Estimating Toxicity Equivalents in the Stack Gas of a Hazardous Waste Incinerator From the Concentrations of Chlorinated Benzenes and Biphenyls

Kaune, A.[A], Lenoir, D.[B], Nikolai, U.[C]
[A] GSF-Forschungszentrum für Umwelt und Gesundheit GmbH, Projektgruppe Umweltgefährdungspotentiale von Chemikalien, Postfach 11 29, D–85758 Oberschleißheim, Germany
[B] GSF-Forschungszentrum für Umwelt und Gesundheit GmbH, Institut für Ökologische Chemie, Postfach 11 29, D–85758 Oberschleißheim, Germany
[C] Gesellschaft zur Entsorgung von Sondermüll in Bayern, Winzererstraße 47d, D–80797 München, Germany

Abstract

We investigated the relationships between concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), chlorobenzenes, chlorophenols, polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) measured in the stack gas of a hazardous waste incinerator. Toxicity equivalents (I-TE) were calculated according to the international toxicity equivalency factor scheme. I-TE values correlated significantly with chlorobenzenes and PCB concentrations. We therefore propose to utilize these classes of compounds as indicator parameters from which I-TE values can be estimated. The most accurate estimates were made using pentachlorobenzene (Cl_5Bz) or heptachlorobiphenyl (Cl_7B).

Introduction

Öberg and Bergström[1] proposed to estimate PCDD/F concentrations in exhaust gases of waste incinerators from the concentrations of other chloroaromatics which can be analyzed more rapidly and with lower costs. The most promising indicator parameters for PCDD/F were chlorinated benzenes and phenols. Relationships between these compounds and PCDD/F have also been reported by Oehme et al.[2] and Sandström[3] using linear regression techniques. Besides this method, multiple regression and partial least squares regression (PLS) were used[4,5,6]. These methods may improve the accuracy of estimating PCDD/F and I-TE values from indicator parameters, but have the disadvantage that many substances (at least two in the case of a multiple regression) rather than a single one have to be measured. Thus, these methods do not take full advantage of the indicator parameter concept. In the present paper we therefore focus on linear regression equations to study the dependence of I-TE on indicator parameter concentrations. However, the results of linear regressions will be compared to those of a multiple regression using two independent variables.

Materials and Methods

The hazardous waste incinerator investigated consists of two rotary kilns which are operated at a temperature of about 1000 °C. The flue gas is heated to 1200 °C in a post combustion chamber, then passes an energy recovery boiler and enters the flue gas cleaning system with a temperature of about 300 °C. The air pollution control device consists of a two-stage electrostatic precipitator, a two-stage wet scrubber, a condensing system and a wet electrostatic precipitator. Sampling and analyses were performed by the Gesellschaft für Arbeitsplatz- und Umweltanalytik (Münster, Germany) according to methods previously described[7]. Besides PCDD/F, the following substances were analyzed: tri- to decachlorobiphenyl (Cl_3B to $Cl_{10}B$), six PCB and seven chlorophenols congeners, penta- and hexachlorobenzene, CO, O_2, and 16 polycyclic aromatic hydrocarbons. Concentration values were expressed in ng per m^3 of dry air under standard conditions at 11 % O_2. Values below the detection limit were treated as missing.

Results and Discussion

International toxicity equivalents (I-TE) in the stack gas of the incinerator ranged from 63.83 to 0.74 ng/m^3 and decreased in the period from September 1988 to June 1991 in which 19 measurements were performed. The decrease of the I-TE values was due to improvements in the feeding of the waste which minimized incomplete combustion. A further reduction of I-TE levels was achieved by adding active carbon to the second stage of the wet scrubber and removing fly ash and active carbon particles, to which PCDD/F were adsorbed, from the circulating washing water. In the regression analyses, I-TE values were chosen as the dependent variable because the emission limit set forth by the 17th Ordinance of the German Federal Law on Ambient Air Quality (17th BImSchV) is expressed on the basis of the international toxicity equivalents. However, if the correlation between I-TE and one of the potential indicator parameters was statistically significant the same was true for many PCDD/F congeners and homologues used as dependent variables. On the 0.0001 level of significance, I-TE correlated with Cl_5Bz (Figure 1), hexachlorobenzene, the sum of penta- + hexachlorobenzene, and penta- to decachlorobiphenyl (Cl_7B: Figure 2). I-TE did not correlate significantly with 2,4,4'-Cl_3B because this isomer was detected in 2 samples only. The distributions of 3 PCB congeners (2,2',4,5,5'-Cl_5B, 2,2',4,4',5,5'-Cl_6B, and 2,2',3,4,4',5'-Cl_6B) were not normal and hence did not allow Pearson's correlation coefficients to be calculated, but Spearman's rank correlation coefficients were significant ($P < 0.01$). 2,2',5,5'-Cl_4B and 2,2',3,4,4',5,5'-Cl_7B did not correlate significantly with I-TE although the normality assumption held true ($P > 0.10$) and there were 6 and 9 data above the detection limit, respectively. On the 0.05 level of significance, I-TE correlated with pentachlorophenol (PCP) and with incinerator operating parameters (CO, O_2). I-TE values decreased with increasing O_2 concentrations. All substances not mentioned above but listed in the experimental section did not reveal any relationship to I-TE. The lack of relation between I-TE and tri- and tetrachlorophenols and the relatively weak relation between I-TE and PCP confirms results by Öberg and Bergström[4] indicating that the estimation of PCDD/F congener and homologue concentrations from the concentrations of chlorobenzenes is much more accurate than the estimation from chlorophenols levels.

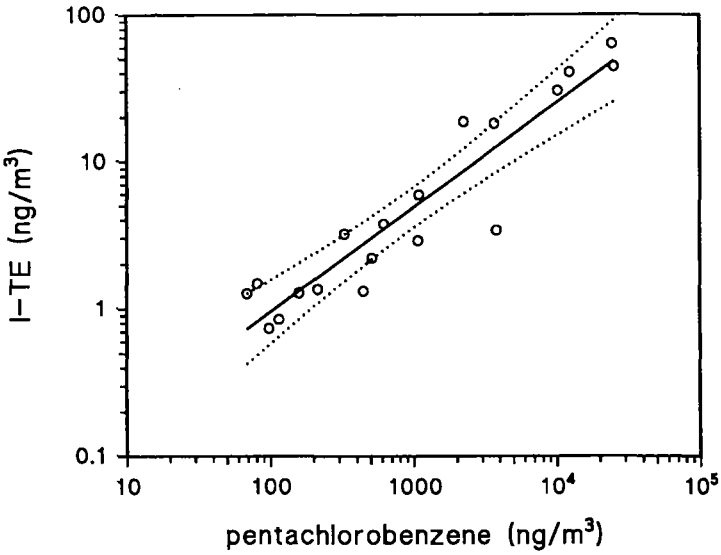

Figure 1. Regression of I-TE versus pentachlorobenzene in the stack gas of a hazardous waste incinerator. The dotted line represents the 95 % level of confidence.

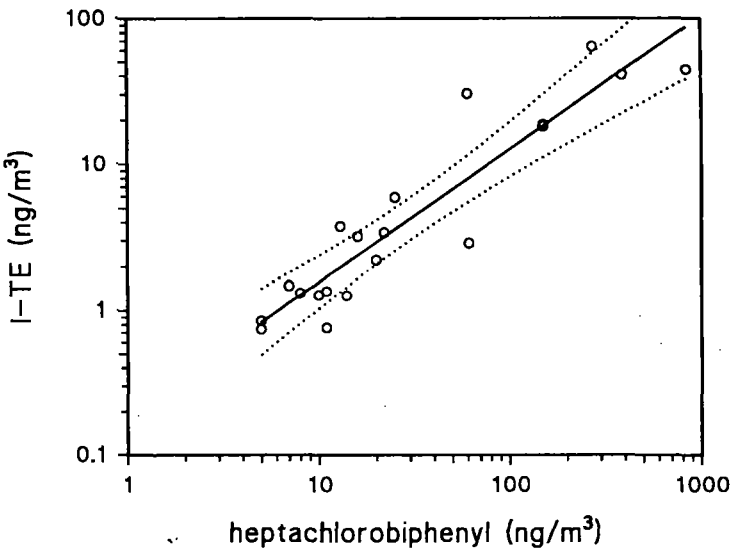

Figure 2. Regression of I-TE versus heptachlorobiphenyl in the stack gas of a hazardous waste incinerator. The dotted line represents the 95 % level of confidence.

The best multiple correlation using I-TE as dependent variable and two independent variables included Cl_5Bz and Cl_7B. The regression equation was:

$$\log \text{I-TE} = -1.17 + 0.395 \log Cl_5Bz + 0.443 \log Cl_7B. \quad \text{(Eq. 1)}$$

The two independent variables were those with the highest correlation coefficients and were highly intercorrelated (R = 0.90, P < 0.0001). It can therefore not be assumed that the inclusion of Cl_7B into the regression of I-TE versus Cl_5Bz will add

any significant information. This is reflected by the correlation coefficient which increased only slightly from 0.939 for I-TE versus Cl_5Bz and 0.933 for I-TE versus Cl_7B to 0.961 for the multiple regression (equation 1). The same increase was observed for R adjusted for the degrees of freedom (R_{adj}). R_{adj} was 0.935 for I-TE versus Cl_5Bz and 0.930 for I-TE versus Cl_7B compared to 0.957 for the multiple regression. Plotting predicted versus measured I-TE values (Figure 3) also reveals that the prediction using the multiple regression equation is only slightly better than that using the linear regression equation. As a consequence, utilizing a multiple rather than a linear regression equation does not seem necessary.

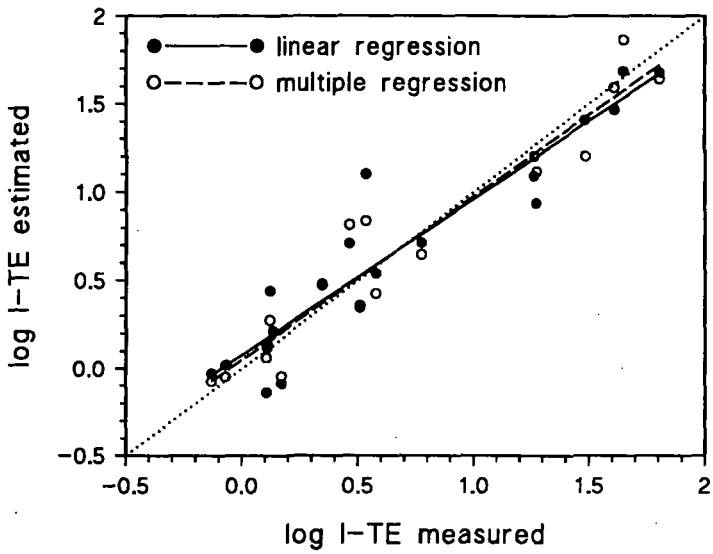

Figure 3. Comparison of measured I-TE values with those estimated from the concentration of Cl_5Bz and of Cl_5Bz + Cl_7B using equation 1. I-TE values were expressed in ng/m^3.

REFERENCES

1 Öberg T, Bergström J. Hexachlorobenzene as an indicator of dioxin production from combustion. *Chemosphere* 1985; 14: 1081–1086.
2 Oehme M, Manø S, Mikalsen A. Formation and presence of polyhalogenated and polycyclic compounds in the emissions of small and large scale municipal waste incinerators. *Chemosphere* 1987; 16: 143–153.
3 Sandström G. Adjusting the operation conditions of waste incinerators for minimized dioxin formation by "in-line" monitoring of chlorobenzenes and chlorophenols. *Organohalogen Compounds* 1990; 3: 151–156.
4 Öberg T, Bergström J. Emission and chlorination pattern of PCDD/F predicted from indicator parameters. *Chemosphere* 1987; 16: 1221–1230.
5 Öberg T, Bergström J. Indicator parameters for PCDD/F. *Chemosphere* 1989; 19: 337–344.
6 Öberg T, Bergström J. Indicator parameters for PCDD/PCDF – Plant specific models. *Organohalogen Compounds* 1992; 8: 197–200.
7 Funcke W. Emissionsmessungen von mittel- und schwerflüchtigen organischen Substanzen. *VDI-Berichte* 1990; 838: 345–370.