CHARACTERISTICS OF PCDD/Fs IN FLY ASH FROM WASTE INCINERATERS IN EAST CHINA USING CALUX ASSAY WITH HRGC/HRMS

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Introduction

Since 2000 the construction of new incinerators in China has been booming and by 2003, 70 Municipal Solid Waste Incinerators (MSWIs) were operational, with a daily treatment capacity of 16.5 million kg[1]. However, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are typically found in flue gases and fly ash generated by MSWIs. The major and important source of PCDD/Fs at present is waste incineration, with most being formed in combustion processes or cooling stage of flue gas[2-5]. From the report of Ministry of Environmental Protection of China, the local department must supervise the emission of waste incinerators at least every two months[6], so the amounts of fly ash samples must be large, and it is important to have a reliable, fast and inexpensive method to monitor. However, since HRGC/HRMS analysis is an expensive and time consuming method, the CALUX (Chemically Activated LUciferase gene eXpression) bioassay is a fast, sensitive, and inexpensive tool for the analysis of a high number of samples, the use of this technique in routine analysis of fly ash samples may be a valuable alternative for HRGC/HRMS. In this paper, sixteen fly ash samples from waste incinerators in east China were analyzed and compared using the CALUX assay and HRGC/HRMS.

Materials and methods

The fourteen fly ash samples are collected from municipal solid waste incinerators (MSWIs), medical waste incinerators (MWIs), and industrial waste incinerators (IWIs) in Zhejiang Province in east China. The left two samples are international calibration samples of 2010.

For HRGC/HRMS analysis, about 1 g (dry matter) of fly ash samples were taken out, clean-up procedure and analytical determination, described as the previous research[7]. The sample was immersed in HCl for one hour, and then filtering separated. The liquid was then liquid-liquid extracted and the solid was soxhlet extracted. Each sample was spiked with a mixture of ^{13}C-labelled PCDD/Fs compound stock solution (5μl) before extraction. The extracts were subsequently passed through multilayer silica gel column and activated carbon column following USEPA Method 1613. The extracts were blow down to 20μl by nitrogen (N_2), and 5μl internal standard solution were added before sample were subjected to PCDD/Fs analysis by using HRGC/HRMS (JEOL JMS-800D, Japan) with a DB-5MS column (60m×0.25mm×0.25μm).

Fly ash samples (about 2 g) were immersed in HCl for one hour, and then filtering separated. The liquid part was then liquid-liquid extracted and the solid part was soxhlet extracted for 16 hrs. After the rotary evaporation, the extraction was loaded onto an acid-silica gel and XCARB (XDS Inc., USA) bigeminal columns. The DL-PCBs and PCDD/Fs fractions were then eluted with different solution only onto XCARB column respectively, and the PCDD/Fs fraction was selected for CALUX assay in this

study. The CALUX assay was carried out using a recombinant H1L6.1 cell line. The cells were seeded on 96-well microplates, and after 24 hrs of incubation, cells were exposed in duplicate to the purified sample extracts and 2,3,7,8-TCDD standard solution for 20-24 hrs of incubation. The luciferase activity was measured using a Lucy I luminometer (Antos, Salzburg, Austria).

Results and discussion

The TEQ of PCDD/Fs determined by CALUX assay and HRGC/HRMS with WHO-TEF (2006) are written as "CALUX-TEQ" and "WHO-TEQ", respectively. WHO-TEQ of the sixteen fly ash samples collected from different waste incineration plants in east China are in the range of 0.008 to 116 ng WHO-TEQ/g (Table 1), and CALUX-TEQ is 0.01~123 ng WHO-TEQ/g (not shown in this paper). CALUX-TEQ and WHO-TEQ values are compared graphically in Fig.1. It is obvious that CALUX-TEQ is highly correlated with WHO-TEQ, and the correlation coefficient is 0.99. The average ratio of CALUX-TEQ to WHO-TEQ is 1.30; so generally, CALUX-TEQ shows higher values than WHO-TEQ[8]. The use of CALUX in routine analysis of fly ash samples may be a valuable alternative for HRGC/HRMS, although we need more correlation data between WHO-TEQ and CALUX-TEQ for fly ash samples in China to support the conclusion in the future.

A higher CALUX value for PCDD/Fs could be ascribed to various factors including (i) the difference between toxic equivalence factors (WHO-TEFs, 2006) and CALUX relative potency (REP) values, and (ii) the presence of other AhR ligands that are not quantified during HRGC/HRMS analysis. To examine the factors affecting the discrepancy found by TEQ determined by bioassay and chemical analysis, we multiplied the PCDD/F concentrations measured by HRGC/HRMS by the corresponding REP values instead of the WHO-TEF values (2006) (the corresponding REP were shown in another paper) [9] to get REP-TEQ. Interestingly, CALUX-TEQ was found to be close to WHO-TEQ, except that the REP values of 1,2,3,7,8-PeCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,7,8,9-HpCDF and OCDF were much higher than the corresponding WHO-TEF values. Possibly, the response of the CALUX assay to PCDFs is higher. However, the REP-TEQ values did not change significantly from WHO-TEQ values, indicating that the difference between WHO-TEF (2006) and REP values were not responsible for the observed discrepancy[10]. Furthermore, the presence of other compounds that bind to the AhR-receptor may explain the observed discrepancy. Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs), polyhalogenated dibenzo-p-dioxins and dibenzofurans (PXDD/Fs; X=Br/Cl) and a few polychlorinated naphthalene (PCNs) congeners, but also less persistent pollutants like polyaromatic hydrocarbons (PAHs), and even natural compounds, also have dioxin-like activities[11].

Table 1 shows the PCDD/F contents in sixteen fly ashes from different waste incinerators. The MWIs fly ashes (FA-1 to FA-3) are found to have very high PCDD/F concentration, at 47.2~116 ng WHo-TEQ/g, compared to the other fly ashes and – in fact – to the typical dioxins load of MSWIs. This could be related to the fuel characteristics, distinct with MSW and common industrial waste. There are different characteristics of MW compared with MSW: more plastics, e.g. disposable medical apparatus, human tissues and organs, and expired drugs, which may cause the higher dioxin contents.

In general, the ratio of [PCDDs]:[PCDFs] is suggestive of the route by which PCDD/Fs is produced. If

this ratio is smaller than 1, PCDD/Fs probably are formed mainly via the de novo route; if the ratio is greater than 1, other routes like the precursor route prevail[12]. Table 1 shows that the values for PCDDs/PCDFs are different according to the different sources of fly ash samples. The ratios of [PCDDs]:[PCDFs] are very closely grouped for the fly ash samples from industrial waste liquid and residue incinerators (0.10-0.15). It is concluded that the samples from industrial waste liquid and residue incinerators may be characterized by this specific character - the remarkably highter contributor to TEQ values is PCDFs, which account for about 90% of the total TEQ values. The ratio values for MWIs and MSWIs are grouped respectively in the range of 0.27~0.56 and 0.44~0.86, which is indicated that although PCDFs is also the higher contributor, PCDDs in fly ash samples from MSWIs contribute higher WHO-TEQ values than that from MWIs. Generally speaking, the ratios of [PCDDs]:[PCDFs] for waste incinerators are lower than 1, which is an indicative of de novo formation, except for the fly ash sample from waste resin fluidized bed incinerator (the ratio is 1.82).

PCDD/Fs congener profiles of the sixteen fly ash samples are shown in Table 1. 2,3,4,7,8-PeCDF is the predominant congener of all the seventeen toxic congeners, which may be the characteristics of fly ash from waste incinerators, except for FA-13 from waste resin fluidized bed incinerator. The most abundant PCDD congener in samples from MSWIs, MWIs, industrial waste melting incinerator, and waste resin fluidized bed incinerator is 1,2,3,7,8-PeCDD, except for FA-4 from MWIs (1,2,3,4,7,8-HxCDD). For the fly ash samples from industrial waste liquid and residue incinerators, the highest contributor to PCDDs is 1,2,3,7,8,9-HxCDD. Along with the remarkably low ratios of [PCDDs]:[PCDFs], these two characteristics may make the ash samples from this kind of incinerator quite distinct.

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Table 1 PCDD/Fs congener profiles of sixteen fly ash samples collected from east China

		FA-1	FA-2	FA-3	FA-4	FA-5	FA-6	FA-7	FA-8	FA-9	FA10	FA11	FA12	FA-13	FA-14	FA15	FA16
Sources		**MWIs**				**MSWIs**					**Industrial waste liquid and residue incinerators**			**Waste resin fluidized bed incinerator**	**Industrial waste melting incinerator**	**International calibaration 2010**	
PCDDs ng/g	**2378-TCDD**	3.73	1.66	12.6	0	0.13	0.25	0.16	0.15	0.25	0	0	0	0.01	0.05	0.05	0.01
	12378-PeCDD	19.9	5.27	22.3	0	0.31	0.56	0.34	0.29	0.31	0	0	0	0.02	0.46	0.49	0.01
	123478-HxCDD	2.07	0.70	1.41	0.001	0.03	0.04	0.03	0.03	0.03	0.002	0	0.44	0	0.05	0.09	0.001
	123678-HxCDD	3.15	1.43	2.29	0	0.05	0.06	0.05	0.07	0.05	0.003	0.001	0.52	0.001	0.10	0.35	0.002
	123789-HxCDD	3.32	0.89	2.04	0	0.04	0.05	0.04	0.06	0.05	0.004	0	0.82	0.001	0.09	0.18	0.001
	1234678-HpCDD	2.02	1.20	0.97	0	0.03	0.04	0.03	0.05	0.03	0.003	0	0.25	0	0.06	0.50	0.001
	OCDD	0.06	0.06	0.02	0	0.001	0.001	0.001	0.001	0.001	0	0	0.02	0	0.002	0.05	0
	Total	34.2	11.2	41.6	0.002	0.59	0.99	0.63	0.64	0.72	0.01	0.002	2.05	0.03	0.80	1.71	0.03
PCDFs ng/g	**2378-TCDF**	2.22	1.03	18.1	0	0.10	0.19	0.11	0.16	0.20	0.003	0.001	2.09	0.002	0.12	0.01	0.006
	12378-PeCDF	1.89	0.67	2.21	0	0.03	0.07	0.03	0.03	0.04	0.002	0	0.78	0	0.02	0.02	0.002
	23478-PeCDF	27.8	13.2	29.5	0.002	0.54	1.11	0.42	0.43	0.56	0.04	0.006	6.66	0.01	0.77	0.34	0.02
	123478-HxCDF	11.7	5.92	7.09	0.001	0.08	0.27	0.05	0.06	0.09	0.02	0.001	1.96	0.002	0.17	0.17	0.005
	123678-HxCDF	11.7	4.73	7.67	0.001	0.08	0.27	0.05	0.05	0.10	0.01	0.001	1.68	0.002	0.16	0.22	0.005
	123789-HxCDF	1.68	1.11	1.29	0	0.02	0.03	0.05	0.05	0.01	0.003	0.001	00	0	0.04	0.04	0.001
	234678-HxCDF	15.6	7.06	7.09	0.001	0.09	0.26	0.01	0.007	0.07	0.02	0	2.48	0.003	0.22	0.34	0.004
	1234678-HpCDF	3.34	1.81	1.52	0	0.01	0.05	0.007	0.007	0.01	0.01	0	0.83	0.001	0.05	0.13	0.001
	1234789-HpCDF	0.70	0.38	0.20	0	0.003	0.007	0.001	0.001	0.001	0.001	0	0.19	0	0.01	0.02	0
	OCDF	0.07	0.05	0.01	0	0	0	0	0	0	0	0	0.02	0	0.001	0.003	0
	Total	76.7	36.0	74.65	0.007	0.95	2.26	0.73	0.79	1.08	0.11	0.011	16.7	0.02	1.56	1.30	0.04
HRGC/HRMS ng WHO-TEQ/g		111	47.2	116	0.008	1.54	3.25	1.36	1.42	1.80	0.12	0.012	18.7	0.05	2.36	3.01	0.07
CALUX ng -TEQ/g		122	76.8	123	0.01	1.27	3.99	1.25	1.57	2.70	0.42	0.01	26.2	0.04	2.97	2.24	0.12
Ratios*		0.45	0.31	0.56	0.27	0.63	0.44	0.86	0.81	0.67	0.10	0.15	0.12	1.82	0.51	1.31	0.71

* "Ratios" mean the ratios of PCDDs to PCDFs.

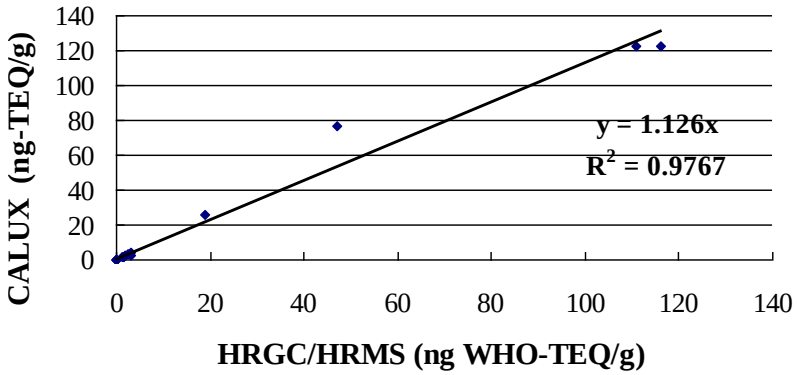

Fig. 1 Correlation relationship of CALUX-TEQ and WHO-TEQ for sixteen fly ash samples collected from waste incineration plants in east China.