

# MONITORING OF PCDDs/PCDFs BY USING THE PASSIVE AIR SAMPLER

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## Introduction

Passive air sampling with polyurethane foam (PUF) disk for seasonal monitoring of PCDDs/PCDFs have been conducted by us in a city, Northern Vietnam<sup>1,2</sup>. The experiment area is dominated by tropical climate with four distinct seasons: spring, summer, autumn and winter. In order to continue evaluation of the application of this sampling method, we have carried out experiment around an area of in-pile thermal desorption, in Central Vietnam. This region is of tropical climate with only two seasons: dry and rainy seasons. This study indicated that passive sampling method is conformable with the purpose of monitoring of PCDDs/PCDFs in the ambient air in Central 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 disk. The PUF disks are round shape with 5.5 inch diameter and 0.5 inch thick. The disk 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°C for 5 h and kept in tight condition before sampling.

### *PCDD/PCDF standards:*

We prepared the spiking solution (signed C<sub>LDF</sub>), which includes 15 congeners of <sup>13</sup>C-labeled PCDDs/PCDFs with code EDF-8999 from Cambridge Isotope Laboratories for adding to the PUF disks. The concentration of C<sub>LDF</sub> is 2000 pg/mL for each <sup>13</sup>C-labeled PCDD/PCDF and 4000 pg/mL for <sup>13</sup>C-labeled OCDD in acetone. The standards of native and other labeled PCDDs/PCDFs are from Cambridge Isotope Laboratories and also Wellington Laboratories as described in the US.EPA method 1613B<sup>3</sup>.

### *Experiments:*

The experiments have been carried out in an area of In-Pile Thermal Desorption (IPTD) where treats dioxin-contaminated soil, in Central Vietnam where dominated by tropical climate with 2 distinct seasons: dry and rainy seasons. Dry season is typically between January and August. Rainy season is from September to December. However, it rained in January and February 2014 as affected by northeast monsoon.

We selected two sites for hanging passive air samplers around the IPTD. The samplers were hanged outdoor, at a high of 2.5 m from the ground level. At the first sampling site we hanged a sampler at a distance of 250 m to the east of IPTD. At the second site were two samplers (sampling duplicate) at a distance of 500 m to the north-northwest of IPTD. At the first site, we added congeners of <sup>13</sup>C-labeled PCDDs/PCDFs (1 mL of solution C<sub>LDF</sub>) on the PUF disk at the beginning of sampling. At the second site, 1 mL of solution C<sub>LDF</sub> was only added on either of two PUF disks. The experiments have been carried out with the aim to evaluate the stability of the <sup>13</sup>C-labeled PCDD/PCDF congeners and efficiency of their retention on the disks during the sampling period, determine concentration of native PCDD/PCDF congeners in the ambient air absorbed on the disk and evaluate the replication of the sampling method.

PUF disks have been collected after each experiment interval as follows: DNP1 and DNP2: 6 weeks from March 14<sup>th</sup> 2013; DNP3 and DNP4: 8 weeks from April 23<sup>rd</sup> 2013; DNP5, DNP6 and DNP7: 4 weeks from June 20<sup>th</sup> 2013; DNP8, DNP9 and DNP10: 8 weeks from July 19<sup>th</sup> 2013; DNP11, DNP12 and DNP13: 12 weeks from September 12<sup>th</sup> 2013; DNP14, DNP15 and DNP16: 12 weeks from December 3<sup>rd</sup> 2013.

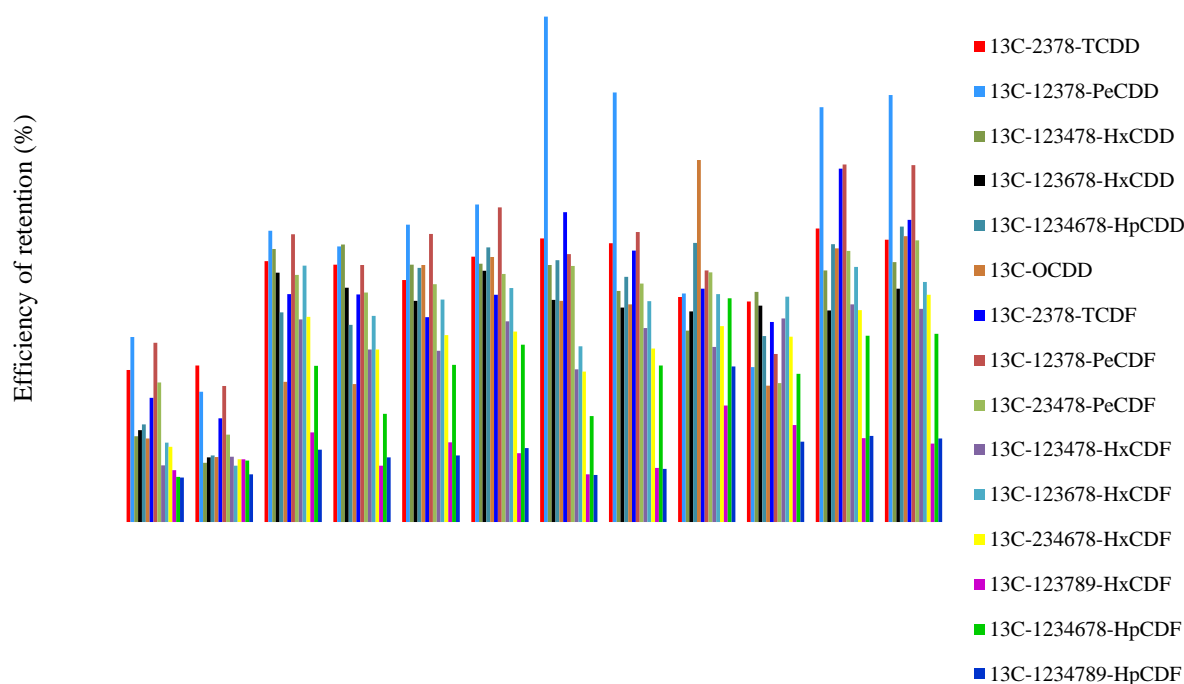
### *Analysis of PCDD/PCDF congeners:*

The PUF disks with spiked solution C<sub>LDF</sub> are not requiring the extraction standards <sup>13</sup>C-labeled PCDDs/PCDFs but requiring recovery standards <sup>13</sup>C-labeled PCDDs before sample extraction. The PUF disks without spiked solution C<sub>LDF</sub>, were added extraction standards and other labeled standards. The sample preparation was carried out according to the US.EPA method 1613B<sup>3</sup>. Congeners of PCDDs/PCDFs 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

Efficiency of  $^{13}\text{C}$ -labeled PCDDs/PCDFs retention on the PUF disks during different experiment interval and seasons is showed in Figure 1.

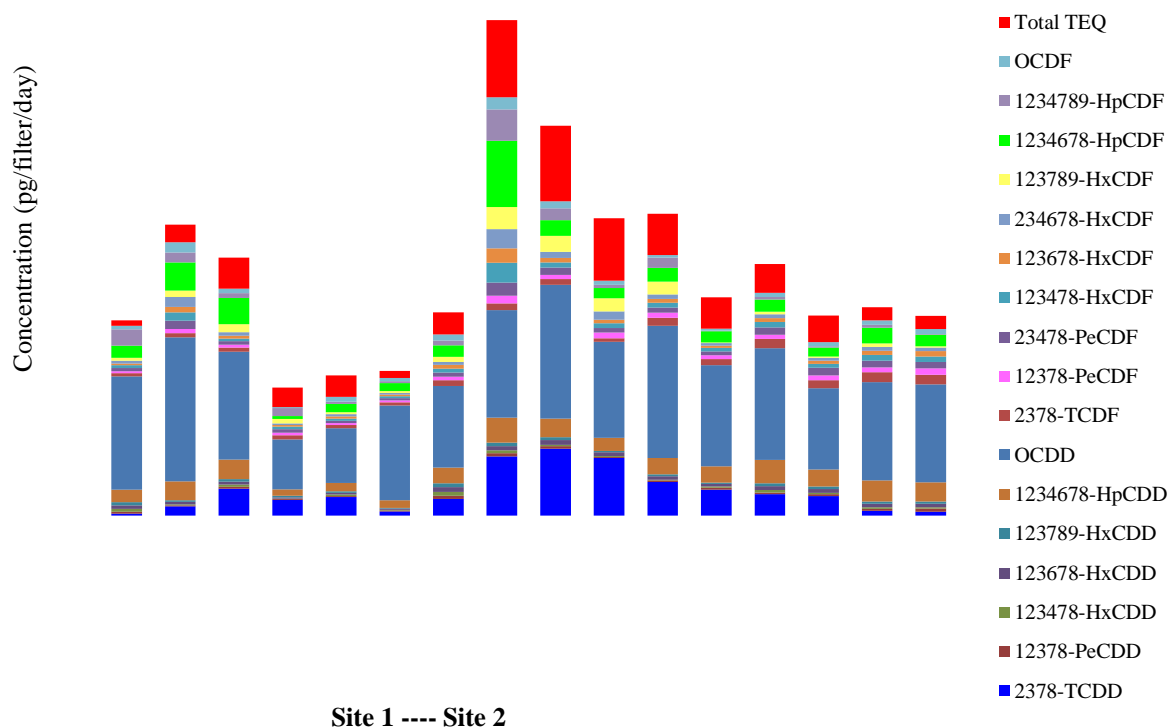


**Figure 1.** Efficiency of  $^{13}\text{C}$ -labeled PCDDs/PCDFs retention on the PUF disks

As from March to August 2013 it is characterized by dry season with very high temperature (min: 21°C, avg: 29°C, max: 40°C) we have carried out 4 experiments with different sampling periods: 4, 6 and 8 weeks. From September 2013 to February 2014 is rainy season with lower temperature (min: 13°C, avg: 24°C, max: 33°C) so we have spent 12 weeks for 2 experiments. The Figure 1 indicated that the efficiency of  $^{13}\text{C}$ -labeled PCDDs/PCDFs retention ranged from 16.3% to 185% (avg: 66.5%) in dry season and 28.7% to 156.3% (avg: 81.9%) in rainy season. Thus, the efficiency of all  $^{13}\text{C}$ -labeled PCDDs/PCDFs retention on PUF disks in dry season and rainy season satisfied the requirement of US.EPA method 1613B (from 17% to 185%)<sup>3</sup>. The  $^{13}\text{C}$ -labeled PCDD/PCDF standards have been stable and maintained during the sampling period. Therefore, they may be added directly on PUF disks at the beginning of the monitoring period.

Concentration of the native PCDD/PCDF congeners on PUF disks is showed in Table 1 and illustrated in Figure 2. Table 1 indicated that may detect most of PCDD/PCDF congeners by using passive air sampler with PUF disk. Total TEQ<sub>PCDDs/PCDFs</sub> of the air samples at the first site is from 0.16 to 0.97 pg/disk/day, at second site from 0.40 to 2.41 pg/disk/day. And at both sites 2,3,7,8-TCDD contributes from 31.7% to 92.4% of the total TEQ. This ratio is similar to the air samples taken by high volume air sampler with PUF disks.

The comparison of native PCDD/PCDF congeners (table 1) found on PUF disks with and without addition of  $^{13}\text{C}$ -labeled PCDDs/PCDFs at the second site during the same experiment in both seasons (sampling duplicates) showed that: almost all (84.9%) PCDD/PCDF congeners have the concentration with a coefficient of variance < 35%. And the coefficient of variance of other congeners is < 50%. The concentration of PCDD/PCDF congeners on the disks added with  $^{13}\text{C}$ -labeled PCDDs/PCDFs is substantially higher than that on the disks without addition of  $^{13}\text{C}$ -labeled standards. This is very logical as addition of  $^{13}\text{C}$ -labeled PCDDs/PCDFs has eliminated the loss of native PCDDs/PCDFs on the disks during the monitoring period.



**Figure 2.** Amount (pg/disk/day) of PCDD/PCDF congeners on the PUF disks (U = Unspiked  $^{13}\text{C}$ -labeled PCDD/PCDF standards)

Quality insurance and quality control have been implemented. The analytical result of method blank samples with clean PUF disk 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 several times higher than their detection limit in the blank samples. The lab duplicate samples have a coefficient of variance < 35%.

#### Acknowledgements

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#### References:

1. Sau TK, Thu NT, Dung NT (2013); *Organohalogen Compounds* 75: 418-421.
2. Sau TK, Truong NX (2013); *Organohalogen Compounds* 75: 554-557.
3. US. Environmental Protection Agency (1994); *Method 1613B: Tetra- through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS*.

**Table 1.** Amount (pg/disk/day) of PCDD/PCDF congeners on the PUF disks

Sample code	DNP1	DNP3	DNP7	DNP10	DNP13	DNP16	DNP2	DNP4	DNP5	DNP6	DNP8	DNP9	DNP12	DNP11	DNP15	DNP14	
Sampling site	Site 1						Site 2										
Sample type	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Spiked C <sub>LDF</sub>	Un- spiked	Spiked C <sub>LDF</sub>	Un- spiked	Spiked C <sub>LDF</sub>	Un- spiked	Spiked C <sub>LDF</sub>	Un- spiked
Test interval	Mar- Apr 2013	Apr- Jun 2013	Jun- Jul 2013	Jul- Sep 2013	Sep- Dec 2013	Dec- Feb 2014	Mar- Apr 2013	Apr- Jun 2013	Jun- Jul 2013	Jun- Jul 2013	Jul- Sep 2013	Jul- Sep 2013	Sep- Dec 2013	Sep- Dec 2013	Dec- Feb 2014	Dec- Feb 2014	
Temperature (°C) Min - Avg - Max	21-27- 40	22-30- 39	21-30- 38	23-29- 37	19-26- 33	13-21- 29	21-27- 40	22-30- 39	21-30- 38	21-30- 38	23-29- 37	23-29- 37	19-26- 33	19-26- 33	13-21- 29	13-21- 29	
2378-TCDD	0.064	0.287	0.844	0.489	0.581	0.132	0.524	1.847	2.088	1.798	1.047	0.809	0.667	0.613	0.150	0.127	
12378-PeCDD	ND	0.039	ND	0.028	ND	0.028	ND	0.103	ND	ND	0.051	0.066	0.054	0.053	0.063	0.099	
123478-HxCDD	ND	0.025	ND	0.012	ND	0.018	ND	0.084	0.034	0.022	0.022	0.032	ND	ND	#0.047	0.039	
123678-HxCDD	ND	0.077	0.098	ND	#0.056	0.044	0.146	#0.135	0.157	0.128	0.109	#0.080	0.117	#0.118	0.111	0.107	
123789-HxCDD	ND	0.057	0.072	0.047	ND	#0.019	0.118	0.105	#0.087	0.034	#0.057	0.039	0.092	0.082	0.072	0.072	
1234678-HpCDD	0.386	0.584	0.612	0.205	0.265	0.243	0.490	0.783	0.573	0.416	0.511	0.514	0.722	0.530	0.658	0.593	
OCDD	3.536	4.493	3.367	1.548	1.707	2.952	2.549	3.349	4.173	2.988	4.128	3.157	3.484	2.532	3.063	3.055	
2378-TCDF	0.100	0.127	0.123	0.134	0.103	0.099	0.175	0.208	0.186	0.113	0.249	0.184	0.287	0.243	0.311	0.300	
12378-PeCDF	#0.063	0.132	0.093	0.082	0.055	0.058	0.115	0.244	0.126	0.174	0.154	0.121	#0.136	0.158	0.143	0.203	
23478-PeCDF	0.094	0.259	#0.108	0.108	0.068	0.068	0.131	0.412	0.226	0.143	0.159	0.124	0.225	0.233	0.215	0.196	
123478-HxCDF	ND	0.256	#0.081	0.083	#0.070	0.065	0.112	0.615	0.159	0.147	0.156	#0.102	0.172	0.118	0.175	0.175	
123678-HxCDF	0.056	0.176	0.088	#0.046	0.067	0.050	#0.124	0.450	0.139	0.114	0.114	0.071	0.122	0.105	0.131	0.169	
234678-HxCDF	#0.084	0.304	0.112	0.053	0.072	0.050	0.094	0.598	0.191	0.255	0.141	0.085	0.116	0.090	0.123	0.109	
123789-HxCDF	ND	0.200	0.250	#0.139	ND	0.063	ND	0.688	0.498	0.409	0.400	ND	#0.085	#0.036	0.111	#0.033	
1234678-HpCDF	0.382	0.878	0.819	0.087	0.260	0.244	0.361	2.071	0.498	0.323	0.431	0.344	0.380	0.280	0.486	0.361	
1234789-HpCDF	0.509	0.308	ND	0.250	ND	ND	ND	0.977	#0.361	0.096	0.318	ND	0.079	ND	0.091	#0.019	
OCDF	#0.112	0.325	0.137	0.033	0.151	0.093	0.185	0.380	0.222	0.136	0.081	0.059	#0.122	0.124	0.144	0.167	
<b>Total TEQ</b>	<b>0.164</b>	<b>0.549</b>	<b>0.972</b>	<b>0.605</b>	<b>0.675</b>	<b>0.228</b>	<b>0.698</b>	<b>2.405</b>	<b>2.357</b>	<b>1.946</b>	<b>1.289</b>	<b>0.978</b>	<b>0.905</b>	<b>0.827</b>	<b>0.401</b>	<b>0.401</b>	

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