

## Seven-year Decreasing Trend of PCDD/F Emissions from a Waste Incinerator Showing Importance of Primary Measures

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### 1. Introduction

The limit value of 0.1 ng I-TE/m<sup>3</sup> set forth for emissions of polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) from waste incinerators can only be complied with if incinerator operating conditions are optimized and effective flue gas cleaning devices are installed. These measures are often referred to as primary, secondary and tertiary measures. Primary measures are related to waste input, waste feeding and the furnace section of the incinerator and lead to optimized burning. This definition is also used in this paper. However, the addition of chemicals to the flue gas, inhibiting fly-ash catalysed PCDD/F formation, is sometimes also called a primary measure<sup>1)</sup>. Similarly, the terms secondary and tertiary measures were defined in many different ways<sup>2,3)</sup> and are thus avoided in this paper.

Optimization of incinerator operating conditions are determined by factors like temperature, residence time, turbulence and air flow rate. Among others<sup>4)</sup>, we investigated some of these factors at a pilot-scale fluidized-bed incinerator<sup>5)</sup>. Since extrapolations from pilot-scale plants to full-scale incinerators are difficult and deductions are not always valid, we studied the influence of primary measures and of improved flue gas cleaning on the emission of PCDD/F and other organic compounds from a full-scale hazardous waste incinerator (HWI).

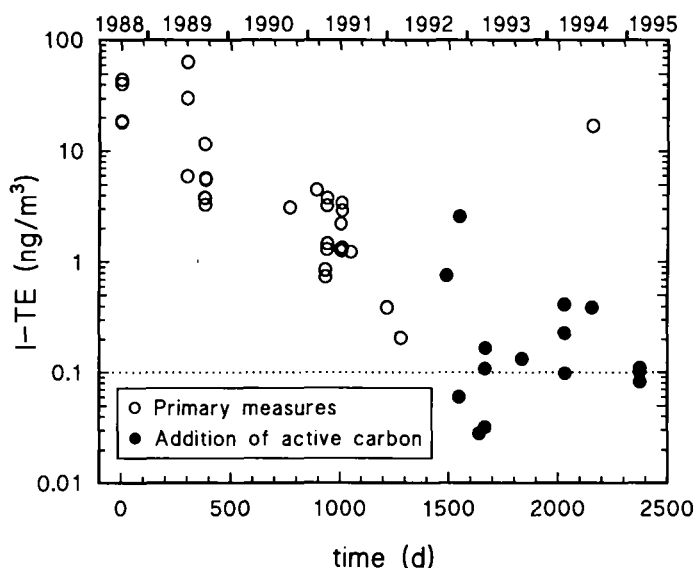
### 2. Materials and Methods

The HWI consists of two rotary kilns operating at a temperature of about 1000 °C. The flue gas is heated to 1200 °C in a post combustion chamber, then passes an energy recovery boiler and enters the flue gas cleaning system with a temperature of about 300 °C. The air pollution control device consists of a two-stage electrostatic precipitator, a two-stage wet scrubber, a condensing system and a wet electrostatic precipitator.<sup>6)</sup> Sampling and analyses of the stack gas were performed by the Gesellschaft für Arbeitsplatz- und Umweltanalytik (Münster, Germany) according to methods previously described<sup>7)</sup>. Among PCDD/F,

the following substances were analyzed: tri- to decachlorobiphenyl homologues, the six Ballschmiter PCB congeners, seven chlorophenols congeners, penta- and hexachlorobenzene and 16 polycyclic aromatic hydrocarbons (PAH). Toxicity equivalents (I-TE) were calculated using the international (NATO/CCMS) toxicity equivalency factors. Concentrations were expressed in ng per m<sup>3</sup> of dry air under standard conditions at 11 % O<sub>2</sub>.

### 3. Results and Discussion

Large within-day and day-to-day variations of the concentration of all analytes (PCDD/F, PCB, chlorobenzenes, chlorophenols, PAH) were observed. For example (Figure 1), I-TE values obtained on a single day differed by factors of up to 2.1. When measurements were performed within a few days, the maximum I-TE values were 1.1 to 43 times larger than the minimum. Thus, the maximum deviation was much greater than the factor of two, which, for normal operation, is considered normal based on the results of a German measurement programme at municipal solid waste incinerators<sup>8</sup>). The maximum deviation was also much greater than that obtained at a municipal waste incinerator (Spittelau, Vienna)<sup>9</sup>). The reason for the large variability in concentration is unknown. Unusual operating conditions could only be identified for two measurements which even did not exhibit the maximum concentration difference. The large differences in PCDD/F emissions may to some extent result from the variability of the waste input.



combustion. These data illustrate the importance of primary measures. Even though it appears that primary measures alone are not sufficient to comply with the emission limit of  $0.1 \text{ ng I-TE/m}^3$  they are able to reduce I-TE emissions to values very close to it.

After September 1992, a further reduction of I-TE levels was achieved by adding active carbon to the second stage of the wet scrubber and removing fly ash and active carbon particles, to which PCDD/F were adsorbed, from the circulating washing water. This measure led to a minimum I-TE value of  $0.028 \text{ ng/m}^3$ . Its effect could also be seen in August 1994. Adding active carbon resulted in an emission of  $0.39 \text{ ng I-TE/m}^3$  but when this measure was not operating the emission increased to  $17 \text{ ng I-TE/m}^3$ . Even with the addition of active carbon it is, however, not always possible to comply with the emission limit. Some I-TE values were even higher than the minimum value of the unmodified air pollution control device. Therefore, additional measures are necessary to reduce PCDD/F concentration in the stack gas to values well below the emission limit.

The trend of concentrations decreasing with time was also observed for PCB, chlorobenzenes, chlorophenols and PAH. For example, maximum PAH concentrations of up to  $240 \text{ } \mu\text{g/m}^3$  were found in September 1988 for fluoranthene and pyrene (the most abundant PAH in the stack gas). Then, concentrations decreased ten- to hundredfold within one year and reached minimum concentrations of  $10 \text{ ng/m}^3$  in April 1991. This is roughly four orders of magnitude lower than the maximum concentration. Benzo[a]pyrene, perylene, dibenz[a,c+h]anthracene and anthanthrene were never found in stack emissions. The levels of all other individual PAH measured were at least two orders of magnitude lower than those of fluoranthene and pyrene and fell below the detection limit in April 1991. At that time, total PAH concentrations (just comprising fluoranthene and pyrene) were  $10\text{--}30 \text{ ng/m}^3$ .

### 3.1 Calculation of loads

The average stack gas flux of the incinerator was  $60000 \text{ m}^3/\text{h}$ , the average operation period 300 d/a. The annual median I-TE values were used because the data are not normally distributed and the median thus represents an average I-TE concentration much better than the arithmetic mean.

By primary measures, the load was reduced from 12.8 to  $0.13 \text{ g I-TE/a}$  (Table 1). Addition of active carbon further reduced the load to a minimum of  $0.044 \text{ g I-TE/a}$ . This is exactly the load that corresponds to the emission limit of  $0.1 \text{ ng I-TE/m}^3$ .

The load of the HWI investigated cannot easily be extrapolated to that of all HWIs operated in Germany because stack gas fluxes (expressed in  $\text{m}^3/\text{h}$ ), operation period and emission concentration may differ considerably. However, the annual load of  $1.3 \text{ g I-TE/a}$  estimated for this single HWI in 1990 is only slightly lower than the value of  $1.6 \text{ g I-TE/a}$  estimated by Fiedler et al.<sup>10)</sup> for the same year and the total of HWIs operated in Germany. Therefore, the value given by Fiedler et al. for the year 1990 may underestimate the load of all German HWIs. This is probably due to the relatively low average I-TE stack gas concentration of  $0.24 \text{ ng I-TE/m}^3$  assumed by these authors. This emission concentration, which is also low compared to that of municipal waste incinerators (estimated to be  $8 \text{ ng I-TE/m}^3$  in 1990<sup>10)</sup>), was assumed because HWIs operate at higher temperatures leading to a better destruction of PCDD/F. Thus, this assumption underestimates the formation of PCDD/F in the postfurnace section of HWIs. Fiedler et al. also calculated that the annual I-TE load of all combustion sources (including HWIs) account for only 66 to 85 % of the total deposition-derived I-TE burden in Germany<sup>10)</sup>. This may partly (but not totally) be explained by underestimating the load of HWIs.

**Table 1.** I-TE concentration in the stack gas and annual loads of I-TE when primary measures were improved (P) and active carbon was added to the wet scrubber (A).

year	mean <sup>a</sup> (ng I-TE/m <sup>3</sup> )	median (ng I-TE/m <sup>3</sup> )	n <sup>b</sup>	load (g I-TE/a)	type of measure
1988	30.5 ± 14	29.7	4	12.8	P
1989	14.9 ± 20	5.7	9	2.5	P
1990	3.1	3	3	1.3	P
1991	2.1 ± 1.2	1.4	14	0.61	P
1992 Jan–Aug	0.30 ± 0.1	0.30	2	0.13	P
1992 Sep–Dec	1.1 ± 1.3	0.76	3	0.33	A
1993	0.093 ± 0.06	0.11	5	0.047	A
1994	0.28 ± 0.14	0.31	4	0.13	A
1995	0.10 ± 0.01	0.10	3	0.044	A

<sup>a</sup> arithmetic mean concentration ± standard deviation; <sup>b</sup> number of measurements

#### 4. References

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