LONG TERM MEASUREMENT OF I-TEQ$_{PCDD/PCDF}$ IN CORRELATION TO PM1, PM2,5 AND PM10 MEASUREMENTS

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Introduction

In 2004, a new measurement technology was introduced which allows the measurement of POP´s depending on their origin by including wind direction measurement. It was first used in the Monarpop project[1] as a fixed installation for ambient air sampling in the Alps. In 2005 this measurement technology was improved to a compact sampling system for easy transport to different sources, using 2 or 3 cartridges[2]. In 2006 this measurement technology was adapted for additional measurement of the fine dust fractions PM10, PM2,5 and PM1 by the use of impactor stages.

Same particulate impaction technology was introduced to the DioxinMonitoringSystem® in stacks. The DioxinMonitoringSystem® is a continuous isokinetic long term sampling system for PCDD/PCDF emissions, which uses the dilution method. By the adjustment of the mixed gas flow through the impactor stages to a fixed volume of 4,2 m3, the cutpoints at 1, 2,5 and 10 µm are defined. By the adjustment of the dilution air volume in dependence to the velocity of the flue gas, the isokinetic sampling is performed. The use of dilution air enables a dry sampling of the PM10, PM2,5 and PM1 dust fractions at temperatures of 40°C analogue to ambient air sampling. In addition to the ISO/FDIS 23210 standard this sampling technology includes volatile Ammonium salts to the measured PM10 and PM2,5 results of the stack sampling.

This presentation introduces the use of impactors for continuous isokinetic long term samplers (DioxinMonitoringSystem®) and discusses obtained PM10, PM2,5 and PM1 values in comparison to the measured I-TEQ$_{PCDD/PCDF}$ values. Based on interesting results this presentation discusses the use of the DioxinMonitoringSystem® to check the performance of the flue gas cleaning system by evaluation of the particulates using PM2,5 and PM10 cut points together with the long term sampling of PCDD/PCDF.

Methods and Materials

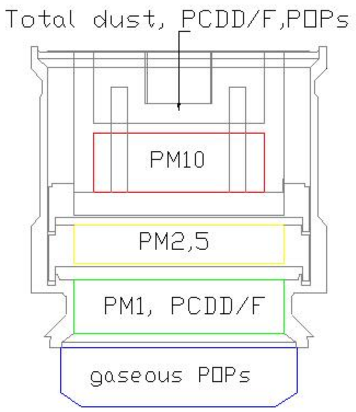
The ambient air sampling system WindSelect $^{+}$® uses three cartridges. Each of the cartridges can be correlated to a defined sector. The software allows to define 6 sectors and each of sectors can be correlated to 3 cartridges. For example cartridge 1 can be used for air downstream related to the emitter and cartridge 2 can be used to sample air upstream the emitter, corresponding to the back ground levels, Cartridge 3 is used to sample during calm periods (e.g. below 0,5 m/sec wind speed) to take into account small, but close emitters (e.g. household stoves).

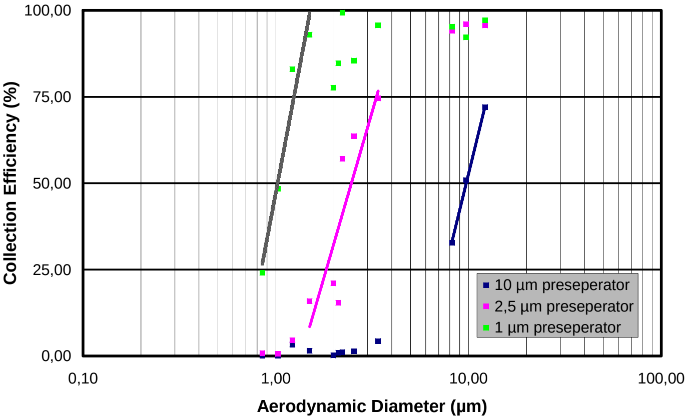
Picture 1: field sampling

Picture 2: WindSelect $^{+}$® system

Picture 3: PM10/PM2.5/PM1

The cartridges allow the use of Polyurethane foam together with XAD2 for improved adsorption of the POP´s, a plane filter with high efficiency for small particulates (99,9999% for 0,3 µm particulates) and up to 3 Preseperators with cut points at 10 µm, 2,5 µm and 1 µm.





Picture 4: principle of impactor

Picture 5: Cut points graph of preseperator stages

Picture 4 shows the principle of the impaction system, which is called ParTrace® system: First a dust fraction with a cut point of 10 µm, second a fraction with a cut point of 2,5 µm, third a fraction with a cut point of 1 µm separates the dust to 4 fractions (>10 µm, 2,5 to 10 µm, 1 to 2,5 µm, < 1 µm) on 4 quartz filters.

Picture 5 shows the obtained evaluation of the cut points. Cut points were checked by the use of a TSI 3321 aerodynamic particle sizer spectrometer (www.tsi.com). The cut points of 10, 2,5 and 1 µm are adjusted with a flow of 4,2 m3/h, enabling the sampling of 100 m3 of air every day.

The DioxinMonitoringSystem® uses the same impactors design, enabling the sampling of fly ash and dust with cut points of 10 µm, 2,5 µm and 1 µm. While flue gas and dilution air are adjusted to 4,2 m3/h, the flue gas sampling is adjusted to isokinetic sucking.

Picture 6 shows the sampling unit, for the sampling of PCDD/PCDF together with a fractioning of the particulates. Pictures 7 and 8 show the cartridge, which is named ParTrace® cartridge.

Picture 6, 7, 8: DioxinMonitoringSystem® with PM10 and PM2,5 cut points (ParTrace® cartridge)

For more detailed resolution in the range below 2,5 µm, the particulate distribution was additionally measured by the use of a Grimm 1.108 portable laser aerosol spectrometer (www.grimm-aerosol.com), directly from the diluted flue gas of the DioxinMonitoringSystem®.

Results and discussion

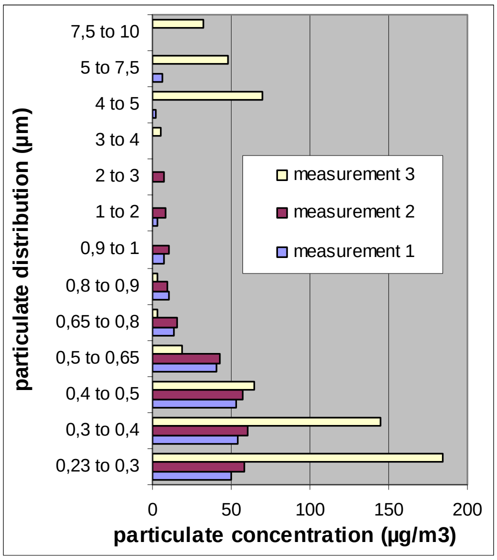
Kaup H. and McLachlan[4] M.S. showed for ambient air samples, that in the winter time 60% of the PCDD/F is adsorbed on 0,45 - 1,35 µm particles, 30% is adsorbed on particles smaller than 0,45 µm. He found 90% of the PCDD/F adsorbed on particulates smaller than 1,35 µm. In the summer time a higher amount of the PCDD/F is adsorbed on the smaller particles.

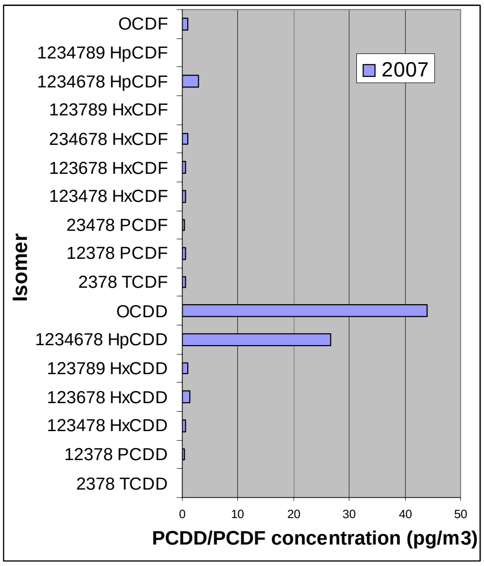
Tirler W., Angeluggi G., Bedin K. and Voto G[5]., showed by the use of the WindSelect + ® sampling technology with dust preseperator, that in the area of Bolzano 90% of the PCDD/F is adsorbed on the particulates smaller than 1 µm. They explained that the PM1 fraction has much higher surface to adsorb PCDD/PCDF than the coarser fractions.

Measurements performed during the CEN validation measurements[3] at the waste incinerator Flötzersteig in June 2007 showed very low $I\text{-}TEQ_{PCDD/PCDF}$ and $I\text{-}TEQ_{PCB}$ values. Laser particulate measurements from the diluted flue gas as well as long term sampling with the ParTrace® cartridge showed very low particulate concentrations of the flue gas. Most of the particulates are smaller than 1 µm (measurement 1 and 2 of picture 9).

As picture 9 shows, 95% of the emitted particulates are smaller than 1 µm. Increasing particulates in the fraction below 0,5 µm (measurement 3) are mainly caused by increased emissions of ammonium salts, which can vary by a factor of 5.

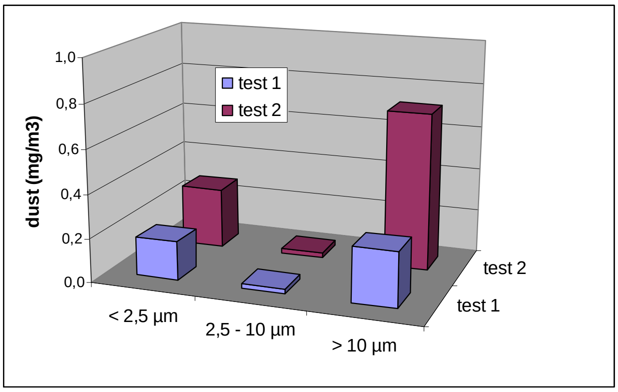
Long term sampling of the PCDD/PCDF, using the PM10 and PM2,5 impactor stages showed PM2,5 values of 200 µg/m3, which are comparable to the Laser particulate measurements, but significant higher levels for particulates bigger than 10 µm. As picture 13 shows, these particulates are mainly activated carbon and corrosion products from the duct walls.





Picture 9: Particulates in the waste incinerator   Picture 10: PCDD/F in correlation

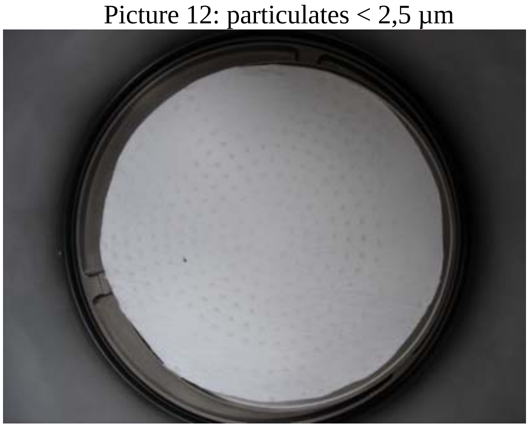
Short term measurements with Laser photometers show systematic lower concentrations of coarse particulates than long term sampling with the ParTrace® cartridge of the DioxinMonitoringSystem®.



Picture 11: long term sampling results

Picture 12: particulates < 2,5 µm

Picture 13: cut point 10 µm



Picture 14: cut point 2,5 µm

The use of the ParTrace® cartridge with the DioxinMonitoringSystem® enables the user to distinguish between particulates below 1 µm, which contain 90% of the PCDD/PCDF and the coarse particulates (cut points 2,5 and 10 µm), which are an indicator for increasing leakages and corrosion in the flue gas cleaning.

Laser particulate measurements from the bypass of the DioxinMonitoringSystem® sample only 0,3 liters of diluted flue gas per measurement, which represent 30 ml of the flue gas. This amount of flue gas is sufficient to count particulates smaller than 2,5 µm, but not sufficient to quantify coarse particulates. Long term sampling with the DioxinMonitoringSystem® samples approximately 100 m3 of flue gas, which gives more representative results for the particulate range from 2,5 to 100 µm.

Laser particulate measurements from the bypass of the DioxinMonitoringSystem® include emitted ammonium salts. The plane filter of the DioxinMonitoringSystem® samples fly ash and ammonium salts. Gravimetric analysis of the plane filter and later thermal treatment of the plane filter enable the quantification of the PM2,5 with and without ammonium salts. Comparing WindSelect+® measurements with DioxinMonitoringSystem® measurements enables to quantify the relevance of a source to the local environment.

Picture 11, 12, 13 and 14 show the particulate fractions of the waste incinerator Flötzersteig, which uses as primary dioxin removal step a baghouse filter with activated carbon. Picture 13 shows the PM10 cut point, which shows some activated carbon particulates and some corrosion products from the duct wall. Quantifying these coarse particulates gave emissions of 200 to 600 µg/m^3.

In correlation to the measured concentration of the coarse particulates, the emitted I-TEQ of this plant was in the range of 0,001 ng I-TEQ/m3, as the validation measurements of the CEN EN 1948 validation work group has shown in 2007.

The particulate fraction below 2,5 µm was measured in the range of 200 µg/m3. Installed dust measurements of the plant showed total dust concentrations of 200 to 2500 µg/m3. Especially in this range optical dust measurements are operated near the detection limit and have increased uncertainty.

Actual legislation in Europe requires measurements of PM2,5 and PM10 for ambient air. Using the DioxinMonitoringSystem® together with the ParTrace® cartridge enables to measure long term mean values of PM10, PM2,5 and I-TEQ$_{PCDD/PCDF}$ with one measurement. Measured PM2,5/PM10 values in the vicinity of an emitter, using the WindSelect $^{+}$® can be correlated to the PM2,5/PM10 emissions of the emitter. Chemical characterisation of the fly ash on the quartz fibre filters, allows to distinguish the traffic related PM2,5/PM10 part from the emitter related part[5].

Visual inspection and mass quantification of the PM10 and PM2,5 impactor stages enables the operator of the waste incinerator to check the performance of the dioxin removal in the flue gas cleaning system. Dust precipitations on catalyst surfaces and leakages in dust filter systems increase I-TEQ$_{PCDD/PCDF}$ levels. Low dust concentrations in the components of the flue gas cleaning system reduce dioxin emissions to very low levels.

Evaluation of the PM10 impactor stage detects break through of activated carbon particulates, because the activated carbon, which is added in the flue gas system has particles size bigger than 10 µm. Possible break through causes for activated carbon particulates can be:

- Small leakage of closed by pass vent in the flue gas cleaning system
- Holes in the bags of the baghouse filters, caused by hot spots of the activated carbon
- Seams of the bags with small leakage
- Aged bags

Increasing dust concentrations of the PM2,5 impactor stage detects increasing precipitation of dust on the catalyst surfaces, which can also lower irreversible the catalytic efficiency and as a result increasing I-TEQ$_{PCDD/PCDF}$ levels.

Picture 15, 16: 4 stage catalyst box without dust precipitations give very low I-TEQ$_{PCDD/PCDF}$ of 0,001 ng/m3

CEN validation measurements, performed in June 2007, have shown very low I-TEQ values at the waste incinerator Flötzersteig. Pictures done after the validation measurements (pictures 15 and 16) show very low dust precipitations in the catalyst box.

Picture 17, 18: Catalyst box with dust precipitations 2 years before with I-TEQPCDD/PCDF of 0,03 ng/m3

Pictures done 2 years ago in 2005 (picture 17 and 18), show higher dust precipitations in the catalyst box, related with higher levels of PCDD/F.

This research work has shown, that the DioxinMonitoringSystem® is suitable to measure PM2,5, PM10 together with I-$TEQ_{PCDD/PCDF}$ in one step.

As by result there is an interesting application, to check the performance of efficient flue gas cleaning systems for removal of PCDD/PCDF by the evaluation of the PM10 and PM2,5 cut points. This application supports also plant manager on the scheduling of the maintenance of the abatement system in order to prevent high emission levels.

Acknowledgements

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