PFOA AND OTHER UPOPs EMISSIONS OF A MODERN INCINERATOR IN THE NETHERLANDS

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Introduction

Currently there are 12 waste incinerators in operation in the Netherlands, all with energy recovery from waste. The last incinerator was built in 2011 and presented as "State of the art" Waste to Energy installation fulfilling all modern concepts of sustainable waste disposal with applying of Best Available Techniques (BAT) / Best Environmental Practices (BEP). Because of this modernity the government set the emission limit for dioxins ten times lower than the obliged EU-norm of 0.1 ng TEQ/Nm^3. After finding high levels of dioxins in the food chain a long-term sampling research was started with analysis on PCDD/F, dl-PCB, PBB, PBDD/F, PBDE, PFOS, PFOA and PAH.

Materials and methods

The incinerator *Reststoffen Energie Centrale* (abbreviated as REC) works like all other installations in the Netherlands with transforming thermic energy into electrical (17 MW). The location of this incinerator is at the UNESCO WaddenSea, 2 km from the centre of the harbour city Harlingen, the Netherlands (16.000 inhabitants). Research of backyard chicken eggs are performed with a composite sampling of 10 - 20 eggs and analysed with DR CALUX and HR/GC/MS. The continuous sampling of flue gas is done by the **A**dsorption **ME**thod for **SA**mpling (abbreviated as AMESA) by the company Environnement[1]. Analyses of PCDD/F/dl-PCBs, PBB, PBDE, PBDD/F, PFOS and PFOA are performed by Eurofins, Hamburg, Germany. The official mandated dioxin emission control by the government is a preannounced short term sampling of 2 x 6 hours/year, which are performed by Promonitoring, Deventer, The Netherlands. Measurements of start-up events (2015, 2016 and 2017) are performed by OmgevingsDienst Regio Arnhem, the Netherlands (ODRA) and analysed with HR/GC/MS by Al-West, Deventer, the Netherlands.

Results and discussion

Do incinerators still contribute substantially to dioxins levels nowadays? The incinerator industry claims to have reach a maximal reduction of emissions of dioxins, leaving backyard burning as a number one source. Still population all over the world are worried about health effects of incineration in their neighbourhood. The incinerator industry claims to be nearly clean due complying all the BAT and BEP practises in order to fulfil the emission limits set in the international and national regulation.
After findings of high levels of dioxins in eggs of backyard chickens[2,3,4] in the environment of the incinerator in Harlingen the question of dioxin emissions by incineration arises again. For the first time in the history of the Netherlands a long-term sampling of emissions of the most modern incinerator of the Netherlands was started in August 2015 and lasted till December 2017, with one measurement during the annual maintenance stop in May 2018. Already in the third month of the long term AMESA sampling exceeding dioxins were measured, but not reported by the incinerator, nor detected by the governmental enforcement, only admit 4 weeks later when analysis results reveal exceeding levels.

Sampling	hours	ng TEQ/Nm3	Factor
Short-term, April 2016	**6**	**<0,00001**	
Long-term April 2016	**256**	**0,01290**	**1290**
Short-term, 8 March 2017	**6**	**0,00001**	
Long-term March 2017	**690**	**0,00460**	**460**

Table 1: Simultaneous short- and long-term measurements (flow 230.000 Nm3)

Incinerators are obliged to measure dioxin emissions 2 times preannounced 6 - 8 hours a year, only 0,1 % of the operating time, and only analysis on PCDD/F. In Table 1 simultaneous measurements of long and short term show a difference of a factor 460 - 1200. This evidence strongly advocates to prefer long term sampling for regulation. Long term sampling should be applicate to all other incinerators, to protect human health and the environment for pollutions of this extreme toxic substances.

The results of a **20,139** hours long-term sampling of dioxins are shown in Figure 1 (log PCDD/Fs). The measured emission levels are far above the regulatory determined level, red line at the bottom with the number of 0,0001 ng TEQ/Nm3. The second red line is the legal permit of 0,01 ng TEQ/Nm3 which is exceeding 7 times. Even the EU limit of 0,1 ng TEQ/Nm3 is two times exceeded, at the beginning and in the end. The graph clearly shows exceeding levels are not exceptional.

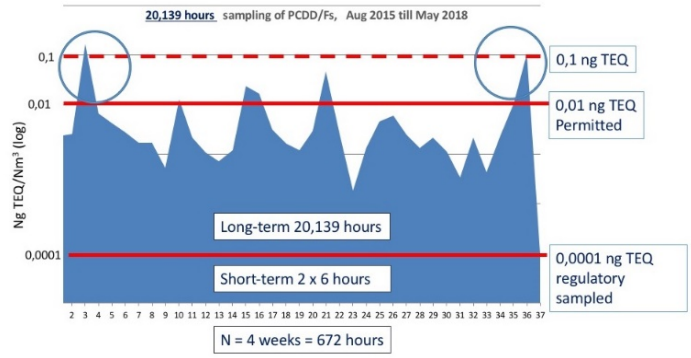

Figure 1: Results of 20,139 hours AMESA long-term sampling PCDD/Fs, REC Harlingen

Start-ups

Exceeding releases of dioxins during start-ups are described in literature before[3], but no data is available in the first phases, when there's no isokinetic flow, like in the flushing and preheating phase of the start-up procedure. Long-term sampling like AMESA works only in relative optimal conditions, but have trouble in transient phases, when the flow is irregular and comes below 1,5 m/s. Measurements of the first phases of the start-up, only can be done by indicative gravimetrical and short-term sampling methods, which are been taken by the ODRA during the start-ups after the annual maintenance stops of 2015, 2016 and 2017.

In the flushing and heating-up phase, all short-term measurements show dioxin emissions in access of the Industrial Emissions Directive (IED) limit of 0.1 ng TEQ/Nm^3. The reason of elevated dioxins is flushing (at different temperatures) of dust (soot) *without filtering* into the environment. Exceeding of dioxin emissions 'posed no legal problem' for the facility because the norms are stipulated to 'apply only to steady state operation'. Bypassing has economical reason: changing of filters, especially the bag or fabric filter is an expensive operation. From the very first start-up of the incinerator in Harlingen in 2011 more than 60 start-ups and shutdowns have been *registered,* officially. In the period of AMESA measurement also start-ups were seen in log data of AMESA (parameters of oxygen, carbon dioxide and flow), never have been passed to the enforcement. In December 2017 the admission permit for this long-term sampling program was terminated by plant management (for unstated reasons), neglecting the wish of both the Dutch government and the concerned population to continue publicly controlled monitoring during all stages of operating or calamities.

In all breaches of the permit emission limit (> 0,01 ng TEQ/Nm3), the long-term sampling was interrupted by low velocity of flow (< 1,5 m/s). In a total period of 20,139 hours sampling of the REC incinerator, AMESA was 1,676 hours off-line (8,3 %), included 1,159 hours during the annual maintenance. The total off-line except the annual maintenance stops was 517 hours (2,6 %).

The AMESA is a very good step forward in determining the load of POPs in the stack. It's only sad to observe that in moments the AMESA didn't and couldn't work – no waste to burn - dioxins or POPs in general are emitted exponential. The little we could measure with other techniques, come to estimated figures far above specified annual emissions loads. Calculated emissions of one start-up can be from 3 – 85 mg TEQ, which correlate with an annual emission load of one start-up of 60 – 1,700%. The REC incinerator operates with a frequency of 5 start-ups a year, emission load counts for decades of normal operation.

Total dioxin emissions by public electricity and heat production in Netherlands for 2004[5] was reported as 3.24 g I-TEQ while from residential heating it was 4.22 g I-TEQ, with total releases estimated at 39.4 g I-TEQ[6]. Just for 5 start-up events can reach between 0.015 – 0.425 g I-TEQ of PCDD/Fs in total. This comparison shows that national inventory can change significantly. It can be more than for example reported by single municipal waste incinerator in South Netherlands (BV Afvalverbranding Zuid Nederland (AZN) and Duiven which reported 0.134 and 0.129 g TEQ in air emissions for year 2017 respectively[7].

Unintentionally produced persistent organic pollutants (UPOPs)

Another important combustion topic needs to be regarded: temperatures in the post combustion zone. Are these temperatures really homogenous above the 850° C during 2 seconds residence? In a conducted study performed by the German company TÜV[8], irregularities were observed in homogeneity of oxygen and temperature. In the governmental committees the management of the incinerator refuse to give details of temperature measured as was promised. So still the question is there: does the incinerator meets its regulations, set by the guideline of the Stockholm and Basel Convention.

Results of other POPs in long-term sampling program

1. Dioxin-like polychlorinated biphenyls (Dl-PCBs) are 8,5% of the total TEQ (n = 36 total 20,139 hours). Sakurai et al[9] come to less than 3% contribution of dl-PCBs TEQ in the flue gas.
2. Polybrominated diphenyl ethers (PBDEs): 0.434 ng PBDE/Nm^3 (n=1)
3. Polybrominated dibenzodioxines and furans (PBDD/Fs): 5.4 – 8.9 pg PBDD/F/Nm^3 (n=2)
4. Polybrominated biphenyls (PBBs): 0.038 – 0.133 ng/Nm^3 (steady state). Normally, these compounds decompose above 300 ^{0}C.
5. PAH: 2,4 – 314,8 ng/Nm^3 (steady state, n=3, total sample time 1,700 hours)
6. Perfluorooctanoic acid (PFOA): 0,013 – 0,041 ng/Nm^3 (n = 6, sampling time 3,929 hrs). PFOS was only detectable (above LOQ) in one shutdown event with 8,23 pg/Nm^3.

The finding of a broad scale of UPOPs indicates strongly the incompleteness of destruction and contribute as contamination to the environment. The question arises if modern waste combusting has to be performed at 1100^0 C to destroy chemical cocktail, the household/municipal waste anno 2019, completely? But on the other hand, we still don't know if the 'modern' incinerators meet the obliged temperature of 850^0 C. Measurements in 2017 (6 years after the start in 2011) by TÜV Rheinland Energy GmbH showed a lack of homogeneity of temperature and oxygen in the post-combustion zone[10], while this is required in the technical guidelines of proper combustion of waste. Also there's still no prove that incinerator REC meets the obligation of the residence of 2 seconds above the 850^0 C in the post combustion zone.

Conclusions

Every source of PFAS or PFOA needs to be considered. PFOA is recently at the Basel, Rotterdam Stockholm Conventions (COPs 9) of 2019 listed as an urgent contamination issue and needs to consider with greatest care. An annual load of 40 mg PFAS seem to be low, but this figure is underestimated by limited techniques we've have today[7]. In addition, the 12 other waste incinerators in the Netherlands never been researched with long term sampling at all. Incinerators of biomass (>100 now in the Netherlands, but much more will coming up), most of the time don't have any air pollution control at all and a very low priority is given at enforcement of co-incineration.

The finding of PFOA in all eggs of backyard chickens in the Netherlands[11], surprisingly linear correlated with the presence of dioxins showing the strong association with the unintentional POPs. More research is needed, introduction of measurement of a much a broader spectrum of POPs in flue gases is strongly advised to meet the need of elimination of POPs in the environment, which is major objective of the Stockholm Convention.

While the data presented in this study provide a conservative estimate of UPOPs-related pollution in the area, the actual impact can be higher, as long-term sampling is interrupted structurally when relevant POPs emissions occur. Long-term sampling shows clearly short-term sampling of dioxins to be non-representative. Also the wide range of other POPs show regular measurement need to be updated to protect human health and environment. The technique of incineration and the recovery of energy, is exponentially promoted in the world as answer to waste crisis. But the question arises if we are not facing a very regrettable solution, because of producing extremely toxic substances persist in human and environment for years and some forever. In this research we focus at a few disadvantages of incineration and its monitoring but there are more in reality. We only stipulate

here the low quality of measurements of emissions, not only POPs. This observation underlined the need to update the data reported by Harlingen waste incinerator or at least thoroughly being controlled by engaged enforcements to be in line with the guidance documents of the Stockholm and Basel Conventions such as for example BAT/BEP Guidelines for technologies listed in Annex C[12].

In using approaches like AMESA for long-term sampling special attention should be paid to the interruptions in the sampling, when transient occasions occur. In other words, long-term sampling must be a continuous process and not being interrupted at moments of emissions. Subsequently excluding emissions occurring during transient stages (like start-ups) from monitoring regulations should be stopped immediately. In agreement with Cheruiyot et al. [13] this study shows that dioxin and other UPOPs emissions should be re-considered during start-up stages in waste incineration[14]. List of monitored POPs should be even broader than suggested inclusion of PBDD/Fs in new BREF document.

Moreover, the results of the measurements in the REC incinerator raise important questions for future policy-making concerning what can be accepted as *normal* operating – and monitoring- conditions for incinerator plants with respect to their potential effects on public health and the environment. The studies reviewed here show unequivocally that dioxins are *still* a serious issue, that measurement programs *still* show serious shortages, that the health of the population is *still* under threat and there is unfortunately *still* a long way to go to totally eliminated dioxin emissions to the environment.

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