

## PCDD/F, PCB, Chlorobenzene and Chlorophenol Emissions Of A Municipal Solid Waste Incineration Plant (MSWI) - Variation Within A Five Day Routine Performance And Influence Of $Mg(OH)_2$ -Addition

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### 1. Objectives

The MSWI Bielefeld-Herford is in operation since 1981. Its PCDD/F emission concentrations amount to 4 - 5 ng TE (BGA)/Nm<sup>3</sup> during routine operation<sup>1</sup>. Due to a luff/lee-study, these emission levels have probably raised soil contamination by PCDD/F for about 1 ng TE/kg in the neighbourhood<sup>2</sup>. PCDD/F-emission will be reduced to less than 0.1 ng I-TEQ/Nm<sup>3</sup> by several means like exclusion of PVC and computer scrap in the input, optimizing combustion operation<sup>3</sup>, installation of a high-performance quasi-dry flue gas purification system (already realized) and by (projected) selective catalytic nitrogen reduction followed by lime/activated-carbon addition and subsequent fibric textile filter<sup>4</sup>.

Within the debate about the environmental input from this plant, citizen's organization doubted the reliability of former emission measurements and judged them as random hits. Plant management therefore decided to attempt a new approach: For a period of five days, clean gas samples were collected quasi-continuously, and citizen's organization selected the samples to be analyzed. Additionally, the effect of an additive on PCDD/F emission concentration was investigated. Finally, the objectives of this investigation were to clarify two questions:

- a) What is the range of PCDD/F emissions of a MSWI during routine performance? How reliable are single emission measurements?
- b) Can the emission of halogenated hydrocarbons be reduced by the addition of  $Mg(OH)_2$  analogous to the addition of  $Ca(OH)_2$ ?

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## 2. Approach and methods

Sample collection was performed from december 16 to 20, 1991 during routine operation. At combustion line No. 1, clean gas samples were taken every three hours without stops. This shortened collection period was chosen for a better association of the organic substance concentrations to continuously measured flue gas parameters. Sample collection took place at the linkage between scrubber outlet and chimney inlet. Here, two sampling devices were installed such a way that they could quickly be exchanged for starting a new sample collection. In addition, flue gas temperature was discontinuously measured with a NiCrNi-thermoelement. Further flue gas parameter (total dust,  $C_{org}$ , CO, O<sub>2</sub>, HCl, HF, SO<sub>2</sub>, NOx, flue gas volume in operating and in standard status) were measured by plant personnel and valuated by the authors. In total, 40 clean gas samples were taken, from which 15 (# 1, 4, 9, 12, 17, 20, 21, 22, 23, 24, 25, 26, 27, 35, 40) were selected for analysis. As during the first half of the test period (samples 1 to 20) Mg(OH)<sub>2</sub> was added for reduction of cauldron deposits, samples in the beginning of the twenties were preferably chosen to register the suspected rise in PCDD/F concentration in clean gas. Later on, further four clean gas samples (# 7, 31, 37, 39) and two mixed electro filter dust samples (one with and one without Mg(OH)<sub>2</sub> addition) were analyzed.

Sample collection followed VDI<sup>6</sup> (condensatio) method with adsorption of not condensable and gaseous substances on a XAD 2-resin. Immediately before starting sample collection, the particle filter in front of the condensate sampler was spiked with a <sup>13</sup>C<sub>12</sub>-dioxin standard. Analytical methods follow procedures referring to German (semi-)official standards, like VDI 3499 for PCDD/F, and DIN 51 527, part 1 for PCB. Before extraction, all sub-samples are spiked with a mixture of a <sup>13</sup>C<sub>12</sub>-labelled PCDD- and PCDF-standard per degree of chlorination and with an unlabelled standard for identifying PCB-, chlorobenzene- and chlorophenol-compounds. Afterwards, the sub-samples "filter material" and "adsorption material" are extracted with toluene, "condensate" and "rinsing liquid" with dichloromethane. From the unified raw extracts a smaller part is taken for chlorophenol detection, while the larger one did undergo clean-up and fractioning by adsorption chromatography on silicagel- and aluminum oxid columns. The PCB containing fraction is concentrated and a defined aliquot of the final volume is injected into a GC with a non-polar capillary column (DB-5 by J&W). PCB congeners are detected by ECD. Quantification is based on standard addition and is performed with six single congeners given in DIN 51 527 part 1 (Ballschmitter Nos. 28, 52, 101, 138, 153, 180). Total PCB is calculated by multiplying this result with a factor of 5. The PCDD/F containing fraction is concentrated and a defined aliquot of the final volume is injected into a GC/MS. Screening analysis and detection of higher chlorinated congeners is performed with a non-polar DB-5 capillary column, isomer specific detection uses a

polar capillary column (CP Sil 88), the MS performing in MID-mode (multiple ion detection). Quantification is based on standard addition, with a recovery rate of the internal standard of at least 70 %. The chlorophenol containing fraction is cleaned, too. An increase in sensitivity and selectivity is achieved by derivation of chlorophenols.

### 3. Results

Table 1: Emission of organohalogen trace compounds in clean gas, in ng/Nm<sup>3</sup>

Test run	PCDD/F, I-TEQ	PCB sum	Chlorobenzenes	Chlorophenols
1	8.09	84.0	1,057	2,103
4	9.19	106	2,000	2,301
7	5.41	88.3	1,667	2,422
9	5.99	96	1,276	2,738
12	5.53	111	1,296	2,939
17	5.17	105	1,571	2,002
20	5.06	77.8	1,320	1,369
median	5.53	96	1,320	2,301
average	6.21	95.4	1,455	2,268
21	2.29	57.1	1,023	2,279
22	3.17	70.3	851	1,398
23	2.90	44.5	857	2,178
24	3.35	41.9	1,196	1,641
25	2.87	63.6	1,010	1,618
26	2.62	54.7	1,255	1,379
27	2.81	65.9	1,162	1,201
31	2.64	55	1,170	1,634
35	2.07	65.2	1,092	1,837
37	1.88	55.8	1,261	1,809
39	2.93	54.7	1,225	3,685
40	7.76	61.2	1,287	2,666
median	2.84	56.5	1,166	1,725
average	3.11	57.5	1,116	1,944
average of all	4.25	71	1,241	2,062

The results of halogenated hydrocarbon trace analysis are given in table 1. Except clean gas sample # 40, all samples of performance without Mg(OH)<sub>2</sub> addition (# 21 - 40) show less PCDD/F (in I-TEQ) than during addition of this substance. Medians are 5.53 and 2.84 ng I-TEQ/Nm<sup>3</sup> respectively. Following the U-test (Mann-Whitney-Wilcoxon), PCDD/F results of test runs # 1 - 20 differ to the results of test runs # 21 - 40 with a level of significance of  $p < 0,05$ . The same is true for PCB,

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chlorophenol and chlorobenzene in the gas phase. In the filter dust, PCDD/F concentration (in I-TEQ) slightly decreased when the addition of  $Mg(OH)_2$  was stopped, while chlorobenzene concentration significantly increased (factor 2.5). Chlorophenol concentrations differed only less than 10 %.

## 4. Conclusions

Following our measurements, PCDD/F concentration in clean gas varies for a factor of 5 (min.: 1.88, max.: 9.19 ng I-TEQ/Nm<sup>3</sup>). Regarding routine operation without  $Mg(OH)_2$  addition, this factor can reach 4 (min.: 1.88, max.: 7.76 ng I-TEQ/Nm<sup>3</sup>). Standard deviation is 25.6 % with and 15.1 % without  $Mg(OH)_2$  addition. For PCB, chlorobenzenes and chlorophenols, the range of deviation seems to be much smaller. Medians and averages of all PCDD/F measurements show a sufficient agreement to analytical results of previous emission measurements, though the latter were obtained without  $Mg(OH)_2$  addition. Not considering the values of the  $Mg(OH)_2$  addition test, 11 of 12 values lie below former emission measurements (about 4.5 ng TE/Nm<sup>3</sup>). This may indicate a first success of measures to optimize this plant. The same trend can be observed for PCB, but not for chlorobenzenes and chlorophenols. While  $Mg(OH)_2$ -addition reduces acid flue gas components like HCl, HF and SO<sub>2</sub> to a considerable extent, it seems to cause an increase in the concentration of trace organohalogen compounds. This is supported by the findings of Oehme et al.<sup>6</sup>, who could identify considerable amounts of PCDD and especially PCDF in waste water samples of a MgO-production plant. The use of Mg- instead of Ca(OH)<sub>2</sub> as additive for PCDD/F reduction in MSWI should not be practiced until further analyses have cleared the possibility of an increasing effect on PCDD/F emissions.

## 5. References

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