Secondary Analysis of Dioxin Emission Data of a Municipal Solid Waste Incinerator

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Introduction

In the course of the start-up and optimization phase of the municipal solid waste incinerators (MSWI) MVB Borsigstr. GmbH, Hamburg, more than 200 polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) emission samples were measured in flue gas simultaneously at up to five test points between 1994 and 1998[1]. Overall 28 measurement campaigns are available from the 5-year investigation period that comprise between 2 to 5 data records related to the single series of measurements and determined at the following sampling points: "A" downstream of the boiler, "B" behind a fabric filter, "C" behind a 2-step HCl-scrubber, "D" behind an alcaline scrubber, "E": behind a wet electrostatic precipitator (ESP).
In various series of measurements, an increase in the I-TEQ-value was determined in the course of passing the flue gas cleaning system (FCS). Comparable observations which are also connected to plastic-coated and gummed surfaces of scrubber systems of MSWI and justified with adsorption/desorption effects by the majority have been published during the past few years[2,3,4,5,6]. Within the framework of the present document, the substantiated pairs of measured values of the sampling points "B" and "E" are evaluated by means of statistical methods. The measured values of the sampling points "C" and "D" are not considered in detail here due to the limited data record (n=10) and the sampling points that are not in accordance with the directive. Furthermore it is examined whether and to what extend there is a modification of the homologue and isomer profile via the FCS provided that the plant is operated as usual.
Finally the PCDD/F concentration profile of the plastic-coated scrubber wall is qualitatively represented by means of measured values that resulted from wipe and material samples of HCl-scrubbers in the area of the scrubber bottom of a fluidized-bed incinerator fed with domestic waste[7].

Plant Description

MVB (Fig.1) has 2 identical combustion lines equipped with a forward feed grate (5 grate zones and 2 grate steps) designed for incinerating 21.5 tons of waste per hour. The flue gas cleaning system for each combustion unit consists of a selective non-catalytic reduction of NO_x (SNCR) by injection of steam-dispersed ammonia into the post-combustion chamber, a high temperature dust-removal system within the boiler between the super heater section and the economizer, an evaporative cooler, the injection of activated carbon, a bag, a two step scrubber, an alcaline scrubber and a wet electrostatic precipitator (ESP).

Sampling Treatment and Analysis

PCDD/F sampling and analysis of emissions were performed by MPU according to the German guideline VDI 3499 part 2 using HRGC/HRMS [8]. Details are described in reference [9]. At the test points "B" and "E", the requirements regarding the upstream and downstream paths according to German guideline VDI 2066 are met[10]. The detection limit was 0.001 ng/Nm³ for all 2,3,7,8-substituted isomers.

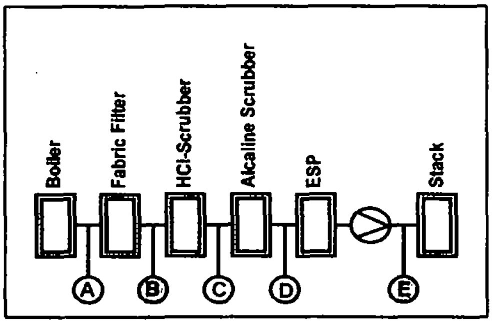

Fig.1 PCDD/F sampling points in the flue gas cleaning system of MVB

Statistic Analysis

The statistical analysis serves the purpose of checking whether the measured values at test points "B" and "E" significantly deviate from each other. This analysis is done step by step:

- A sign check is carried out regarding related value pairs.
- By means of the t-test it is checked whether the Y-values (measurements at the test point "E") significantly differ from the X-values (measurements at the test point "B") and in which direction.

The observed pairs (Xi; Yi) are linked random samples, with Xi representing the measurements after the fabric filter and Yi the results measured simultaneously in the pure gas. In order to facilitate the comparability of the value pairs, the X- and Y-values adjusted to masses have been standardized to standard conditions (273 K, 1013 hPa) and a uniform oxygen content of 10 Vol.%.

Table 1: PCDD/PCDF-Data at sampling points "B" and "E" (excerpt: 8 campaigns out of 22)

plant	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB	MVB
incineration line	L1	L1	L1	L1	L2	L2	L1	L1	L2	L2	L2	L2	L2	L2	L2	L2
sampling date	03.02.94	03.02.94	21.04.94	21.04.94	14.09.94	14.09.94	05.10.94	05.10.94	11.05.95	11.05.95	11.09.96	11.09.96	12.09.96	12.09.96	27.03.98	27.03.98
sampling time	18.00-21:00	18:00-21:00	09:30-12:30	09:30-12:30	15:15-18:15	15:15-18:15	16.45-19:45	16:45-19:45	08:00-14:00	08:00-14:00	13:00-19.00	13:00-19:00	12:30-18:30	12:30-18:30	16:15-22:15	16:15-22:15
remark	startup	startup	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.	optim.
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
sampling campaign no.	2	2	6	6	12	12	14	14	19	19	22	22	23	23	28	28
sampling no.	3	4	15	19	46	49	56	59	72	75	87	88	90	91	105	106
samplin point	B	E	B	E	B	E	B	E	B	E	B	E	B	E	B	E
oxygen content [Vol. -%]	8,1	8,7	8,4	8,3	9	8,9	9	9,3	8,2	8,3	7,3	7,5	8,8	8,9	4,6	5,8
PCDD/F	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]	[ppq]
sum TetraCDD	14,0	264	3,31	33,5	5,57	15,0	4,45	24,2	2,67	10,3	6,58	14,0	8,28	13,7	2,75	3,79
sum PentaCDD	16,1	145	5,15	15,5	10,4	25,2	6,03	25,7	2,95	8,73	9,47	18,0	10,9	18,5	6,53	5,76
sum HexaCDD	14,9	46,7	6,33	4,06	14,6	36,9	5,62	13,6	7,36	7,96	13,5	18,5	13,8	18,0	10,4	7,33
sum HeptaCDD	8,62	6,63	4,82	0,95	13,5	19,1	2,53	3,40	4,59	2,64	9,23	8,52	8,60	8,77	10,6	3,58
OctaCDD	0,39	0,67	2,55	0,46	17,7	12,0	1,95	1,00	2,92	0,78	6,27	2,17	4,07	2,71	3,89	0,65
sum PCDD	54	463	22,2	54,5	61,7	110	20,6	67,9	20,5	30,4	45,0	61,3	45,6	61,7	34,1	21,1
sum TetraCDF	13,6	147	4,39	23,9	111	39,6	12,2	41,9	2,88	19,1	7,37	21,3	8,35	20,2	3,96	5,61
sum PentaCDF	11,1	62,8	5,33	10,3	31,5	37,1	9,87	31,7	1,23	11,3	5,19	12,7	6,02	14,4	1,78	3,12
sum HexaCDF	4,80	12,5	3,19	2,37	13,5	26,3	5,44	9,81	0,95	3,73	3,45	4,99	4,64	5,16	1,09	1,27
sum HeptaCDF	1,78	1,92	1,41	0,47	11,5	9,39	2,63	2,36	0,21	0,72	0,67	1,56	0,54	1,79	0,44	0,30
OctaCDF	0,41	0,11	0,39	0,10	12,9	2,85	3,28	1,29	0,14	0,10	0,53	0,31	0,20	0,40	0,15	0,12
sum PCDF	31,7	224	14,7	37,1	180	115	33,4	87,1	5,42	35,0	17,2	40,8	19,8	42,0	7,43	10,4
total PCDD+PCDF	85,7	687	36,9	91,6	242	225	53,9	155	25,9	65,4	62,2	102	65,4	104	41,5	31,5
tox. equivalents I-TEQ [ng/Nm3]	0,019	0,125	0,010	0,018	0,055	0,065	0,016	0,047	0,006	0,015	0,008	0,026	0,008	0,025	0,009	0,007
2,3,7,8-TetraCDD	0,12	2,99	0,04	0,33	0,14	0,21	0,07	0,14	0,06	0,07	0,04	0,25	0,04	0,35	[illegible]	[illegible]
1,2,3,7,8-PentaCDD	0,30	2,69	0,18	0,42	0,44	0,75	0,31	0,90	0,12	0,24	0,11	0,39	0,19	0,37	0,14	0,10
1,2,3,4,7,8-HexaCDD	0,29	1,03	0,11	0,11	0,34	0,68	0,12	0,29	0,11	0,16	0,20	0,36	0,23	0,40	0,21	0,09
1,2,3,6,7,8-HexaCDD	1,09	3,27	0,49	0,38	1,03	2,56	0,57	1,12	0,43	0,43	0,60	0,97	0,62	0,97	0,71	0,38
1,2,3,7,8,9-HexaCDD	0,67	1,86	0,33	0,22	0,80	1,31	0,12	0,47	0,22	0,16	0,25	0,51	0,28	0,51	0,34	0,18
1,2,3,4,6,7,8-HeptaCDD	4,28	2,86	2,56	0,50	6,79	8,41	1,21	1,57	2,12	1,09	4,38	3,56	3,68	3,76	4,20	0,92
2,3,7,8-TetraCDF	0,44	5,11	0,14	0,90	5,27	2,25	0,59	2,48	0,55	0,83	0,32	1,17	0,43	1,23	0,21	0,46
1,2,3,7,8+1,2,3,4,8-PentaCDF	0,54	2,47	0,25	0,37	2,70	1,76	0,46	1,89	0,19	0,62	0,17	0,53	0,19	0,46	0,10	0,21
2,3,4,7,8-PentaCDF	0,69	3,9	0,44	0,68	3,03	3,20	0,72	3,17	0,12	0,75	0,23	0,99	0,26	0,98	0,14	0,31
1,2,3,4,7,8+1,2,3,4,7,9-HexaCDF	0,45	1,22	0,34	0,23	1,73	2,49	0,78	1,35	0,11	0,34	0,11	0,43	0,12	0,42	0,09	0,19
1,2,3,6,7,8-HexaCDF	0,58	1,45	0,40	0,23	1,73	2,79	0,66	1,10	0,06	0,34	0,11	0,48	0,18	0,47	0,13	0,28
1,2,3,7,8,9-HexaCDF	0,07	0,06	0,06	0,03	0,24	0,42	0,03	0,12	[illegible]	0,03	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2,3,4,6,7,8-HexaCDF	0,63	1,43	0,40	0,23	2,21	3,85	0,48	1,10	0,39	0,51	0,16	0,64	0,29	0,71	0,22	0,33
1,2,3,4,6,7,8-HeptaCDF	1,22	1,44	0,99	0,31	8,32	6,89	1,59	1,68	0,15	0,52	0,43	1,07	0,27	1,14	0,28	0,39
1,2,3,4,7,8,9-HeptaCDF	0,14	0,05	0,05	0,03	1,09	0,54	0,27	0,11	0,05	[illegible]	0,05	0,10	[illegible]	0,16	0,04	[illegible]

highlighted values: concentration below detection limit, value calculated with 1/2 detection limit

Results

Within the framework of this evaluation, a total of22 value pairs of sampling point "B" and "E" have been taken into account, see table 1 (excerpt of complete results). What has been characteristic of all of the 22 examination periods is an almost stationary and nearly undisturbed plant operation of the two identically constructed incineration lines. Three measuring campaigns in the course of which there were breakdowns as well as another three series of measurements that showed no PCDD/F clean gas data have been rejected for this consideration.

As result of the sign check can be noticed a rather significant increase via the FCS for the sums of TCDD/F-HxCDD/F, the significance level is at least 98.5%. The sum of HpCDD as well as of 1,2,3,4,7,8,9-HpCDF are identical regarding the concentration level. A concentration inversion is noticed at the OCDD/F as well as at the 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDF. A significant increase via the FCS could also be noticed for any other single isomers with the significance level being at least 86%.

The t-test analogously shows a very significant increase in the ITEQ (> 99%), sums and the predominant number of isomers of TCDD/F - HxCDD/F (at least 95%). The results regarding the HpCDD/F are not significant. However, a somewhat lower significance of about 80% at a decrease in concentration can be noticed for the OCDD/F. Rejecting the measured values of the measuring campaign 7, you also get a significance level of 95% for the 2,3,7,8 TCDF and also some change in significance for other sums and isomers. We consider this procedure justified since there has been a plant failure prior to measuring campaign 7.

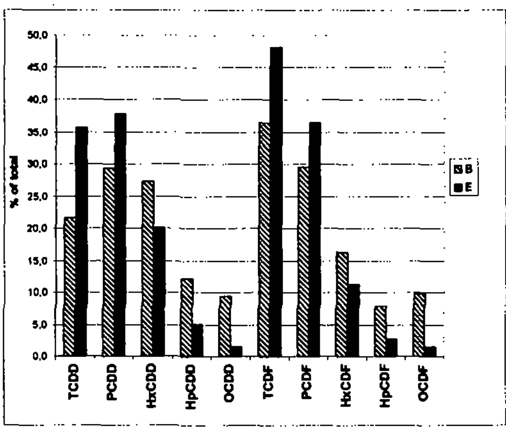

Fig. 2: PCDD/F distribution [%] at sampling points B and E, campaign no.11

At the example of a selected serie of measurements (with an average emission level) it can be shown that there is not only a modification in concentration but also in the PCDD/PCDF-distribution profile via FCS, see fig. 2.

Fig. 3 qualitatively shows to what extend the inside of a channel or wall surface in a wet scrubber system can be enriched with PCDD/F under unfavorable operating conditions that extend over a operating period of approx. 1-year. The PCDD/F values measured at wipe and material samples of a drilling core which were taken about 0.3 m below the liquidity level of a HCl scrubber bottom of a fluidized bed incinerator fed with domestic waste, clarify that the PCDD/F load primarily occurs in the plaque as well as in the utmost surface layer of the GFK scrubber wall coated with plastic material. At a material thickness of about 1mm, a decrease in the PCDD/F concentration by factor 30 could be determined. It can furthermore be derived from other sample results that the PCDD/F load of the plaque or the inner wall surface in the area of the scrubber bottom is about 2 dimensions higher than in the spraying zone.

Discussion

First of all it is postulated that there is no PCDD/F formation from precursors under the conditions of wet-operated components of a flue gas cleaning system and that a chlorination of the Mono-TriCDD/F can be neglected as far as quantity is concerned.

PCDD/F bound to dust and soot particles in the flue gas of a MSWI is separated at the inner surfaces of scrubber systems, with a little share of which being taken out by means of the liquid and solid substance streams of the gas path. The gaseous PCDD/F emissions are bound to the inner channel or plaque surfaces of the scrubber components. On account of the rather low PCDD/F concentration in the flue gas, the PCDD/F coverage density at the wall surface is proportional to the partial pressure analogue to Henry's law. It has to be assumed that, apart from steric influences, mainly van der Waals forces dominate the adsorption of PCDD/F at the non-polar surfaces. The affinity on a non-polar surface generally follows the sequence of molecular weights. With regard to those effect mechanisms, it can be explained that, on the one hand, the low-chlorinated PCDD/F is increasingly desorbed compared to the high-chlorinated PCDD and on the other hand, PCDF is increasingly released from the plaque or inner wall compared to dioxins.

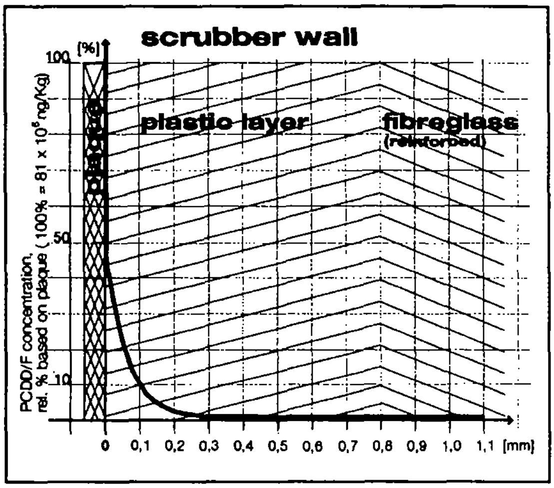

Fig. 3: PCDD/F load at scrubber wall surface

The source of the PCDD/F load at the scrubber wall surface or its coating is obviously the gas phase either directly via the gas path or indirectly via the gas over the plaque towards the plastic wall. An estimate via an e-function shows that the PCDD/F load of the plastic layer can be described according to figure 3.

In our opinion, the following operating conditions can be considered to be a cause for the critical operating conditions of a MSWI and are thus partially connected to the danger of increased PCDD/F input into the FCS: startup/shutdown, soot blowing, non-stationary plant operation, unexpected failure or malfunction of plant components

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