

Long-term sampling emission of PFOS and PFOA of a Waste-to-Energy incinerator

Arkenbout, Abel

NGO ToxicoWatch, Harlingen, 8862 VS, arkenbout@toxicowatch.org

Introduction

In 2011 a 'state of the art' incinerator was established in Harlingen, The Netherlands, with a stringent permit for dioxin emissions of 0,01 ng TEQ/Nm³. In 2013 NGO ToxicoWatch found high concentration PCDD/Fs/dl-PCBs in eggs of backyard chicken in the surroundings of the incinerator [1]. To determine or to exclude the source in August 2015 a long-term sampling program of flue gases was started on halogenated UPOPs. In this report we present the results of perfluorooctanesulfonic acid, PFOS and perfluorooctanoic acid (PFOA) in flue gas and discussed these results in relation with other UPOPs, heterogeneous temperatures in the post combustion zone and interruptions in long-term sampling.

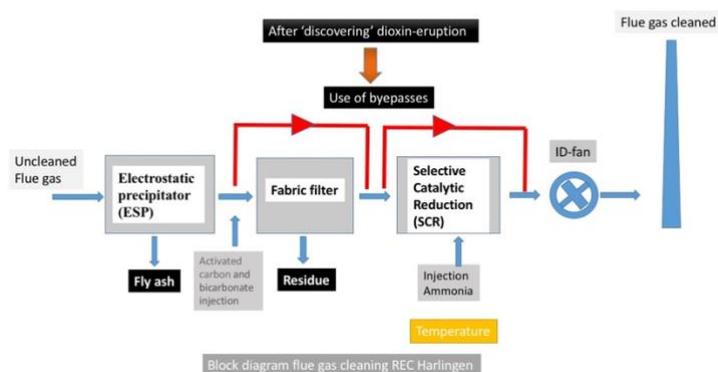
Methods

The waste incinerator is a Waste-to-energy installation, a *Reststoffen Energie Centrale* and is abbreviated as REC, located in Harlingen, The Netherlands. Annual waste combustion is 228,000 tons with a flow of 170,000 Nm³/hour. The emissions of flue gas of the waste incinerator in Harlingen, The Netherlands (REC) is measured by continuous sampling method AMESA (Adsorption METHOD for SAMpling of dioxins) [2]. The principle of measuring is explained in article of Reinmann (2006). Analyses are performed every 4 weeks by Eurofins, Hamburg, Germany on PXDD/Fs, PXBs, PFOS and PFOA (X=Chlorine, Bromine). Total sample time PCDD/F/dl-PCB was 20,748 hours (n=36), for PBDD/F, PBB, PBDE, PFOS and PFOA sampling time was 3,942 hours (n=6). TÜV Rheinland Energy GmbH measured the temperature and oxygen content in two measurement planes (18 meter and 24 meter) in the post-combustion chamber of the incinerator. The waste had a calorific value of 10.3 MJ/kg (Full Load) and 10,1 MJ/kg (Part Load), while 'the most unfavourable conditions' refer to waste of 9 MJ/kg. Short term samplings of start-ups during annual maintenance are performed by Odra (OmgevingsDienst Regio Arnhem), Arnhem, The Netherlands.

Results and discussion

Nowadays thousands of synthetic organic fluorine substances are produced for a wide range of applications; one of the large groups are per- and polyfluoroalkyl substances (PFASs) with an estimate of 3000 compounds. Since the late 1990s, multiple long-chain PFASs, in particular perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), have attracted worldwide attention in the scientific and regulatory community and among the public. PFOS and its precursors are now listed and PFOA and related precursors are being evaluated for listing, under the Stockholm Convention on Persistent Organic Pollutants (POP).

Taylor et al. (2014) [3] concluded incineration of fluorotelomer-based polymers does not result in the formation of detectable levels of PFOA under conditions representative of typical municipal waste combustor (MWC) and medical waste incinerator (MWI) operations in the U.S. Therefore, waste incineration of these polymers is not expected to be a source of PFOA in the environment.



Afbeelding 1: Block diagram flue gas cleaning REC Harlingen

In this study, flue gas of the REC incinerator in Harlingen was analysed on UPOPs in a long-term sampling program of the AMESA. A side research took place in 6 samples of 3,929 hours of measurements of brominated and fluorinated compounds. The fluorinated compounds were PFOS and PFOA. The results show PFOS only detectable (above LOQ) at one shutdown event with 8,23 pg/Nm³. PFOA was detectable in all (n=6) long-term sampling periods (433 – 794 hours). Minimum-maximum is 0,0134 – 0,004 ng/Nm³, average emissions are 0,002 ng/Nm³, which results in a yearly load estimate of 40,1 mg PFOA and 4,9 mg PFOS. In the same period 0,0002 – 0,1828 ng TEQ PCDD/F/dl-PCB was measured. No correlation could be found with transient conditions, like start-up of shutdown, in all samples PFOA was detectable (Fig. 2).

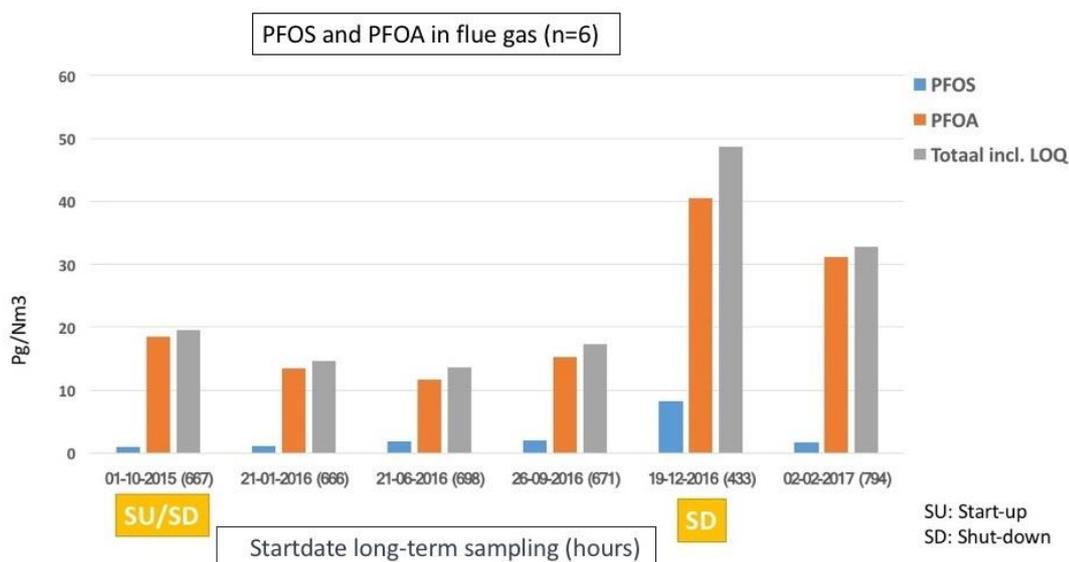


Fig 2: Longterm sampling of 3,976 hours of PFOS and PFOA in flue gas REC Harlingen (pg/Nm³)

However, PFOA and PFOS should not be detectable at all in modern waste incineration processes [3]. Finding of PFOA in the stack can be an indicator of incomplete combustion, i.e. not complying with a minimum 2 seconds residence time at 850 °C. Another study conducted by ToxicoWatch and performed by TÜV Rheinland shows heterogeneous temperatures in the post-combustion zone. Another UPOP PolyBrominated Biphenyl (PBB) was found two times during steady state conditions 0,038 – 0,133 ng/Nm³, while these compounds normally totally decompose at 300⁰ C.

Sakurai et al [4] finds a minor impact of coplanar PCBs from combustion sources, because its contribution of 3% in the total TEQ PCDD/F/dl-PCBs. In this study of 20,139 hours long-term sampling, the average contribution of dl-PCB is 8,5% of the total TEQ (n = 36). Presence of high UPOP content can be the result of uncomplete combustion and/or structural use of two bypasses over bag filter and DeNOx during start-ups and shutdowns.

Gravimetric measurements performed by ODRA [5] of start-ups after the annual maintenance stop show exceeding dioxin emissions not covered by AMESA long term sampling. It means dioxin emissions are far more than could be measured by AMESA, because of interruption sampling. It should be noted, that long term sampling by AMESA is far more superior to the regulatory obligated short term sampling (2x 6 hours pre-announced), but attention is needed this sampling interruptions. In Figure 3 is show the long-term results of 20,748 hours sampling of PCDD/F/dl-PCBs. All the peaks with exceeding dioxin emissions were characterised with more or less long sample interruptions (min/max time 0:04 – 8:33) when AMESA was set off-line. The total time of interruptions in the 20,748 hours sampling-time was 1,496 hours.

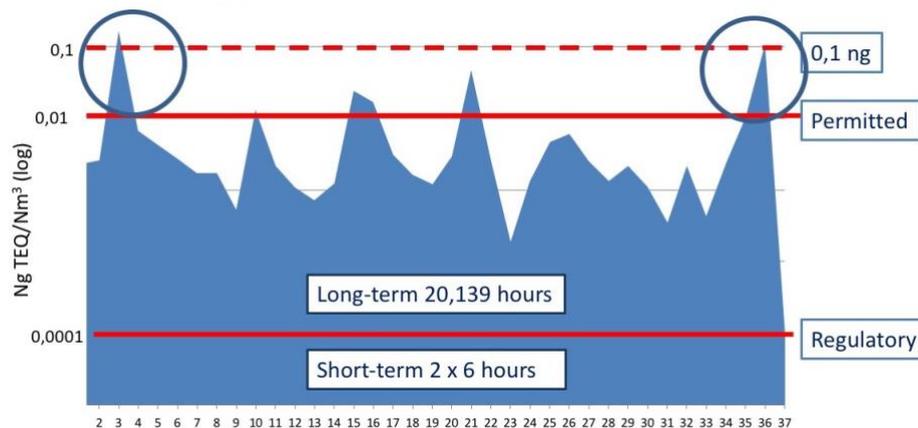


Fig 3: Results long-term sampling REC Harlingen

In Fig. 3 are the results of 20,139 hours long-term sampling in the flue gas of the incinerator REC Harlingen summarized. The first red line is the result of the regulatory 2 x 6 hour short-term measurements: 0,0001 ng TEQ/Nm³. The second red line is the regulatory limit of 0,01 ng TEQ/Nm³, set because of the modernity of the incinerator. The third broken line is the EU-limit of 0,1 ng TEQ/Nm³, which is exceeded two times. All the peaks in this Fig 3 are characterized by interruptions of sampling; in the circles in this Figure 3 the interruptions were more than 8 hours.

Essentially, 'small' emissions of PFOA from a steady state operational incinerator are just the tip of the iceberg when all the potential 'upset' conditions are considered. It conveys the impression that modern incinerators cannot fully destroy UPOPs like PCDD/F, PBB, PCB or even PFOA - even under optimal operating conditions. The interrupted sampling of UPOPs in flue gas indicate the real emissions are higher, in what degree more research is needed. Maybe temperatures in the post-combustion zone should be elevated anyhow to the level of 1100⁰ for an actual complete destruction of all relevant UPOPs, meant in the Stockholm Convention 2004 to eliminate or reduce UPOPs.

Acknowledgements

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References

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