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

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Introduction

Belgium was a precursor in the domain of the continuous sampling to monitor PCDDs and PCDFs emissions from municipal waste incinerators. EU emission limit value of 0.1 TEQng/Nm³ PCDDs/PCDFs was already transposed in the Walloon Environmental law at the end of 2000. Regional authorities have directly chosen to impose an extensive compliance control. All the ovens of municipal waste incinerators (MWI) were equipped with an automatic continuous sampling system at the end of 2000. For ten years, ISSeP has supervised this equipment and analysed the samples.

Methods and Materials

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

Main operations are similar to those for the manual method as in the EN 1948-1 standard. The differences are:

- Fix sampling point for automatic measurement against grid measurement for punctual EN 1948 sampling
- All researched analytic compounds 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 extractors are necessary)
- Sampling duration is 6 to 8 hours for punctual EN 1948 sampling (usual volume between 3 and 10 Nm³) against 24 hours to 1 month for continuous sampling (usually volume between 10 and 400 Nm³).
- A back-flush 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.
- The probe is cleaned from time to time or after a significant problem, but not before each sampling period.

The same plants are controlled since the beginning of the network. Number and size of ovens have varied in time. Position and number of samplers (around ten) have followed these modifications. From 2001 to 2007, sampling time was 14 days and then move progressively to 28 days as the results of the diminution of exceeding. Results are available 2 weeks after sample collection and are posted on Environment Directorate's web site[1].

Analytical Procedure

The methods of extraction, purification and HRGC-HRMS analysis were improved by the traces analysis laboratory of ISSeP throughout these 10 years and the following ones are actually applied. XAD-2 cartridges are spiked with ^{13}C 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 ^{13}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 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.

Results and discussion

Infringements evolution

Numbers of infringements of the 0.1 ng TEQ/Nm³ limit value during the last 10 years and the justifications when identified are presented in Table 1.

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Results (number of cartridges)	227	182	263	289	261	275	254	251	224	174
Infringements of Limit Value	31	9	5	5	0	1	2	1	3	2
Identified / Unidentified infringements	23 / 8	6 / 3	2 / 3	2 / 3		0 / 1	0 / 2	1 / 0	3 / 0	2 / 0
Older ovens shut down since then	5									
Damage around filters	7			1				1	1	1
Broken joint	1			1						
Recurrent difficulties of load feeding on one oven	3	6								
Memory effect of installation after significant infringement	7		1						1	
Emergency stop – leak on boiler										1
Fuel burners start-up after a long break			1						1	

Table 1: Results, Infringements and Causes from 2001 till 2010

Evolution of results since the launching of the programme shows the benefits brought. The number of infringements has strongly decreased at the beginning of the network and remains very low for several years. Continuous monitoring with fast availability and publicity of results triggered efforts of operators. They shall manage their process and prevented breakdowns of their abatement system. Most of the time infringement gives prominence to problem in the process or abatement techniques and monitoring remains thus an asset even after several years of operation.

Emitted mass evolution

The mass of emitted dioxins and furanes is compared to the mass of incinerated wastes in figure 1.

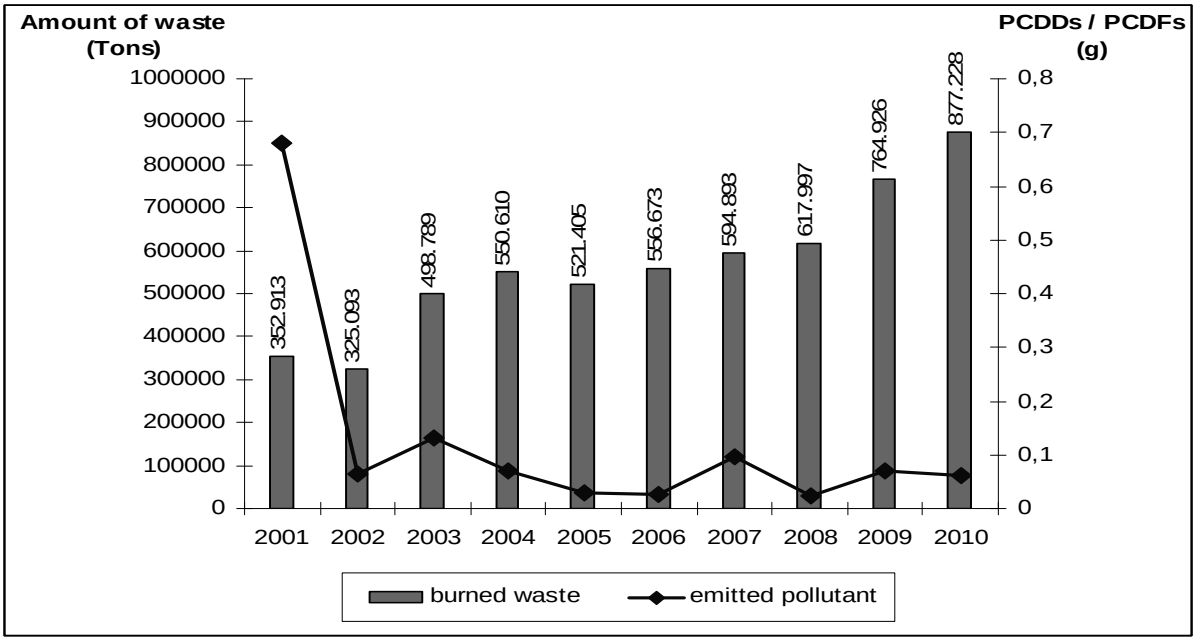

Figure 1: Mass of PCDDs/PCDFs *vs.* mass of incinerated wastes

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. Emitted concentration has indeed been decreased with a factor of around 30 since the beginning of the network.

Implementation costs

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

The running cost was estimated at around 1 € per ton of incinerated waste while the cartridges were changed each 14 days and decreases to 0.7 € per ton since the frequency have been enlarged to 28 days. This cost is accepted to be reasonable by the Walloon government in front of the benefits for the health of the population and is afforded by the plants operators. The functional cost of the network includes all personal charge, reagents (± 20 kg of XAD-2 a year, solvents, ^{13}C spikes solutions, Power-Prep© cartridges…), equipments maintenance and reparation (samplers, HRGC-MS), data treatment and valorisation (publication of the data on the net[1]) and annual control (one double parallel sampling of 6 to 8 hours with AMESA© and with manual method EN 1948).

Reference method

A new European standard EN 1948-5[2] dealing with the problematic of continuous monitoring of dioxins from stationary sources is actually in preparation. This standard will include all recommendations needed for the users to implement and validate a continuous sampling system. Regarding continuous monitoring of dioxins Belgium was a precursor and is nowadays at the top with more than 50 samplers in use in a lot of industrial sectors. More and more other countries in Europe and Asia are now installing such systems. For example, in France, all ovens of MWI shall be equipped with a long term sampler by the end of 2014. We can expect that this standard will probably reinforce interest to continuous sampling in the near future.

Continuous sampling is unquestionably more representative of the yearly running of the plants than episodic samples of 6 to 8 hours. Moreover, the large volumes sampled during 4 weeks periods allow the minimization of the problems due to detection and quantification limits that occur regularly on small size samples obtained during punctual measurement.

Nevertheless for practical reason some operation procedures are different and these points could have an important impact on the result:

- Grid measurement is not possible with the continuous system and the measurement is thus less representative of the whole section of the chimney.
- A systematic cleaning of the probe is not performed after each sampling period.
- Condensed water is not analysed. Indeed it is really difficult to extract a volume between 50 and 100 litres of water. ISSeP have performed several tests and proved that the mass of PCDD/PCDFs in water is negligible.

Among other ones, all these points are under discussion within the working group in charge of the redaction of the EN 1948-5.

To our personal point of view, continuous and punctual samplings are perfectly complementary and that's why both controls are performed for more than ten years on all municipal waste incinerators in Wallonia.

Regulation improvement

Actual regulation and plant authorisations have been developed when only punctual sampling results were available. European and local authorities will probably update legislations taking into account the advantages of long term sampling. Among these points the following ones could be mentioned:

- Including or not start-up and shut-down procedures of oven. Despite a very high level of pollution during these steps, such periods are not taken into account for the moment. Indeed, measurements are performed only during stable phases and results may be quite far from the real impact of the source in term of health.
- Using or not continuous monitoring results for air emission inventories in place of emission factors.
- Defining or not new infringement rules and re-examining the emission limit value of 0.1 TEQng/Nm³ PCDDs/PCDFs for long term sampling.
- Integrating or not the amount of the 12 PCBs dioxin-like to the sum of the 17 PCDDs/PCDFs congeners.

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References

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