

PCDDs AND PCDFs EMISSIONS OF WASTE INCINERATORS: FROM MEASUREMENT UNCERTAINTY TO DECISION MAKING

B. Bergmans, F. Idczak, P. Maetz*, C. Nadin, S. Petitjean

Environmental Monitoring Direction, Institut Scientifique de Service Public (ISSeP), rue du Chéra 200, 4000 Liège, Belgium

*Present address: IRCEL/CELINE, 10-11, Avenue des Arts, 1210 Bruxelles, Belgium

INTRODUCTION

In order to check the compliance with the EU emission limit value of 0.1 TEQ ng/Nm³, a continuous sampling network to monitor PCDDs and PCDFs emissions has been implemented on the 11 municipal waste incineration ovens in the Walloon Region of Belgium since the end of 2000. As uncertainty could have an impact on the final judgment of the decision makers, it needs to be involved in the decision making process. Uncertainty estimation shall include both sampling and analytical steps. To this end, the uncertainty was estimated annually over six years using a top-down approach based on replicate measurements¹. Based on this result, a guard band has been calculated and will be proposed to the regulatory body as the bases of the decision rule.

MATERIAL AND METHOD

Description of the Plant

One of the incineration ovens of the Walloon monitoring network is equipped with two separate stacks, each one with its own emission treatment line, but these ones are identical. Both include an activated carbon injection, an acid gas scrubber, a basic scrubber with lime injection and a baghouse filter. Therefore, from this specific furnace, PCDDs and PCDFs can easily be sampled and analysed in duplicate with the same equipments and procedures.

Sampling System

The AMESA[®] system (Environnement SA – Becker Messtechnik), a full automatic one, samples all original phases for PCDDs and PCDFs on XAD-2 cartridges. As isokinetic sampling is maintained, particulate collection remains representative of particles present in the stack flow. The sampling volume is usually between 50 and 200 Nm³ and the sampling period 14 days. A back flush of the probe during long shutdown periods of the plant is used in order to avoid eventual contamination, especially during the drying of the refractory bricks of the oven.

Analytical Procedure

XAD-2 cartridges are spiked with ¹³C PCDDs / PCDFs extract standards and extracted in toluene (24h, large volume Soxhlet extractors). The concentrated extract is subjected to a full automatic (Power Prep^(c)) multistep clean-up (Silica-Alumina-Carbon). All ¹³C spiking levels are adapted to the high sampled volume of flue gas. The final extract (100 µl, in n-nonane) is analysed by HRGC-HRMS, using a MICROMASS Autospec ULTIMA (SIM Mode, RP 10000, 10% Valley) equipped with a HP-Agilent (GC 6890 Series) chromatograph. The 2,3,7,8-congeners are separated by a 60m x 0.25mm x 0.25µm CP-Sil 8 CB Low Bleed/MS CHROMPACK-VARIAN column (5% Phenyl - 95% Dimethylpolysiloxane). The injected volume is 1.5µl (Splitless, EPC Flow Ramp Mode), using a HP-Agilent 7683 Series autosampler. All steps are in compliance with EN 1948.

Uncertainty Evaluation

The uncertainty was calculated following ISO 20988². The formula has been slightly adapted to express the result as a relative value instead of an absolute value.

$$u_{(\%) } = 100 \times \sqrt{\frac{\sum_{i=1}^n \left[\frac{(x_{i,1} - x_{i,2})}{\bar{x}_i} \right]^2}{2 \times n}}$$

u = uncertainty estimation

n = sample size

x_{ij} = jth result of the ith duplicate sampling

\bar{x}_i = mean value of the two replicates

RESULTS

The uncertainties were estimated annually for each congener using the above formula over the last 6 years with a maximum of 26 samples a year (table 1). As the PCDDs / PCDFs concentration of the plant is very low, some results are below the quantification limit of the analytical method. As statistical analysis can only take the quantified results into account the number of results involved in each calculation is varying from 11 to 26, depending on the congener and the year involved. For a sampling period from 2003, a result four times higher was found for one line with respect to the other; these results were considered as abnormal values and were removed. 90% of the annual uncertainty results are lying between 20 and 70%. The uncertainty presents a good stability from one year to another. Except for two congeners, 2378-TCDF and 123789-HxCDD, the dispersion of the results is less or equal to 20% and even below 10% for some compounds (see table 1).

Congener	Uncertainty (%)							Standard deviation
	2002	2003	2004	2005	2006	2007	u mean	
2378-TCDD	22%	47%	35%	43%	42%	30%	39%	9%
2378-TCDF	28%	45%	18%	39%	44%	41%	40%	11%
12378-PeCDD	28%	42%	26%	31%	36%	27%	35%	6%
12378-PeCDF	31%	44%	12%	35%	37%	32%	36%	11%
23478-PeCDF	30%	42%	21%	30%	28%	36%	35%	7%
123478-HxCDD	26%	33%	31%	26%	25%	20%	30%	5%
123678-HxCDD	30%	38%	36%	26%	34%	18%	34%	7%
123789-HxCDD	39%	41%	39%	32%	29%	25%	38%	6%
123478-HxCDF	32%	38%	35%	34%	22%	31%	35%	5%
123678-HxCDF	37%	39%	37%	31%	20%	30%	36%	7%
234678-HxCDF	48%	40%	46%	33%	20%	39%	42%	10%
123789-HxCDF	40%	38%	19%	27%	22%	33%	31%	9%
1234678-HpCDD	36%	39%	53%	32%	27%	34%	41%	9%
1234678-HpCDF	49%	41%	62%	47%	36%	54%	54%	9%
1234789-HpCDF	67%	50%	63%	51%	39%	56%	56%	10%
OCDD	44%	29%	42%	39%	36%	39%	40%	5%
OCDF	71%	57%	68%	59%	51%	68%	65%	8%

Table 1: Uncertainty results

The average fraction of each congener of the plant, calculated on results obtained during the last 6 years and taking the Toxic Equivalent Quantification factor² (TEQ) into account, is presented in table 2. Using uncertainty of each congener, the uncertainty of this annual average could be determined (table 2). This uncertainty value will be used in the decision rule.

Congener	TEQ	Average fraction			u mean %	u contribution %
		pg/Nm ³	pg/Nm ³ TEQ	%		
2378-TCDD	1	1.08	1.08	11%	39%	4%
2378-TCDF	0.1	0.80	0.08	1%	40%	0%
12378-PeCDD	0.5	3.19	1.59	16%	35%	5%
12378-PeCDF	0.05	1.03	0.05	1%	36%	0%
23478-PeCDF	0.5	10.33	5.17	51%	35%	18%
123478-HxCDD	0.1	1.61	0.16	2%	30%	0%
123678-HxCDD	0.1	3.78	0.38	4%	34%	1%
123789-HxCDD	0.1	1.90	0.19	2%	38%	1%
123478-HxCDF	0.1	2.74	0.27	3%	35%	1%
123678-HxCDF	0.1	3.38	0.34	3%	36%	1%
234678-HxCDF	0.1	6.25	0.63	6%	42%	3%
123789-HxCDF	0.1	0.25	0.03	0%	31%	0%
1234678-HpCDD	0.01	7.87	0.08	1%	41%	0%
1234678-HpCDF	0.01	8.93	0.09	1%	54%	0%
1234789-HpCDF	0.01	1.95	0.02	0%	56%	0%
OCDD	0.001	7.01	0.01	0%	40%	0%
OCDF	0.001	5.10	0.01	0%	65%	0%
Tot PCDD/PCDF	-	67.21	10.16	100%	-	36%

Table 2: Annual average fraction of each congener and relative contribution to uncertainty

In order to reduce the risk of false positive, a guard band should be used in the decision making process. Any analytical result above the EU limit (specification zone), but lying in the “guard band zone” will be considered as an acceptable result. Only results lying in the rejection zone will be considered as non-compliant (figure 1). This approach could be considered as more favourable for plant operators, but is necessary to avoid any possible contestation. By following this rule the risk of false positive is reduced to 5%, which could be considered as an acceptable level.

Using a k value of 2.015 (1-sided tail, $\alpha=95\%$, $n=5$) and the uncertainty determined for the annual average concentration, a guard band of $36\% * 2.015 = 73\%$ can be calculated.

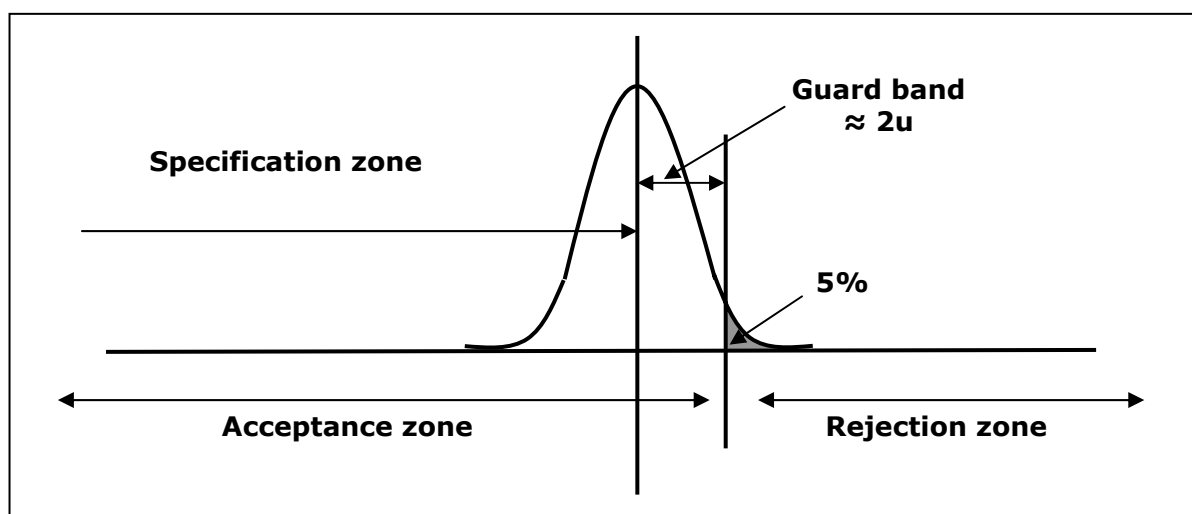


Figure 1: Guard band for decision making

DISCUSSION

For a given compound, a good stability of the uncertainty over the six years considered was observed. This is probably the consequence of a combination of the following points. The assessment is done over one year of results, so really under reproducibility conditions. In addition, the uncertainties are calculated via a top-down approach which is surely including all possible contributions. We would like to stress that this doesn't mean that a top-down approach should be considered a better way than a bottom-up one, as only the latter one permits to identify the main contributions and is therefore necessary if one wants to reduce the uncertainty. In addition, the number of results involved in each calculation is sufficient to obtain a representative assessment.

Therefore, using the calculated uncertainties and the annual average fraction of each congener, one can easily make a good estimate of the uncertainty of the total PCCD/PCDF concentration. This latter result can be used to set up a guard band which could be involved in the decision making process and this tool will be proposed to the regulatory body in Wallonia.

ACKNOWLEDGMENTS

The authors wish to thank A. Galloy and P. Duchateau from ISSeP analytical laboratory for technical help. ISSeP and the authors are also indebted to the Walloon Environment Directorate and the MWI which funds the monitoring network.

REFERENCES

¹ ISO 20988 "Air Quality – Guidelines for estimating measurement uncertainty" (Experimental design A6, Paired measurements) – June 2007.

² Council Directive 2000/76/EC of 4 December 2000 on the incineration of waste.