

Validation Tests for PCDD/F Long-Term Monitoring Systems: Short Comings of Short Term Sampling and Other Lessons Learned

Reinmann Jürgen^{1*}, Weber Roland², Watson Alan³

¹Environnement S.A Deutschland, Kölner Straße 6, 65760 Eschborn, Germany

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

³PIC, Public Interest Consultants, Oakleigh, Wernffrwd, Swansea, Wales, UK

Introduction

Over the past 10 years it was discovered that especially during start-up periods of (even state of the art) incinerators^A the dioxin emissions in the flue-gas can increase compared to normal operation¹⁻⁵ up to factors of 1000 in raw gas and after bagfilters¹. Other studies quantified that around 40 %³ (or 60 %⁵) of the yearly dioxin emissions of a plant are produced and emitted during the 4 start-ups in one year. These findings revealed and demonstrated that dioxin and POPs emissions of incinerators cannot be reliably monitored by manual short term sampling since such spot measurements represent only 1 – 2 % of the yearly operating time of the plants during normal operating conditions. Hence it is obvious that short term measurements are not suitable for compliance measurements of the actual average PCDD/F emissions of a plant. Since continuous online monitoring of PCDD/F is not feasible for compliance measurements⁶, the continuous sampling with e.g. AMESA (Adsorption Method for Sampling of dioxins and furans) is the method of choice for supervision of facilities. Therefore the interest in continuous dioxin monitoring has increased over recent years (which has resulted in many installations mainly in Belgium, France and Italy). The increasing interest can be noted also by the fact that the European CEN/TC 264 WG 1 applied in March 2008 for a project to establish a standard for long-term sampling of PCDD/F and dioxin-like PCBs (as EN 1948-5). Additionally, in the assessment of Directive 2000/76 EC⁷ the long-term sampling of dioxins/furans and PCBs was included as a proposed amendment of considerable interest. One important topic for the standardization of sampling procedures is the application of validation measurements and consequently, the consideration of possible bias influences on the results of such validation tests. One intensive comparison of manual sampling and long term monitoring systems was conducted by the Environment Agency of England and Wales (UK). In this test systematic differences between the automatic and the manual systems were found for some test periods. These differences were not satisfactorily explained and were incorrectly interpreted in the published test report⁸.

This paper reveals and discusses the reasons for the inconsistencies between the AMESA and the manual short term measurements and gives some recommendations of what needs to be considered when performing long-term and short-term monitoring tests in one series. The experiences of this work can be used as an important input for further validation tests including, for example EN 1948-5.

Additionally the detailed evaluation of the results demonstrates again the insufficient monitoring capability by manual short term sampling for evaluation of the real dioxin emissions of an incinerator when not considering start-up and shut down phases. This is particularly important when these phases occur several times a month.

Materials and Methods

The general principle of the AMESA system has already been described in several publications^{9,10,11}. AMESA extracts a part of the flue-gas isokinetically through a cooled sampling probe. The flue-gas passes an adsorption cartridge filled with quartz wool and XAD-II. Due to the special design of the adsorption cartridge all dioxins/furans (gaseous, particle and liquid bound) are adsorbed. During the sampling period the system runs completely automatically and stores important plant and sampling parameters as electronic data. After the sampling period, which can be between 4 hours and 6 weeks, the adsorption cartridge is exchanged and sent to a dioxin laboratory where it is analysed with GC/MS.

^A The emissions during start-ups could be significantly reduced by optimizing the start-up procedures (Gass et al 2003). This optimisation should be required for each incinerator.

The Environment Agency comparison tests were carried out in two 3 month long field tests. First in a municipal waste incinerator (MWI) followed by a test in a cement plant (CP). For these tests AMESA, another automatic sampling system (AMS) and 2 manual sampling trains (MST) were installed in the same stack. Firstly several parallel short-term samples were taken, followed by some long-term ones (up to 28 days) by the AMS's with short term sampling being carried out in parallel on a few days by the MST's.

The field tests were conducted by Netcen and AES for the sampling and the analysis was carried out by the Environment Agency's National Laboratory Service (NLS) in Leeds.

The measurements in the incinerator were performed in a reciprocating grate facility with a dry absorption unit (dry lime/activated carbon) for the removal of pollutants from the flue gases (approx. 135°C at the sampling point). The cement plant was a dry kiln fired with coal, tyres and sewage sludge and had an ESP as dust abatement for the kiln off gas with around 20-30 mg dust/Nm³ and 100-110 °C at the sampling point.

In this paper only the results of the AMESA system in comparison to the MST's are discussed in detail because the authors had no access to the detailed results of the second installed AMS. However some comments are also made on the results of the second AMS that were included in the published report on the tests..

Results and Discussion

Measurements in the waste incinerator

During the measurement series four long term measurements (No 9 to 12) were conducted with durations of 14, 14, 28 and 10 days respectively (Figure 1). During measurement 10 (28 days) the incinerator had a shut down and cold start-up and one severe operation failure with grate cleaning (which required the feeding of waste to stop and a hot start-up)^B. This resulted in elevated PCDD/F emissions (0.06 ng TEQ/Nm³ for AMESA and 0.25 ng TEQ/Nm³ for the other AMS which had started a few hours before AMESA and just after the start-up of the incinerator) (Figure 1). Additionally a shift in the pattern was observed: During the period with start-ups and operation failure the ratio of PCDD:PCDF decreased from average of 1.4 (measurements 1 to 8) to 0.84 to 1 in long term measurement 10-12. A shift in patterns and PCDD:PCDF ratio were also reported in other incinerators

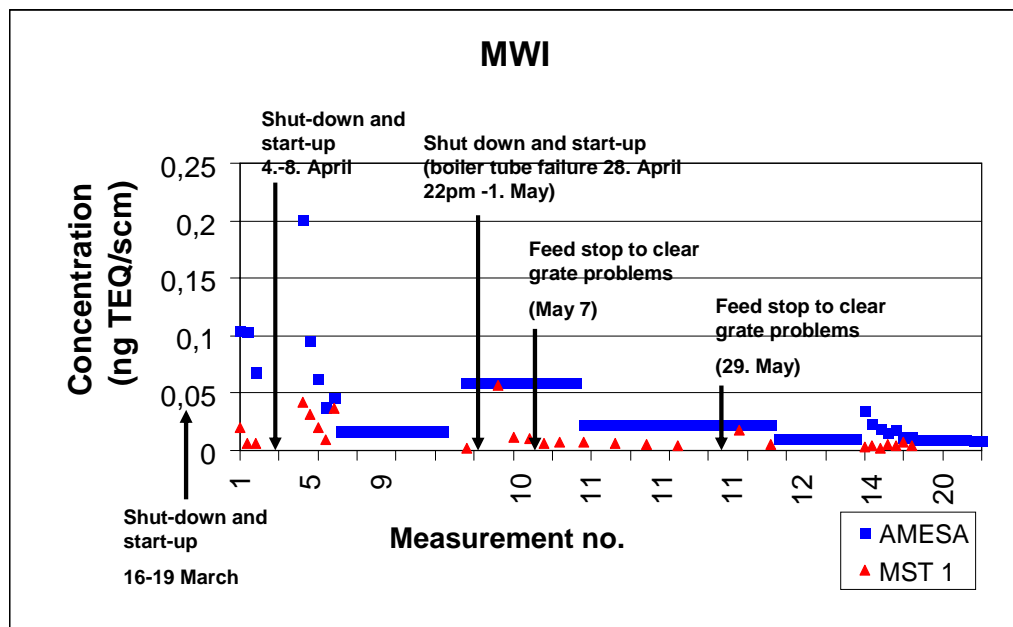


Fig. 1 Short and long-term emission concentrations of the MST and AMESA in the MWI with history and special events.

during start-ups along with the elevated PCDD/F¹⁻⁵. The manual short term samplings performed during the long term measurements were not taken during the days of the start-ups/operation failures but performed one to several day(s) after these events. The results of e.g. the 6 manual samplings performed during measurement No 10 showed an average 0.019 ng TEQ/Nm³ and therefore ca. 30% of the values of the continuous AMESA sampling and ca 8% of the second AMS (Figure 1). In the short term measurements the memory effect of the start-up/operational failures were revealed with decreasing PCDD/F over time (short term measurements 10/2, 10/3 and 11/5, 11/6) (Figure 1).

However the relatively low values in these measurements and the high PCDD:PCDF ratio of 1.2 to 1.6. reveals that the short term samplings only monitored the 'tail' of the start-up releases and that most of PCDD/F were released within less than 24 hours and were monitored partly by the continuous sampling which started shortly after the start-ups. Also the significant difference of AMESA long term monitoring (0.06 ng TEQ/Nm³ for the 14 days) and the second AMS which restarted sampling just a few hours earlier close to the start-up (0.25 ng TEQ/Nm³ for the 14 days) demonstrate that most PCDD/F were released from this start-up during the first hours of the 14 days measurement. The main release duration of several hours is in accordance with observations in an incinerator similarly equipped with dry adsorption/carbon spray were the main PCDD/F release where within 8 hours after disturbances¹² and the finding of 100 to 1000 times higher gas values during the start-up period^{1, C}.

The AMESA short term measurements No 13 to 19 following the long term sampling showed still slightly elevated concentrations compared to the manual short term samples (13-19) (Figure 1). The pattern in the AMESA short term samples AMS 13-19 had a similar PCDD/F pattern as the AMESA long term measurements AML 11/12 with a PCDD:PCDF ratio around 1 and a similar homologue pattern shifting (with decreasing TetraCDD/F homologue compared to AMS 11 and 12) while the parallel manual samplings 11 to 19 showed a PCDD:PCDF ratio between 1.2 and 8. This shows that PCDD/F had been deposited in the AMESA probe which was not cleaned between and after the highly contaminated long term samplings 10 and 11 (4793 pg TEQ total and 4758 pg TEQ) having approximately two orders of magnitude higher total concentrations which then contaminated the AMESA short term samples 13 to 19 (Figure 2).

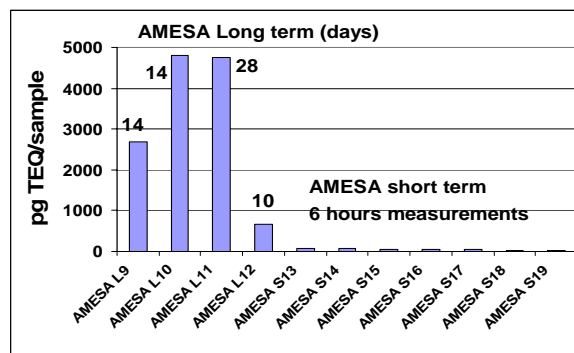


Fig. 2: Total PCDD/F concentration in AMESA long term and short term measurements 9 to 19 in the incinerator

Before long term measurements No 9 to 12, eight short term samples were performed. Also in the measurements 1 to 7 the AMESA long term sampling had higher values compared to the manual short term samplings (Figure 1). In this case no long term sampling test has been run before but the AMESA probe had been installed in the incinerator stack since 3rd March - four weeks before the first measurement started on 2nd April. During this time the plant had a shut down (16th March) and a cold start-up (19th/20th March). Although there was no active suction in the probe, PCDD/F were deposited in the probe (most probably on fine dust particles). The probe was not cleaned before the testing and thus contaminated the first AMESA short term measurements nos. 1 to 3. The higher homologue patterns of the AMESA short term samplings compared to the manual sampling (Figure 3a/3b) support the conclusion that the deposition was mainly caused by particles which contain on average the

^B Both continuous long term monitoring samples were stopped during shut down and started sampling again during the start-up phase.

^C In incinerators with wet scrubbers the PCDD/PCDF can be adsorbed on the plastic in the wet scrubber and can result in significant memory effects over days¹ or even weeks⁴.

more highly chlorinated PCDD/F homologues^D. In short term measurements 1-3 the memory effect of the start-up was detected by decreasing values indicating high emissions during start-up two weeks before (Figure 1). As it can be seen in figure 3a also the measurement no. 1 of the MST showed a different pattern which could however had three reasons:

- End of the memory effect from the start-up some days before
- Contamination of the sampling probe (actually the short term sampling in particular probe 2 were contaminated in a range of measurements),
- contamination in the lab (in particular the Accelerated Solvent Extraction system).

After measurement No 3 again the plant had a shut-down (4th April) and a start-up (8th April) with the long term probe remaining in the chimney. Again in the following short term measurements No 4 to 7 the concentrations in the AMESA sampling with the newly impacted probe were higher compared to manual sampling which was much less affected by the higher start-up emissions. Again however the manual short term sampling 4 to 7 revealed the memory effect of the start-up^E (Figure 1).

It should also be noted that the second AMS showed higher concentrations than the MST's although not as high as AMESA (generally 30 – 40 % less). One reason for the lower values of this AMS compared to the AMESA results was probably the back-flush operation of that sampling probe during periods of no sampling which reduced the level of particulate contamination of the probe. However, the higher values in comparison to the MST's demonstrated also for this system contamination with following memory effects.

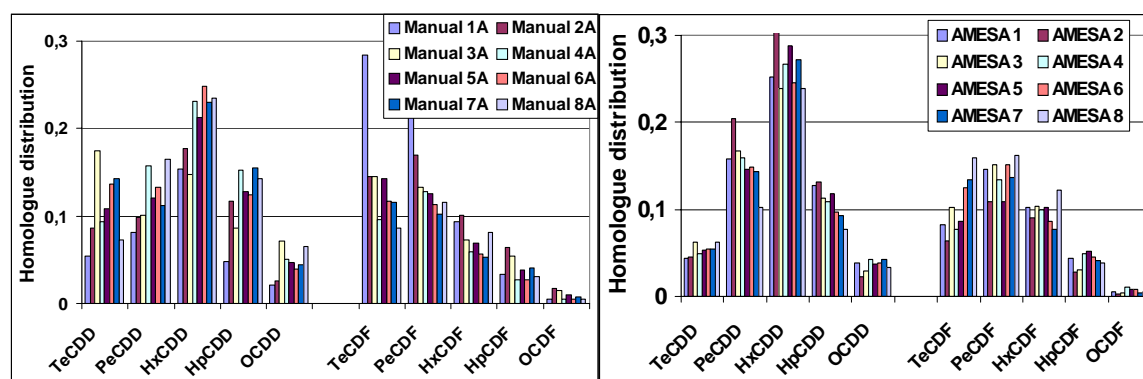


Figure 3: PCDD/F sum homologues distribution in manual short term sampling (A) and AMESA short term sampling.

Measurements in the cement kiln

The manual measurements in the cement kiln showed a significantly different pattern compared to the waste incinerator (Figure 4 in comparison to Figure 3). The lower chlorinated PCDFs (TetraCDFs) were the dominant homologue and the PCDD:PCDF ratio in the non contaminated short term samples were around 0.15 (Figure 4). For short term sample 8, with very low PCDF, the PCDD:PCDF ratio was 1 (Figure 4). The laboratory HpCDD/OCDD blank of 10 to 30 pg was thought to contribute to this (the laboratory used an Accelerated Solvent Extraction system for extraction).

The short term AMESA samples (AMESA cement No 1-3 and 5-7) were elevated in the short term samples compared to the manual ones (Figure 5). The patterns in these elevated AMESA short term samples however

^D In start-ups the bagfilters are frequently bypassed especially in facilities with carbon spray to avoid fires in the BF at the high oxygen concentration. This practice results in elevated PCDD/F and particle emissions during start-ups.

^E The higher PCDD:PCDF ratio in the AMESA can be seen as a memory effect from the start-up/shut down processes.

showed consistently the homologue pattern of the waste incinerator with a PCDD:PCDF ratio between

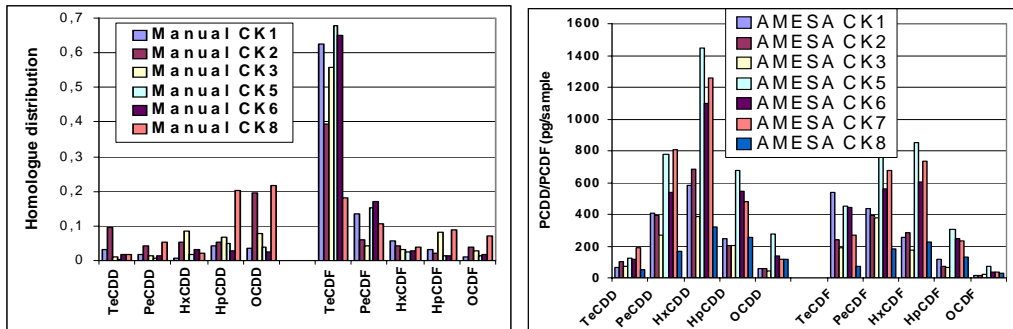


Figure 4: PCDD/F sum homologues pattern in the MST and AMESA short term sampling measurements in the cement kiln (OCDD and HeCDD in MST are laboratory blanks).

1 and 1.48 and not the cement plant pattern at all (Figure 5). Only the two AMESA long-term samples No 4 and No 9 showed a mixed pattern of the cement plant and the incinerator with a PCDD:PCDF ratio of 0.5 and 0.6 (Figure 5).

Therefore nearly all of the PCDD/F in the AMESA short term samples (1-8) sampled in the cement kiln stem from a contamination from the incinerator. Since for the cement kiln a new probe was used in the AMESA, a memory effect from the probe can be excluded. Therefore the most probable sources for contamination were the XAD-cartridges: For the whole testing series 10 AMESA sampling cartridges were sent to the UK. Each cartridge was at least used twice in the 22 incinerator tests and then they were re-used in the 17 cement kiln tests. The contamination path via the cartridges is supported by the much lower values for AMESA cement plant samples 11 to 17 (Figure 5) where the cartridges were used a second time in the cement plant and therefore had two treatments in the laboratory after having been used in the incinerator. These patterns were mainly a mixture of the cement pattern and laboratory blanks. It could not be clarified if the cartridge itself was contaminated or if the XAD was re-used after extraction (which is common practice in some laboratories). The cartridges returned after the completion of the test series had a soot layer on the cartridge wall revealing that the cartridges were not effectively cleaned in the laboratory. It should be noted that the laboratory had no previous experience with the extraction of the large long term cartridges before the test.

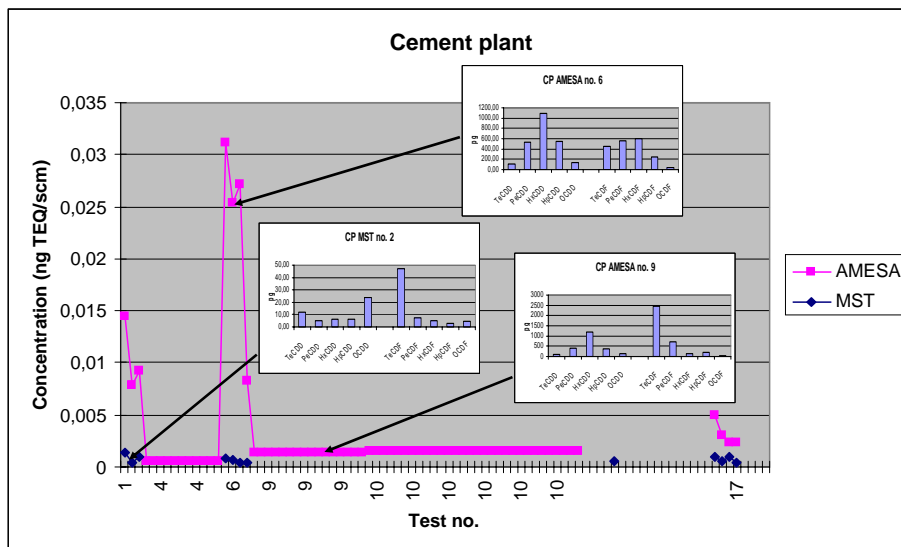


Figure 5: PCDD/F concentration and homologue pattern of AMESA short term (A) and long term (B) measurements in the cement kiln

Lessons learnt

The high emissions during the forced shut down/start-up processes and the disturbed combustion due to grate trouble were revealed due to the long term monitoring sampling in this testing series. During these disturbances high emissions were generated resulting in concentrations above the Waste Incineration Directive emission limit (0.1 ng TEQ/Nm³). This test series shows that with short term sampling these releases are not adequately detected even during a measurement campaign with approx. 30 short term samples in approx. three months. The higher emissions were only recognised as slight memory effects even if they were sampled shortly after the start-up/disturbance with manual samplers. This shows that even with several short term measurements a year, the real emission of an incinerator cannot be monitored at all effectively. These short term measurements present a misleading impression of the real evaluation of the emission from an incinerator and fail to ensure it's compliance with the guidelines.

The test further revealed that care has to be taken when highly impacted long term sampling (>4000 pg TEQ/sample) and short term sampling (with two order of magnitudes lower concentrations) are done within one series. Ideally the less contaminated source would be tested first but obviously the probe or the liner in the probe has to be exchanged or thoroughly cleaned in any case. Further the probe should not be left in the flue gas weeks before and the days between the measurements (particularly with the nozzle in the flow direction!). Further it needs to be ensured that the cartridges are exhaustively extracted and cleaned and the XAD is not reused. This is contrary to the standard AMESA operation in which the cartridges and the XAD is normally reset to the same facility with the same sampling duration. Finally it is important that the laboratory performing such a test is experienced and accustomed to the different type of sampling equipment used in the test. When analysing samples in cement kilns with emissions in the low or sub pg TEQ range, care has to be taken to minimise the risk of cross-contamination from sampling equipment or the laboratory where they are treated in a high contamination area/room, which is reasonable since some samples from cement plants can contain high levels of PCDD/F¹³.

After these experiences a manual has been produced for guidance in future comparison tests using AMESA long term sampling and short term measurements. Additionally the AMESA sampling probes are delivered as standard with changeable liners to assure an easy method for handling and cleaning it.

References

- 1a. Gass H.C, Lüders K and Wilken M. *Organohalogen Compounds* 2002; 56: 193-196.
- 1b. Gass H.C, Lüders K, Wilken M. *Organohalogen Compounds* 2003; 63: 25-28.
2. Wilken M., Marsch F. and Dehoust G. *Organohalogen Compounds* 2003, 63, 29-32
3. Tejima H., Nishigaki M., Fujita Y., Matsumoto A., Takeda N. and Takaoka M. *Chemosphere* 2007: 66: 1123.
4. Loethgren C.J. and van Bavel B. *Chemosphere* 2005: 61:405-412.
5. Wang L.C., His H.C., Chang J., Yang X, Chang-Chien G, Lee W, *Chemosphere* 2007, 67: 1346-1353.
6. Weber R. *Organohalogen Compounds*. 2005; 67:321-325.
7. Knut Sander, Christian Tebert, Stephanie Schilling, Dirk Jepsen, Assessment of the application and possible development of community legislation for the control of waste incineration and co-incineration Final Report, European Commission Service Contract No.070501/2006/446211/MAR/C4, November 2007, Oekopol Report
8. Environment Agency, Use of Continuous Isokinetic Samplers for the Measurement of Dioxins and Furans in Emissions to Atmosphere, April 2006
9. Reinmann J., Kuch B., Weber R. *Organohalogen Compounds*, 2006, 68:852-855.
10. Funcke W., Linnemann H. and Phillipp Ch. *Chemosphere* 1993; 26, 2097-2101
11. Becker E, Reinmann J., Rentschler W., and Mayer J., *Organohalogen Compounds* 2000; 49: 21-23
12. Weber R., Sakurai T., Ueno S., Nishino J. *Chemosphere* 2002; 49: 127-134.
13. Karstensen, K. H., *Chemosphere* 2008, 70, 543-560.