Prediction or detection of I-TEQ emission from PCDD/F congeners, PCBz and process parameters in a WTE plant

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Introduction

The Waste Incineration Directive 2000/76/CE sets legally binding limit values for the emission of polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/F) of 0,1 $ng_{I\text{-}TEQ}/Nm^3$ at 11% O_2 dry gas for WTE (Waste To Energy) plants. In order to check the compliance of PCDD/F emissions, two measurements per year are performed by manual sampling during 6-8 hours and analysis according to the standard EN 1948-1, 2, 3. Presently, there is no on-line monitoring of PCDD/F emissions. Continuous sampling systems of PCDD/F have been implemented. However the report on the results requires time. Moreover those systems provide an average value of PCDD/F emissions. It does not allow continuous monitoring of the process in order to limit PCDD/F emissions. The aim of this study is to identify indicator parameters in order to assess "real time" emission level of PCDD/F. Several types of parameters have been investigated: PCDD/F congeners, polychlorobenzenes (PCBz) and process parameters. PCBz compounds are involved in the PCDD/F formation as precursors. Many works have been carried out to establish the relationship between PCDD/F and PCBz (1) (2). The indirect continuous measurement of the indicators may improve the knowledge on PCDD/F formation as well as the control and the optimisation of the process.

Materials and methods

Several tests have been performed at a Municipal Solid Waste incineration plant in France. Two campaigns have been carried out in 2007 and 2008. The incineration line consists of a furnace, an energy recovery boiler, a spray tower, a sodium bicarbonate and lignite coke injection, a baghouse filter, a low operating temperature Selective Catalytic Reduction (SCR), an ID-fan and a stack. The removal of PCDD/F is achieved by entrained-phase adsorption (Figure 1). SCR provides further PCDD/F removal (>70%) as final treatment.

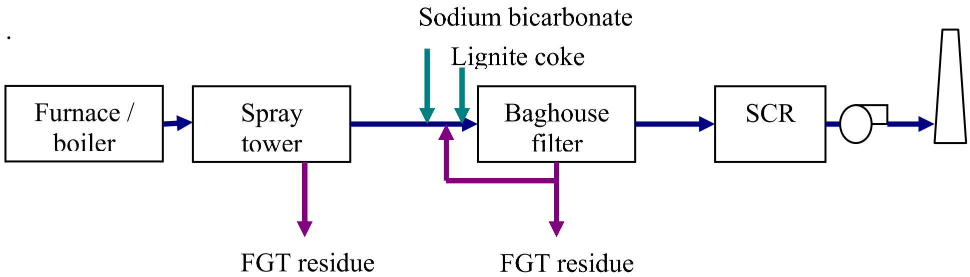

Figure 1 – Schematic diagram of the MSW plant

The present study focused on the dry sorption system which is the most representative of PCDD/F treatment in France. The number of trials have been determined by using a statistical power analysis program (G*power3). We performed 26 trials: 16 trials during normal operations and 10 after a start up. The analytical samples were collected at the boiler outlet and the baghouse filter outlet. Gas is sampled according to the filter/condenser method described in EN 1948-1. A sample period of 3 hours was selected to optimise the number of trials. The quality control was checked (blank field, breakthrough of the sampling train...). The PCDD/F were analysed by high resolution gas chromatography (HRGC)/high resolution mass spectrometry (HRMS) according to EN 1948-2 and -3 standards. The I-TEQ value is the sum of the 17 PCDD/F congeners weighted by the Toxic Equivalent factors (TEF). A fraction of the extracts was used for PCBz analysis (13-DiCBz, 14-DiCBz, 12-DiCBz, 135-TriCBz, 124-TriCBz, 123-TriCBz, 1235-TetraCBz, 1245-TetraCBz, 1234-TetraCBz, PentaCBz, HexaCBz). Those analysis were based on capillary column chromatography coupled with low resolution mass spectrometry (LRMS) using the isotopic dilution method. The results of the measurements were standardised (273 K, 101.3 kPa, 11 % oxygen, dry gas). Process parameters were taken from continuous measurements available at the plant or specific flue gas analyser (Table 1).

Table 1 –Parameters measured at different sampling points

Sampling points	Measured parameters
Boiler outlet	PCDD/F (I-TEQ, 17 congeners, tetra to octachlorinated congener groups), PCBz (11 isomers).
	Combustion parameters: air flow rate, flue gas temperatures (furnace, boiler outlet), flue gas flow rate, oxygen, CO_2, CO, NOx contents.
Bag filter outlet	PCDD/F (I-TEQ, 17 congeners, tetra to octachlorinated congener groups), PCBz (11 isomers).
	Flue Gas Treatment (FGT) parameters: lignite coke flow rate, baghouse filter pressure drop, cleaning cycle of the baghouse filter, face filtration velocity, flue gas temperature, flue gas flow rate, oxygen, CO_2, CO, NOx contents.
Stack	Continuous monitoring parameters: flue gas flow rate, oxygen, CO_2, CO, NOx, TOC, SO_2, HCl contents.

Data sets were established for each sampling point and each group of parameters. An appropriate data treatment was processed for some analytical data below the quantification limit or subjected to interference, in particular for lower chlorinated PCBz.

Statistical analysis was performed by using R software. For each variable the normal distribution was checked by using the Shapiro Wilk test. If the normality assumption did hold on the level of significance ($p<0.05$), the data were considered normally distributed and the Pearson product-moment coefficient (r) was calculated. Otherwise the Spearman's rank correlation coefficient (r_s) was computed (3). Data were also logarithmically transformed to approximate normal distribution. The correlation coefficients and the scatter plot were considered in order to select the parameters well-correlated with the I-TEQ value. The simple regression equations used were $y = b\, x + a$ and $\log y = B \log x + A$ where y and x were respectively the I-TEQ value and the selected parameters. The coefficient of determination R^2 and the level of significance ($p<0.05$) of the intercept and slope coefficients were assessed. If the intercept was not significant, regression equation without intercept was calculated. This type of model could enhance the R^2 level but not necessarily the fitting of the regression line. Furthermore the standardized residuals were analysed such as normal distribution, independence of random residuals etc. Moreover the confidence intervals and the prediction intervals were calculated. Finally, the optimum models were determined by leave-one-out cross-validation due to limited number of trials. The models that presented the lower mean square error were selected.

According to the level of accuracy, the regression equation could be used either to predict the I-TEQ value or to check if the threshold value (s) was exceeded (4). In this case, the probability (Pr) to meet the threshold value was estimated using the standard deviation (σ or σ'), the estimators of the slope and the intercept coefficients as follow:

$$\Pr = P(y \le s) = \Phi\left(\frac{s - bx - a}{\sigma}\right) \text{ or } \Pr = P(\log y \le \log s) = \Phi\left(\frac{\log s - B\log x - A}{\sigma'}\right)$$

For detection purposes, a level of probability (q) was set in order to assess Pr calculation:

- $\Pr \geq q$ means I-TEQ value $\leq s$,
- $\Pr < q$ means I-TEQ value $> s$.

In addition two kinds of error rates were calculated:

- Error type I (false positive): the detection showed that the I-TEQ value was above s whereas the measured I-TEQ value was below.
- Error type II (false negative): the detection showed that the I-TEQ value was under s whereas the measured I-TEQ value was above.

Results and discussion

A significant increase of PCDD/F and PCBz levels has been observed after transiently disturbed operating conditions, in particular after start up phase. The correlations between

PCDD/F congeners and I-TEQ were strong (>0.9). The I-TEQ value could be predicted precisely using 23478-PentaCDF, 123478-HexaCDF, 123678-HexaCDF at all sampling points. At the baghouse filter outlet, additional congeners were identified as indicators: 12378-PentaCDD, 123678-HexaCDD, 1234678-HeptaCDD, 1234678-HeptaCDF. The confidence and prediction intervals showed a good accuracy of estimated values (Figure 2). PCDD/F congeners are good indicators for I-TEQ value prediction, in particular 23478-PentaCDF in agreement with literature (5). Further development is required for on line measurement of individual PCDD/F congener.

The relationship between PCBz and I-TEQ was confirmed but PCBz were less closely correlated (~0.7). The TetraCBz, PentaCBz, sum of PentaCBz and HexaPCBz could be considered as potential indicators at any sampling points (Figure 3).

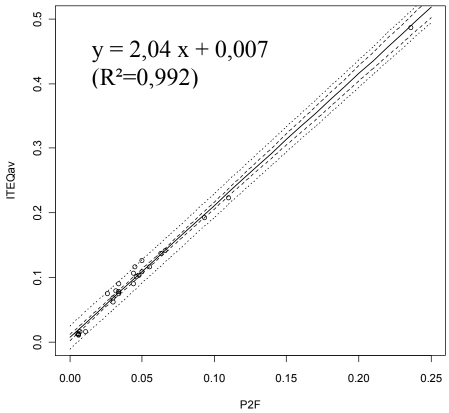

Figure 2 – Regression of I-TEQ versus 23478-PentaCDF both in ng/Nm^3 (at baghouse filter outlet)

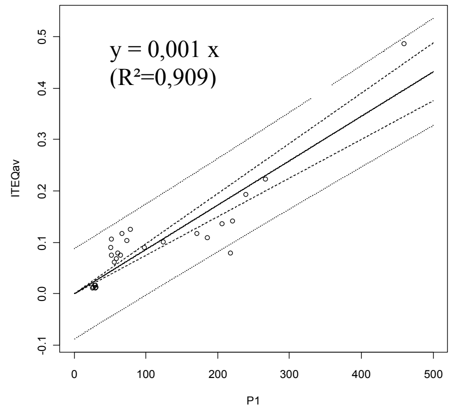

Figure 3 – Regression of I-TEQ versus PentaCBz both in ng/Nm^3 (at baghouse filter outlet)

Other indicators could be identified depending on the sampling point or the logarithmic data transformation (Table 2).

Table 2 – PCBz indicators for I-TEQ values

Boiler outlet	**Baghouse filter outlet**
Sum of TetraCBz, PentaCBz, PentaCBz+HexaCBz	**Sum of TetraCBz, PentaCBz, PentaCBz+HexaCBz,** 123-TriCBz
Data without logarithmic transformation	
1234-TetraCBz, 1235-TetraCBz	**1234-TetraCBz,** HexaCBz
Data with logarithmic transformation	
123-TriCBz, Sum of TriCBz	1235-TetraCBz

Moreover the confidence and the prediction intervals were significantly larger due to limited number of trials and large dispersion between estimated and measured I-TEQ values. The estimation of I-TEQ concentrations from those of PCBz was less accurate compared with PCDD/F congeners. PCBz seemed more appropriate for making detection rather than prediction of I-TEQ emission. For each selected indicator, the probability to have the I-TEQ value below s was assessed. At the baghouse filter outlet, s was set at 0.1 $ng_{I\text{-}TEQ}/Nm^3$. Figure 4 shows the trend of the probability, the estimated I-TEQ values and the measured I-TEQ values for the PentaCBz. The two error rates were also calculated (see Figure 4). The probability level was determined in order to minimise the overall error rates as well as the false negative. This level was of 0.8 - 0.9 corresponding to overall error rates of ~15% (10 – 25%). As a comparison the uncertainty of I-TEQ measurements is of ~20%. PCBz are good indicator for I-TEQ value detection. For practical application, the probability could be derived from the monitoring of those indicators to allow "real-time" detection of exceeding I-TEQ levels. Thanks to this detection, the operating conditions could be checked and adjusted if necessary. Development of continuous measurement of PCBz (e.g. jet resonance-enhanced multiphoton ionization) is under progress (6).

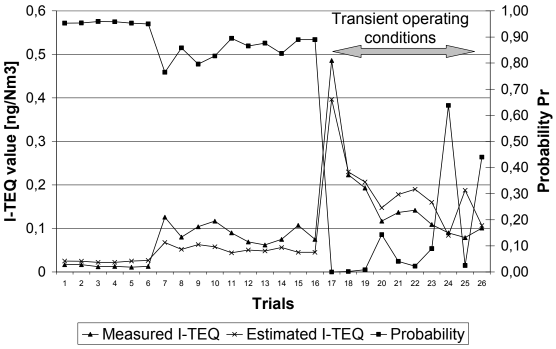

Figure 3 – Detection of the I-TEQ value from the PentaCBz (baghouse filter outlet)

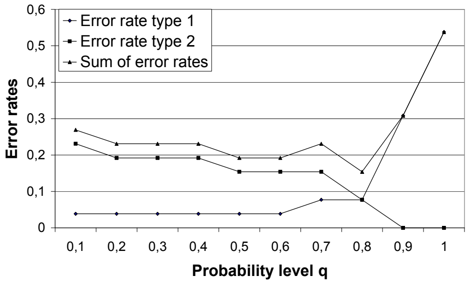

Figure 4 – Error rates versus probability levels from the PentaCBz (baghouse filter outlet)

Few works have been carried out on process parameters as indicators (7) (8). For those parameters, moderate correlations were revealed (0.5 – 0.6). The most correlated parameters were used for linear regression. The face filtration velocity, the cleaning cycle and the flue gas flow rate were selected at the baghouse filter outlet. Concerning boiler outlet, the potential indicators were: flue gas residence time "T2S" (without log transformation), O_2, CO_2 contents, gas flow rate (with log tranformation), O_2 content and gas flow rate at the stack (in any cases). The models did not allow accurate prediction of the I-TEQ value. Following the PCBz, the process parameters could be used for I-TEQ detection. At the baghouse filter outlet, the levels of probability were of 0.5 and 0.7 (respectively for data without and with logarithmic transformation). The corresponding overall error rates were higher compared to PCBz (25%-45%). On the other hand, those parameters are continuously monitored at the plant.

The studied indicators are specific to the plant, the sampling point and the data treatment. They can be implemented for prediction or detection of the I-TEQ emission. In-depth, the knowledge of the dioxin formation and abatement is required to prevent erroneous interpretation (1) (3).

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References

1. Öberg T, Neuer-Etscheidt K, Nordsieck HO, Zimmermann R (2002); *Organohalogen compounds*; 59: 37-44.
2. Lavric ED, Konnov AK, De Ruyck J (2005); *Waste Management ;* 25 : 755 – 765.
3. Kaune A, Lenoir D, Nicolai U, Kettrup A (1994); *Chemosphere;* 29: 2083-2096
4. Kawamoto K, Miyata H, Suyama T (2006); *Organohalogen compounds*; 68: 2260-2263.
5. Fiedler H, Lau C, Eduljee G (2000); *Waste Management & Research*; 18: 283-292.
6. Gullett B, Touati A, Oudejans L, Tabor D (2008); *Organohalogen compounds*; 70: 481-484.
7. Everaert K, Baeyens J (2002); *Chemosphere*; 46: 439-448.
8. Nordsieck HO, Neuer-Etscheidt K, Orasche J, Zimmermann R (2004); *Organohalogen compounds*; 66: 804 - 809.