Levels, Temporal trends of PCDDs/PCDFs at IPTD area using passive air sampler and correlation with active air sampling between 2012-2017

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Introduction

The passive air sampler with polyurethane foam (PUF) disk was applied to monitor PCDDs/PCDFs from March 2013 to February 2014 at a airport in the Central Vietnam, where the in-pile thermal desorption (IPTD) technology is used to remediate dioxin/orange agent contaminated soil [1]. Standards of ^{13}C-labeled PCDDs/PCDFs were spiked on the passive PUF disks as surrogates at the beginning of sampling. The initial results showed the stable operation of passive air sampler, the high repeatability and reliability of the monitoring results, and this sampler is suitable to apply in the tropical climate in Central Vietnam. Up to present, this research has been carried out continuously with a sampling interval of 3 months between February 2014 and February 2017 to monitor the fluctuation and temporal trend of PCDDs/PCDFs contamination in ambient air. The monitoring results by passive air sampler are compared with the ones that are determined by the high volume sampler (active air sampling) to evaluate the correlation between two sampling methods. This research contributes into the global plan for monitoring POPs [2].

Materials and methods

Passive and active air samplers: The sampler TE-200 PAS of Tisch Environmental (USA) was used with PUF disk for passive air sampling [1]. The high-volume sampler 123SL of Kimoto (Japan) with glass fiber filter, PUF adsorbent was used for active air sampling.

Standards of PCDDs/PCDFs: The surrogate standards with sign of C_{LDF} consists of 15 isotopes ^{13}C-labeled PCDDs/PCDFs diluted from the stock solution EDF-8999 of Cambridge Isotope Laboratories. 1 mL of solution C_{LDF} was spiked on each passive PUF disk from the beginning of sampling [1]. The native and other labeled standards are used in compliance with method US.EPA1613B [3].

Experiments: In this research, three sampling sites were selected in the surrounding IPTD area. The first sampling site is at a distance of 250 m to the east of IPTD. The second one is at a distance of 500 m to the north-north west. The third one is at a distance of 100 m to the south. The period of each passive air sampling lasted approximately three months. In order to evaluate reliability of the passive air sampling method, the correlation between the levels of PCDDs/PCDFs in ambient air that were collected by the passive and active air samplers round the IPTD area are reviewed. The high volume sampler was integrated into this research for active air sampling [4]. The frequency of the active air sampling was once a month.

Analysis of PCDDs/PCDFs: The PUF disks were spiked the surrogate standards ^{13}C-labeled PCDDs/PCDFs (C_{LDF} solution), thus only recovery standards ^{13}C-1234-TCDD and ^{13}C-123789-HxCDD shall be added before sample extraction to determine the efficiency of surrogates retention on the passive PUF disks. Samples were prepared in compliance with the US.EPA method 1613B [3]. PCDDs/PCDFs were analyzed by high resolution gas chromatography coupled with high resolution mass spectrometry (AutoSpec Premier, Waters). MS resolution was $\geq$ 10,000 [5].

Statistical analyses: The data was processed by statistical algorithms. The temporal trends of PCDDs/PCDFs level in ambient air were examined by the regression models.

Results and discussion

The efficiency of ^{13}C-labeled PCDDs/PCDFs retention on passive PUF disk:

The efficiency of ^{13}C-labeled PCDD/PCDF surrogates retention on passive PUF disks during the collecting of 47 samples between March 2013 and February 2017 was presented in Table 1.

Table 1: Efficiency of ^{13}C-labeled PCDD/PCDF surrogates retention on passive PUF disks (n=47)

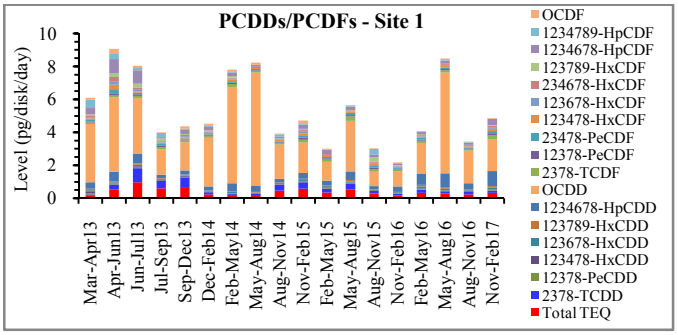
Surrogate standards	Min	Max	Average	%RSD
^{13}C-2378-TCDF	37.9	129.4	86.6	19.3
^{13}C-12378-PeCDF	49.8	160.7	114.9	20.4
^{13}C-23478-PeCDF	32.0	135.1	96.1	21.3
^{13}C-123478-HxCDF	20.7	102.5	74.8	21.2
^{13}C-123678-HxCDF	20.6	118.6	86.0	20.7
^{13}C-234678-HxCDF	23.0	101.5	73.8	20.1
^{13}C-123789-HxCDF	20.6	99.9	39.2	43.3
^{13}C-1234678-HpCDF	38.8	106.2	65.8	22.2
^{13}C-1234789-HpCDF	20.0	123.3	38.8	57.1
^{13}C-2378-TCDD	55.7	108.9	91.2	12.1
^{13}C-12378-PeCDD	47.7	185.0	112.6	23.6
^{13}C-123478-HxCDD	21.6	112.3	88.0	21.4
^{13}C-123678-HxCDD	23.7	121.4	83.2	17.9
^{13}C-1234678-HpCDD	24.3	117.2	91.4	20.4
^{13}C-OCDD	23.8	142.5	85.3	31.8

Table 1 indicates that the efficiency of ^{13}C-labeled PCDD/PCDF surrogates retention in the different sampling intervals are in the range from 20% to 185%. Their average are from 38.8% to 114.9%, with RSD of 12.1% to 57.1%. Only 3.7% of total surrogates that is mostly ^{13}C-123789-HxCDF and ^{13}C-1234789-HpCDF have the efficiency of retention less than 20%. That meets the requirements from 17% to 185% of US.EPA method 1613B [3]. Through the efficiency of ^{13}C-labeled PCDDs/PCDFs retention, the important result of this study illustrates that the PCDD/PCDF congeners were well kept on PUF disk. The ^{13}C-labeled PCDD/PCDF surrogates are stable, persistent during a long sampling duration in the hot, dry and humid tropical climate in the Central Vietnam. They have the important role in controlling the retention and determining the amount of native PCDDs/PCDFs on passive PUF disks. Therefore, the monitoring results of PCDD/PCDF contamination in ambient air shall have the high reliability.

The fluctuation of PCDDs/PCDFs level and temporal trends:

The levels of PCDDs/PCDFs and their total TEQ_{2005} in ambient air that were adsorbed on the passive PUF disks between March 2013 and February 2017 at three monitoring sites around IPTD area, their fluctuation and temporal trends are presented in Figures 1,2,3. The level of PCDDs/PCDFs in ambient air at monitoring sites depends mostly on their emission sources at IPTD area, the main wind direction and the distance to emission sources. The site 3 was directly affected by IPTD area. Therefore, PCDDs/PCDFs level is always the highest, with the average level of total PCDDs is 6.58 pg/disk/day, total PCDFs: 1.43, total TEQ: 3.93, and the fluctuation of total TEQ is in the range from 0.437 to 15.38. The lower level was found at the site 2 with total PCDDs: 4.45, total PCDFs: 1.63, and total TEQ: 0.706 with the fluctuation from 0.138 to 2.41. The lowest level was at the site 1 with total PCDDs: 3.80, total PCDFs: 1.14, and total TEQ: 0.398 with the fluctuation from 0.164 to 0.971.

Figure 1: Levels of PCDDs/PCDFs on passive PUF disks at site 1 (left) and temporal trend of total TEQ (right) between 2013 and 2017



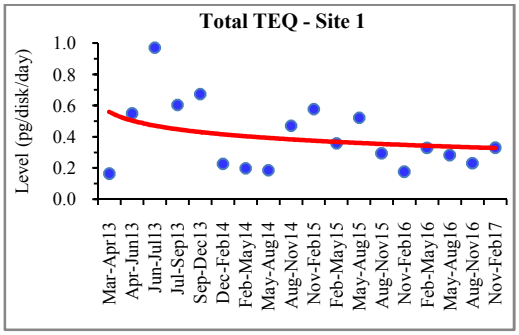
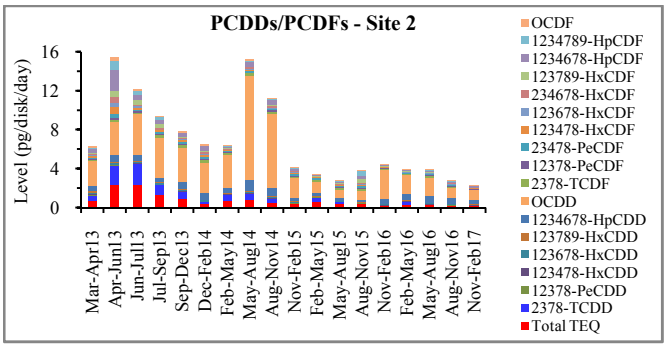


Figure 2: Levels of PCDDs/PCDFs on passive PUF disks at site 2 (left) and temporal trend of total TEQ (right) between 2013 and 2017



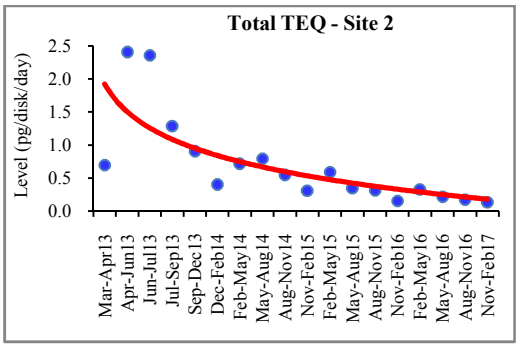
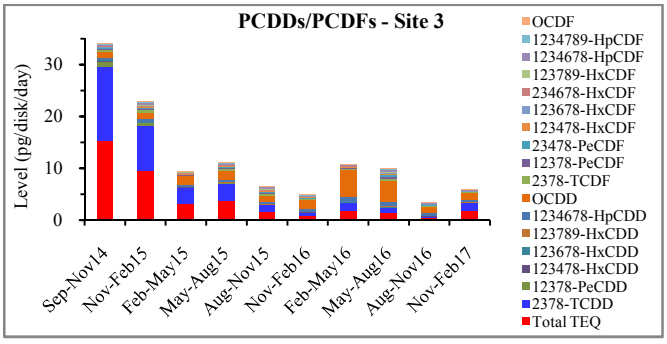
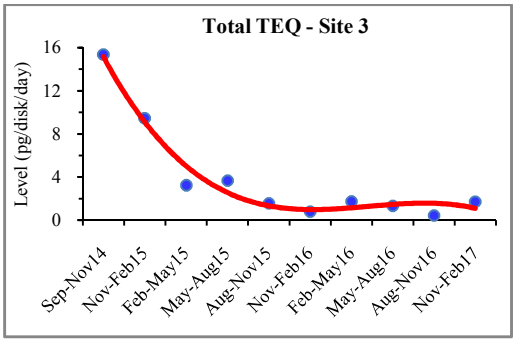


Figure 3: Levels of PCDDs/PCDFs on passive PUF disks at site 3 (left) and temporal trend of total TEQ (right) between 2014 and 2017





When activities of excavation and/or remediation were implemented, the PCDDs/PCDFs levels in ambient air would be increased. In contrast, when there were not those activities, the emission from sources would be reduced. Hence, the decreasing trend in PCDDs/PCDFs levels at the site 3 (Figure 3) is identified to be suitable with a third-order polynomial regression [6]. At the sites 1 and 2, the decreasing trend of PCDDs/PCDFs levels (Figure 1,2) is identified to agree with log-linear regression. In general, there is a significant decrease of PCDDs/PCDFs levels in the ambient air at all three sampling sites. Especially, at the sites 2 and 3 there was a much decrease in PCDDs/PCDFs level and total TEQ between February 2015 and February 2017 in comparison with those at interval between March 2013 and February 2015.

The correlation between PCDDs/PCDFs levels collected by passive and active air samplers:

When the passive air sampling was carried out, the high-volume sampling was also implemented once a month. In order to compare the two sampling methods, the average value of PCDDs/PCDFs levels that was determined by active samplers at the same passive sampling interval is referenced. The linear regression was used to evaluate the correlation between their levels collected by passive and active air samplers. The results are illustrated in Figure 4.

Figure 4: The correlation of total TEQ between the passive (PAS) and active (HV) air samplers

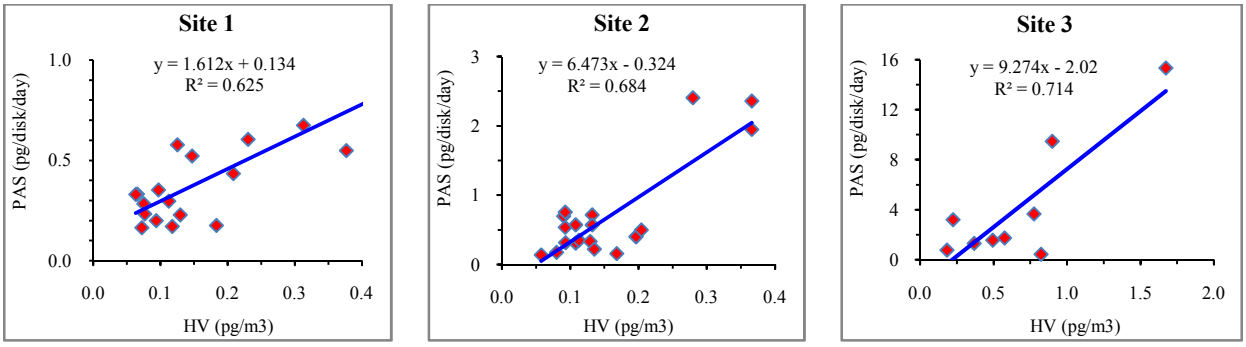


Figure 4 indicates the relatively high compatibility with the correlation factor (R^2) of 0.625 to 0.714 for total TEQs as well as PCDDs/PCDFs levels determined by two passive and active sampling methods at all three sites. Therefore, the monitoring PCDDs/PCDFs by passive air sampler are acceptable and compatible with the active air sampler.

Acknowledgements

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References

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