SEASONAL MONITORING OF dI-PCBs BY USING THE PASSIVE AIR SAMPLER WITH PUF FILTER

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Introduction

Twelve congeners of polychlorinated biphenyls have been considered by WHO to have toxicity similar to dioxin (dl-PCB)¹. We have carried out seasonal monitoring of dl-PCB congeners in ambient air in a city, Northern Vietnam using passive air sampler with polyurethane foam (PUF) filter. ¹³C-labeled dl-PCB standards have been added on the PUF filter at the beginning of sampling to evaluate the efficiency of dl-PCB retention during the monitoring period. Almost all ¹³C-labeled dl-PCB congeners are stable and well maintained on the filters in all seasons, except for ¹³C-labeled PCB#114, #105 and #126 in summer. Concentration of native dl-PCBs found in each season is not very much different between the filters with and without addition of ¹³C-labeled dl-PCBs. The results indicated seasonal monitoring of dl-PCBs may be carried out by using passive air sampler with PUF filter in the tropical climate in Northern Vietnam.

Materials and methods

Passive air sampler:

The passive air sampler of Tisch Environmental Inc. (USA) was used, hanged outdoor. 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. The filter is dried in vacuum oven at 50°C for 5 h and kept in tight condition before sampling.

Native and ¹³*C*-labeled PCB standards:

We prepared the spiked solution (signed C_{LB}), which includes twelve congeners of ¹³C-labeled dl-PCBs EC-4937 from Cambridge Isotope Laboratories for adding to the PUF filters. The concentration of C_{LB} is 2000 pg for each ¹³C-labeled dl-PCB/mL in acetone for the purpose of our experiment. Native dl-PCB and other ¹³C-labeled PCB standards are from Cambridge Isotope Laboratories and also Wellington Laboratories as described in the US.EPA method 1668B².

Experiments:

The experiments have been carried out in a city, Northern Vietnam dominated by tropical climate with four distinct seasons: spring, summer, autumn and winter. In each season, we used two passive air samplers with clean PUF filters. In the first sampler, the ¹³C-labeled dl-PCBs (1mL of solution C_{LB}) were added on the filter when the sampling started. This experiment was carried out to evaluate the stability of the ¹³C-labeled dl-PCB congeners and efficiency of their retention on the filters. In the second sampler, the solution C_{LB} was not added. The purpose of this experiment is to determine the concentration of native dl-PCBs in ambient air absorbed on the filter. The comparison of the concentration of native dl-PCBs on these two filters to evaluate the replication of the sampling method.

The samplers were hanged outdoor 2.5 m high from the ground level, one 10 m far from other. PUF filters have been collected after 12 weeks in each season. The time of experiment is as follows: PAS07 and PAS08 in autumn from 22nd August 2012; PAS09 and PAS10 in winter from 14th November 2012; PAS11 and PAS12 in spring from 4th February 2013; PAS13 and PAS14 in summer from 3rd May 2013; PAS15 and PAS16 in autumn from 26th July 2013; PAS17 and PAS18 in winter from 17th October 2013; PAS19 and PAS20 in spring from 9th January 2014.

Analysis of PCB congeners:

The PUF filters without spiked solution C_{LB} have been added with ¹³C-labeled dl-PCB standards and then labeled clean-up standards and labeled injection internal standards. The PUF filters with spiked solution C_{LB} is not in need to add ¹³C-labeled dl-PCB standards but need to add labeled injection internal standards for

Organohalogen Compounds

determining the efficiency of ¹³C-labeled dl-PCBs retention on the PUF filters and then add labeled clean-up standards. Sample preparation and analysis of dl-PCBs according to US.EPA method 1668B².

Congeners of PCBs were analyzed by high resolution gas chromatography coupled with high resolution mass spectrometry (AutoSpec Premier, Waters). MS resolution was $\geq 10,000$.

Results and discussion

The efficiency of ¹³C-labeled dl-PCBs retention on the PUF filters in the different seasons is showed in Figure 1.



Figure 1. Efficiency of ¹³C-labeled dl-PCBs retention on the PUF filters in difference seasons

The Figure 1 indicated that most of ¹³C-labeled dl-PCBs are stable and well maintained on the PUF filters during sampling period in all seasons. The efficiency of their retention on the filters ranged from 27.2% to 190%. However, in the summer of 2013, the efficiency of ¹³C- labeled PCB#114, #105 and #126 retention is higher than 200%.

The concentration of native dl-PCB congeners found on the PUF filters is presented in Table 1 and showed in Figure 2. Profile of dl-PCBs congeners in ambient air in the study area is showed in Figure 3.

Table 1 indicated that may detect nearly all dl-PCB congeners by using the passive air sampler with PUF filter for seasonal monitoring. In all seasons, PCB#118 always has the highest concentration (Figure 3): from 15.3 to 62.4 pg/filter/day. Next is PCB#105 (6.3-18.7 pg/filter/day), PCB#77 (1.9-10.0) and PCB#156 (1.2-3.1). The congeners with lower concentration are PCB#169 (0.04-0.10 pg/filter/day) and PCB#189 (0.12-0.23). Total TEQ_{dl-PCBs} highest is 0.063 pg/filter/day in winter of 2013 and lowest is 0.023 pg/filter/day in spring of 2013.

Comparison of the concentration of dl-PCB congeners found on PUF filters with or without ¹³C-labeled dl-PCB standards at the beginning of sampling in different seasons (Table 1) indicated that: most (96.4%) received results have a coefficient of variance $\leq 33.7\%$. It means that the sampling method has good replication. Although in summer of 2013, five congeners of ¹³C-labeled dl-PCBs (#123, #118, #114, #105, #126) had the efficiency of retention higher than 190%, only three native dl-PCBs (#123, #118 and #114) had the coefficient of variance 51.3%, 58.5% and 66.6% respectively. This result indicated that the ¹³C-labeled dl-PCB congeners are fairly

stable and well maintained during the seasonal sampling period. Generally, concentration of dl-PCBs on the filters with addition of ¹³C-labeled dl-PCB standards is higher than that on the filters without addition of ¹³C-labeled dl-PCBs. This is highly relevant as addition of ¹³C-labeled dl-PCB standards has excluded the loss of native dl-PCBs on the filters during the monitoring period. Thus, the received monitoring data are highly reliable.



Figure 2. Concentration of native dl-PCB congeners on the PUF filters in difference seasons

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 dl-PCB congeners from PUF and the sample preparation in the laboratory. The concentration of dl-PCBs found in the passive air samples is several times higher than their detection limit in the blank samples. The lab duplicate samples have a coefficient of variance < 35%.

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References:

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- 2. U.S. Environmental Protection Agency (2008); *Method 1668B: Chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS.*

Sample code	PAS07	PAS08	PAS09	PAS10	PAS11	PAS12	PAS13	PAS14	PAS15	PAS16	PAS17	PAS18	PAS19	PAS20
Sample type					Spiked		Spiked	Spiked	Spiked	Spiked	Spiked		Spiked	
					C _{LB}		C _{LB}		C _{LB}					
Test interval	Autumn	Autumn	Winter	Winter	Spring	Spring	Summer	Summer	Autumn	Autumn	Winter	Winter	Spring	Spring
	2012	2012	2012	2012	2013	2013	2013	2013	2013	2013	2013	2013	2014	2014
PCB#81	0.518	0.530	0.455	0.378	0.213	0.184	0.255	0.293	0.417	0.393	0.623	0.644	0.648	0.554
PCB#77	9.956	9.703	5.381	5.114	2.085	1.867	3.109	2.983	4.862	4.685	6.303	6.600	5.160	4.871
PCB#123	ND	ND	ND	ND	ND	ND	1.414	0.836	1.092	1.059	1.279	1.151	0.736	0.668
PCB#118	36.07	33.87	27.78	36.77	18.55	15.31	62.36	34.12	46.25	43.97	47.96	49.47	25.78	23.35
PCB#114	1.347	1.435	ND	ND	0.565	0.576	2.238	1.120	1.498	1.459	1.837	1.962	1.134	1.023
PCB#105	16.18	15.53	10.53	12.18	7.318	6.344	15.79	12.76	18.67	16.87	17.30	18.51	10.24	9.715
PCB#126	0.365	0.342	0.350	0.332	0.239	0.207	0.294	0.262	0.316	0.336	0.548	0.587	0.431	0.402
PCB#167	0.836	0.870	ND	1.085	0.556	0.517	1.214	0.864	1.099	1.060	1.151	1.213	0.820	0.790
PCB#156	2.034	2.001	1.980	2.260	1.196	1.193	2.558	1.939	2.714	2.597	2.863	3.068	2.119	2.010
PCB#157	ND	0.679	0.331	0.417	0.324	0.291	0.520	0.430	0.609	0.552	0.698	0.775	0.494	0.484
PCB#169	0.070	0.081	0.069	0.043	0.044	0.039	ND	# 0.047	# 0.044	0.049	0.100	# 0.059	0.086	0.069
PCB#189	0.185	0.166	ND	ND	0.143	0.120	0.185	0.149	0.117	0.162	0.189	0.229	0.221	0.200
Total TEQ	0.041	0.039	0.039	0.037	0.026	0.023	0.032	0.029	0.035	0.038	0.061	0.063	0.048	0.044

Table 1. Amount (pg/filter/day) of dl-PCBs on the PUF filters

ND: below detection limit; #: peak detected but did not meet quantification criteria.



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Figure 3. Profile of dl-PCB congeners in ambient air in the study location Vol. 76, 102-105 (2014)