DISTRIBUTION OF PCDD/FS IN SOIL AND SEDIMENT AT FORMER ASO AIRBASE LOCATED IN CENTRAL VIETNAM

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), known as one category of the most toxic chemicals, are listed in the Stockholm Convention as one of the Persistent Organic Pollutants (POPs) groups[13.] Notable characteristics of PCDD/Fs are their environmental persistence,bioaccumulation through food chains and toxic responses in human being including immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine functions[15]. The lipophilic and hydrophobic properties of dioxin largely determine their distribution in the environment, as well as their fate and distribution in biological organisms, including humans[9]. They can transfer from mothers to infants via breast milk and have long half-lives in the human body[10]

During the Vietnam war, the US army conducted the Ranch Hand Operation (1962-1971) sprayed 77 millions litters of various herbicidesin a region south of former Demilitarized Zone at the 17 parallel in a southern Vietnam[8]. Agent Orange (AO) was the most widely used herbicide containing a 50:50 mixture of n-butyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic (2,4,5-T). It is noted that 2,4,5-T was contaminated to varying degrees with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), which is the most toxic congener of PCDD/F group[11,12]. Actually, other PCDD/Fs also presented in AO because they are by-products of 2,4,5-T production. In fact, OCDD was found as predominant congener in soils and sediments collected from areas storing and sprayed AO in Vietnam

High levels of PCDD/Fs are recently found in various kinds of food and breast milk of nursing mothers living around AO hotspots[4, 12,14], implying the serious problem caused by AO contamination. After released to environment, PCDD/Fs contaminated in AO are mainly adsorbed into soil and remain in soil for a longtime afterward due to their persistence. High concentrations of PCDD/Fs are recently found in soils and sediments collected from surrounding regions and areas storing or sprayed AO[17] although the Vietnam war has ended up more than 40 years ago. Importantly, PCDD/Fs releases from soil, accumulate in food chains and finally affect human health in regions of AO contamination. However, there is limited information regarding PCDD/F characteristics including occurrence, distribution and total toxicity in soil environment.

Aluoi District (formerly known as Aluoi Valley) is a part of Thua Thien-Hue province, located in the North Central Vietnam, in the high mountains of the Aluoi valley bordering Laos. The Aluoi Valley was one of the strategic focal points of the war in Vietnam. This was an integral part of the Ho Chi Minh trail where was used as the transported road weapons and foods for Vietnam Army. Therefore, Aluoi was heavily sprayed from approximately 1965 to 1970 principally with AO and to a lesser extent, Agent Blue and Agent White[1,8,16]. Moreover, the US Army used the former military Aso airbase, located in Dong Son commune of Aluoi district, to store herbicides, which potentially causes heavy contamination of AO or PCDD/Fs in soil of Aso airbase and surrounding areas. After the war, Aso airbase was abandoned no longer used, people surrounded it with a fence of banyan trees and forbidden to travel and grazing cattle in the airbase. So far, only one huge investigation of PCDD/Fs occurrences in various environment matrix including soil, sediment, fish fat, duck fat,human blood and breast milk samples collected from Aluoi valley has been conducted by Hatfield Consultants Ltd. in between 1996 and 1999[2]. It was concluded that "Aluoi Valley is a microcosm of southern Viet Nam, where numerous reservoirs of TCDD exist in the soil of former military installations south of the former demilitarized zone. Large quantities of Agent Orange were stored at many sites, used inground and aerial applications, and spilled. TCDD, through various forms of soil disturbance, can be mobilized fromthese reservoirs after decades below the surface, and subsequently, introduced into the human food chain". The results obtained from this study also indicated that the highest TEQ concentration measured in soils collected from Aso airbase.Therefore, Aluoi valley is of high potential for PCDD/Fs accumulation and Aso airbase is the most priority area to conduct an investigation of PCDD/Fs occurrence for understanding characteristics of PCDD/Fs after 20 years of the first investigation without any remediation method applied for reducing contaminated level.

In order to investigate occurrence and distribution characteristics of PCDD/Fs in study area, in April and May, 2014, forty sites were chosen to collect surface soil and sediment samples in the contaminated areas of Aso airbase, including zone A (28 sites) and zone B (12 sites) with the approximate areas of 5.12 and 10.73 ha, respectively, as presented in Fig. 1. Core soil samples were also collected to evaluate the distribution and characteristics of PCDD/Fs in different soil layers. Different from other AO hotpots in Vietnam, this airbase is located in Aluoi Valley, where is extremely affected by soil erosion [6,] which might influence the characteristics

and transportation of PCDD/Fs in surface soil. The topography of zone A appears to be higher than zone B. During the war, zone A was a storage for herbicides, therefore, soil samples were collected from zone B in order to assess the spread of PCDD/Fs from zone A to zone B. Results obtained from this study will provide the information for further understanding the current characteristics of PCDD/F contamination in Aso airbase, which is necessary for proposing remediation method.

2. Materials and methods

Among 40 sampling sites, 4 sites (including A9, A13, A15, B4) are bomb craters, where 4 surface sediment samples (0-10 cm). For other sites, 36 surface soil samples (0-10 cm) were collected using a stainless steel shovel, each samples consisted of five sub-samples composites collected from area of 2 m^2. The sampling procedure followed strictly those used in previous studies implemented by Hatfield Consultants [2]. Furthermore, core soil samples were collected from 4 sites (including A7, B18, B10, and B11), at each site, sub-samples were collected from 4 soil layers: 0-50 cm, 50-100 cm, 100-150 cm and 150-180 cm.

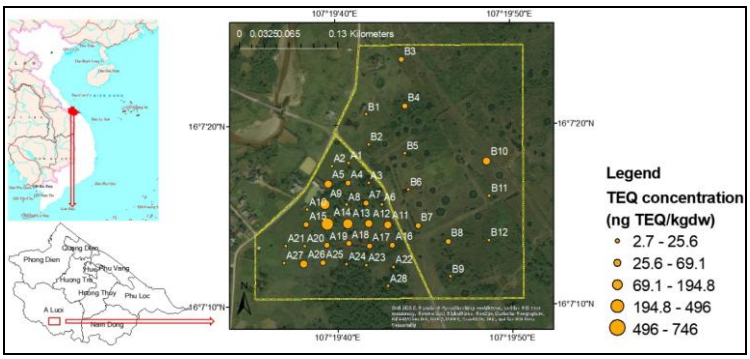

Fig.1. Sampling sites and TEQ concentrations of PCDD/Fs measured at different sites in zone A and B

Analytical procedure for determination of seventeen 2,3,7,8- substituted PCDD/Fs follows US EPA method 1613 with minor modifications considering available recent advanced techniques. All modifications were adequately validated prior to regular usage. The soil and sediment samples were dried at room temperature, crushed and sieved to less than 1 mm. Cleanup steps were performed by the Fluid Management Systems (FMS, USA) following the recommended procedure by the manufacturer (FMS, 2008) and were validated in our laboratory. Basically, pre-packed silica column (Silica #PCBS-ABN-STD, FMS), alumina column (Alumina #PCBA-BAS-011, FMS) and carbon column (Carbon #PCBC-CCE-034) were used for cleanup and fractionation of PCDD/Fs. Finally, 13C-labelled injection standards were added to the concentrated aliquot of the sample and further evaporated under gentle nitrogen stream of 20 µL prior to quantification.

3. Results and discussion

3.1. Concentration of PCDD/Fs in soil and sediment samples

The TEQ concentration and spatial mass distribution of PCDD/Fs measured in surface soil and sediment samples collected from the study area are presented in Fig. 1 and Fig. 2, respectively. Generally, the average concentrations of PCDD/Fs measured in zone A are significantly higher than those measured in zone B (in terms of both mass and TEQ concentrations). The mass concentrations of PCDD/Fs measured in zone A ranges from 95.0 to 4534 ng kg_{dw}^{-1} (4.58 to 746 ng TEQ kg_{dw}^{-1}), while the mass concentrations of PCDD/Fs found in zone B are in range of 80.8-4150 ng kg_{dw}^{-1} (2.70-89.0 ng TEQ kg_{dw}^{-1}). The higher concentration of PCDD/Fs measured in zone A compared with that in zone B might be due to the fact that zone A was the area storing herbicides during Vietnam war. As showed in Fig.2, it looks like the PCDD/Fs from the central area of zone A diffusing into surrounding area, including zone B. The zone B is of lower elevation compared with zone A, which may result in PCDD/Fs measured in zone B drifting from zone A to zone B.

In zone A, the highest mass concentration found at A13 (4534 ng kg_{dw}^{-1}), followed by A5 (3322 ng kg_{dw}^{-1}) and A14 (3296 ng kg_{dw}^{-1}), while in zone B, the highest mass concentration measured at B4 (4150 ng kg_{dw}^{-1}), followed by B7 (1623ng kg_{dw}^{-1}) and B3 (1338ng kg_{dw}^{-1}). Interestingly, the samples of A13 and B4 are sediments collected from bomb craters in zones A and B, respectively. The results reveal that high level of PCDD/Fs are accumulated in bomb craters, which might result from drifting surface soil in adjacent areas through rainwater to bomb craters. For the TEQ concentration, the highest concentration is found at A14 (746 ng TEQ kg_{dw}^{-1}), followed by A9 (496 ng TEQ kg_{dw}^{-1}) and A13 (358 ng TEQ kg_{dw}^{-1}). The concentration of PCDD/Fs in these samples exceed the level of 300 ng TEQ kg_{dw}^{-1}, regulated by Vietnam national technical regulatory QCVN:45/2012/BTNMT on the limitation values of dioxin in soil according to land use, which require there mediation or rehabilitation[3]. On the other hand, three samples collected from zone A (A12, A12, A11) are of PCDD/Fs levels range from 138 to 195 ng TEQ kg_{dw}^{-1}, which are higher than the limit level of 120 ng TEQ kg_{dw}^{-1} regulated for soil in rural area[3]. All samples collected from zone B have the concentrations lower that 100

ng TEQ kg_{dw}^{-1}. Many samples have the concentration higher than 40 ng TEQ kg_{dw}^{-1} (A4, A7, A15, A19, A15, A16, B3, B4, B7 and B10), which is the maximum level regulated for soil used for planning short-term crops. Excluding sediment samples, the TEQ concentrations of PCDD/Fs measured in surface soil collected from Aso airbase range from 2.7 to 496 ng TEQ kg_{dw}^{-1}, which are comparable or even higher than those reported by Dwernychuk et al. (2002) for samples collected in 1999 (4.9-360 ng TEQ kg_{dw}^{-1}). This result indicates that in about 20 years after the first investigation, the PCDD/Fs contamination in Aso airbase did not improve much, even worse for some sites which are lower elevation. Obviously, applying suitable methods is necessary and urgent for effectively removal of PCDD/Fs and controlling the spread of PCDD/Fs in study area to other regions surrounding Aso airbase.

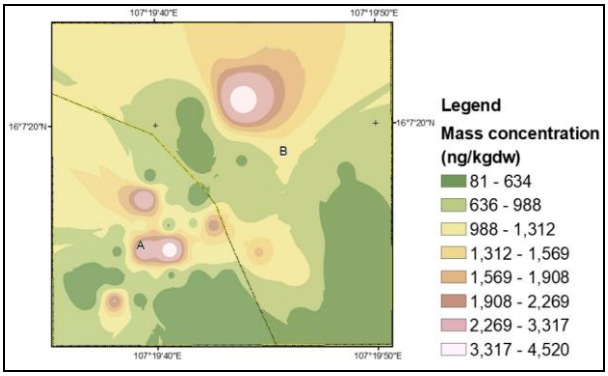

Fig 2. Spatial distribution of PCDD/Fs concentration in study area

3.2. Distribution of PCDD/Fs in surface soil samples

Result obtained from 40 soil samples are clustered into 4 groups. The congener distributions characterized for 4 groups. Group 1 includes 33 samples characterized by the predominance of OCDD, accounting for 86.2±5.7%, followed by 2378-TCDD (4.8±3.2%). Group 2 including samples of B6, B11, B4 is characterized by OCDD contributing 73.1±0.6% and 1234678-HpCDD (19.3±4.4%). Group 3 is composed of A12, A14, B10, which is dominated by OCDD (66.2±6.3%), followed by 2378-TCDD (17.0±3.5%) and 1234678-HpCDD (9.7±4.3%). While the group 4 is only sample of A9 with different congener distribution from other samples, which is characterized by OCDD (50.5%) and high contribution of 2378-TCDD (43.5%). The predominance of OCDD in soil contaminated by herbicides production (PCP, Na-PCP) are observed[19]. The dominances of OCDD, 1234678-HpCDD and 2378-TCDD are also observed in soil and sediment collected from an AO hotspot in Bien Hoa airbase (Minh et al., 2015). In case of sample A9, which is sediment collected from a bomb crater in zone A, which might be related to a prominent contribution of 2378-TCDD. 2378-TCDD is of water solubility lower about 4 orders compared with that of OCDD [5,6] which suggests that 2378-TCDD might be washed out from surface soil in higher elevation and accumulate in sediment in bomb crater. 2378-TCDD predominates for contributing to total TEQ concentration, accounting for 91±9% and 72±17% in zones A and B, respectively. In fact, the predominance of 2378-TCDD contributing to TEQ concentration is a feature characteristic of AO contamination. Minh et al. (2005) reported that 2378-TCDD contributes extremely high (98%, on average, of total TEQ concentration) in surface soil samples collected from hotspot of AO contamination in Bien Hoa Airbase. The lower contribution of 2378-TCDD to TEQ concentration measured in zone B compared with that in zone A might be due to the degradation of this congener during transportation from zone A to zone B.

3.3. Characteristics of PCDD/Fs in subsurface soil samples

Generally, the trend of decreasing PCDD/Fs concentration as the depth of soil layer increases, are found for all four sampling sites. However, the difference of PCDD/Fs level are clearly observed for three top layers, the PCDD/Fs levels of two last layers (100-150 cm and 150-180 cm) are relatively comparable.The TEQ concentrations measured in the surface soils range from 17.6 to 51.6 ng TEQ kg_{dw}^{-1}, the levels measured in layer of 50-100 cm ranges from 13.9 to 28.4 ng TEQ kg_{dw}^{-1}, while TEQ concentration in two last layers (100-150 and 150-180 cm) are quitelow and in a narrow range of 3.8 to 4.4 ng TEQ kg_{dw}^{-1}. The decrease of PCDD/Fs concentration with the death was also reported by Mai et al. (2007) for sediment samples collected from Bien Hung lake, located nearby the AO hotspot, Bien Hoa airbase. If we consider the TEQ contribution of each layer to total TEQ level of PCDD/Fs measured in a unit of area, two top layers (0-50 and 50 -100 cm) contribute to 81-95% of total TEQ level.PCDD/Fs in soil are mainly associated with organic matter and black carbon[9], which are prominent in top soil, resulting in high level of PCDD/Fs in top soil layer. The result indicates that the remediation applied for reducing PCDD/Fs level in study area should focus on the top layer of soil (1m).

Mass distribution of PCDD/Fs in different soil layers (Fig. 3) indicates that the distributions of PCDD/Fs in soil layers collected from zone A relatively differ from those found in zone B. For zone A, OCDD predominates in all soil layers collected from two sites, accounting for 94±3%, however, the decreases of 2378-TCDD with

depths of soil layers are found in both sampling sites. The contribution of 2378-TCDD found in the surface layer are 6 and 5%, decreasing to 2 and 3% in layer of 50-100 cm and only 1 and 0% in two last layers for site A7 and A18, respectively. As we know, the dominance of 2378-TCDD characterizes for AO contamination, the results suggest that the upper layer of soil (1m) is mainly contaminated by AO. On the other hand, different profiles of PCDD/Fs are found in different soil layers collected from sites B10 and B11. For site B10, two upper layers (0-50 and 50-100 cm) are of similar congener distribution, characterized by OCDD (61-64%), followed by 1378-TCDD (13%) and 1234678-HpCDD (12-15%), while, the higher contribution of OCDD (69%) and lower composition of 1378-TCDD (7%) and 1234678-HpCDD (9%) are observed in layer of 100-150 cm. It is noted that the higher contributions of HxCDDs in three soil layers collected from site B10 compared with other site. For site B11, two top soil layers are dominated by OCDD, followed by1234678-HpCDD and 1378-TCDD, while two bottom soil layers are characterized by OCDD (44-48%) and significant contribution of 1234678-HpCDD (34-38%). Interestingly, the 2378-TCDF and 1234678-HpCDF also contribute 5 to 9% of total PCDD/Fs in two bottom layers of soil collected from site B11. The different distributions of PCDD/Fs between soil layers collected from sites B10 and B11 may be attributed to the shifting PCDD/Fs from other areas (i.e zone A) to these sites.

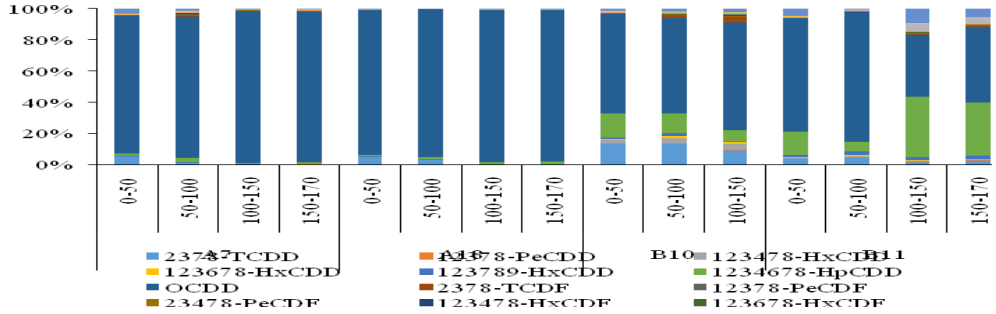

Fig 3. Distribution of 17 2378-substituted PCDD/Fs in different soil layers

Based on the investigation of PCDD/Fs occurrences and distribution in soil and sediment samples collected from Aso airbase, it is concluded that the level of PCDD/Fs contamination in Aso airbase has not been improved much since the first investigation was conducted about 20 years ago. The TEQ concentrations measured in 40 soil and sediment samples range from 2.7 to 746 ng TEQ $kgdw^{-1}$, which require appropriate remediation for agricultural and living purposes. The lower concentrations of PCDD/Fs observed in zone A are higher than those in zone B suggests that PCDD/Fs are shifted from zone A to zone B through surface soil erosion. The different distributions of PCDD/Fs in different soil layers collected from zones B, while similar distribution of PCDD/Fs found in different soil layers in zone A. The top soil layer (>1m) contributes 81-95% of total PCDD/Fs in study area, which indicate that remediation should conduct for this layer as a priority. The predominance of 2378-TCDD contributing to TEQ concentration indicate that Agent Orange is the main source of PCDD/Fs measured in study area. Applying suitable methods is necessary and urgent for effectively removal of PCDD/Fs and controlling the spread of PCDD/Fs in study area to other regions.

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