EVALUATING APPLIED CAPACITY OF POLYURETHANE FOAM FILTER IN PASSIVE AIR SAMPLING FOR ANALYSIS OF PCDDs/PCDFs

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Introduction

Polyurethane foam (PUF) has been widely used in daily life. Owning to the porous structure, PUF can adsorb and retain the harmful organic substances, metals from the atmosphere. PUF filter has been recommended by US. Environmental Protection Agency to use in ambient air monitoring studies for determination of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), pesticides, polychlorinated biphenyls with low volume and high volume air samplers according to the US.EPA methods: TO-9A, TO-10A[1-2]. The Global atmospheric passive sampling Network of Environment Canada and MONET-CEECs Project in the Central and Eastern European Region uses PUF filter in air passive samplers for the measurements of persistent organic pollutants such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, organochlorine pesticides, polybrominated diphenyl ethers[3-8] for the effectiveness evaluation of the Stockholm Convention. In this study, we have conducted the experiments for evaluating the applied capacity of PUF filter in the air passive sampling in the tropical climate condition in Vietnam for analysis of congeners PCDDs/PCDFs.

Materials and methods

Materials:

Passive air sampling device:

The passive air sampling device LAE-PS1 (Russia) consists of two stainless steel domes attached to the common axes to form a protective chamber for the PUF filter and air is allowed to flow over. The pollutants and particles will be retained on the PUF filter. The device have hanged outdoor, 2 m high from the ground level. It is used easily, not requiring electricity, sampling period may be consecutive from 4 to 12 weeks depending on the desired purpose.

PUF filter:

PUF are cut off to have round filters, 150 mm diameter, 20 mm thick. Each filter is pre-cleaned by soxhlet extraction with 200 ml toluene for 16 h and then solvent is sucked dry. The filter is dried in vacuum oven at 50 ºC for 5 h and tightly maintained before use.

Spiked solution of PCDDs/PCDFs:

The commercial standards of native PCDDs/PCDFs for this study are limitation. We have created the native PCDDs/PCDFs congeners by extracting and separating them from the dioxin/furan heavily contaminated soil[9]. The received solution of PCDDs/PCDFs is significantly meaningful as both having native congeners with the concentration suitable for the purpose of experiment and the profile of congeners has the characteristics of dioxin pollution in hotspot. The PCDDs/PCDFs solution to be spiked on the PUF filters is marked Control C_0 in hexane. The concentration of the seventeen 2,3,7,8-substituted congeners and total $TEQ_{PCDD/PCDF}$ in 150 µl of the Control C_0 is showed in table 1.

Methods:

Evaluating the efficiency of PCDDs/PCDFs retention on PUF filter:

In order to evaluate the retaining of PCDDs/PCDFs on PUF filter in the tropical climate condition, we added the equal volume of Control C_0 to the PUF filters. Clean PUF filter has been put into the device, using syringe to take exact 150 µl of Control C_0 and drip evenly on the filter surface, hanging the device outdoor. The test has been conducted for 4 weeks from 17th January 2012 and 8 weeks from 15th February 2012.

Checking the operation of the air passive sampling device:

In order to check the operation of the air passive sampler, we have installed clean PUF filter without adding Control C_0, hanged the sampler outdoor in the same study location for the same time has been above mentioned.

Analysis of congeners PCDDs/PCDFs:

PUF filters were sent to the laboratory, adding more 15 internal standards ($^{13}C_{12}$-labeled PCDDs/PCDFs). The filters have been soxhlet extracted with toluene for 16 hours. The extract was added the cleanup standard ($^{37}Cl_4$-2,3,7,8-TCDD) and cleaned up by acid/salt/base solutions followed on multilayered column of silicagel, then on micro columns of activated carbon and alumina. The final extract was added 2 recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD, $^{13}C_{12}$-1,2,3,7,8,9-HxCDD)[10].

Analyse PCDDs/PCDFs by high resolution gas chromatography (Aligent 7890A) and high resolution mass spectrometry (AutoSpec Premier, Water). HRGC/HRMS analysis was carried out according to the US.EPA method 1613B[10]. 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: 60m length, 0.25mm id., 0.25µm film thickness. MS resolution ≥ 10,000.

Quality assurance and quality control procedures have been applied. The method blank samples with draw PUF and clean PUF filters were analysed to make sure no cross-contamination of PCDDs/PCDFs from PUF and the sample preparation in the laboratory.

Results and discussion

The concentration of 2,3,7,8-substituted PCDDs/PCDFs congeners and total $TEQ_{PCDD/PCDF}$ in the Control C_0 and testing samples are showed in table 1. The profile of 2,3,7,8-substituted congeners and their concentration in the samples PAS01 and PAS03 are illustrated in figure 1.

Table 1. Concentration of PCDDs/PCDFs on PUF filters (pg/filter)

Sample	C_0	PAS02	PAS04	PAS01	PAS03	MB	PUF Blk
Sample type	Control sample	Spiked sample	Spiked sample	Unspiked sample	Unspiked sample	Method blank	Raw PUF blank
Sampling interval	-	4 weeks	8 weeks	4 weeks	8 weeks	-	-
2,3,7,8-TCDD	52716	50843	50915	4.97	8.42	< 0.53	< 0.90
1,2,3,7,8-PeCDD	43.7	37.2	35.8	2.20	2.17	< 0.44	< 0.69
1,2,3,4,7,8-HxCDD	1.69	1.75	2.20	< 1.51	0.83	< 0.48	< 0.70
1,2,3,6,7,8-HxCDD	20.2	19.0	19.1	# 3.03	2.38	< 0.59	< 0.84
1,2,3,7,8,9-HxCDD	6.18	8.95	9.68	# 1.72	1.29	< 0.50	< 0.72
1,2,3,4,6,7,8-HpCDD	50.1	65.9	54.5	6.50	8.82	< 0.37	< 0.63
OCDD	1296	1262	1364	25.7	36.1	< 0.67	< 9.80
2,3,7,8-TCDF	68.1	57.1	59.9	5.61	9.60	< 0.38	< 0.69
1,2,3,7,8-PeCDF	2.72	4.79	8.84	3.20	6.71	< 0.50	< 0.86
2,3,4,7,8-PeCDF	3.31	7.90	11.61	2.52	8.09	< 0.51	< 0.88
1,2,3,4,7,8-HxCDF	2.36	3.98	9.57	1.93	5.61	< 0.32	< 0.56
1,2,3,6,7,8-HxCDF	1.14	2.47	5.66	# 1.36	4.82	< 0.27	< 0.51
2,3,4,6,7,8-HxCDF	4.29	4.83	7.50	1.30	5.09	< 0.31	< 0.59
1,2,3,7,8,9-HxCDF	< 0.99	# 1.05	2.11	< 0.77	1.59	< 0.43	< 0.68
1,2,3,4,6,7,8-HpCDF	9.16	11.7	20.4	4.97	11.45	< 0.50	< 1.31
1,2,3,4,7,8,9-HpCDF	# 0.62	0.98	1.58	< 1.00	1.35	< 0.49	< 0.71
OCDF	6.86	7.13	7.99	4.28	5.12	< 0.62	< 1.16
Total $TEQ_{PCDD/PCDF}$	52773	50895	50970	10.1	18.3	< 1.59	< 2.64
Efficiency of PCDDs/PCDFs retention on PUF filter	-	96.4%	96.6%	-	-	-	-

Notes: Mark <: peak not detected in the sample and number after < is detection limit. Mark #: peak detected but did not meet quantification criteria, result reported represents the estimated maximum possible concentration.
We evaluate the retaining of PCDDs/PCDFs on PUF filter by calculating the percentage ratio of the concentration of PCDDs/PCDFs and total $TEQ_{PCDD/PCDF}$ found on PUF filters in comparison with the Control sample C_0. Table 1 indicated the efficiency of PCDDs/PCDFs retention on PUF filters after test intervals in 4 weeks (PAS02) and 8 weeks (PAS04) are very high, ranged from 96.4% and 96.6%. The concentration of PCDDs/PCDFs on PUF filter is not decreased when the sampling period is longer. The efficiency of PCDDs/PCDFs retention on PUF filter is a bit higher due to more adsorption and deposition of PCDDs/PCDFs from the atmosphere. This is suitable to the increasing of PCDDs/PCDFs concentration in the sample PAS03 (18.3 pg/PUF filter) in comparison with that of the sample PAS01 (10.1 pg/PUF filter).

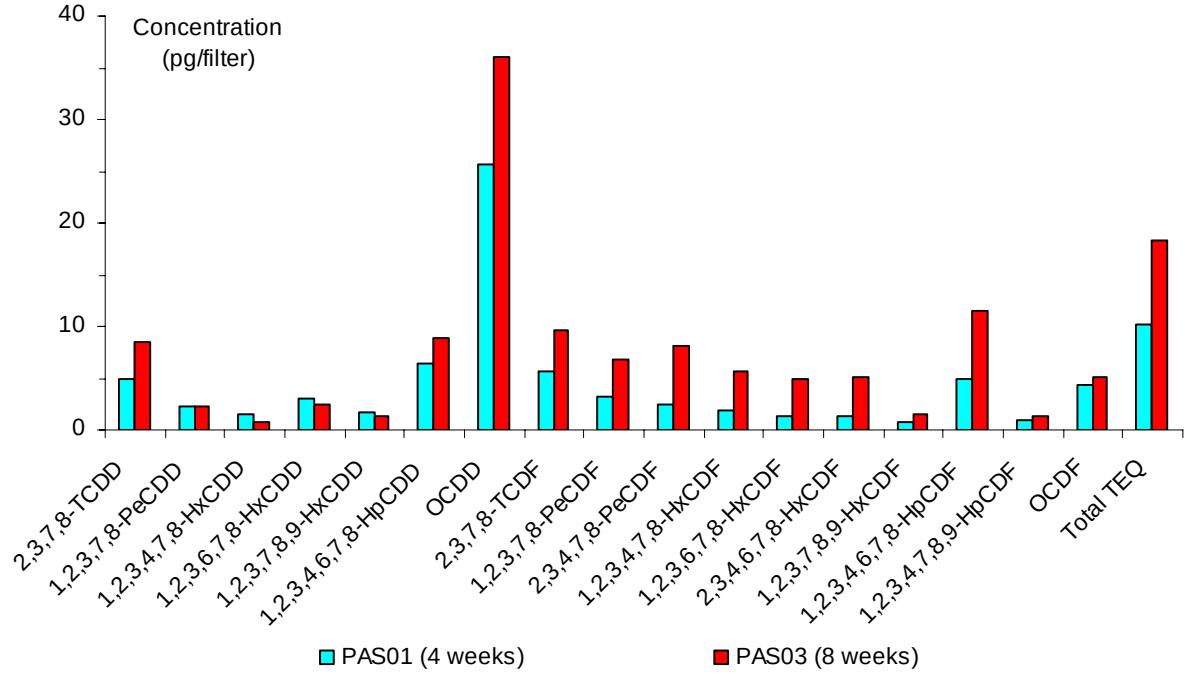

Figure 1. Profile of 2,3,7,8-substituted PDCDs/PCDFs congeners in the passive air samples

Figure 1 indicated that the profile of 2,3,7,8-substituted PDCDs/PCDFs congeners in atmosphere is quite similar in the same site where the air passive sampling devices are deployed at intervals of 4 weeks and also 8 weeks. That means the device operated fairly stably. Thus, it is showed that PUF filter is capable of adsorbing PCDDs/PCDFs from the atmosphere and well retaining them in tropical climate condition in Vietnam.

The analysis result of samples with raw PUF filter (PUF blank) and with clean PUF filter (method blank) as showed in table 1 indicated that there is no any cross-contamination of PCDDs/PCDFs from PUF and the sample preparation in the laboratory. Detection limit of PCDDs/PCDFs in the blank samples is always many times lower than concentration of PCDDs/PCDFs found in the passive air samples. However, with the short sampling period of 4 weeks as for PAS01 the concentration of some congeners of PCDDs/PCDFs is only about 4-5 times higher than the detection limit of method blank sample. In our opinion, the minimum sampling period of 8 weeks for air passive sampler is reasonable and reliable for analysis of PCDDs/PCDFs.

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