CORRELATIONS BETWEEN PCDD/F HOMOLOGUE CONCENTRATIONS AND TEQ VALUES IN LABORATORY-, BOILER-, AND PRACTICAL-SCALE INCINERATORS

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Introduction

Recent proposed formation mechanisms of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and measured data from practical-scale incineration have enabled researchers to make statistical analyses and correlations which can further contribute to control or prevention of PCDD/F formation[1-12]. One of the most remarkable findings reported by several different research groups is a linear correlation between the 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-P5CDF) concentration and toxic equivalent (TEQ) values[6, 9, 11] obtained from more than 100 municipal waste incinerators (MWIs). Another important correlation was found between the total tetra- to octa- PCDD/Fs and the conventional International TEQ (I-TEQ) values from more than 150 incineration facilities[11]. However, the theoretical basis for these observed correlations is still unknown.

Iino et al.[13, 14] proposed a PCDD/F isomer pattern prediction model (termed "IIG") based on the N-1 chlorinated species isomer patterns (N = the number of chlorine atoms of the fully chlorinated species). This model also implies that each of the 17 toxic congeners has a constant relative concentration to its respective total homologue concentration. In this paper, we attempted to validate the model by comparing the measured TEQ values with the predicted TEQ values calculated from the measured homologue concentrations. The data used for this validation were collected from a laboratory-scale reactor[15, 16], a commercial package boiler[17], and operating MWIs in Japan[9].

Methods

The prediction equations of PCDFs and PCDDs are described elsewhere[13, 14]. The equations were corrected to allow the coefficients of the prediction equations to adequately represent an inversed symmetry number of each isomer[15]. Based on the prediction equations, the TEQ

prediction equations from homologue concentrations can be described as:

$$TEQ(PCDFs)_{IIG} = 0.0001 \times H_8 + 0.01 \times \frac{a+d}{T_7} \times H_7 + 0.1 \times \frac{a^2+4ad+d^2}{2T_6} \times H_6 + (0.05 \times \frac{ad^2}{T_5} + 0.5 \times \frac{a^2d}{T_5}) \times H_5 + 0.1 \times \frac{a^2d^2}{2T_4} \times H_4 \quad (1)$$

$$TEQ(PCDDs)_{IIG} = 0.0001 \times H_8 + 0.01 \times \frac{a}{T_7} + 0.1 \times \frac{3a^2}{2T_6} \times H_6 + 1 \times \frac{a^3}{T_5} \times H_5 + 1 \times \frac{a^4}{4T_4} \times H_4 \quad (2)$$

where Hj is the measured concentration of homologue j (number of chlorine atoms = j), and Tj is the sum of the predicted isomer values in homologue j of PCDD and PCDF. The values of **a**, **b**, **c**, and **d** for equation (1) are 0.630, 0.166, 0.129, and 0.075, and the values of **a** and **b** for equation (2) are 0.468 and 0.532, respectively. These values were obtained from one or two typical stoker-type MWI isomer patterns of heptachlorodibenzofuran (H7CDF) and heptachlorodibenzo-*p*-dioxin (H7CDD) isomer patterns[13, 14].

This current work includes 124 data points from the laboratory-scale reactor, 61 data points from the commercial package boiler, and 114 data points from the MWIs. The data from the laboratory-scale reactor were collected from experiments with combinations of non-flame or premixed flame conditions and as-received (AR), oxidized (OX) , or extracted (EX) fly ash samples. The OX fly ash was prepared by treating AR fly ash in flowing air at 500 °C for 24 h, and the EX fly ash was prepared by extracting AR fly ash with toluene over 48 h, followed by heating to 500 °C in a nitrogen (N_2) atmosphere for 24 h. Details of the experimental conditions are described elsewhere[16, 17]. The emissions and deposited solids from the 732 kW North American Package Boiler were sampled while burning #2 oil or natural gas with 2,4-dichlorophenol/copper naphthenate, 1,2-dichlorobenzene/copper naphthenate, or no dopants. The two chlorinated chemicals were doped to simulate co-firing hazardous materials[18]. In order to obtain data from operating MWIs, emission gas samples before and after fly ash collectors and stack gas samples were taken from more than 30 MWI facilities in Japan. Some of the facilities have several incinerators.

Results and Discussion

The correlation plots of PCDF TEQ values from the prediction by equation (2) and the measurement are shown in Figs. 1 – 3. The data are sampled from the laboratory-scale reactor, the package boiler, and the MWIs in Japan, respectively. The trend lines obtained by the least square method are also shown on each plot. Regardless of the three scales and types of equipment, the different temperature profiles, and the various chemical and physical properties of the starting materials, all the plots of PCDFs showed highly linear correlations. The fact that the trend line is linear means that the TEQ values of the samples are proportional to the homologue

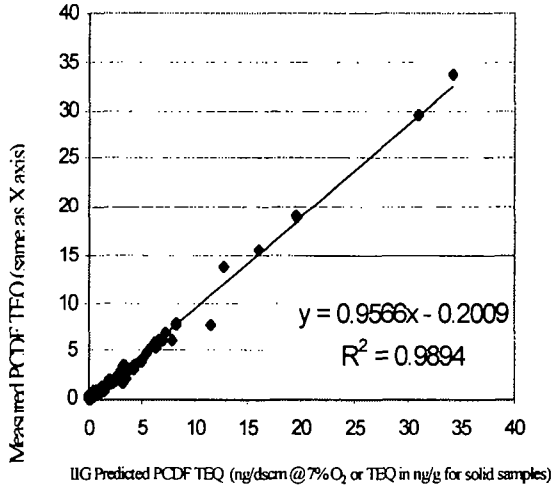

Figure 1 Predicted and measured PCDF TEQ from laboratory-scale reactor

concentrations, which was pointed out b

ato[11] with data from the field scale of incineration. A perfect prediction of TEQ values from homologue values would provide the trend line of y = x. The data from the MWIs in Fig.3 resulted in a slope of 0.85, but the fitting line still indicates a reasonable correlation (R^2>0.99).

The plots of PCDD TEQ values obtained by equation (2) were also investigated from the laboratory-scale reactor, the package boiler, and the MWIs in Japan. The plots from the laboratory-scale reactor and the MWIs showed scattered points within a range, and didn't make any significant correlations. A better relation was found from the package boiler, probably because of the limited species of the dopants (2,4-dichlorophenol/copper naphthenate or 1,2-dichlorobenzene/copper naphthenate). These plots of the PCDD TEQ correlation imply that PCDD formation is more subject to reaction condition than PCDF formation. Hence, the variability in experimental conditions has a greater effect on PCDD homologues and the 17 toxic congeners than with PCDFs.

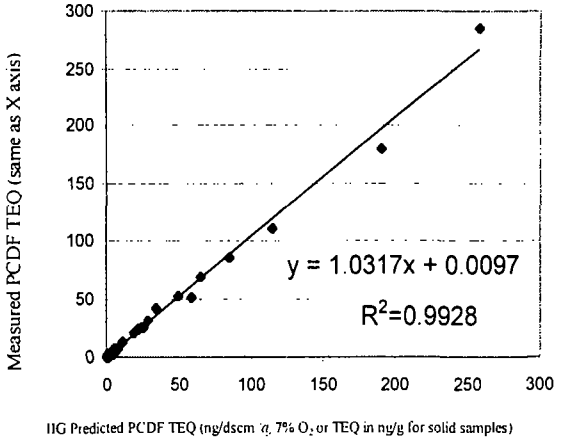

Figure 2 Predicted and measured PCDF TEQ from package boiler

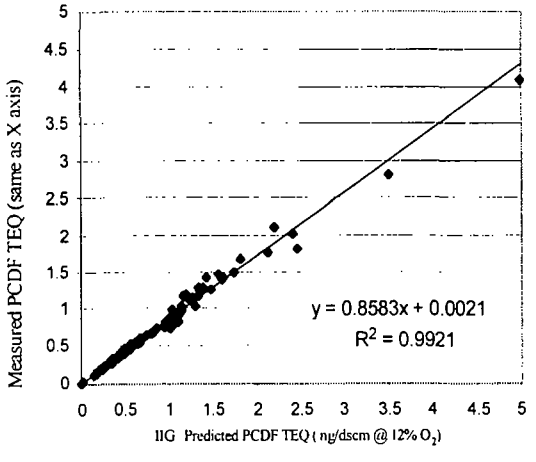

Figure 3 Predicted and measured PCDF TEQ from MWIs

Although it is still uncertain whether dechlorination is a controlling reaction for PCDF formation[13, 14], this model is capable of predicting PCDF TEQ values from the measured homologue concentrations. It can be also concluded that PCDF TEQ values are proportional to the homologue concentrations, whereas the PCDD TEQ values are not.

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