Homologue Profile and Congener Pattern of PCDD/Fs at Different Positions of a Municipal Waste Incineration Plant

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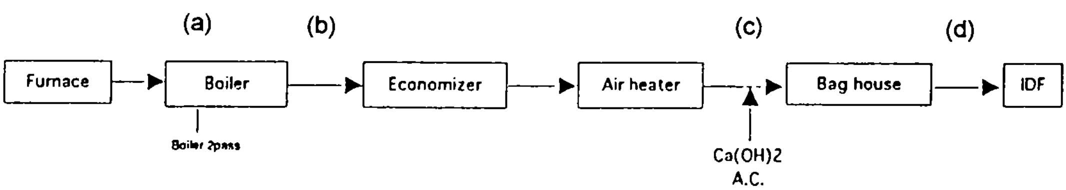
Introduction

In order to find the optimal operating conditions for minimizing dioxin emissions, we have recently utilized mathematical modelling analysis to study the dioxin measurement data in an industrial-scale fluidized-bed incinerator[1]. The toxic equivalent (TE) total for practical application purposes has been used as the response variable in the modelling. The study of homologue profile and congener pattern of PCDD/Fs can still provide some information about the PCDD/F formation mechanism in actual incineration operation and show whether some less toxic isomers may be produced under certain operating conditions. Therefore in this paper we examine the homologue profile and congener pattern of PCDD/Fs measured at different positions of an MSWI plant using the mathematical method of principal component analysis (PCA) and discuss the mechanistic implications.

Experimental Methods

The schematic flow of the MSWI plant studied is shown below:



The incineration furnace is of the revolving twin-interchanging fluidized-bed (TIF) type. The operating conditions and example performance data are given in Table 1. For PCDD/F measurement six experimental runs have been conducted, each with four sampling positions indicated by (a) to (d) in the diagram. Sampling and analysis methodology of PCDD/Fs was according to the procedure of the Waste Research Foundation (Japan). Concentrations of homologue total and the 2,3,7,8-substituted isomers in flue gases were determined.

Table 1. Operating conditions and example performance data of the MSWI plant

Temperature(°C)		Flue gas CO level at baghouse out (ppm)	40
Furnace bed	635		
Furnace top	879	Unburned carbon content in boiler ash (mg/g)	5.6
Boiler 2nd pass	457		
Boiler out	253	Total chloro organic compounds in boiler ash (mg/g)	61.2
Baghouse in	164		
Retention time in frunace (sec)	3	Dioxin at boiler out (ng-TE/Nm^3)	2.99
Flue gas O_2 level at boiler out (%)	11.5	Dioxin at baghouse out (ng-TE/Nm^3)	0.08

Results and Discussion

The TIF fluidized-bed combustor has the advantage of intensive material mixing, rapid heat transfer and uniform bed temperature. In Table 1 the unburnt carbon content in fly ash and the CO level in flue gas are low, indicating that the combustion conditions in the TIF type incinerator are favourable. The flue gas PCDD/F concentration is about 3 ng-TE/Nm^3 at boiler out and decreased to below 0.1 ng-TE/Nm^3 at baghouse out.

The homologue profile and congener pattern of PCDD/Fs at different sampling positions are studied using PCA. PCA is a statistical method for examining the similarity or dissimilarity of a large array of experimental data, and is well suitable for studying PCDD/F data[2,3]. The results of PCA of the homologue profile are shown in Fig. 1. The first principal component accounts for 76.5% of the variance of the homologue profile data; and the second accounts for 18.6% of the variance. From Fig. 1 it is seen that the data points of positions (a), (b) and (c) tend to be clustered below, around and above the x axis respectively, which is indicative of some differences of the homologue profiles at positions (a), (b) and (c), although broadly speaking they are similar as all data points are located at about the same

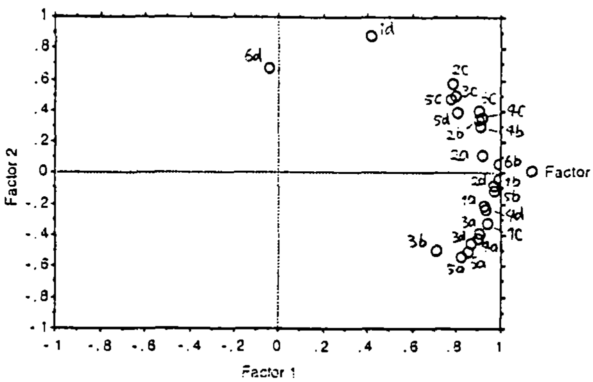


Fig. 1 Principal component analysis of PCDD/F homologue profile at different sampling positions of the MSWI plant. The numbers 1 to 6 indicate the experimental runs; the letters a to b indicate the sampling positions.

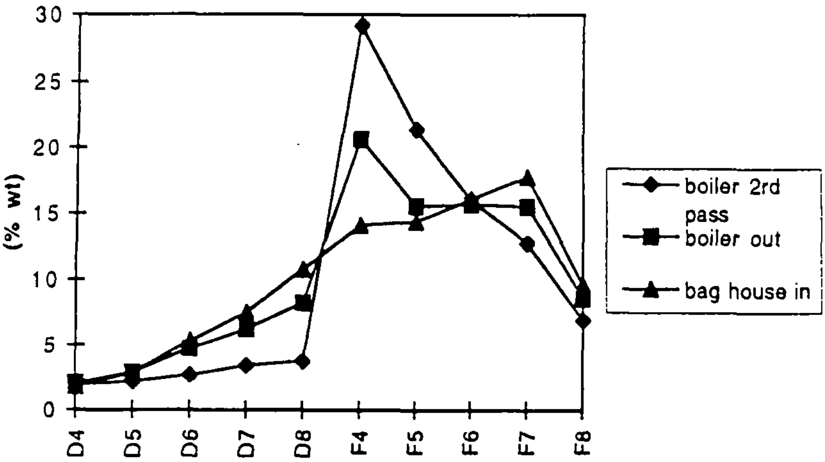


Fig. 2 The PCDD/F homologue profile at different sampling positions of the MSWI plant (average values of six experimental runs for each sampling position).

position of the x axis. The PCDD/F homologue profiles for the different positions are shown in Fig. 2. It is evident that the PCDD/F homologues are representive for the combustion "fingerprint" of PCDD/Fs, i.e. PCDF/PCDD > 1, the distributions of PCDDs are weighted towards higher chlorinated homologues, and that of PCDFs may show a maximum between T_4CDF and H_6CDF. Comparing the three sampling positions the change of the homologue profile is such that while the flue gases are traversing the postcombustion zone of about 500 to 150°C, the distribution of the higher chlorinated PCDDs are increased, and that of the lower chlorinated PCDFs are decreased. The PCDF/PCDD ratio is 6.5, 3.2 and 2.7 at boiler 2nd pass, boiler outlet and baghouse inlet, respectively (average values of six experimental runs).

The congener pattern is defined as the amount of 2,3,7,8-substituted isomers devided by the corresponding homologue total. The PCA of the congener patterns

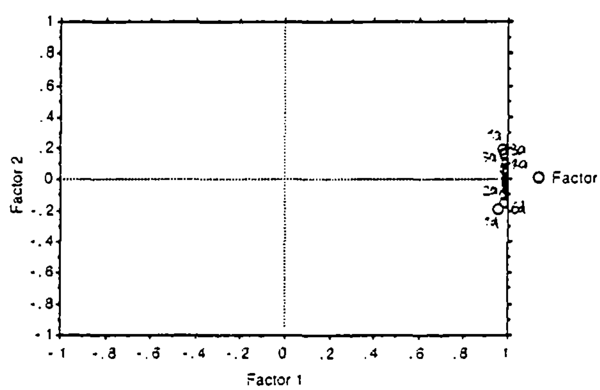


Fig. 3 Principal component analysis of 2,3,7,8-substituted congener pattern of PCDD/Fs at different sampling positions of the MSWI plant. All data points are overlapped at (1,0) except those shown.

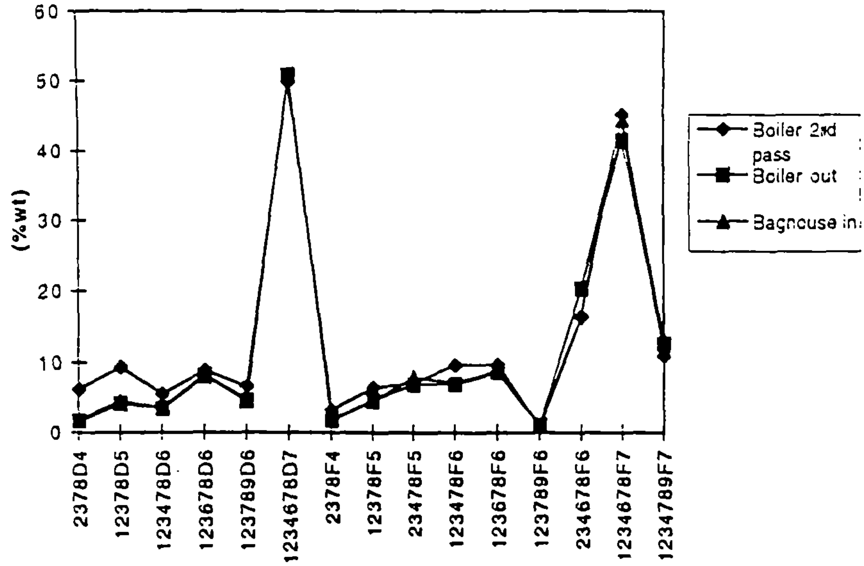


Fig. 4 The 2,3,7,8-substituted congener pattern of PCDD/Fs at the MSWI plant

is shown in Fig. 3. The first principal component accounts for 99.1% of the variance of the congener pattern data and the second accounts for 0.9% of the variance. Fig. 3 suggests that the congener patterns at all positions are nearly constant; Fig. 4 gives the average values for each sampling position.

The very stable congener pattern of PCDD/Fs throughout the postfurnace region may be explained by thermodynamic control of the isomeric distribution of PCDD/Fs. As to the PCDF/PCDD ratio, it is known that the solid carbon precursor pathway leads to PCDF/PCDD > 1, but the organic precursor condensation pathway produces only PCDDs. Thus the measurement data of PCDF/PCDD > 1 at all sampling positions from 500 to 150°C indicate that overall the solid carbon precursor pathway is likely to be more important than the organic precursor condensation pathway for this MSWI plant.

Conclusion

Measurements in a modern twin-interchanging fluidized-bed incinerator have shown that the PCDD/F stack emissions are below 0.1 ng-TE/Nm^3. Detailed study of the data revealed that in the postfurnace zone the 2,3,7,8-substituted congener pattern remain nearly constant, but the homologue profile exhibit certain changes. The amount of PCDF is larger than PCDD at all sampling positions indicating that the PCDD/Fs are probably mainly from solid carbon precursors in fly ashes.

Literature Cited

(1) Ishikawa, R.; Buekens, A.; Huang, H; Watanabe K. *Chemosphere*, in press.
(2) Fangmark, I.; van Bavel, B.; Marklund, S.; Stromberg, B.; Berge, N.; Rappe, C. *Environ. Sci. Technol.* **1993**, 27, 1602-1610.
(3) Ruuskanen, J.; Vartiainien, T.; Kojo, I.; Mannien, H.; Oksanen, J.; Frankenhaeuser, M. *Chemosphere*, **1994**, 28, 1989-1999