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Correlation between PCDD/F, PCB and PCBz in coal/waste combustion. Influence of various inhibitors

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Abstract

In the flue gas of co-combustion of solid waste and coal in a laboratory scale furnace high concentrations of polychlorinated dibenzo-*p*-dioxin and furans (PCDD/F), polychlorinated biphenyls (PCB) and polychlorinated benzenes (PCBz) have been detected. These toxic emissions have been reduced by the help of various inhibitors added to fuel before incineration. Knowledge of the congener pattern and homologue profiles of PCDD/F, PCB and PCBz is important to elaborate the mechanism of formation and inhibition of the toxic compounds formed during co-combustion of solid waste and coal. Principle component analysis (PCA) is used in order to find the similarity between the samples and separate them according their toxicity. By the help of the component analysis (CA) the best correlated congeners are effectively detected. Using linear regression between the independent variables and the indicator parameters various good correlated pairs between PCDD/F, PCB and PCBz have been elaborated. Generally it was found that the samples with higher toxicity show a good correlation between tetra- and pentachlorinated benzenes and tetra- and pentachlorinated dibenzo-*p*-furans. The best indicator parameter for PCDD/F World Health Organization toxic equivalent (WHO-TEQ) among the PCBz congeners investigated is 1,2,4,5-TCBz. This isomer is also significantly correlated with PCDD/F WHO-TEQ and with the sum of PCDD/F WHO-TEQ and PCB WHO-TEQ. However for samples with higher percentage of inhibitors the above mentioned relationship between the surrogate and WHO-TEQ disappeared. The PCB homologues and congeners show no correlation with PCBz and PCDD/F homologues and congeners.

Keywords: PCDD/F; PCB; Chlorobenzenes; PCA; CA; Indicator parameter

1. Introduction

Routine measurements of PCDD/Fs in the effluent of incinerators are difficult and expensive. As a consequence, there is growing tendency to find surrogates of PCDD/Fs. In particular chlorobenzenes have attracted much attention because of their good correlation with PCDD/F international toxic equivalent (I-TE) value (Öberg and Bergström, 1985; Oehme et al., 1987; Kaune et al., 1994, 1998; Blumenstock et al., 1999, 2001; Zimmermann et al., 1999). The first relationship of PCDD/F on chlorobenzenes in emissions has been reported by Oehme et al. (1987) using linear regression techniques. To improve the accuracy of the prediction, multiple regression (Öberg and Bergström, 1989) and

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partial least square (PLS) (Manninen et al., 1996) was used. Multiple regression may improve the accuracy of estimating PCDD/F and I-TE values from indicator parameters but has the disadvantages that many parameters rather than a single one have to be measured. Thus, these methods do not take full advantages of the indicator parameter concept. Statistical analysis of the results is useful, if performed in order to determine whether relationship exist between the investigated compounds (Manninen et al., 1996; Blumenstock et al., 2000; Gullett and Wikström, 2000).

PCBz is present in incinerator emissions at much higher concentrations than PCDD/F (Fängmark et al., 1993). Among the PCBz, either pentachlorobenzene or hexachlorobenzene (Kaune et al., 1994) are the dominating congeners in full scale incinerators stack gas. I-TE and PCDD/F concentrations are most accurately predicted from the concentrations of pentachlorobenzene (Kaune et al., 1994). However Öberg proposed hexachlorobenzene as an indicator of dioxin production (Öberg and Bergström, 1985). Some lower chlorinated PCDD, PCDF and PCBz were identified as surrogate for the emission of the toxicity carried by the PCDD/F in the flue gas at hazardous waste incinerator (HWI) plants (Blumenstock et al., 2001). The most promising candidates for an easily accessible compound group of I-TE surrogates at the HWI plant are chlorinated benzenes. 2,3,7,8-Tetrachlorodibenzodioxin was closely correlated with the concentrations of pentachlorophenol, pentachlorobenzene and hexachlorobenzene in the flue gas of three waste incinerators (Kaune et al., 1998). The proposed correlation is valid for all sampling points of the waste incinerators including the dry electrostatic precipitator (ESP) and wet scrubber where the I-TE values are much lower. Furthermore it was found that all isomers of PCBz, which are good surrogates for the emissions of the I-TE in the flue gas, show similar correlation coefficient values also in the stack gas (Blumenstock et al., 1999).

The correlation between PCDD/F and PCB is not so widely investigated as other indicator parameters such as PCBz and polychlorinated phenols (PCPh). On the other site the correlation between the PCB and PCDD/F is important in order to understand the mechanisms of PCDD/F formation. It is already known that PCB molecules are also precursors of PCDD/F formation (Lenoir et al., 1998; Tuppurainen et al., 1998). Investigations at hazardous waste incinerators from (Kaune et al., 1994) for example, pointed out that some PCBs are good indicators for I-TE values. Using principal component analysis Fängmark et al. (1993) reported a positive correlation among PCDD/F and the three planar PCB analysed. However Blumenstock suggested that the formation of PCB seems to be different from the other chlorinated aromatics, which may be hind of different formation mechanisms of PCDD/F and PCB.

The present study is based on statistical analysis like principle component analysis (PCA) and correspondent analysis (CA) and focused on linear regression equations between different PCDD, PCDF, PCB and PCBz values. Furthermore, the influence of different inhibitors on these correlations is studied.

2. Materials and methods

2.1. Combustion samples

A mixture of lignite coal, solid waste and PVC was thermally treated in a laboratory-scale furnace at 400 °C. The total amounts of PCDD, PCDF, PCB, and PCBz generated during experiments were substantial enough to investigate the effect of inhibition (Pandelova et al., 2005). Three different additives namely $(NH_4)_2SO_4$, $(NH_4)_2S_2O_3$ and $(NH_2)_2CO + S$ (1:1) used at level of 10% could suppress the PCDD/F, PCB and PCBz emission to an extended of more than 95–99%. Therefore, further experiments were performed in which these substances constituted a lower fraction of the fuel. Experiments wherein $(NH_4)_2SO_4$ and $(NH_4)_2S_2O_3$ were studied at 5%, 3% and 1% of the total fuel weight were performed in triplicate and $(NH_2)_2CO + S$ (1:1) studied at 3% and 1% of the total fuel weight. One sample of 5% $(NH_4)_2S_2O_3$ added to the fuel was excluded in this serial of investigations. Totally 21 samples including one sample combusted without inhibitor and 20 other samples treated with different percentage of inhibitors was used in this investigation (Table 1). It was found that with decreasing percentage of inhibitor the effect is correspondently reduced.

2.2. PCDD, PCDF, PCB and PCBz data set

Once the experiment of thermal treatment was completed, the sample was processed by further specific clean-up steps. Quantification of PCDD/F, PCB and PCBz was performed on a high-resolution gas chromatograph coupled with a high-resolution mass spectrometer (HRGC/HRMS). The tetra- to octachloro-PCDD and PCDF, the tetra- to hepta-PCB and the tetra- to hexa-PCBz congeners were identified and quantified in pg/g combusted material (Schramm et al., 1995; Henkelmann et al., 1996).

Here 17 PCDD/PCDF congeners and 12 PCB are included in the WHO-TEQ (WHO, 1998). Table 2 presents the sum and WHO-TEQ of different chlorinated levels of homologues of PCDD, PCDF and PCB. The concentration of the three tetrachloro-PCBz congeners and the single sum amount of PeCBz, and HxCBz together with the sum of the tetra- to hexa-PCBz were also included in this study. Furthermore the total toxicity including the WHO-TEQ values of PCDD/F and PCB