

A PRIMARY INVESTIGATION ON LEVELS OF PCDD/Fs IN SOIL OF FOUR HAZARDOUS WASTE INCINERATOR PLANTS IN CHINA

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Abstract

The polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) levels in soil samples collected from four hazardous waste incinerator plants and their vicinities from different sites of China were investigated respectively. Soil samples collected in Plants showed concentration ranging from 1.9 ng I-TEQ/kg to 13 ng I-TEQ/kg with an average value of 8.2 pg I-TEQ/g while the soil sample collected from in the vicinity of HWI Plants range from 0.41 to 2.0 ng I-TEQ/kg with an average value of 1.19 pg-TEQ/g. The PCDD/Fs levels in this work could be comparable to the results from other countries. PCDD/Fs pattern and Factor analysis were also employed to explore the characteristic and possible source of the PCDD/Fs in soil.

Introduction

In presenting UNEP inventories toolkits¹, Hazardous waste incinerators (HWI) were catalogued as important potential emission sources of PCDD/Fs. In China, The stringent emission control regulations took effort for HWI emissions from 2000. However, there was still little information known about the environmental impact of HWI²⁻⁶. In this investigation, soil samples at different sites of four HWI plants and their vicinity were collected to evaluate PCDD/Fs contaminated levels.

Materials and Methods

The four HWI plants here assessed located in different Provinces of China. Major characteristics of the selected HWI plants were shown in table 1. Four Soil samples were collected from four sites at each plant, one in the HWI plants and the others in the range 0.5-1.5km to HWI plants (estimated maximum concentration points from emissions). For the analysis of the relationship between stack emission and soil, the corresponding HWI PCDD/Fs stack emission profiles were also provided. 16 soil samples were collected in total in 2006. Each soil sampling was carried out by five-points- averaging method to represent average sampling point conditions and to avoid interference from possible local variations in soil characteristics. In each site, 500 g of soil was collected with a metal hand-operated sampler at the depth of about 20cm. All samples were sent to laboratory after sealed with aluminum foil.

Table 1 Major characteristics of the selected HWI plants

	HWI-A	HWI-B	HWI-C	HWI-D
Type	Rotary Kiln	Rotary Kiln	Pyrolysis furnace	Pyrolysis furnace
Maximum capacity(t/d)	45	15	24	25
Flue gas cleaning Technology	Semi-dry method+ Bag filter	Wet method+ Bag filter+Active Carbon adsorption	Wet method + Bag filter+Active Carbon adsorption	Wet scrubber + Wet method
Year of start-up	2001	2002	2004	2003
Stack height(m)	45	35	35	45

All samples were analyzed according to the laboratory SOP adapted from US-EPA method 1613B. The soil samples were air dried at ambient temperature. After sieved and homogenized, samples were spiked with ¹³C-labelled isotope standards EPA 1613 LCS and Soxhlet-Dean stark extracted by 300ml toluene, pesticide-grade, for 19-24h. then the

extracts were solvent transferred to hexane and concentrated for H₂SO₄ purification. After H₂SO₄ treatment the extracts were cleaned up by a multi-layer silica column which described by JIS 0311K. Then an active carbon impregnated silica column was used to separate the PCDD/Fs from PCBs. The third toluene fraction containing PCDD/Fs congeners was collected and concentrated to 0.5ml by rotary distillation, and then final extracts were concentrated to 50 ul by gentle nitrogen blow. After EPA 1613 ISS internal standard added, the extracts were transferred to a PTFE sealed vial for HGRC/HRMS analysis.

PCDD/F analysis was conducted by a HRGC/HRMS Autospec Ultima NT equipped with Agilent 6890N. The mass spectrometer was operated in Electron Impact Mode at 35 eV ionizing potential and 10 000 resolution power (10% peak valley definition). For the analysis of PCDD/F isomer, both DB5-MS 60 m long, i.d.0.25 mm, film thickness 0.25 um and DB17-MS 60m long, i.d. 0.25 mm, film thickness 0.25 um, were used to ensure that all 2378 substituted congeners could be separated from other non 2378substituted congeners.

Results and Discussion

The PCDD/Fs levels in soil expressed in I-TEQ were given in table 2. For those congeners below the detection limit the actual concentration was assumed to be zero during the calculation of I-TEQ. Soil samples collected in Plants showed concentration ranging from 1.9 ng I-TEQ/kg to 13 ng I-TEQ/kg with an average value of 8.2 pg I-TEQ/g. Whereas the soil sample collected from in the vicinity of HWI Plants range from 0.41 to 2.0 ng I-TEQ/kg with an average value of 1.19 pg-TEQ/g. PCDD/Fs levels of soil in Plants were obvious higher than levels of the soil in the vicinity of plants. Compared with average values from different sites in Italy (0.95)³,(2.68-6.91)⁴,USA (4.0)⁵, Spain (1.08,12.24) and Japan(1.8,6.0,6.1 and 7.1) ⁶,the PCDD/Fs levels in this work could be comparable. Compared with the soil guideline in Germany and Sweden, which are 5 and 10 pg-TEQ/g, respectively, It seems that the soil from the vicinity of all selected HWI Plants could be considered safe till 2006 and further consideration to evaluate environmental risk maybe needed for the soil from HWI-A,HWI-B and HWI-D plants in case necessary. However, due to the working time of all investigated plants maybe not long enough to make a notable PCDD/Fs levels in the soil from the vicinity of HWI plants; further long-term monitoring would be expected.

Table 2 PCDD/Fs levels in soil ,I-TEQ (ng/kg)

ng I-TEQ/kg	Near plants			In Plants
	Site 1	Site 2	Site 3	Site 4
HWI-A	1	1.6	1.7	7.9
HWI-B	0.61	0.41	2.0	13
HWI-C	0.83	0.53	0.61	1.9
HWI-D	1.6	0.57	0.74	10

Figure 1 showed the composition of 2378-substituted PCDD/F congeners in soil and corresponding stack emission from selected HWI plants respectively. It could be seen that highly chlorinated PCDD/F congeners, especially OCDD and OCDF, were prevailing in soil samples. It also could be observed that the percentage ratio of furans in soil from in plants were greater than that in soil from the vicinity of various HWI plants respectively. For soil samples from HWI-A and HWI-B, except the sample from B-site2, the OCDD percentage ratio was larger than 59% while the OCDF percentage ratio was less than 8%. For the soil samples from HWI-C and HWI-D, the percentage of OCDF (10-32%) was higher than those from HWI-A and HWI-B, but still less than the percentage of OCDD (29-58%) in most cases. There might be a reasonable implication that OCDDs were more stable than OCDFs in soil.

The PCDD/Fs congener patterns in soil from HWI-A and HWI -B were obvious different from those in corresponding stack emission, however the PCDD/Fs congener patterns in soil from HWI-C and HWI -D were similar in some extent with those in corresponding stack emission. The difference may be caused by following two possible reasons: one reason was that there might be another PCDD/Fs source. The other reason might be, considering different physicochem property of each PCDD/Fs congener and longer working time of HWI Plants A and B, that the PCDD/Fs patterns could be changed observably due to PCDD/Fs congener's evaporation,

transformation and transportation in soil. The study on PCDD/Fs behaviors in soil would be helpful to understand the patterns differences.

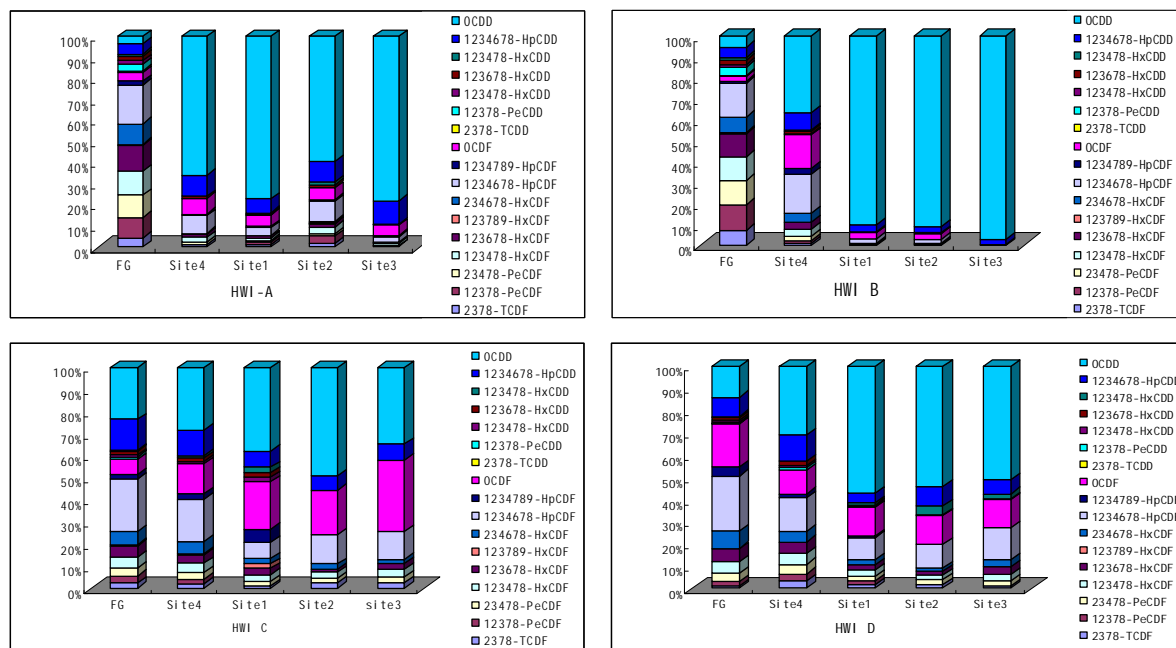


Figure 1 the composition of 2378 substituted PCDD/F congeners in soil and flue gas from selected HWI plants.

Factor analysis results including all soil samples and corresponding stack emission samples were shown in Figure 2. the factor 1 scores (first factor -axis) of the plot explained 58% and factor 2 (secondary factor -axis) explain 17% of the total data variation. The data points in FA plot appeared to cluster together to 4 groups. Group 1 contains flue gas samples from HWI-A, B, C and D. Group 2 consisted of soil samples collected in HWI-B, C and D plants. Group 3 and Group 4 comprised soil samples collected from the vicinity of HWI-A, B and those from the vicinity of HWI – CD respectively. The cluster results were matched with the PCDD/Fs pattern described in figure 1 approximately. It should be noted that soil sample collected in HWI-A belonged to Group 4 while soil sample collected from HWI-C site 1 was not assembled to any group. From the Fig 2, it could be seen that the distance between points D-FG and D-4 represented were close to each other, same for points C-FG and C-4, which supported the similar conclusion shown on Fig 1 and implied that these samples might have similar pattern and stack emission might be important PCDD/Fs source for soil from HWI-C and HWI-D. As for HWI-A and HWI-B, further researches and discussions would be needed.

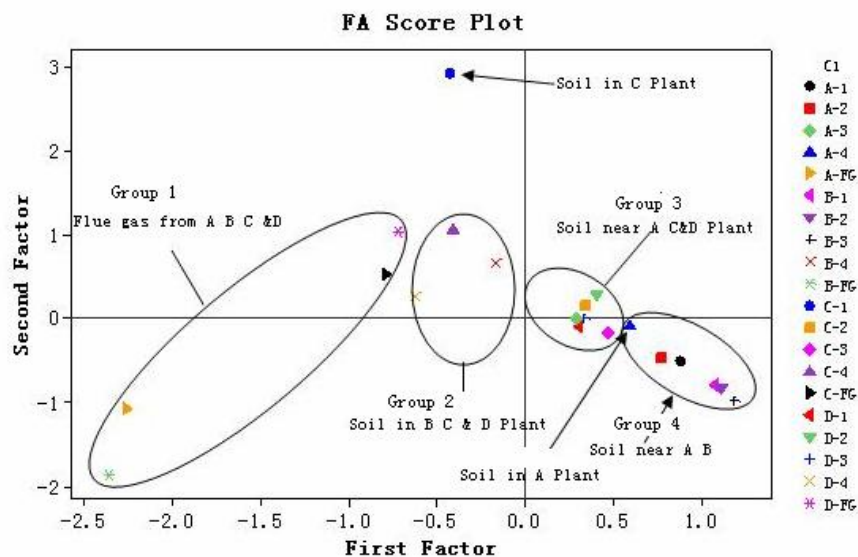


Fig 2 Factor Analysis plot of stack emission and soil samples collected from selected HWI plants

Conclusion

The PCDD/Fs levels in soil samples from the vicinity of investigated HWI Plants were found in very low level while those in soil samples inside the HWI plants seemed a little higher than the guideline value of Germany and Sweden in a few cases. However all PCDD/Fs levels in this study could be comparable to data from other researches in different countries. Pattern analysis and FA analysis revealed that stack emission from HWI might be direct sources for PCDD/Fs in soil of some HWI plants. For other instances, further research on the behavior of PCDD/Fs in soil or other potential source near HWI would be helpful to understand.

Reference

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