

LONG-TERM MONITORING OF PCDD/PCDF – CONCEPTS AND CASE STUDIES FROM EUROPE

Reinmann Jürgen^{1*}, Weber Roland²

¹Environnement S.A Deutschland, Benzstrasse 11, 61352 Bad Homburg, Germany,
j.reinmann@environnement-sa.com

²POPs Environmental Consulting, Ulmenstraße 3, 73035 Göppingen, Germany

Abstract

During start-up and unstable combustion periods, even state-of-the-art incinerators can emit PCDD/F in stack gases at concentrations that are up to 1000 times higher than normal operation. Therefore, incinerators and other sources with variation of PCDD/F release to air cannot be reliably monitored by conventional short term sampling that covers only 0.1 to 0.2 % of the yearly operating time. A more comprehensive monitoring regime is required. This paper describes different applications of continuous PCDD/F sampling in some European countries. The cases demonstrate that flexible regimes for continuous sampling can be crafted and applied by governments or regional/local authorities. Such regimes range from a countrywide, continuous requirement for selected facility types (e.g., waste incinerators) to a facility-specific regime that applies, for example to new facilities for a defined time period until the facility has demonstrated continuous compliance with regulatory limits.

We suggest as a practical approach, that countries implementing the Stockholm Convention should evaluate in their BAT/BEP activities the usefulness of long-term sampling by, for example, designating institutes related to the environmental ministry or regional authorities to supervise long-term sampling regimes at relevant facilities in their country/areas, beginning with priority sources (e.g. facilities used for PCB/POPs destruction or hazardous waste processing).

Introduction

In most countries, PCDD/F emission monitoring currently entails short term sampling with a maximum sampling time of approximately 8 hours under normal condition as e.g. described by the European standard¹. Over the last years it was, however, discovered that, during start-up and unstable combustion periods, even state-of-the-art incinerators can emit up to 1000 times higher PCDD/F levels compared to normal operation²⁻⁶. Therefore incinerators cannot be reliably monitored by manual short term sampling that covers only 0.1 to 0.2% of the yearly operating time. More comprehensive monitoring is needed for all facilities with potentially high PCDD/F release and in particular for facilities destroying POPs or having a variation in feed materials (e.g. secondary metal industries, cement kiln processing hazardous waste, etc.). Continuous online monitoring systems for PCDD/F are not sufficiently well-developed and, in addition, online monitoring is not feasible for compliance measurements.⁷ However, continuous sampling with AMESA (Adsorption Method for Sampling of PCDD/F, uPOPs and inorganic/organic micro-pollutants) can be used to document the total air releases of PCDD/F and other micro-pollutants, allowing continuous supervision of facilities.

Interest in continuous PCDD/F monitoring has increased in recent years. For example, approximately 100 European facilities are now using long-term monitoring systems and an European CEN working group has started to establish a standard for long-term sampling of PCDD/F and dioxin-like PCBs (EN 1948-5).

The present paper describes monitoring regimes based on continuous sampling that are in use in some European countries. In addition to the standard approach of having a long-term sampler stationary in a facility, they demonstrate flexible uses of PCDD/F long term sampling for a range of facility types.

Material and Methods

The operating principles and functionality of the AMESA system have been proven through 12 years of long-term sampling of PCDD/F^{8,9}. The system was approved in 1997 by TÜV Rheinland¹⁰ and validated against EN 1948 by comparison measurements with the cooled probe method. The performance test standard which was used followed the "German Guidelines for the Qualification Testing of Continuous Emission Monitors (CEMS)"¹¹, which were notified by the EU. These guidelines define minimum requirements for CEMS in the qualification test and under chapter 1.7 requirements for Long-Term Sampling systems.

The functional principle of the system (see fig.1) was described previously⁸.

A cooled probe (<50°C) is used to extract a part of the flue gas isokinetically from the stack. PCDD/Fs which are combined in the gas, the dust and the condensate of the flue gas are adsorbed in a specific cartridge filled with XAD-2 and quartz-wool as dust filter. An automatic leakage test is performed before and after the sampling cycle to ensure that no leakage biased the sampling.

After adsorption, the measured gas is pumped through a flexible tube to the control cabinet, where the gas is cooled down (<5°C) to completely remove the condensate. The isokinetic extraction is controlled continuously as a function of the flue gas velocity, temperature and pressure, by use of a thermal mass flowmeter and a frequency controlled pump. The dried measured gas flow is determined twice by means of a calibrated gas meter and a thermal mass flowmeter. AMESA® operates fully automatically and all necessary data are stored internally and can be transferred to an USB flash drive. Both the XAD-2 cartridge and the USB flash drive are sent to a specialized laboratory for further analysis of PCDD/PCDF. The cartridge containing the PCDD/F is evaluated together with the data medium in an accredited laboratory. This process not only monitors PCDD/F, but also other organic substances with a similar volatility and polarity including all unintentionally produced POPs listed in the Stockholm Convention (PCB, Hexachlorobenzene and Pentachlorobenzene). By variation of the sampling probe and adsorption cartridge other key pollutants -- mercury, general heavy metals, dust, and particulate matter (PM) can be continuously sampled

One AMESA® can be equipped with maximum 4 sampling units, thus allowing successive automatic sampling of up to 4 stacks or different emission points in a facility (multiplexing). Alternatively also the different key pollutants (dioxins/uPOPs, heavy metals, mercury, dust, PM) can be sampled in parallel at the same stack or other sampling point

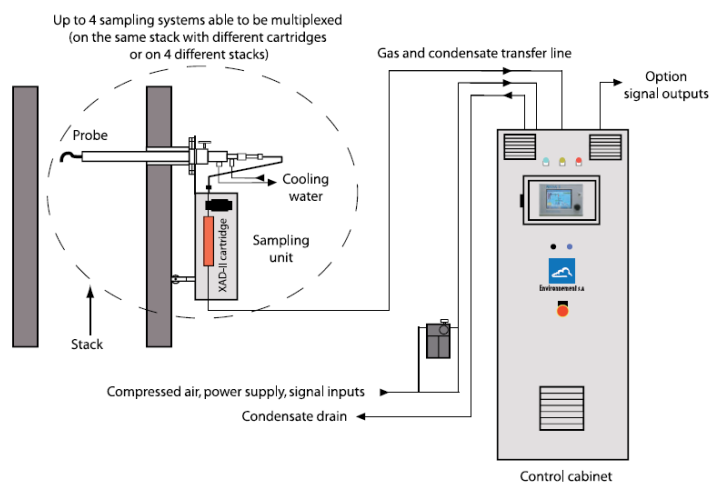


Fig. 1: Functional principle of AMESA continuous sampling

Quartzwool



Figure 2: Cartridge box with XAD-II adsorption cartridge

In principle the AMESA method complies with the cooled probe method of EN-1948 with the exception that the condensate flask is installed after the XAD-II cartridge and that therefore the condensate does not need to be collected and analysed. This is in accordance to US EPA method 23A. The plane filter for the dust collection is replaced by quartz wool placed at the top of the XAD-II cartridge (see Fig. 2). It was confirmed in our studies and from other experienced monitoring groups that the usage of a plane filter is not necessary^{12, 13}.

Results and Discussion

During the past decade, not only the facility operators using PCDD/F long-term monitoring but also environmental ministries and competent authorities have gained a range of experience and confidence in the application and benefits of continuous PCDD/F monitoring and are extending the application portfolio.

1. Long-Term PCDD/F Sampling as country wide approach (Belgium)

Belgium has required nationwide continuous sampling for all hazardous and municipal waste incinerators since 2000. One impetus for the Belgian program was a 1998 study that revealed that the short term monitoring at Belgian incinerators can underestimate the actual PCDD/F releases of an incinerator by more than an order of magnitude¹⁴. After the installation of continuous sampling in all Belgium incinerators, several facilities struggled in the first two years to continuously meet the 0.1 ng TEQ/Nm³ standard¹⁵. However within the first two years all operators of incinerators learned to operate their facilities better and optimized flue gas treatment systems and incineration operation that facilities succeeded in continuously meeting the 0.1 ng TEQ/Nm³ standard. Today it is very rare that any of the approximately 50 incineration lines are close to or even exceed the 0.1 ng TEQ/Nm³ limit. Average emission concentrations are around 0.02 ng TEQ/Nm³ (measurement results for the Walloon region are available on the internet: <http://environnement.wallonie.be/data/air/dioxines/>).

Due to these efforts the total yearly dioxin air emissions for the Walloon region in Belgium were reduced from approximately 5 g TEQ/year in 1999 to 0.7 g/year in 2001 and further to 0.02 g/year even though the amount of incinerated waste increased by 75 % between 2001 and 2007 (Figure 3).

In the Walloon region of Belgium the continuous sampling systems has been financially supported for the municipal waste incinerators while the operators cover the cost of analysis.

In the Flemish region of Belgium, continuous sampling of PCDD/F taking 2-week samples is obligatory for all incineration plants since 2000. However if the operator can demonstrate for one year that emissions are continuously below the limit then 4-week samples can be authorised¹⁷.

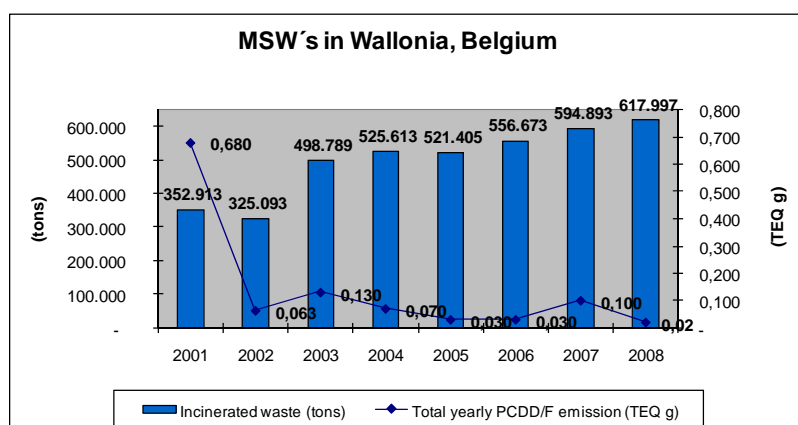


Figure 3: Total burned waste (tons/year) and total yearly PCDD/F air emission (g TEQ/year).

2. Continuous PCDD/F monitoring of hazardous waste incinerators in Europe

Plants with comparatively high risk of generating and releasing PCDD/F are in particular facilities destroying PCB/POPs or wastes with elevated chlorine or bromine concentrations. Therefore such facilities should have specific emission monitoring requirements which for air can best be secured by continuous sampling. To meet this need, hazardous waste incinerators are equipped with continuous PCDD/F sampling systems in various European countries including Austria, Belgium, Finland and Sweden⁶. Furthermore, currently France, Italy and Spain are also installing continuous monitoring systems in hazardous waste incinerators. In Germany continuous PCDD/F monitoring of hazardous waste incinerators has only been applied for a certain time span (see below) to evaluate releases after certain changes in operation parameters¹⁶.

3. Use of continuous monitoring systems for evaluation of emission sources for a specific time span – examples of flexible approaches of competent authorities

In most cases continuous monitoring systems stay in the facilities and operate the whole year with sample spans of 2 or 4 weeks. However in some facilities continuous sampling is used for a specific period, for example after a facility is newly constructed or if lower emission standards are set for a facility.

3.1 Flexible and comprehensive monitoring of municipal waste incinerators

For a German incinerator equipped with a continuous monitoring system, the city authority requests 6 times a year by a phone call to start the monitoring system for a period of several days up to 1 month. By this approach the plant is monitored approximately 33% of the year instead of the 0.2% with the short term sampling. The price for the monitoring is however about the same.

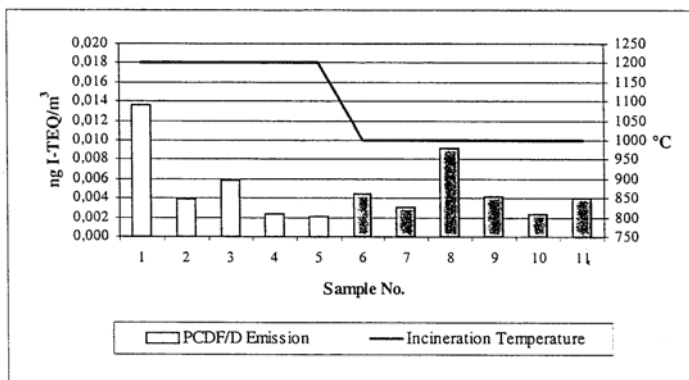
3.2 Continuous sampling for certain facilities for a limited period of time

For several facilities in Belgium, authorities required continuous monitoring for a period of time necessary for establishing that the facility is not a source of PCDD/F or can adequately control their PCDD/F releases. This included some facilities with fluctuating material input (e.g. power plant with co-incineration) and facilities where PCDD/F releases were unknown (e.g. sulphuric acid plant). In most cases the systems were installed for 1 to 2 years and then moved to other facilities.

3.3 Continuous monitoring of a hazardous waste incinerator after reducing the combustion temperature.

The continuous monitoring system was used to demonstrate that PCDD/F emissions of a German hazardous waste incinerator did not increase after the burner temperature was reduced from 1.200 °C to 1.000 °C¹⁴, but remained at a level below 0.01 ng TEQ/Nm³ (Figure 4). After this demonstration the local authority allowed the reduced combustion temperature. In this case, the continuous monitoring system was used to prove that the incinerator could operate at a lower temperature, thus securing economic benefits for the operator by reducing operation costs through lower fuel consumption, which also reduced CO₂ emissions.

Figure 4: PCDD/F concentrations (ng I-TEQ/m³) in stack gas of a hazardous waste incinerator study for permission of reduced incineration temperature (refers to 0°C, 101,3 kPa, dry, related to 11% O₂).



3.4 Long-term sampling in sinter plants

In a sinter plant in central Europe the local authority required continuous PCDD/F monitoring for some months after more stringent emission limits entered into force for the plant. After the facility demonstrated for the required time span that the new limit was met, no further continuous PCDD/F monitoring was required by the authority.

4. Mobile system for continuous PCDD/F and UPOP monitoring as tool for governments and competent authorities for screening facilities in their country/region

Normally continuous PCDD/F sampling systems are installed in one facility for the monitoring PCDD/F release over years. However, while incinerators and cement plants are still required to have their own fixed system in Belgium, there is a current initiative in the Belgium Walloon region to have mobile AMESA systems for time-limited screening of thermal sources among the metal industries and other industries that are potential sources of PCDD/F or PCB). These mobile AMESA systems^A are equipped with different sampling probes for adjustment of stack size and flue gas velocity for a wide range of facilities.

Lessions learned

The approach of Belgium to have continuous monitoring of all incinerators analysing every 2-4 weeks demonstrated a range of advantages including not only reduced air emissions but also the pressure of a timely optimization of all facilities including education of all plant operators, enhanced public trust, and a clear position of the competent authority. After facilities have demonstrated for a reasonable time span that regulatory limits are continuously met, authorities can allow reduced sampling intervals, thereby reducing costs for the operators. For example, with long-term sampling 6 times a year, a facility can be monitored up to 50% of the time at a cost comparable to that of the 3 short term samplings per year required under the EU regulations, which represent only 0.2% of the total operating time.

The examples from European countries demonstrate that continuous sampling can be required/applied in flexible ways by governments or regional/local competent authorities for a limited time period (three months up to two years) to document the total PCDD/F air release of a facility and thereby provide impetus for release reductions. For these projects, continuous monitoring systems are often rented. One very practical approach in this respect is that an institute related to the competent authority owns long-term sampling equipment and successively monitors the facilities of interest in their areas.

By the selection and further development of concepts of flexibly applying continuous PCDD/F/UPOPs monitoring, a better supervision of PCDD/F/UPOP air emissions from incinerators and a wide range of other facilities/industries can be achieved with an acceptable economic burden for the operators.

The positive experience and increasing demand for long-term monitoring in Europe recently lead to the establishment of a European CEN working currently developing a standard for continuous sampling of PCDD/F and PCBs.

We suggest as a practical approach, that countries implementing the Stockholm Convention should evaluate in their BAT/BEP implementation activities the usefulness of long-term sampling and e.g. assign institutes related to the environmental ministry or regional competent authorities to supervise with long-term sampling successively at relevant facilities in their country/areas starting with priority emission sources (e.g. facilities used for PCB/POPs destruction or hazardous waste processing).

^A The AMESA systems used for this purpose are former stationary used systems which operated for 9 years in an incinerator. After a new facility with less stacks was constructed, 2 systems were not needed anymore and the local authority had the option for an alternative use of the equipment. This example demonstrates also the long life time and reliability of the AMESA system.

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