDDs/PCDFs. Assessing the operation of the passive air sampler through appraising the adsorption of PCDDs/PCDFs from the air on the PUF filters, which were spiked ^{13}C-labeled PCDDs/PCDFs only. Clean PUF filter is put into the sampler. In the first sampler, native PCDDs/PCDFs in 50 µl of solution C_N is added on the filter surface. In the second sampler, only ^{13}C-labeled PCDDs/PCDFs is added by using pipette to suck 1 mL of solution C_L then drip evenly on the filter. The samplers are hanged outdoor at the same site. Testing period for each paired samples was equal: 8 weeks during the summer from 11th April 2012, 12 weeks in autumn from 22nd August 2012, 12 weeks during winter from 14th November 2012 and 12 weeks in spring from 4th February 2013.

Analysis of congeners PCDDs/PCDFs:

The PUF filters with spiked solution C_N, were added extraction standards ^{13}C-labeled PCDDs/PCDFs, cleanup standard (^{37}Cl-labeled 2,3,7,8-TCDD) and recovery standards (^{13}C-labeled PCDDs). And, the PUF filters with

spiked solution C_L are not requiring the extraction standards but requiring recovery standards before sample extraction and cleanup standard. Extracting, separating, cleanup and enriching analytes was carried out according to the US.EPA method 1613B. Congeners PCDDs/PCDFs were analyzed by high resolution gas chromatography coupled with high resolution mass spectrometry (AutoSpec Premier, Waters). MS resolution ≥ 10,000.

Results and discussion

The concentration of 2,3,7,8-substituted PCDDs/PCDFs congeners, total $TEQ_{PCDD/PCDF}$, the efficiency of PCDDs/PCDFs retention on the PUF filters in the comparision with Control C_N and the recovery of ^{13}C-labeled PCDDs/PCDFs are shown in Table 1.

Table 1. Concentration of PCDDs/PCDFs and efficiency of their retention on PUF filters

Sample	C_N	PAS06	PAS08	PAS10	PAS12	PAS05	PAS07	PAS09	PAS11
Sample type	Control C_N	Spiked C_N	Spiked C_N	Spiked C_N	Spiked C_N	Spiked C_L	Spiked C_L	Spiked C_L	Spiked C_L
Test interval	t = 0	8 summer weeks	12 autumn weeks	12 winter weeks	12 spring weeks	8 summer weeks	12 autumn weeks	12 winter weeks	12 spring weeks
Analytes	Amount of PCDDs/PCDFs (pg/filter)					Recovery of ^{13}C-PCDDs/PCDFs (%)			
2,3,7,8-TCDD	4930	4294	4376	4394	4357	105.4	111.5	116.3	108
1,2,3,7,8-PeCDD	4.09	3.44	5.66	8.59	6.13	117.3	124.4	127.5	124.2
1,2,3,4,7,8-HxCDD	0.44	0.86	1.58	2.76	2.06	114.8	110.7	115.2	102.9
1,2,3,6,7,8-HxCDD	1.89	3.95	5.49	8.03	8.10	94.4	98.3	94.3	88.5
1,2,3,7,8,9-HxCDD	0.86	2.09	3.29	4.93	4.13	-	-	-	-
1,2,3,4,6,7,8-HpCDD	4.68	10.9	17.5	31.8	28.4	98.1	83.1	110.8	116.2
OCDD	121	133	163	229	272	82.3	76.9	108.8	82.8
2,3,7,8-TCDF	6.37	12.4	21.8	22.7	21.6	98.0	109.2	111.1	83.4
1,2,3,7,8-PeCDF	0.53	4.64	12.1	17.1	10.9	114.3	110.3	146.3	116.9
2,3,4,7,8-PeCDF	0.59	5.61	13.8	19.9	12.6	107.3	112.9	118.5	104.7
1,2,3,4,7,8-HxCDF	0.50	4.88	11.2	16.7	11.0	85.9	91.8	95.8	92.4
1,2,3,6,7,8-HxCDF	0.38	3.97	9.82	15.3	9.66	93.6	95.7	110.7	102.3
2,3,4,6,7,8-HxCDF	0.68	4.79	8.60	13.1	10.7	86.3	99.2	97.6	92.5
1,2,3,7,8,9-HxCDF	0.37	1.21	2.99	5.55	3.40	60.8	89.5	69.3	65.2
1,2,3,4,6,7,8-HpCDF	1.14	10.2	18.5	35.3	26.5	69.9	80.9	80.8	96.7
1,2,3,4,7,8,9-HpCDF	0.34	1.12	1.41	9.68	3.57	56.5	75.6	77.4	76.7
OCDF	0.93	2.71	4.30	17.1	13.7	-	-	-	-
Total $TEQ_{PCDD/PCDF}$	4936	4304	4396	4423	4377	-	-	-	-
Retention efficiency (%)	-	87.2	89.1	89.6	88.7	-	-	-	-

The efficiency of PCDDs/PCDFs retention was evaluated by calculating the percentage ratio of total $TEQ_{PCDD/PCDF}$ found on PUF filters, which were added native PCDDs/PCDFs, in comparison with the Control C_N. Table 1 indicate the efficiency of PCDDs/PCDFs retention after 8 summer weeks in sample PAS06 is 87.2%. The test interval for samplers conducted in autumn PAS08, winter PAS10, and spring PAS12 with lower temperature than in summer has been lengthened to be 12 weeks. However, the efficiency of PCDDs/PCDFs retention on such PUF filters is not decreased and remains high, ranged from 88.7% to 89.6% and 1.5% to 2.4% higher than that in summer. The highest retention efficiency is 89.6% in winter with sample PAS10. It means that the efficiency of PCDDs/PCDFs retention on PUF filters depends on environment temperature. At high temperature as in summer, the retention of PUF filters is a bit lower than in other seasons. The higher temperature decreases the adsorption of PCDDs/PCDFs the on PUF filter. This is suitable to total $TEQ_{PCDD/PCDF}$ seasonally as mentioned in Table 1.

The efficiency of PCDDs/PCDFs retention on PUF filters is also evaluated through recovery of ^{13}C-labeled PCDDs/PCDFs in the samples spiked with solution C_L (Table 1). Recovery efficiency of ^{13}C-labeled PCDDs/PCDFs in the sample PAS05 tested in summer is 56,5% to 117.3%; sample PAS07 in autumn: 75.6% to 124.4%; sample PAS09 in winter: 69.3% to 146.3%; sample PAS11 in spring: 65.2% to 124.2%. The recovery efficiency is highest in winter and lowest in summer. This is also suitable to the efficiency of PCDDs/PCDFs retention mentioned above.

The recovery efficiency of all ^{13}C-labeled PCDDs/PCDFs in different seasons is 56.5% to 146.3%, satisfying the requirements of the US.EPA method 1613B (from 17% to 185%)[10] and the UNEP guidance on the global monitoring plan for persistent organic pollutants (from 40 to150%)[12]. Thus, ^{13}C-labeled PCDDs/PCDFs have been also well retained on PUF filters. They are stable and maintained within long term of up to 12 weeks in different seasons. Therefore, they may be spiked directly to PUF filters at the beginning of sampling and used for determining PCDDs/PCDFs adsorbed on the filters. This is the advantage possible to compare with the active air sampling methods.

Due to high amount of 2,3,7,8-TCDD spiked to PUF filters, its concentration found upon sampling completion is decreased in comparison with the Control C_N (Table 1). As other congeners have lower spiked amount than amount of PCDDs/PCDFs adsorbed from the atmosphere, their concentration found is higher than the Control C_N. It means that the PUF filters also adsorb PCDDs/PCDFs from the ambient air. This is suitable to the concentration of PCDDs/PCDFs found on the filters of samples PAS05, PAS07, PAS09 and PAS11 shown in Table 2. Such filters are spiked with only ^{13}C-labeled PCDDs/PCDFs at the beginning of sampling.

Table 2. Amount (pg/filter/day) of PCDDs/PCDFs adsorbed on the filters

Sample	PAS05	PAS07	PAS09	PAS11
Test interval	Summer	Autumn	Winter	Spring
2,3,7,8-TCDD	0.050	0.041	0.058	0.039
1,2,3,7,8-PeCDD	0.029	0.035	0.079	0.038
1,2,3,4,7,8-HxCDD	0.019	0.018	0.047	0.023
1,2,3,6,7,8-HxCDD	0.054	0.068	0.077	0.055
1,2,3,7,8,9-HxCDD	0.032	0.028	0.050	0.030
1,2,3,4,6,7,8-HpCDD	0.139	0.181	0.303	0.308
OCDD	0.408	1.374	1.479	1.412
2,3,7,8-TCDF	0.133	0.218	0.321	0.201
1,2,3,7,8-PeCDF	0.077	0.141	0.200	0.110
2,3,4,7,8-PeCDF	0.131	0.168	0.328	0.151
1,2,3,4,7,8-HxCDF	0.092	0.130	0.220	0.110
1,2,3,6,7,8-HxCDF	0.090	0.117	0.188	0.091
2,3,4,6,7,8-HxCDF	0.102	0.108	0.232	0.126
1,2,3,7,8,9-HxCDF	0.059	0.026	0.119	0.049
1,2,3,4,6,7,8-HpCDF	0.252	0.232	0.569	0.340
1,2,3,4,7,8,9-HpCDF	0.033	0.031	0.115	0.047
OCDF	0.075	0.064	0.216	0.126
Total $TEQ_{PCDD/PCDF}$	0.211	0.242	0.447	0.235

Table 2 indicates the amount of PCDDs/PCDFs was adsorbed from the ambient air on the filters in 4 tested seasons. For easy comparison, in this table we converted the unit of seasonal concentration (pg/filter/season) into the daily concentration (pg/filter/day). The amount of PCDDs/PCDFs on the filters is ranged from 0.211 to 0.447 pg-TEQ/filter/day. We can see that the lowest pollution of PCDDs/PCDFs is in summer and highest is in winter.

Figure 1 illustrates the profile of 2,3,7,8-substituted PCDDs/PCDFs congeners and total $TEQ_{PCDD/PCDF}$ in the ambient air at the study location of passive air samplers. It can be seen that the characteristics of seasonal pollution of PCDDs/PCDFs is rather similar. It means that the passive air sampler operate stably.

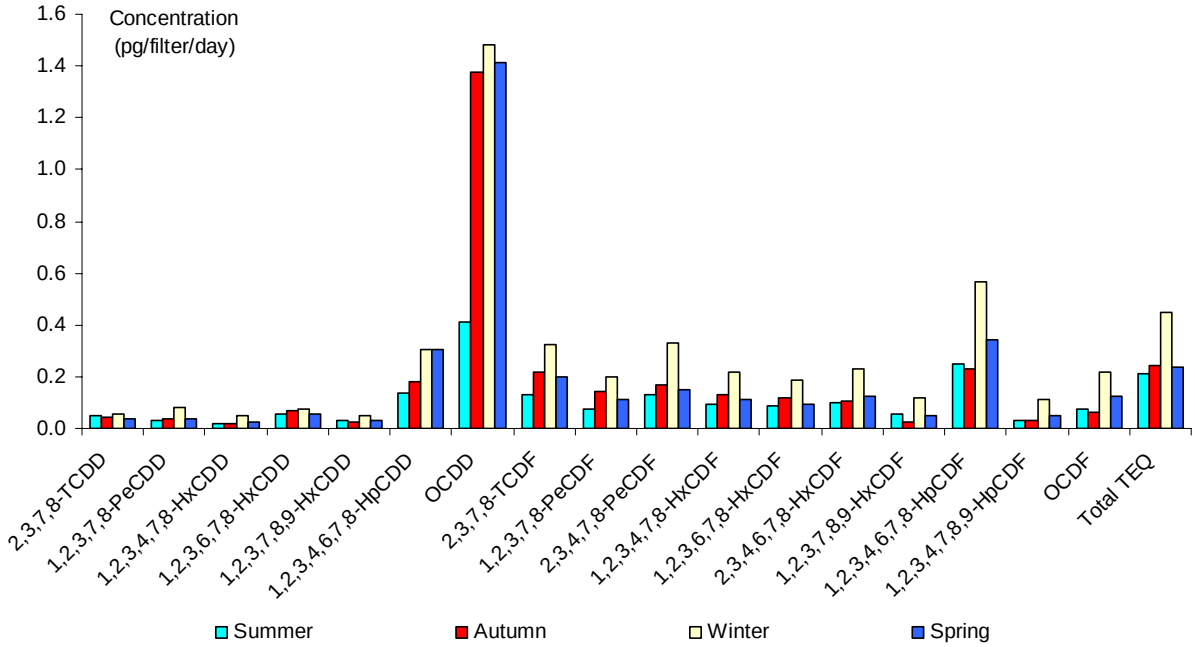

Figure 1. Profile of PCDDs/PCDFs congeners in the ambient air in the study location

Quality insurance and quality control have been implemented. The analytical result of method blank samples with clean PUF filter indicates that there is no any cross-contamination of PCDDs/PCDFs from PUF and the sample preparation in the laboratory. The concentration of PCDDs/PCDFs found in the passive air samples is many times higher than their detection limit in the blank samples. The duplicate samples with a coefficient of variance < 35% indicates that the passive air sampler operate stably and the analytical result is acceptable.

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