

## LOW PCDD/F- AND POP-EMISSIONS FROM MWI EQUIPPED WITH SMALL DRY FLUE GAS CLEANING SYSTEM

Gass H.C., Schneider C., Sünderhauf W.<sup>1</sup>, Pot E.<sup>2</sup>

<sup>1</sup>Müller-BBM GmbH, Schöneberger Str. 15, D-10963 Berlin, Germany; <sup>2</sup> EVI Abfallverwertung B.V.&Co. KG, Vosmatenweg 6, D-49824 Laar, Germany

### Introduction

Emissions measurements at two lines of the municipal solid waste incinerator EVI, Laar, Germany, have been carried out since the start of operation in 4/2008. The incineration of waste leads to the emission of inorganic and organic gases, even of PCDD/F<sup>1,2</sup>. With optimized combustion in combination with minimal, but effective dry flue gas cleaning system it can be shown that the emission limit values (ELV) due to permit (Table 1) can be met for PCDD/F and POP as well as for other components.

An identical measurement campaign over 3 years at another MWI plant with wet flue gas cleaning has been described earlier<sup>3</sup>. Here, PCDD/F emission concentrations have been significantly higher, still meeting the ELV (17. BImSchV<sup>4</sup>).

### Plant description

EVI (Fig.1) has two identical combustion lines equipped with 3-zones grate design for the incineration of

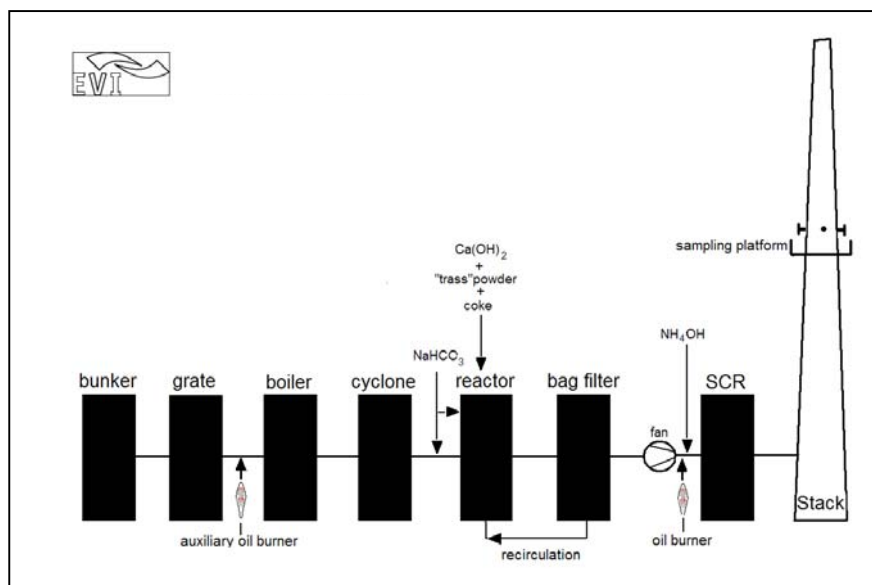


Fig. 1 Plant scheme and sampling location

approx. 25 Mg waste per hour ( $H_u = 12$  MJ/kg), generating ~ 83 t steam (60 bar) per hour. The flue gas cleaning system is identical for each incineration line and consists of a double cyclone,  $\text{NaHCO}_3$ -injection after the cyclones, an absorber reactor with injection of  $\text{NaHCO}_3$  and injection of  $\text{Ca}(\text{OH})_2$ , “trass” powder with coke (HOK) (50/45/5%), a bag filter with PTFE/PI-fabric and with  $\text{NH}_4\text{OH}$ -injection in front of the low temperature catalyser (SCR-DeNOx). A part of the precipitated reaction products/sorbent from the bag filter is recycled into the reactor. Oil firing with auxiliary burner in the post-combustion

Table 1 Emission limit values (ELV) due to permit of EVI (selection) and in accordance to 17. BImSchV

component	unit	ELV	
		due to permit	17. BImSchV
PCDDF I-TEQ	[ng/m <sup>3</sup> ,N]	0,005	0,1
Benzo(a)pyren	[mg/m <sup>3</sup> ,N]	0,6E-06	0,05 *)
PCP	[mg/m <sup>3</sup> ,N]	0,21	-
PCB (WHO)	[mg/m <sup>3</sup> ,N]	0,0015	-

\*) sum B(a)P,As,Cd,Co,Cr (according to §5, point 3c of 17. BImSchV)

chamber and in front of the DeNOx is done only during the start-up procedure and if a temperature drop below 850 °C occurs. Clean gas is released into atmosphere via a 80 m-stack.

## Materials and methods

The sampling point is situated in the stack at a height of 30 m. All requirements of EN 15259<sup>5</sup>, especially for inlet/outlet path length at the sampling location are fulfilled. All sampling and calibration (AST/QAL2) of continuous emission monitoring systems (CEMS) has been carried out by Müller-BBM. Sampling of PCDD/F,

Table 2 PCDD/PCDF data for line 1 and line 2 (emissions clean gas)

Polychlorinated Dibenzo-dioxins and -furans (PCDD/F)	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1	Stack L1
	18.04.08	19.04.08	19.04.08	05.05.09	16.06.09	22.09.09	19.01.10	23.03.10	06.05.10	07.07.10	26.08.10	Stack L1	Stack L1	Stack L1
	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]
sum TetraCDD	0.0019	0.0067	0.015	0.00132	0.0011	0.0040	0.0034	0.0019	0.0018	0.0023	0.0023	0.0023	0.0023	0.0102
sum PentaCDD	0.0022	0.006	0.0135	0.00176	0.0012	0.0050	0.0042	0.0020	0.0016	0.0041	0.0026	0.0044	0.0044	0.0044
sum HexaCDD	0.0091	0.0117	0.0197	0.00237	0.0018	0.0077	0.0075	0.0022	0.0023	0.0051	0.0039	0.0057	0.0057	0.0057
sum HeptaCDD	0.0115	0.0065	0.0103	0.00355	nc	0.0057	0.0076	nc	nc	nc	nc	nc	nc	nc
OctaCDD*)	0.0118	< 0.009	< 0.009	0.00502	< 0.0065	< 0.0090	< 0.009	< 0.009	< 0.008	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009
sum PCDD	0.0385	0.0309	0.0585	0.01402	0.0041	0.0224	0.0227	0.0062	0.0057	0.0114	0.0088	0.0203	0.0203	0.0203
sum TetraCDF	0.0046	0.0193	0.0212	0.00478	0.003	0.0060	0.0042	0.0087	0.0037	0.0029	0.0039	0.0286	0.0286	0.0286
sum PentaCDF	0.0074	0.0118	0.0172	0.00273	0.0008	0.0021	0.0016	0.0044	nc	0.0027	0.0019	0.0056	0.0056	0.0056
sum HexaCDF	0.0179	0.0089	0.0141	0.00195	nc	0.0007	0.0007	0.0027	nc	0.0011	nc	0.0007	0.0007	0.0007
sum HeptaCDF	0.0233	0.0049	0.0087	nb	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
OctaCDF*)	0.013	< 0.009	< 0.009	< 0.0045	< 0.0065	< 0.0090	< 0.009	< 0.009	< 0.008	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009
sum PCDF	0.0662	0.0449	0.0612	0.00946	0.0038	0.0088	0.0065	0.0157	0.0037	0.0067	0.0058	0.0349	0.0349	0.0349
sum PCDD+ PCDF	0.1027	0.0758	0.1197	0.02348	0.0079	0.0312	0.0291	0.0219	0.0094	0.0181	0.0145	0.0552	0.0552	0.0552
I-TEQ excl. LOD *)	0.00124	0.00115	0.00217	0.00022	nc	0.00021	0.00004	0.00030	0.00002	nc	nc	0.00004	0.00004	0.00004
I-TEQ incl. LOD *)	0.00191	0.00180	0.00275	0.00074	0.00085	0.00137	0.00118	0.00136	0.00118	0.00117	0.00117	0.00121	0.00121	0.00121
2378-TetraCDD	< 0.0002	< 0.0002	< 0.0002	< 0.0001	0.00015	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002
12378-PentaCDD	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0003	< 0.0005	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
123478-HexaCDD	< 0.0006	< 0.0006	< 0.0006	< 0.0003	< 0.0004	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123678-HexaCDD	0.0007	0.0006	0.0013	< 0.0003	< 0.0004	0.0015	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123789-HexaCDD	< 0.0006	< 0.0006	0.0009	< 0.0003	< 0.0004	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
1234678-HeptaCDD	0.0061	0.0034	0.0055	0.00185	< 0.002	0.0030	0.0040	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
OctaCDD	0.0118	< 0.009	< 0.009	0.00502	< 0.0065	< 0.0090	< 0.009	< 0.009	< 0.008	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009
2378-TetraCDF	< 0.0004	0.0011	0.0012	0.00024	0.00015	0.0003	< 0.0002	0.0018	0.0002	< 0.0002	< 0.0002	0.0004	0.0004	0.0004
12378/12348-PentaCDF	0.0006	0.0008	0.0009	< 0.0002	< 0.0003	< 0.0004	< 0.0004	0.0008	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
23478-PentaCDF	0.0006	0.0011	0.0023	0.00028	< 0.0003	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
123478/123479-HexaC	0.0027	0.0015	0.0016	< 0.0003	< 0.0004	< 0.0006	< 0.0006	0.0008	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123678-HexaCDF	0.0019	0.0008	0.0013	< 0.0003	< 0.0004	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123789-HexaCDF	< 0.0006	< 0.0006	< 0.0006	< 0.0003	< 0.0004	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
234678-HexaCDF	0.0015	0.0009	0.0022	0.00038	< 0.0004	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
1234678-HeptaCDF	0.0142	0.0036	0.0067	< 0.0015	< 0.002	< 0.0030	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
1234789-HeptaCDF	< 0.003	< 0.003	< 0.003	< 0.0015	< 0.002	< 0.0030	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
1,2,3,4,6,7,8,9-OCDF	0.013	< 0.009	< 0.009	< 0.0045	< 0.0065	< 0.0090	< 0.009	< 0.009	< 0.008	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009

nc = not calculated (all isomers below detection limit)  
 \*) I-TEQ = NATO/CCMS TEQ values

Polychlorinated Dibenzo-dioxins and -furans (PCDD/F)	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2	Stack L2
	05.05.09	16.06.09	30.06.09	03.11.09	04.12.09	20.01.09	24.03.10	05.05.10	06.07.10	03.11.10	Stack L2
	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]	[ng/Nm <sup>3</sup> ]
sum TetraCDD	0.0010	0.0007	0.0021	0.0018	0.007	0.0023	0.0028	0.0032	0.0018	0.0071	0.0071
sum PentaCDD	0.0009	0.0016	0.0033	0.0015	0.011	0.0021	0.0014	0.0023	0.0033	0.0035	0.0035
sum HexaCDD	0.0016	0.0029	0.0084	0.0018	0.016	0.0046	0.0011	0.0033	0.0043	0.0037	0.0037
sum HeptaCDD	0.0029	0.0032	0.0117	nc	0.018	0.0104	nc	nc	nc	nc	nc
OctaCDD*)	< 0.0045	< 0.0045	0.0214	< 0.0045	0.016	0.0184	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009
sum PCDD	0.0064	0.0084	0.0469	0.0051	0.067	0.0377	0.0052	0.0088	0.0094	0.0143	0.0143
sum TetraCDF	0.0041	0.0029	0.01	0.0023	0.009	0.0009	0.0036	0.0053	0.0007	0.0184	0.0184
sum PentaCDF	0.0017	nc	0.0063	0.0008	0.006	0.0012	0.0009	0.0011	0.0005	0.0027	0.0027
sum HexaCDF	0.0008	nc	0.0032	0.0004	0.005	0.0007	nc	nc	nc	0.0007	0.0007
sum HeptaCDF	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
OctaCDF*)	< 0.0045	< 0.0045	< 0.009	< 0.0045	< 0.008	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009
sum PCDF	0.0066	0.0029	0.0195	0.0035	0.019	0.0029	0.0045	0.0064	0.0012	0.0218	0.0218
sum PCDD+ PCDF	0.0130	0.0113	0.0664	0.0086	0.086	0.0406	0.0098	0.0152	0.0105	0.0361	0.0361
I-TEQ excl. LOD *)	0.00019	0.00004	0.00103	nc	0.00051	0.00008	0.00003	nc	nc	0.00005	0.00005
I-TEQ incl. LOD *)	0.00072	0.00061	0.00164	0.00068	0.00160	0.00121	0.00118	0.00119	0.00117	0.00122	0.00122
2378-TetraCDD	< 0.0001	< 0.0001	< 0.0002	< 0.0001	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002
12378-PentaCDD	< 0.0002	< 0.0002	< 0.0004	< 0.0002	< 0.0006	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
123478-HexaCDD	< 0.0003	< 0.0003	< 0.0006	< 0.0003	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123678-HexaCDD	< 0.0003	< 0.0003	0.0011	< 0.0003	0.001	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123789-HexaCDD	< 0.0003	< 0.0003	0.0007	< 0.0003	0.001	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
1234678-HeptaCDD	0.0015	0.0018	0.0076	< 0.0015	0.008	0.0059	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
OctaCDD	< 0.0045	< 0.0045	0.0214	< 0.0045	0.016	0.0184	< 0.009	< 0.009	< 0.009	< 0.009	< 0.009
2378-TetraCDF	0.0002	0.0002	0.0012	< 0.0001	0.000	< 0.0002	0.0003	< 0.0002	< 0.0002	0.0005	0.0005
12378/12348-PentaCDF	< 0.0002	< 0.0002	0.0009	< 0.0002	< 0.0006	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
23478-PentaCDF	0.0003	0.0002	0.0007	< 0.0002	< 0.0006	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
123478/123479-HexaC	< 0.0003	< 0.0003	0.0008	< 0.0003	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123678-HexaCDF	< 0.0003	< 0.0003	0.0008	< 0.0003	0.001	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006	< 0.0006
123789-HexaCDF	< 0.0003	< 0.0003									

PCB (WHO), chlorophenols (Tri- to PentaCPh) and benzo(a)pyren (B(a)P) was performed according to EN 1948-1, method B3, suitable for net measurements. Analysis of PCDD/F and POP has been done by mas GmbH<sup>\*)</sup> in compliance with EN 1948-2 and -3<sup>6</sup> using HRGC/HRMS.

### Results and discussion:

First measurements at line 1 have been done during start-up of the incinerator, i.e. first fire with waste, during test operation in 4/2008. As it can be seen in Table 2 the concentrations of PCDD/F were slightly increased (0,0012 – 0,0022 ng ITEQ/Nm<sup>3</sup>) on a low level, but nevertheless below ELV. The slightly increased PCDD/F concentrations may be explained by contamination of the inner surface of boiler, duct and gas cleaning system in combination with “memory-effect”<sup>7,8,9</sup> due to incomplete burning conditions of the auxiliary oil burner during hot commissioning, i.e. drying, blow-out and boil-out operations<sup>10</sup>.

Table 3 Concentrations of POPs during measurements from 5/2009 until 11/2010

		line 1	line 2
PCB (WHO) TEQ	ng/Nm <sup>3</sup>	nc - 0,00005	nc - 0,00002
PCB (WHO) sum	ng/Nm <sup>3</sup>	nc - 0,42	nc - 0,16
BaP	ng/Nm <sup>3</sup>	< 0,1 - 0,22	< 0,05 - 0,64
Tri- to PentaCPh	µg/Nm <sup>3</sup>	nc	nc

nc = not calculated (all isomers below detection limit)

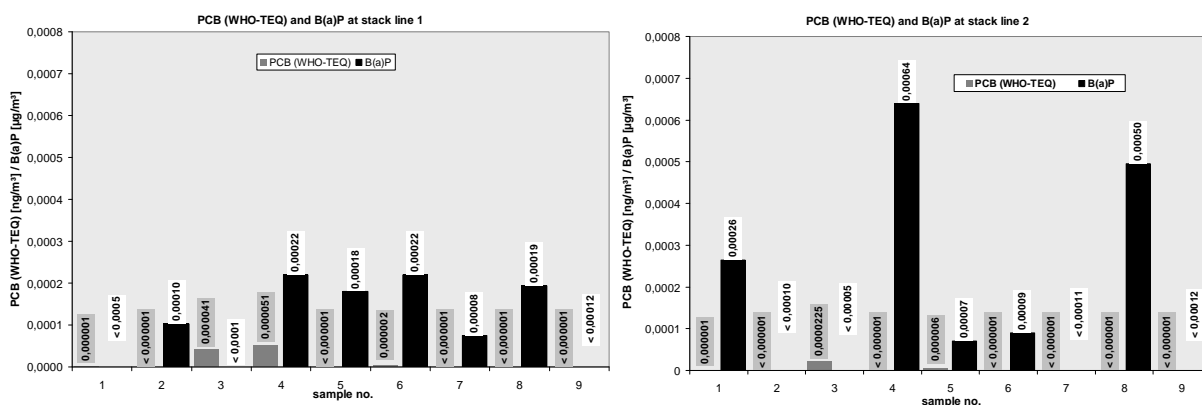


Fig. 2 Concentrations of PCB (WHO-TEQ) and B(a)P emissions from line 1 and line 2

With the beginning of normal operation of the MWI on both lines in 5/2009, PCDD/F concentrations measured were even lower (line 1: nc – 0,00030 ng ITEQ/Nm<sup>3</sup>, line 2: nc – 0,00051 ng ITEQ/Nm<sup>3</sup>). Simultaneously, all other POP values measured had low levels (Table 3 and Fig. 2).

We see the following causes for the low emission concentrations:

- By controlling primary and secondary air injection via prism tube by means of ultrasonic grid temperature measurement in the first flue / combustion zone to realize post combustion temperatures of > 900 °C during full load operation (100-110%), optimized combustion conditions are achieved (CO < 10 mg/m<sup>3</sup>, total organic carbon TOC < 1 mg/m<sup>3</sup> during all measurement campaigns).
- Very low dust concentrations, due to a combination of double cyclone and bag filter and effective even for small particles, are achieved due to the tight (no leakage) membrane bag filters (PTFE filter material). All dust measurements over two years showed total dust concentrations below 0,2 mg/m<sup>3</sup>, with a PM 10 contribution to the total of 78 % (line 1) resp. 71 % (line 2) and a PM 2,5 contribution of 59 % (line 1) resp. 49 % (line 2).

<sup>\*)</sup> mas | münster analytical solutions gmbh, 48149 Münster

- The gas cleaning device with the injection of coke and the dust/coke layer on the bag filter removes nearly the total amount of POP components as well as the heavy metals. Thus, the heavy metals also are below ELV (individual limits due to permit, e.g. Cd 0,001 mg/m<sup>3</sup>, Sb 0,0006 mg/m<sup>3</sup>, As 0,0005 mg/m<sup>3</sup>, Cr 0,002 mg/m<sup>3</sup>). No impact of various coke (HOK) amounts injected on sum PCDD, sum PCDF and sum PCDD/F could be observed (Fig. 3).

The amount of coke (HOK) used is only guided by the Hg-emission as observed and controlled with the CEMS.

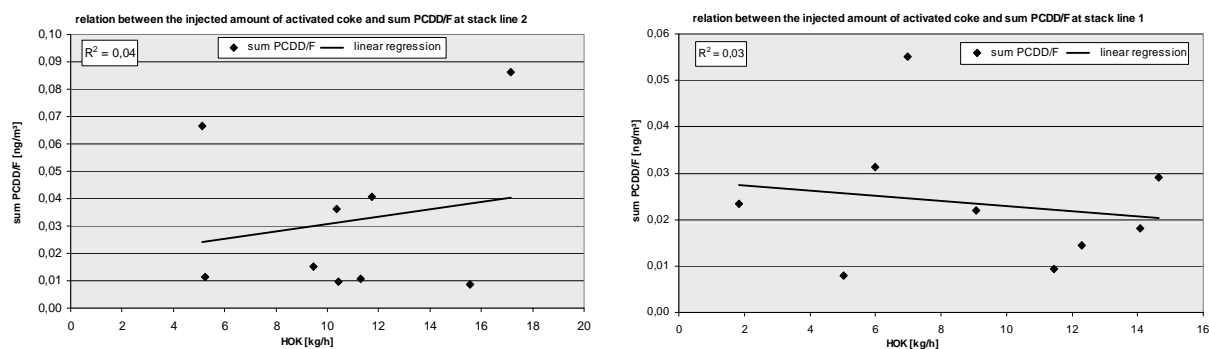


Fig. 3 Sum PCDD/F as function of coke (HOK) amount injected for line 1 and line 2.

Further measurements will be carried out in the raw gas (behind boiler) and in clean gas to assess the impact of primary combustion conditions and the efficiency of the cleaning system (e.g. pressure drop of bag house, amount of coke) to the clean gas emissions in detail.

#### Acknowledgements:

The authors would like to thank the EVI staff for providing the necessary data.

#### References:

1. Nestruck TJ, Lamparski LL. *Anal. Chem* 1982; 54: 2292
2. Stieglitz L, Vogg H, Zwick G, Beck J, Bautz H. *Chemosphere* 1991; 23: 1255
3. Gass HC, Jager E, Menke D, Lüder K (1998); *Organohalogen Compounds Vol. 36*: 175-78
4. Verordnung über die Verbrennung und die Mitverbrennung von Abfällen in der Fassung der Bekanntmachung vom 14. August 2003 - 17. BImSchV) (8/2003); *BGBl. I*: 1633
5. Air quality – Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report; German version EN 15259 (2007)
6. EN 1948/1-3; Stationary source emissions – Determination of mass concentration of PCDDs/PCDFs, Part 1: Sampling; Part 2: Extraction and clean-up; Part 3: Identification and qualification; German version EN 1948 (2006)
7. Kreis S, Hunsinger H, Vogg H (1996); *Chemosphere Vol.32, No.1*: 73-78
8. Gass HC, Sünderhauf W, Rotard W, Jager J. (2000); *Organohalogen Compounds Vol.46*: 154-57
9. Gass HC, Werner C, Sünderhauf W, Meisser J, Schulte J. (2005); *Organohalogen Compounds Vol.67*: 2265-67
10. Hunsinger H, Jay K, Vehlow J (2002); *Chemosphere Vol.46*: 1263-72