Emissions of dl-PCB, PBB, PBDD/F, PBDE, PFOS, PFOA and PAH from a waste incinerator

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Introduction

Since 2011 a 'state of the art' incinerator is established in Harlingen, The Netherlands, with a stringent permit for dioxin emissions of 0,01 ng TEQ/Nm3. In 2013 ToxicoWatch found high concentration PCDD/Fs/ dl-PCBs in eggs of backyard chicken in the surroundings of the incinerator [1]. In August 2015 a long-term sampling program of flue gases was started with analyses of PCDD/F and an extended program analyse of UPOPs on PBDD/F, dl-PCB, PBB, PBDE, PFOS, PFOA and PAH was realized. A summary of the results we present here.

Methods and materials

The emissions of flue gas of the waste incinerator '*Reststoffen Energie Centrale*' (REC) in Harlingen, The Netherlands is measured by semi-continuous sampling method AMESA (**A**dsorption **ME**thod for **SA**mpling of dioxins) [2] and analyses are performed by Eurofins, Hamburg, Germany. Total sample time dl-PCB was 20,748 hours (n=36), the other UPOPs was 3,942 hours (n=6).

Results

PBDE

Polybrominated diphenylethers were detected during an incomplete combustion event in October 2015: 0,434 ng PBDE/Nm^3, predominantly tetra and penta-BDEs. In two out of six measurements results were above the limit of detection.

PBDD/F

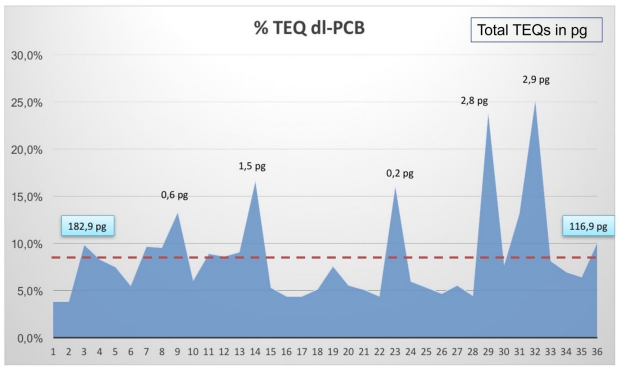
Levels of PBDD/F of 0,01 ng/Nm^3 were found during transient phases of the incinerator. One time the limit of quantification (LOQ) was very high, 3,700 ng PBDD/F. No reason for these high LOQ was given.

pg/Nm3	1 (REC 3)	2 (REC 7)	REC 3 (13)	REC 4 (18)	REC 5 (21)	REC 6 (23)
Date	01-10-15	21-01-16	21-06-16	26-09-16	19-12-16	02-02-17
Hours	667	666	698	671	433	794
Event	sd/su				sd	
PBDDs (UB)	**0,4 (1,3)**	**0 (1,1)**	**0 (950)**	**0 (1,1)**	**4,6 (5,5)**	**0 (0,9)**
PBDFs (UB)	**5,0 (7,2)**	**0 (3,1)**	**0 (2717)**	**0 (2,9)**	**4,3 (8,2)**	**0 (2,4)**

PBDD/F in flue gas (n=6)

Dl-PCB

Sakurai et al (2003) suggest 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 sampling, the average contribution of dl-PCB is 8,5% of the total TEQ (n = 36). PCB 126 is with 85% the most prominent PCB congener and PCB 169 as second (14%) in the TEQ contribution.



% TEQ dl-PCB in flue gas (n=36)

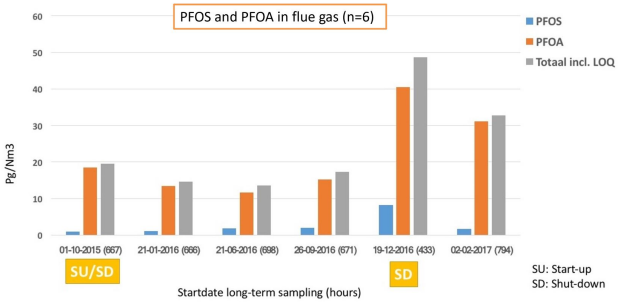
PBB

PBB decompose above 300^0 C, however two times PBB was detected during steady state conditions 0,038 – 0,133 ng/Nm^3

PFOS, PFOA

Fluorinated compound in the long-term sampling program: PFOS was only detectable (above LOQ) in one shutdown event with 0,008 ng/Nm3. PFOA was detectable in all (n=6) samples (433 – 794 hours, total 3,929 hours): Minimum-maximum 0,0134 – 0,004 ng PFOA/Nm^3. The yearly estimation load is 40,1 mg PFOA and 4,9 mg PFOS.
No correlation found between start-up of shutdown events.

Taylor et all (2014) [3] find incineration of fluorotelomer-based polymers does not result in the formation of detectable levels of PFOA under conditions representative of typical Municipal Waste Combustion (MWC) and Medical Waste Incinerator (MWI) operations in the U.S. 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 uncomplete combustion, i.e. not complying with a minimum 2 seconds residence time at 850 °C, or they could be an accidental product of bypassing of Air Pollution Control Devices during start-ups or shut-downs.



PAH

PAH CALUX on sheep wool and black soot deposition on roofs in the environment of the incinerator show high activity in benzo(a)pyrene equivalence (BEQ). However, benzo(a)pyrene could not be found with GC-MS in flue gas. A request of ToxicoWatch to analyse flue gas samples with PAH CALUX was not performed, because local enforcement (FUMO) was not familiar with CALUX bioassays. A comparison with the CALUX research of ToxicoWatch of PAH on sheep wool and soot in the environment near the waste incinerator is therefore not possible. Although the incinerator has not applied for a PAH emission licence, all samples (n=3) were positive on GC-MS, see table below : 2,4 – 314,8 ng/Nm3. The most dominant congener is naphtalene.

PAH			
GC-MS (excl. LOQ)	23-05-17	21-06-17	08-07-17
Sample time (hrs:min:sec)	*695:09:00*	*408:50:00*	*627:00:00*
Naphtalene	286,0	1,7	282,0
Acenaphthylene	0,4	0,1	3,1
Acenaphthene	0,2	0,1	1,8
Fluorene	0,3	0,1	5,9
Phenanthrene	1,0	0,3	19,1
Anthracene	-	-	0,4
Fluoranthene	0,3	0,1	1,8
Pyrene	0,1	0,1	0,7
Benzo[a]pyrene	-	-	-
Total ng/Nm3	**288,3**	**2,4**	**314,8**

PAH in flue gas (n=3)

Conclusions

The contribution of 8,5% dl-PCBs to the total TEQ is nearly 3 times more than other incinerators emit. The presence of UPOPs like PBB and PFOA and even PAH in flue gas samples could indicate the efficiency of the post combustion zone isn't optimal. PBB and PFOA should not be detected at all and certainly not during normal combustion without failures.

Acknowledgements

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