Estimating I-TEQ emissions of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) from lower chlorinated PCDD/F and benzenes (PCBz) at a hazardous waste incinerator (HWI)

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Introduction

Recently interest was focused on measuring trace pollutants in the flue gas of waste burning processes to estimate I-TEQ emissions of PCDD/F from related compounds. It is known, that hexachlorobenzene is a good indicator parameter for the total TCDD/F emission at waste incinerators (1). Pentachlorobenzene and tetrachlorobenzene were identified by Kaune et al. as substances, which strongly correlated with the I-TEQ values at several waste incineration plants and different sampling points in these plants (2). Lower chlorinated benzenes (mono- to dichloro) could, if they were present in the ppb range of the flue gas, also measured on-line in the flue gas with REMPI-TOFMS (Resonance-enhanced Multiphoton Ionization Time-of-flight Mass Spectrometry) (3). But until now no investigations have been performed to show, that there is also a correlation between the lower chlorinated benzenes and the I-TEQ. Thus, the estimation of the I-TEQ via chlorinated benzenes especially the lower chlorinated isomers is essential for applying REMPI-TOFMS.

Flue and stack gas emissions of a hazardous waste incinerator (HWI) were analyzed for mono- to octachlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF) and mono- to hexachlorinated benzenes (PCBz) to obtain information about the relationship of either parameter. In addition, the profiles of the homologue pattern for PCDD/F and isomeric pattern of the PCBz were compared to elucidate the influence of the flue gas cleaning system. Principal component analysis (PCA) was carried out to find a correlation between the I-TEQ and the lower chlorinated PCDD/F homologues or PCBz isomers.

Materials and Methods

The hazardous waste incinerator (HWI) investigated was exactly described elsewhere (4). Sampling point 1 is located in the flue gas in the middle of the heat recovery boiler before the electrostatic precipitator and showed a temperature range from 310 °C up to 380 °C and a flue gas flow rate of 4 m/s up to 12 m/s. Sampling

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point 2 is at the stack and is characterized by much more stable flue gas flow conditions with a temperature of about 70 °C and a flue gas velocity about of 8 m/s. The sampling of the PCDD/F was performed isokinetically.

For sampling PCDD/F two glass cartridges were used: The first one contained quartz glass wool to avoid breakthrough of fine particulate matter to the second one, which contains 50 g of XAD-2. The adsorbent was spiked with a sampling standard mixture containing one $^{13}C_6$ TCDD and one $^{13}C_6$ labelled HexCDD.

PCBz were sampled on thermodesorption quartz glass tubes (6 mm ID) containing Carbotrap C (100 mg) and Carbotrap (220 mg) spiked with an internal standard containig one PCBz labelled $^{13}C_6$ isomer of each degree of chlorination. Behind this tube a second backup tube was placed filled with Carboxen 569 (200 mg). To avoid condensation of water vapour in the tubes, sampling was performed at 70 °C. The thermodesorption tubes were connected to the sampling units for the PCDD/F after the cooling zone of the probe and before the condensing flask. Sampling volumes for PCDD/F were about 2 m^3/h and 20 l/h for the PCBz.

Before the cleanup-procedure the PCDD/F containing cartridges were spiked with a cocktail of $^{13}C_{12}$ labelled PCDD/F. Cleanup for the PCDD/F are described elsewhere (5). For the PCBz samples no cleanup was necessary. PCDD/F were measured with HRGC/HRMS (HP5890/MAT 95). PCBz were desorbed at a thermodesorber (ATD 400) in a kryofocusing trap connected with a HRGC/LRMS equipment (Varian HRGC 3400/its Tracker 40).

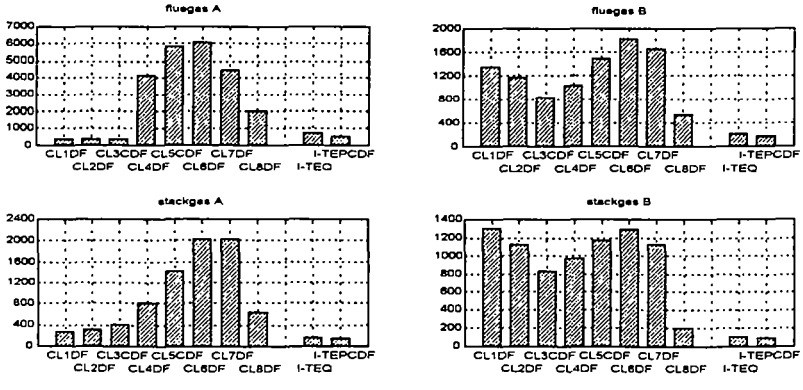
The PCDD/F concentrations of the two PCDD/F cartridges (quartz wool and XAD-2 resign) were added up. All concentrations were calculated at normal conditions: dry air, 273 K, 1013 hPa and 11% O_2 (≡Nm^3).

To reduce the information of the data set and to group the dependent variables, principal component analysis (PCA) was carried out, for further information about PCA see (6).

Results and Discussion

Depending on the grade of chlorination recoveries were between 60% and 100% for both classes of compounds.

To elucidate how the homologue profiles of PCDD/F and PCBz were influenced by the flue gas cleaning system of the plant, two examples (case A and B refer to the figures) are shown in Figure 1 (PCDD/F) and Figure 2 (PCBz isomers).



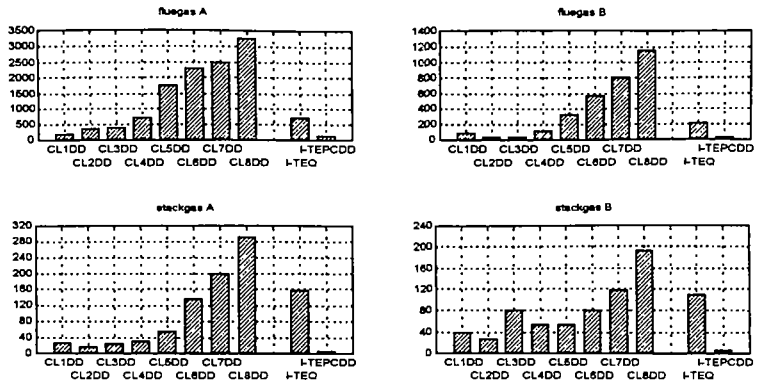


Figure 1: PCDD/F homologue patterns from mono- to octachlorodioxins/furans in the flue gas and stack gas of the HWI in [pg/m^3](I-TEPCDD or I-TEPCDF denote the contribution from the PCDD or PCDF of the total I-TEQ value; samples in the flue/stack gas were taken simultaneously).

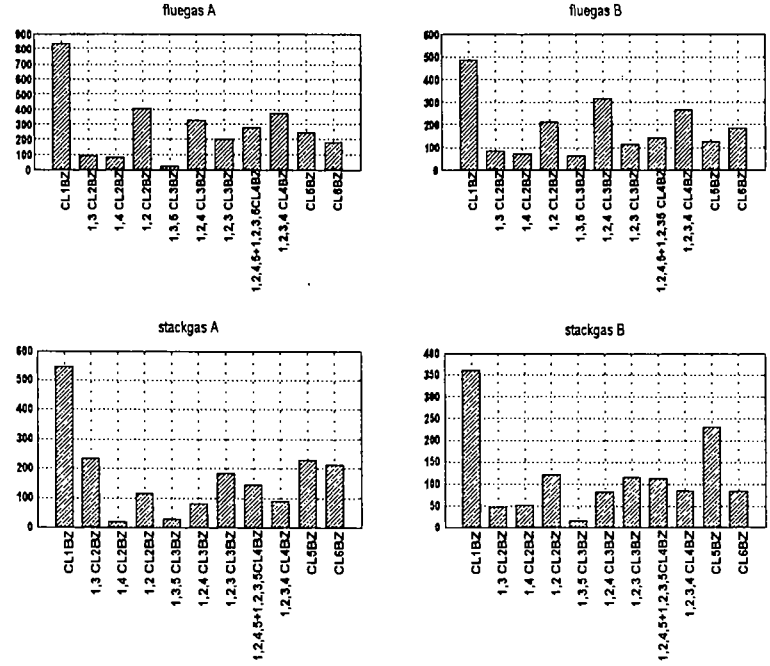


Figure 2: PCBz isomer patterns in the flue gas and stack gas of the HWI in [ng/m^3] (samples in the flue/stack gas were taken simultaneously).

It is very obvious, that the profiles of the different substances are very similar in the stack- and flue gas of the HWI. The homologue pattern (not in the figures) of PCBz is in good agreement with that found by Hunsinger et al. at a waste incineration plant (7). In contrast to that, Ballschmitter et al. described an increasing concentration of the chlorobenzenes with increasing chlorination (8). Till now, the only possible explaination for this contrary results may be the different sampling methods. So it can be suggested, like by Marklund, that the observed patterns of the compounds are a result of a series of formation and degradation reactions (9). Also *it is known, that* PCDD and PCDF do not originate from the same points in an

incineration plant. For HWI investigated it seems, that this does not affect the homologue pattern of PCDD/F and the isomer pattern of the PCBz (10).
The data used for the PCA were taken from the flue- and stack gas (n = 23), because the profiles were very consistant and because for the calculation of the principal components only the correlation matrix is important, not the parameters (regression equation coefficients) as in regression analysis.

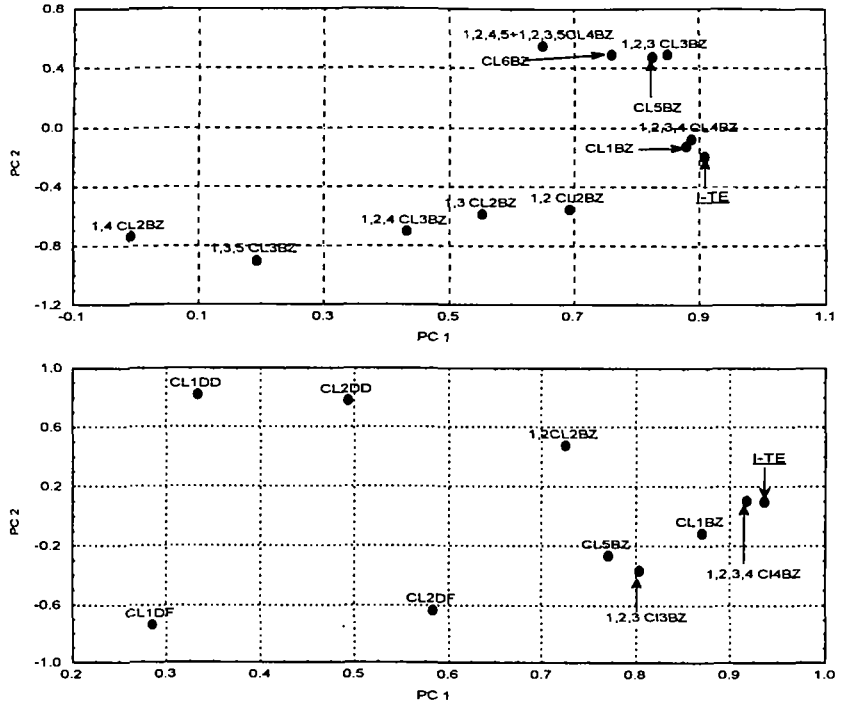


Figure 3: Loading plots of two PCAs with different indicator parameters (e.g. 1,2,3 CL3BZ denotes 1,2,3-trichlorobenzene or 1,2CL2BZ denotes 1,2-dichlorobenzene)

Figure 3 (top) shows a loading plot of the PCA for I-TEQ and chlorobenzene isomers. The second loading plot at the bottom of Figure 3 was derived from PCA, that compares some chlorobenzene isomers with the lower chlorinated PCDD/F (mono- to dichloro) as possible indicator parameters for the I-TEQ. In both PCA the first two principal components can always explain more than 75% of the total variance (PC 1: 50% / PC 2: 25%).
The first PCA in Figure 3 shows, that all chlorobenzene isomers are roughly correlated with the I-TEQ. In this case pentachlorobenzene was still a good indicator parameter as reported by Kaune et al. (11). There are differences between the isomers within a homologue group. For example 1,4-dichlorobenzene (1,4CL2BZ) is much more worse in the correlation with the I-TEQ compared to the 1,2-isomer (1,2CL2BZ), which is much closer to the I-TEQ. Monochlorobenzene seems to be a very sensitive indicator parameter, because it is very close to the I-TEQ. This can perhaps be explained by the high concentration of monochlorobenzene in the flue gas; a variation of the I-TEQ will result in a larger variation at the concentration of monochlorobenzene in comparison with the lower concentrated pentachlorobenzene. So not only the sum of higher chlorinated benzenes like penta- and hexachlorobenzene could be used as indicator parameter for the PCDD/F or I-TEQ emission in the waste incineration process, also lower

chlorinated mono- to trichlorobenzene (12, 13). Surprisingly, the thermodynamic least stable isomers in a homologue group are the most promising indicator parameters. Also Zimmermann et al. (14) reviewed the data of Fängmark et al. (15) for the trichlorobenzene isomers and found out, that 1,2,3-chlorobenzene was the best indicator parameter for the I-TEQ emission. It could be speculated, that this result is an effect of the kinetic control of the PCDD/F formation process, but it is also mentioned by Wehrmeier et al., that the PCDD/F formation is mainly thermodynamically controlled (16).

The second loading plot in Figure 3 shows the results of a PCA in which the sum of the mono- and dichlorodibenzodioxins and -furans, the lower chlorinated „indicator chlorobenzenes" and the I-TEQ were used as variables. It is very clear, that the chlorinated benzenes are better indicator parameters than the lower chlorinated dioxins/furans. As already mentioned above, this could perhaps also be an concentration effect, because the lower chlorinated benzenes are present in the flue gas in a concentration range between 100 and 2000 ppt (v/v) in contrast to the lower chlorinated PCDD/F, which are only present in the range of 20 up to 200 ppq (v/v). So the lower chlorinated PCDD/F were no main products of incomplete combustion like the lower chlorinated benzenes.

For correlation calculation of 1,2-dichlorobenzene only the data from the sampling point in the flue gas were used, because this could be the interesting point in the future to control the combustion process and to minimize both the I-TEQ emission and the cleaning procedure of the flue gas.

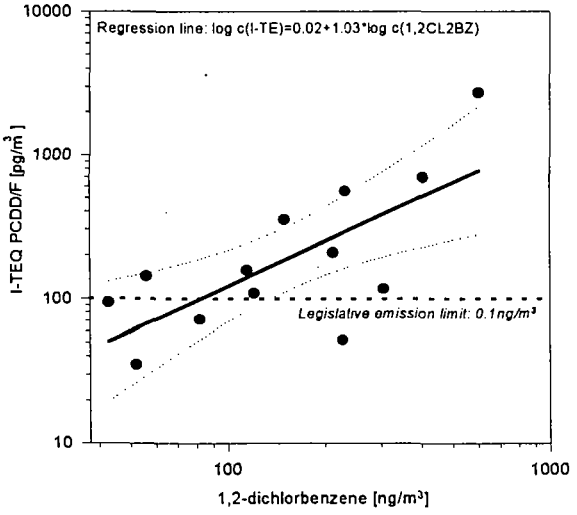


Figure 4: Regression between 1,2-dichlorobenzene and I-TEQ in the **flue gas**

Figure 4 shows the correlation between 1,2-dichlorobenzene and the I-TEQ in the flue gas of the HWI. The correlation coefficient (r^2) for the regression line is about 0,6 (n=13). The relativly high concentrations and the correlation between I-TEQ and 1,2-dichlorobenzene in the flue gas of the HWI plant enables us to use this isomer as on-line indicator parameter for PCDD/F emission control with a REMPI-TOFMS equipment in combustion processes in future.

Conclusions

1. Lower chlorinated (Cl1-Cl3) PCBz are the most abundant chlorobenzene isomers in the flue and the stack gas in the HWI investigated compared to the lower chlorinated (Cl1-Cl2) PCDD/F homologues.
2. The pattern of PCBz and PCDD/F were not effected by the flue gas cleaning system of the plant.
3. 1,2-dichlorobenzene can be an indicator parameter for the I-TEQ emission similar to the higher chlorinated PCBz (Cl5-Cl6). This indicator parameter may be used for on-line measurements.

Acknowledgements

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Literatur

1. Öberg T. and Bergström J.G.T.; *Chemosphere*, **1985**, 14, 1081.
2. Kaune A., Lenoir D., Zimmermann R., Schramm K.-W., Kettrup A., Jaeger K., Rückel H.G. and Frank F.; *Environmental Engineering Process*, **1998**, in press.
3. Zimmermann R., Heger H. J., Kettrup A. and Boesl U.; *Rapid communications in mass spectrometry*, 11, **1997**, 1095.
4. Kaune A., Lenoir D., Nikolai U. and Kettrup A., *Chemosphere*, **1994**, 29, 2083.
5. Schramm K.-W., Merk M., Henkelmann B., and Kettrup A.; *Chemosphere*, **1995**, 30, 2249.
6. Harmann H.; *Modern Factor Analysis*, **1970**, Chicago. London, The University of Chicago Press, 2nd edition.
7. Hunsinger H., Kreisz S. and Vogg H.; *Chemosphere*, **1996**, 32, 109.
8. Ballschmitter K., Braunmiller I., Niemczyk R. and Swerev M.; *Chemosphere*, **1988**, 17, 995.
9. Marklund S., Fängmark I. and Rappe C.; *Chemosphere*, **1992**, 25, 139.
10. Osamu F., Yoji S., Yasuhiro I. and Makato S.; *Organohalogen Compounds*, **1997**, 32, 397.
11. Kaune A., Lenoir D., Nikolai U. and Kettrup A., *Chemosphere*, **1994**, 29, 2083.
12. Oehme M., Mano S., Mikalsen A.; *Chemosphere*, **1987**, 16, 143.
13. Kaune A., K.-W. Schramm; Kettrup A. and Jaeger K.; *Organohalogen Compounds*, **1996**, 27, 163.
14. Zimmermann R., Boesl U., Heger H.-J., Rohwer E.R., Ortner E.K., Schlag W. and Kettrup A.; *Journal of high resolution chromatography*, **1997**, 20, 416.
15. Fängmark I., Bavel v.B., Marklund S., Strömberg B., Berge N. and Rappe C.; *Environmental Science and Technology*, **1993**, 27, 1602.
16. Wehrmeier, A., Lenoir D., Schramm K.-W. and Kettrup A.; *Chemosphere*, **1998**, 36, 2775.