

## **FIVE YEARS OF CONTINUOUS SAMPLING TO MONITOR PCDDs AND PCDFs EMISSIONS OF WASTE INCINERATORS IN WALLOON REGION OF BELGIUM**

François Idczak<sup>1</sup>, Serge Petitjean<sup>1</sup>, Benjamin Bergmans<sup>1</sup>

1. Environnemental Monitoring Direction, Atmospheric Emissions Departement , Institut Scientifique de Service Public, rue du Chéra 200, 4000 Liège, Belgium

### **Introduction**

Wallonia in Belgium is typically one region where incineration remains needed to cope with waste. EU emission limit value of 0.1 TEQng/m<sup>3</sup> PCDDs/Fs was transposed in the Walloon Environmental law at the end of 2000. Regional authorities chose for extensive compliance control through implementation of an automatic continuous sampling system, for each of the 11 municipal waste incineration ovens of Wallonia<sup>1</sup>. The firm Becker-Messtechnik won the procurement tender with its AMESA<sup>®</sup> equipment<sup>2</sup>. For five years, ISSeP has supervised this equipment and analysed the samples.

### **Methods and Materials**

The AMESA system samples all three original phases for PCDDs/PCDFs on XAD-2 cartridges. Isokinetic sampling is maintained so that particulate collection remains representative of particles present in the stack flow. Relevant physical parameters on oven, stack and sampling system are stored on a memory card. Data are also available from ISSeP with an ordinary phone line.

Main operations are similar to those for the manual method as in the EN 1948 standard. The differences are:

- The position of the probe never changes
- All researched analytes are collected on the XAD-2 resin (instead of on three phases for EN 1948)
- Resin cartridges are larger than those used with the manual method (larger Soxhlet are necessary)
- The sampling duration: 6 to 8 hours according to EN 1948 against 6 hours to 1 month for continuous sampling.

The continuous sampling system has been validated by both German TUV and English MCERTS.

Sampling time used for this control network is 14 days, and the sampling volume approximately 50 to 200 Nm<sup>3</sup>. Results are available 2 weeks after sample collection and are posted on Environment Directorate's web site at the authorities' request<sup>3</sup>.

A backflush of the probe during long shutdown periods of the plant was added in 2002. This system was implemented in order to avoid eventual contamination of the probe especially during the drying of the refractory bricks of the oven.

XAD-2 cartridges are spiked with EN 1948 <sup>13</sup>C PCDDs/Fs extract standards and extracted in toluene (24h, large volume Soxhlet extractors). The concentrated extract is subjected to a full automatic (Power-Prep<sup>®</sup>) multistep clean-up (Silica-Alumina-Carbon), according to EN 1948. All <sup>13</sup>C 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 2378 congeners are separated by a 60m x 0.25mm x 0.25µm Df CP-Sil 8 CB-MS Low Bleed CHROMPACK-VARIAN (5% Phe-95% Me silicon gum) column. The injected volume is 1.5µl (Splitless, EPC Constant Flow Mode), using a HP-Agilent 7683 Series autosampler.

Concentrations calculations are reported in compliance with EN 1948.

## Formation, sources and source inventories

### Results

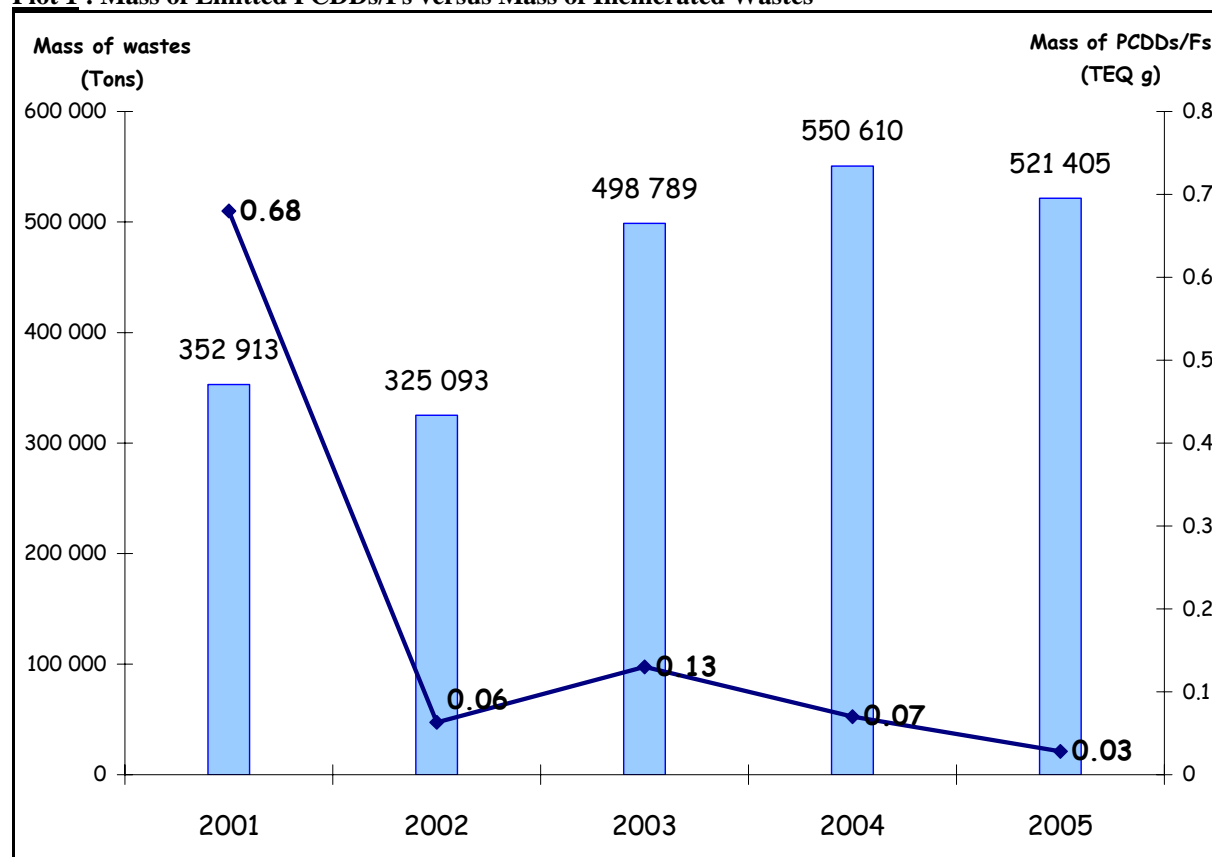
Table 1 shows the evolution of the infringements number during these five years. As shown, this number decreases continuously to reach zero in 2005.

**Table 1 : Results, Infringements and Causes from 2001 till 2005**

Numbers of	2001	2002	2003	2004	2005
Results (cartridges)	227	182	263	268	237
Infringements of Limit Value	31	9	5	5	0
Identified / Unidentified infringements	23 / 8	6 / 3	2 / 3	2 / 3	
Older ovens shut down since then	5				
Damage around filters	7			1	
Broken joint	1			1	
Recurrent difficulties of load feeding on one oven	3	6			
Memory effect of installation after significant infringement	7		1		
Fuel burners start-up after a long break			1		

The mass of emitted dioxins and furanes is compared to the mass of incinerated wastes in plot 1. We can observe that together with the number of infringements, the amount of emitted dioxins has drastically decreased since 2001, in spite of a significant increasing of the amount of burned waste since 2003.

**Plot 1 : Mass of Emitted PCDDs/Fs versus Mass of Incinerated Wastes**

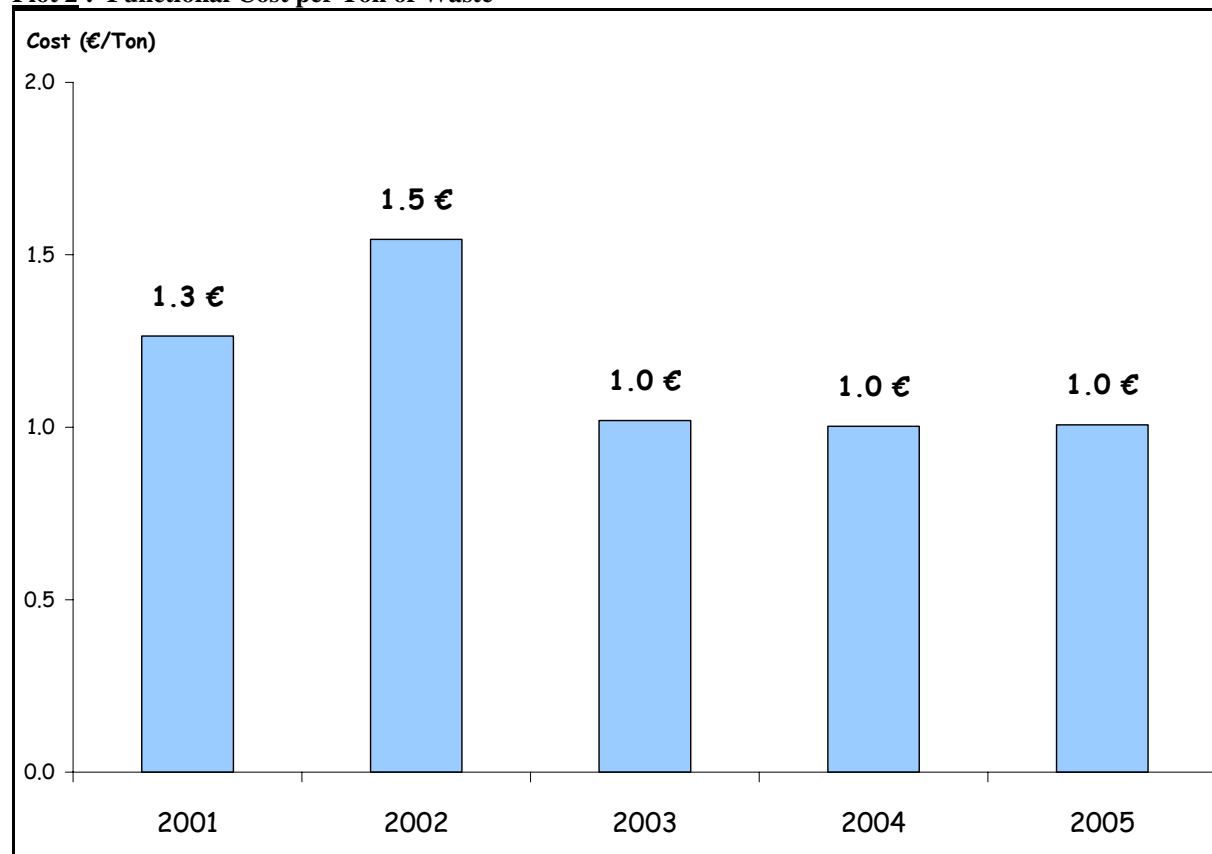


The investment for the samplers and for the HRGC-MS was funded by the Walloon Region at the creation of the network.

## Formation, sources and source inventories

The functional cost of the network is paid by the plants. This functional cost consist in technicians and supplies for: preparation and analysis of the XAD-2 cartridges ( $\pm 20$  kg of XAD-2 a year, solvents,  $^{13}\text{C}$  spikes solutions, Power-Prep<sup>®</sup> cartridges,...), collect of the cartridges and memory cards, maintenance and reparation of the samplers, annual control (one double sampling of 6 to 8 hours with AMESA<sup>®</sup> and with manual method EN 1948) and publication of results on internet site.

**Plot 2 : Functional Cost per Ton of Waste**



### Discussion

Evolution of results since the launching of the programme shows the benefits brought. Continuous monitoring with fast availability and publicity of results triggered efforts of operators. They managed their process and prevented breakdowns of their abatement system so that remaining problems are very limited.

The cost of a complete and continuous control of the MWI remains reasonable ( $\pm 1$  €/per ton) in front of the benefits for the health of the population.

Whereas a 6 to 8 hours sampling according to EN 1948 covers the whole section of the duct, on a very short period, the AMESA<sup>®</sup> continuous sampling covers the whole running period of the controlled plants but at a fixed point. Therefore, both methods are perfectly complementary. Actually consecutive samples for 14 days periods are unquestionably more representative of the yearly running of the plants than episodic samples of 6 to 8 hours duration as usual with the manual method. Moreover, the large volumes sampled during 14 days periods allow the minimization of the problems due to detection and quantification limits that occur regularly for the municipal wastes incinerators with the EN 1948 smaller volumes sampled. Thus, the actual solution applied in Walloon Region (a continuous sampling at a representative point, controlled with a yearly normative sampling) should be the best way to get a really representative control of the emission of PCDDs/Fs.

## Formation, sources and source inventories

Actually, this domain is in expansion with more than 100 continuous sampler systems (from 2 suppliers) running all over the world. In this area, Belgium is at the top with more than 50 systems in use in a lot of industrial sectors.

Thus, for monitoring results with unquestionable compliance control value, inclusion of the automated sampling method in the standard EN 1948, as envisaged by CEN TC264, should be a great benefit for the control of industrial air emissions.

1. F. Idczak, S. François, A. Deboutez, Dioxins in the Air, Bruges (Belgium), November 2001
2. J. Reinman, Dioxin2002, Barcelona
3. <http://environnement.wallonie.be/data/air/dioxines/>