TEMPORAL VARIATION OF PCDD/FS IN SOILS NEAR A NEW HAZARDOUS WASTE INCINERATOR IN EASTERN CHINA

Wang Q*, Lu SY, Li XD, Yan JH

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, PR China

Introduction

Due to the advantages of detoxification, mass reduction and reclamation of incineration technology, the construction of hazardous waste incinerators (HWIs) has been booming up in mainland China[1]. Whereas the unintentional emissions of POPs especially PCDD/Fs from HWIs to the environment[2], the concern about their environmental impact and health risk is notable. At present, many researchers try to investigate the exposure risks by determining PCDD/Fs concentration in different natural medias such as soil, water, air and organism because of the public fear about dioxins[3,4].
Unfortunately, there is still lack of detailed information presented to the public about health risks of hazardous waste incineration in China until now[5]. In order to get the overall information on the environmental impact of HWIs, this study focuses on the levels of PCDD/Fs in soil around a HWI plant before and after one year operation and the relationship between PCDD/Fs emissions and the environmental accumulation by congener pattern comparison and multivariate statistical analysis.

Materials and methods

Location Description
The study area is in the vicinity of a new HWI plant which was finished in the end of 2008, located in the north of Zhejiang province in eastern China. This area is an old industrial estate that farmlands and hills coexist, located 15 km northeast of Hangzhou downtown. The HWI plant referred in this study is situated in the hilly country, which is surrounded by two main roads, and the further around area is farmland and community (Fig.1). The HWI plant is equipped with two rotary kilns, and the gas cleaning system contains a semi-dry scrubber and a bag-house filter. The height of the stack is 45 m, still lower than the close hill. The PCDD/F emission levels of the incinerator measured in 2009 were ranged from 0.021 to 0.845 ng I-TEQ N m^{-3}. It had been in commissioning operation since December 2008 and full operation with a total daily capacity of 0.05 million kg since January 2010.

Sample preparation and analysis
A total of 26 soil samples were collected from hillside and agricultural fields in the vicinity of the HWI plant (Fig.1). Sampling was performed with the aid of a handheld GPS device (Meridian Color, Thales Navigation, US) in December 2008 and 2009 within a period of two days respectively, the sampling method was reported in the previous work[6]. The soil samples firstly were subsequently dried in a ventilated room until constant weight, small rocks and plant materials were manually removed. Then they were ground and passed through a 2-mm sieve, finally, about 500 g soil of each sample was homogenized through a 60-mesh sieve and refrigerated until analysis.

For comparison of PCDD/Fs congener patterns between soil and HWI emission, the flue gas was collected. The flue gas samples were collected with an isostack sampler (M5, KNJ Engineering, Korea) according to USEPA method 23A. The sample collection components included the glass fiber filters, in line with a condenser, the sorbent (XAD-2 resin) module and four impingers. The sampling standard ($^{13}C_{12}$ labelled standard, Cambridge Isotope Laboratories, Inc., USA) was spiked into the XAD-2 resin before sampling of flue gas.

Results and discussion

All the experimental results were expressed on the dry weight basis, and the 2,3,7,8-TeCDD toxic equivalents (I-TEQ) were calculated using NATO/CCMS factor. The 26 soil samples of this study were grouped into 8 clusters by their distances from the incinerator. Table 1 summarized the PCDD/Fs concentration of soil samples collected from different direction but the same distance from the stack, in order to know the temporal variation between the 2008 and 2009 survey. For the samples sampled at sampling sites that same distance from the incinerator, the percentages of temporal variation of the average I-TEQ values are also shown. In the 2008 survey, average I-TEQ values ranged from 0.7 to 29.01 ng I-TEQkg^{-1}, with median and mean values of 7.02 and 8.64 ng I-TEQkg^{-1}, respectively. In the 2009 survey, average I-TEQ values ranged from 0.97 to 28.09 ng I-TEQkg^{-1}, with a median value of 11.18 ng I-TEQkg^{-1} and a mean value of 11.15 ng I-TEQkg^{-1}. From 2008 to 2009, PCDD/Fs levels increased in 7 of 8 average I-TEQ values and they decreased in only 1, a significant increase in the percentages of the mean values was observed from 30.4% to 117.9%.

In order to investigate the spacial variation, PCDD/Fs average concentrations in soil samples with increasing distances of sampling sites from the stack in 2008 and in 2009 were shown in Fig.2. It could be observed a significant increase of PCDD/Fs levels in those sites close to the HWI (<1 km) and slight decline of PCDD/Fs levels in those sites far away from the HWI (>1 km) with the increasing distance. The highest concentrations of PCDD/Fs in two surveys were found in those sites at distance of 1 km from the incinerator.

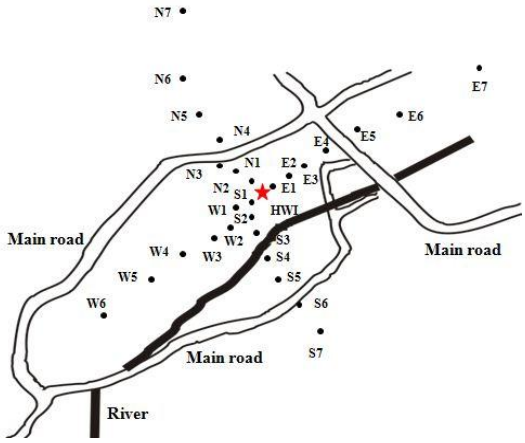

Fig.1 Soil sampling sites around the HWI

Table 1 PCDD/Fs average concentrations (ng I-TEQkg^{-1}) in soil samples collected in different distance of sampling sites from the stack in 2008 and in 2009: Temporal variation

Distance m	Sample numbers	Average value (2008) ng I-TEQkg^{-1}	Average value (2009) ng I-TEQkg^{-1}	Variation %
150	3	9.36	12.21	30.4
250	3	6.26	10.15	62.1
400	3	7.77	12.7	63.4
600	3	8.64	15.08	74.5
1000	2	29.01	28.09	-3.2
2000	5	5.89	6.71	13.9
3500	5	1.51	3.29	117.9
6500	2	0.7	0.97	38.6

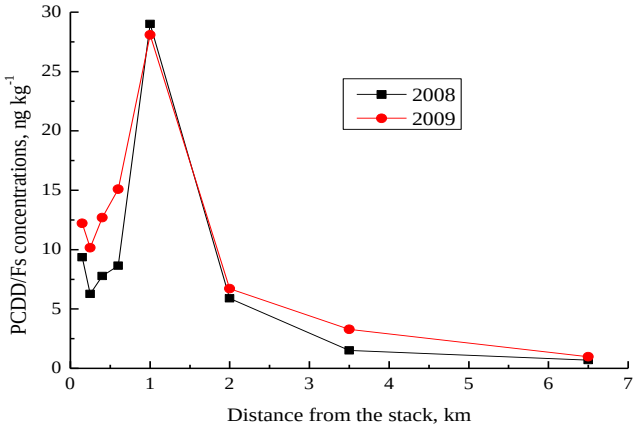

Fig.2 PCDD/Fs average concentrations (ng I-TEQkg^{-1}) in soil samples with increasing distances of sampling sites from the stack in 2008 and in 2009: Spacial variation

PCDD/Fs congener concentration profiles of flue gas samples were shown in Fig.3A. It was a typical HWI gas profile with a dominant homologue of HCDF and relatively low PCDDs. The congener profile of flue gas was dominated by 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD , followed by 2,3,4,6,7,8-HxCDF and 1,2,3,4,7,8-HxCDF. On the contrary, the profile of averaged soil samples (Fig.3B) analyzed in this study had higher fraction of PCDDs than the flue gas samples. The average congener patterns reflected the similarities and differences to the supposed source (HWI emission). Generally, the congener profiles of soils observed in 2009 resembled the fingerprints in 2008, OCDD accounted for approximately 50% in 2008 and 30% in 2009, respectively. After the operation of this HWI, in soil samples, OCDD fraction decreased and PCDFs had higher fraction than the background soil, even though OCDD remained the predominant species. This might result from the emission of the HWI with low fraction of OCDD and the ratio of PCDFs to PCDDs>1.

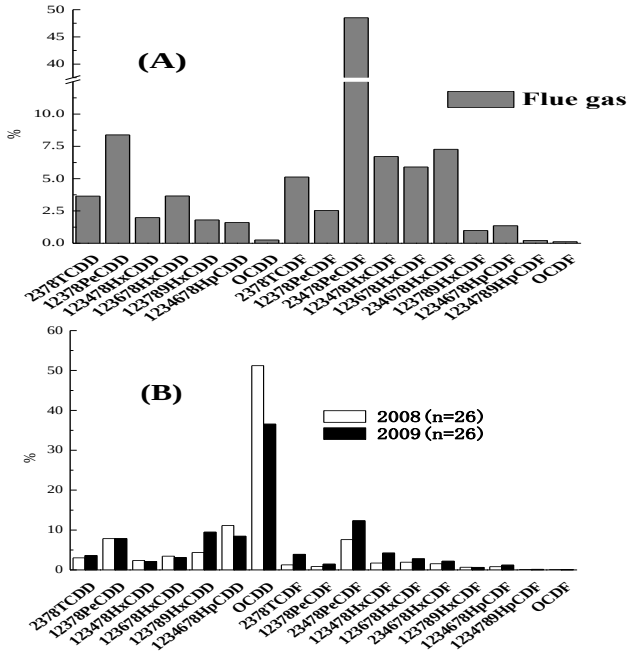

Fig.3 PCDD/Fs congener profiles in flue gas and soil samples during these two surveys

Principal component analysis (PCA) was used to evaluate the potential variation and similarities of the PCDD/Fs congener patterns in soil samples and flue gas, as shown in Fig.4. Soil points separated from flue gas in the score plot, which indicated the difference between soils and flue gas. Also, there were more similarities between 2009 soils and flue gas compare to the relation between 2008 soil and flue gas, especially E5, E7 and W5 collected in 2009. With respect to the annual variations in PCDD/Fs concentrations and the distribution in different distance from the chimney, in the present study, a limited neighbourhood seems to be affected by the emission from the HWI. There must be some other sources of PCDD/Fs responding for the contamination of background soil samples in 2008 survey and the significant difference of PCDD/Fs congener patterns among soil and flue gas. However, there was no enough clear information to identify the pollutant source.

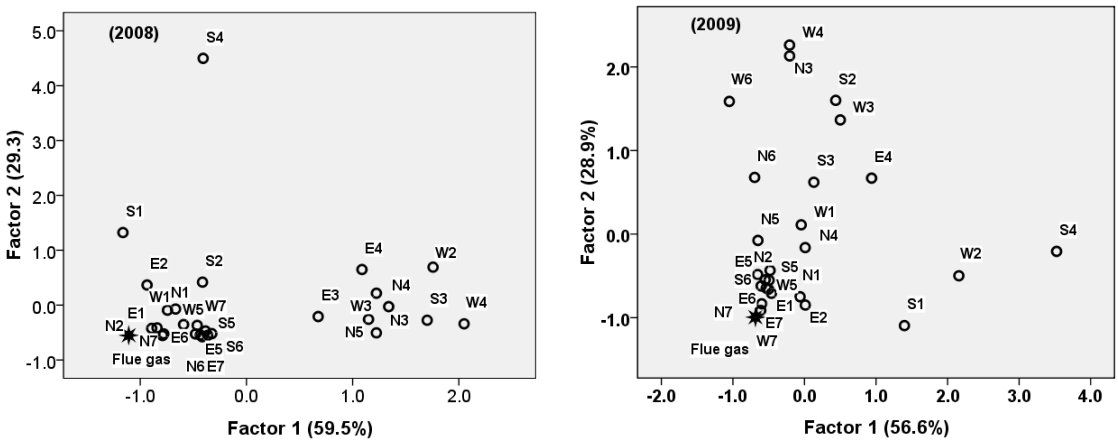

Fig.4 Principal component analysis applied to the soil and flue gas samples

Acknowledgements

The Project is supported by the Major State Basic Research Development Program of China (973 Program, No.2011CB201500) and the Public Welfare Projects for Environmental Protection (No. 201209022). The authors give the grateful acknowledge to the sponsors.

References:

1. Wu HL, Lu SY, Li XD, Jiang XG, Yan JH, Zhou MS, Wang H. (2012) *Chemosphere*. 86(4): 361-367
2. Schuhmacher M, Rodriguez MC, Diaz J, Domingo JL. (2002).*Chemosphere*. 48: 187-193
3 Kulkarni PS, Crespo JG, Afonso CAM. (2008) *Environ Int*. 34: 139-153.
4 Mari M, Domingo JL. (2010) *Environ Int*. 36:131-137
5 Li XD, Yan M, Chen T, Lu SY, Yan JH, Cen KF. (2010) *Journal of Hazardous Materials*. 179 : 783-789
6 Xu MX, Yan JH, Lu SY, Li XD, Chen T, Ni MJ, Dai HF, Wang F, Cen KF. (2009) *Environ Sci Technol*. 43(4): 1023-1029