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THE STUDY AND DIFFERENTIATE OF PCDD/FS DISTRIBUTION FROM HERBICIDE USED IN VIETNAM WAR AND THAT CREATED FROM MEDICAL WASTE INCINERATORS

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*** Introduction**

Dioxin is a common name of 75 congeners of Polychlorinated dibenzo-p-dioixn (PCDDs) and 135 congeners of Polychlorinated dibenzofuran (PCDFs). PCDD/Fs have been list among the Persistent Organic Pollutants (POPs) in Stockholm Convention for long time, which are highly toxic, ubiquitous, and unintentional by- products of several chemical processes. From 210 compounds, only 17 ones, those with Chlorine substitution in 2,3,7,8 positions, these are specially interested due to their high toxicity. Dioxin origin is extremely diversified, created from numerous different activities in industries and people's life such as burning waste, bleaching wood pulp with chlorine, wood processing and so on. Particularly, dioxin is also a kind of impurities created during synthesis 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) from Tetrachlorophenol- a component of herbicide (agent orange, agent pink, agent purple and agent green) used by U.S Army in Vietnam. Therefore, this study focuses on appreciating some main parameters of dioxin originated from herbicide used by U.S Army in Vietnam war that differ with dioxin produced from burning waste sources.

*** Materials and methods**

- Soil, sediment, water and biology samples were collected from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide was stored and spread compounds in Vietnam war. Stack gas, bottom ash, chemical ash were collected from the medical waste incinerators (MWIs) in Ho Chi Minh City (HCMC), Vietnam. They were transferred to Center of Analytical Services and Experimentation (CASE) in Ho Chi Minh City, Vietnam for analysis and determination of concentration of 17 toxic compounds on HRGC/ HRMS with method that was developed based on US.EPA 8280 method with some modification.

- On the results of analysed samples above, we appreciate some following parameters:

+ Toxic concentration (C) percentage of 2,3,7,8-TCDD to TEQ: T% = (C of $_{2,3,7,8\text{-TCDD}}$ / TEQ) x 100

+ Quotient between toxic concentration (C) of 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD:
$P = C_{1,2,3,7,8\text{-PeCDD}} / C_{2,3,7,8\text{-TCDD}}$

+ Quotient between total concentration of 7 toxic congeners of PCDDs and 10 toxic congeners of PCDFs:
$R = (\Sigma\, C_{PCDD}\, (n = 1\text{-}7)) / (\Sigma\, C_{PCDF}\, (n = 1\text{-}10))$

- Statistical methods, such as principal component analysis (PCA) and hierarchical cluster analysis (HCA), are commonly used to evaluate the congener patterns of PCDD/Fs in different environmental matrix, and to reveal the contamination sources of PCDD/Fs. PCA and HCA methods were also used in this study to analyse the probable groups of similar emissions and to determine the predominant PCDD/ Fs congeners in a specific group for the MWIs in HCMC and for the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war. Both the PCA and HCA methods were performed on normalized concentrations of PCDD/Fs using Simca-P. The score plot of PCA shows the relative contributions of 17 toxic PCDD/Fs congeners. The HCA shows the similarities and differences between each waste incinerator and each collected samples from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war.

*** Results and discussion**

- On the results of analysed samples, we appreciate parameters including T%, P, R as below:
For PCDD/Fs (the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war):

T% of soils, sediments, water, biology samples: 99.39, 46.60, 68.75, 35.48, respectively. P of soils, sediments, water, biology samples: 0.005, 0.167, 0, 0.455, respectively and R of soils, sediments, water, biology samples: 63.38, 14.27, 26.74, 2.12, respectively.
While PCDD/Fs (medical waste incinerators), T% of stack gas, chemical ash, waste water (before treatment), bottom ash: 3.18, 2.80, 0, 5.53, respectively. P of stack gas, chemical ash, waste water (before treatment), bottom ash: 3.28, 3.86, 0, 2.85, respectively and R of stack gas, chemical ash, waste water (before treatment), bottom ash: 0.92, 0.58, 0.89, 0.67, respectively.
From study results showed above:
+T% values in samples taken in the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war are from 35.48 to 99.39%. While these values in MWIs are very low between 2.8 and 5.5%. This shows that 2,3,7,8-TCDD had the most contribution to I-TEQ concentration in the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war.
+ P values in all samples from MWIs are higher than 1 (from 2.9 to 3.9), while in all samples from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war are lower than 1 (from 0.005 to 0.455). This shows that 2,3,7,8-TCDD had the most contribution to I-TEQ concentration in the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war.
+ R values in all samples from MWIs are lower than 1 (from 0.58 to 0.92), while in all samples from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war are higher than 1 (from 2.12 to 63.38). The ratios of PCDDs to PCDFs for all samples were more than 1, implied the de no vo synthesis is always dominant.
+ Comparison of T%, P, R in all samples from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war shows the common followings: T% > 35%, P < 1, R >1. This shows that dioxin in these samples from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam have an origin from herbicide containing 2,4,5-T used by U.S. Army in Vietnam war. While T% < 6%, P > 1, R < 1 from all samples in MWIs implied the de no vo synthesis is always dominant.
- To better understand the congener profiles of dioxin in all samples, PCA and HCA were used to evaluate the possible groupings of similar emissions and the dominant congeners in a defined grouping, as well as to illustrate the characteristic profiles for such groupings within the resulting data.
The scope plot of principal component analysis for relative contribution of the 17 toxic dioxin congeners and the similarities and differences in the dioxin patterns were evaluated. Based on the four group extracted from HCA and PCA show that these multivariate pattern comparison results indicated three groups (groups 1 including H_xCDD, 123789-H_xCDD, 123678-H_xCDD, 123789-H_xCDD, 123478-H_xCDD, group 3 including OCDD, 2378-TCDF, 12378-PeCDD, 1234678-H_pCDF, H_pCDF, 1234789-H_pCDF, 1236789-H_pCDF and group 4 focuses on 2378-TCDD) for all congener patterns in the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war.
Group 2 focuses on all samples from MWIs including HxCDF, 123678-HxCDF, 23478-HxCDF, 123478-HxCDF, OCDF, 12378-PeCDF, PeCDF, 13478-PeCDF.
This shows that dioxin in these samples from the vicinity of Bien Hoa airbase, Dong Nai, Vietnam have an origin from herbicide containing 2,4,5-T used by U.S. Army in Vietnam war focused on 2,3,7,8-TCDD. While dioxin in these sample from MWIs focuses on PCDFs, this shows that the de no vo synthesis is always dominant.

References

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Table 1 The concerntration of PCDD/Fs in different matrixes

	PCDD/Fs (*the vicinity of Bien Hoa airbase, Dong Nai, Vietnam where herbicide used in Vietnam war)*				*PCDD/Fs (medical waste incinerators*)			
	Soil (0-30m) (ng/g)	Sediment (ng/g)	Water (ng/L)	Biology samples (ng/g wet)	Stack gas ($pgTEQ/Nm^3$)	Chenical ash, (ng/kg)	Waste water (before treatment) (pg/ml)	Bottom ash (ng/kg)
C (2,3,7,8-TCDD)	0.4886	0.0151	0.0088	0.0011	3.2774	98.6522	0	27.3514
TEQ	0.4916	0.0324	0.0128	0.0031	103.0629	3522.3384	1.4136	494.9280
C (1,2,3,7,8-PeCDD)	0.0025	0.0025	0	0.0005	10.7351	381.0445	0.2229	78.0501
∑ C (PCDD) (n = 1- 7)	0.5768	4.177	1.6257	0.2269	2037.6804	45118.2318	20.4685	3728.8828
∑ C (PCDF) (n = 1-10)	0.0091	0.2927	0.0608	0.1072	2225.1965	78450.6845	22.9183	5557.3952
T%	***99.39***	***46.60***	***68.75***	***35.48***	***3.18***	***2.80***	***0***	***5.53***
P	***0.005***	***0.167***	***0***	***0.455***	***3.275***	***3.863***	**-**	***2.85***
R	***63.38***	***14.27***	***26.74***	***2.12***	***0.92***	***0.58***	***0.89***	***0.67***

Figure 1 The tree HCA in all samples.

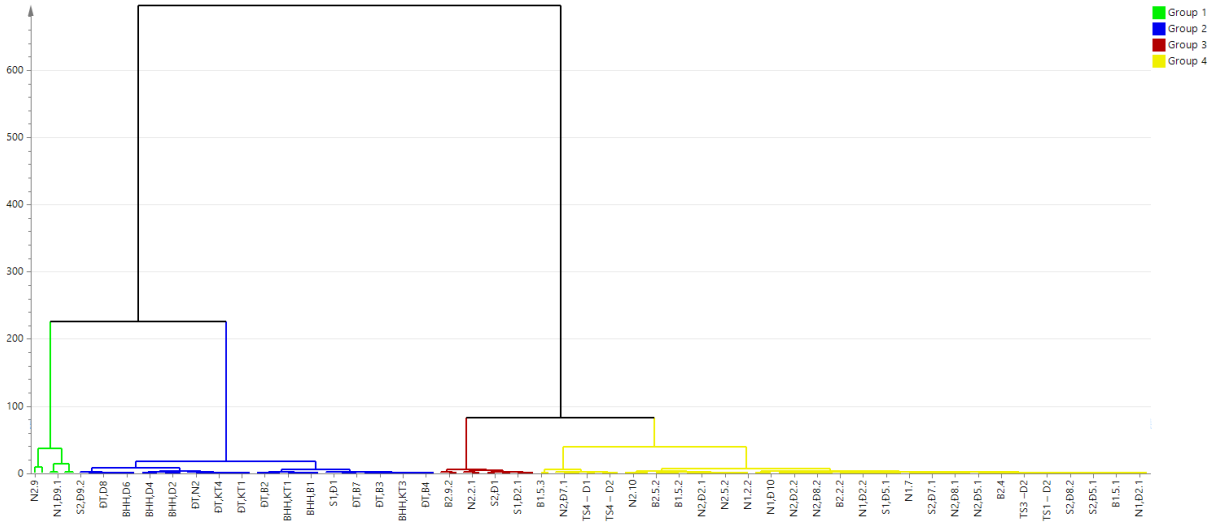

Figure 2 The PCA in all samples.