COMPARATIVE ANALYSIS OF PCDD/FS IN SOIL AROUND WASTE INCINERATION PLANTS IN NORTHEASTERN CHINA USING ELISA AND GC/HRMS

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Introduction

Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) are a group of semi-volatile, hydrophobic and extremely hazardous chemicals, known as dioxins and furans. As the largest developing country in the world, China generated 170 million tons of municipal solid waste in 2009[1]. The lack of landfill sites has led to incineration being an alternative effective and efficient means of treating solid waste. Therefore, large mounts of PCDD/Fs will be released to the environment from municipal solid waste incineration (MSWIs), causing increasing public concern about potential adverse environmental and health effects for human. In order to study the environmental impact of MSWIs on the surrounding soil quality, we collected soil samples around two major MSWIs in Harbin, the capital city of Heilongjiang province in the northeast of China. In this study, ELISA and HRGC/HRMS were used to measure the concentrations of PCDD/Fs. Additionally, TEQ of PCDD/Fs obtained by the ELISA were compared with WHO-TEQ obtained by HRGC/HRMS.

Materials and methods

Sample Collection

The sampling areas were presented in Fig. 1. The soil samples were collected during summer (from August to September) in 2011. 26 soil samples (MSWI A: 13 samples; MSWI B 13 samples) were collected within a 3km radius from the stack, mainly in the downwind directions based on the wind rose resulting from meteorological data. Five top soil samples were taken using a pre-cleaned steel spoon, within a 5-8 m radius, at a depth of 0-10 cm at each site and mixed together in a glass bottle. All the soil samples were dried at room temperature. After being grounded and homogenized through a 60-mesh sieve, the soil samples were stored at -20 °C.
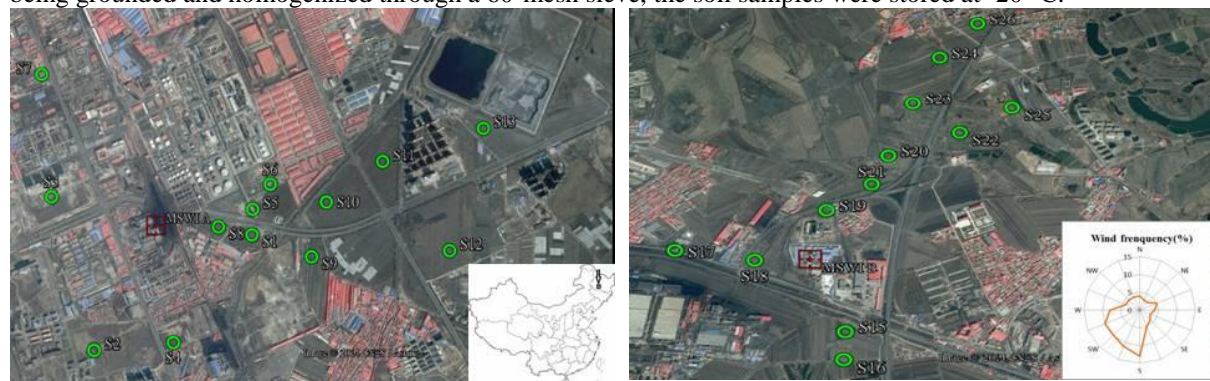

Fig.1. Sample sites in the area of the study with wind rose frequency

Treatment and Analysis

ELISA For ELISA analysis, 40 g soil was used for each sample. The analytical procedure used was a modification of the EPA 4025 method, based on commercially available sample preparation and immunoassay kits. Finally, the optical density at 450 nm was measured immediately after adding 0.5 mL of stop solution to each tube. Dose-response curves were calibrated and a nonlinear least squares curve fit was performed based on a four parameter equation.

HRGC/HRMS For HRGC/HRMS, the PCDD/Fs analysis was performed according to US EPA Method 8092[2] using a HRGC-HRMS. A Trace GC Ultra connected to a MAT95XP mass spectrometer was used. PCDD and PCDF congeners were separated on a DB-5 capillary column (60 m x 0.25 mm i.d. x 0.1 μm) at 1 mL flow rate. The mass spectrometer is operated at an EI energy of 40 eV, ion source of 285 °C, and the ion current was at 650 μA. PCDD/F congeners were monitored by SIM with the two most intensive ions at the molecular ion cluster.

Results and discussion

ELISA and HRGC/HRMS comparison

In this study, the toxic equivalents (TEQ) for PCDD/Fs determined by ELISA and HRGC/HRMS are presented as "ELISA-TEQ" and "WHO-TEQ", respectively. In order to make the comprehensive comparison between ELISA and HRGC/HRMS, three soil samples and three CRM samples were analyzed. The results of the ELISA-TEQ and WHO-TEQ ranged from 2.3 to 936 pg ELISA-TEQ/g and from 1.2 to 710 pg WHO-TEQ/g, respectively. Generally, the values of ELISA-TEQ were higher than those of WHO-TEQ. The mean ratio between ELISA-TEQ and WHO-TEQ is 1.6 ± 0.8. The correlation between the two types of concentrations is shown in Fig. 1. The result indicated that the values of ELISA-TEQ and WHO-TEQ were highly correlated with each other.

Table 1 Concentrations of PCDD/Fs derived from HRGC/HRMS (pg WHO-TEQ/g) and ELISA (pg ELISA-TEQ/g) for three soil samples and three CRM samples

Samples & CRM ID	ELISA (pg ELISA-TEQ/g)	HRGC/HRMS (pg WHO-TEQ/g)	Ratio ELISA TEQ/ WHO-TEQ
1	2.9	1.2	2.4
2	10.1	5.63	1.7
3	15.3	10.11	1.5
4	43	50	0.8
5	270	130	2.0
6	936	710	1.3

Concentration of PCDD/Fs

In this study, acure soil samples were analyzed using ELISA for screening of PCDD/Fs. Eight samples were not detected with PCDD/Fs by ELISA. Other samples were further treated and analyzed by HRGC/HRMS. The values of WHO-TEQ were in the range 0.69-10.11 pg TEQ/g, with a mean concentration of 2.33 pg-TEQ/g. Various levels of PCDD/Fs were reported in soil samples in the world, such as Hang Zhou China (0.39-5.04 pg-TEQ/g)[3], Spain (1.22-34.28 pg-TEQ/g)[4], Taiwan (1.29-5.02 pg-TEQ/g)[5], Korea (1.25-74.98 pg TEQ/g)[6]. The results in this study were comparable with these values. Furthermore, the PCDD/F concentrations are consistent with the soil guidelines in Canada, Germany and Sweden, which are 4, 5 and 10 pg-TEQ/g[7,8], respectively. Although no great variation in the PCDD/F concentrations was observed for most of the soil samples, two higher concentrations were found in S1 and S6 from MSWI A, with concentrations of 5.63 pg-TEQ/g and 10.11 pg-TEQ/g), respectively. These two concentrations are beyond the 5 pg-TEQ/g limit that restricts the cultivation of certain vegetables, but do not exceed the limit for the cultivation of other types of plants (40 pg-TEQ/g) according to the soil dioxin guideline concentrations of Germany[8].
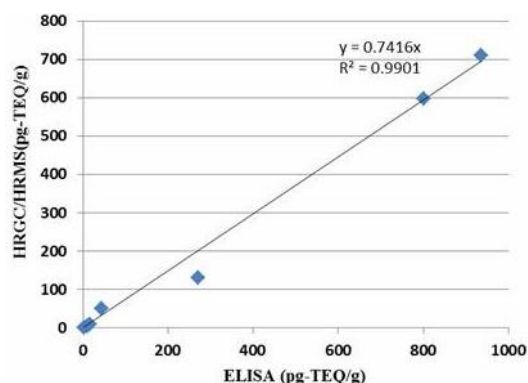

Fig.2. Comparison of PCDD/Fs between HR GC/MS and ELISA for six soil samples
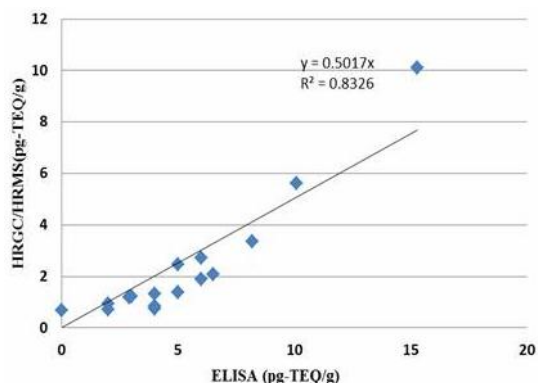
Fig.3. Comparison of PCDD/Fs derived from HRGC/HRMS and ELISA (pg-TEQ/g) for sixteen soil samples from two MSWIs

The relationship of the TEQs between ELISA-TEQ and WHO-TEQ is shown in Fig. 2. The values of ELISA-TEQ were in the range from ND to 15.3 pg-TEQ/g, with a mean value of 5.3 pg-TEQ/g. It is obvious that the ELISA-TEQ is significantly correlated with WHO-TEQ (r=0.83), but lower than for the six samples certified reference material. Notably, it might because the PCDD/Fs concentration in the CRM ranges widely, between

1.2 and 710 pg-TEQ/g, while the distribution in soils from two MSWIs is limited to the range of 0.69-10.11 pg-TEQ/g. A higher ELISA-TEQ value for PCDD/Fs in lower concentration samples could be ascribed to the presence of high levels of congeners that have significant ELISA cross-reactivity but are not determined by the conventional analysis because the contributed minimal toxicity. Such compounds are 2-Br-3,7,8-TriCDD, 2,3-DiBr-7,8-DiCDD, 1,3,7,8-TCDD, 2,3,7-TriDD, 1,2,3,4,7,8-HxCDD with immunoassay cross-reactivity of 110%, 115%, 24%, 6.7% and 1%, respectively[9].

The result indicated that ELISA can be used as a fast monitor tool for PCDD/Fs determination, especially for soil screening. However, much more studied should be conducted for checking the performance of ELISA, especially for low PCDD/Fs concentration.

PCDD/F source identification

The PCDD/Fs homologue patterns of fly ash, petroleum refinery (pref.)[10], agrochemicals PCP[11] and soil samples are shown in Fig. 3. For fly ash, petroleum refinery, PCP samples, OCDD was the major compound, followed by PCDDs, which is a typical MSWI homologue profile. The ratio of $\sum_{4-8}$PCDDs to $\sum_{4-8}$PCDFs was 0.72. The profiles are in accordance with the emission patterns reported for MSWIs. For soil samples from the MSWI B, OCDD was the predominant congener, accounting for 34-62% of the total concentration of 17 congeners, followed by HxCDF, HpCDF and OCDF. But for soil samples from the MSWI A, the percentage of congeners varied greatly, OCDD accounted for 5-44% of the total concentrations. For some samples, like S1, S4, S5, S6, S8, and S9, OCDD was not the dominant congener, which were different from that of soil samples from the MSWI B. Furthermore, when the samples are close to MSWI B, the homologue patterns become uniform, with similar mass percentages of OCDD, which indicated the same source of PCDD/Fs in these soil samples. However, for the soil samples around MSWI A, there may be multiple sources existed.
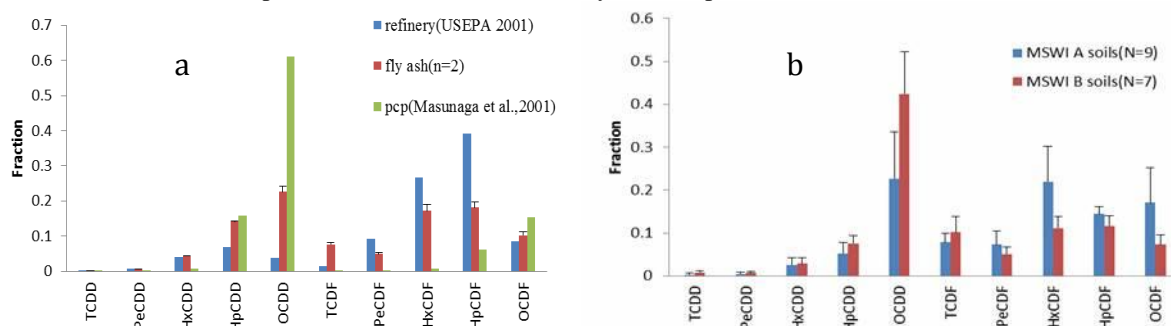

Fig.4. Averaged PCDD/F homologue profiles of combustion sources and impurities in agrochemicals (a) and agricultural soils (b), with the error bars indicating the positive standard deviations

PCA Analysis

PCA Analysis was applied for further sources investigation. Four major factors were extracted after varimax rotation with an eigenvalues greater than 1, which accounted for 77.25% of the total variance (See Fig.4). The soil samples can be divided into three cluster groups (Fig.5).
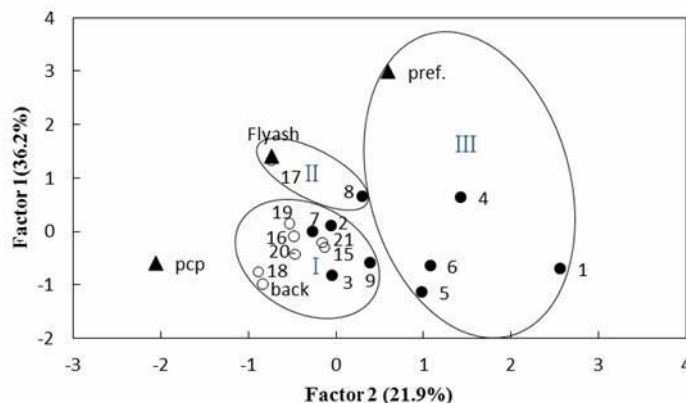

Fig. 5. Congener-specific factor analysis of soil concentration and PCDD/Fs emission sources: factor1 vs factor 2. The soil samples were marked with white (MSWI B) and dark (MSWI A) circles; PCDD/Fs emission sources were marked with dark triangles.

The score plot of factor 1 vs factor 2 indicated that most of the soil samples around MSWI B are in group Ⅰ. It is interesting to note that all the soil samples in this group had uniform compositional pattern, with high proportion of OCDD and low proportion of low-chlorinated PCDDs. When compared with background sample (<2.0pg TEQ/g), relatively higher level of both low-chlorinated PCDFs and high-chlorinated PCDFs was found, which indicated that these agricultural soils may be influenced by the potential combustion emissions of PCDD/Fs. Soil samples in group Ⅱ have close relationships with fly ash from MSWI, which indicated the influence of deposition of fly ash and the potential source of fly ash. Soils in the group Ⅲ are most dioxin-contaminated samples include the two highest concentration samples S1 and S6 (>4 pg TEQ/g). All the samples in this group are located on the downwind of MSWI A, and S1, S5, S6 are closed to the refinery plant, indicating the high PCDD/Fs level observed in these soil samples were primarily attributed to the refinery.

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