

# FORMATION AND SOURCES I -POSTER

## CORRELATION OF PCDD/F AND CO VALUES IN A MSW INCINERATOR - INDICATION OF MEMORY EFFECTS IN THE HIGH TEMPERATURE/COOLING SECTION

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### Introduction

In Japan a "New Guideline For Controlling Dioxin"<sup>1</sup> includes the aim to decrease the total PCDD/F released from all streams of MSWI - air, solid and water - into the environment<sup>2</sup>. In this respect, the importance of primary measures - i.e. minimisation of PCDD/F formation through combustion technology and boiler technologies - became a new actuality for decreasing the total PCDD/F emission from incinerators .

The CO value is one of the parameters reflecting the quality of combustion. Some studies reported on a correlation of CO emission to PCDD/F concentration<sup>3,4</sup> during combustion processes. Generally we observed low dioxin values in stack gas and fly ash<sup>5</sup> from new fluidized bed incinerators (FBI) with excellent combustion control, while older FBI with temporary high CO values had higher PCDD/F emission<sup>6</sup>. However, other studies found no significant correlation of CO values and the PCDD/F in municipal waste incinerators or pilot plants<sup>7,8</sup>.

Therefore it seemed interesting to evaluate the correlation of CO values and the PCDD/F amount formed during an optimisation program for combustion control within one fluidized bed incinerator in more detail.

### Materials and Methods

**Fluidized bed incinerator:** The feed rate of the FBI was more than 150 ton/day municipal solid waste. In a FBI, the waste is decomposed and gasified in an air bubbled sand bed at around 650°C and the emitted volatile compounds are burned in the secondary combustion chamber for more than two seconds above 850°C to complete the combustion process.

The flue gas line of the FBI was equipped with boiler and economiser for heat recovery. Ca-spray (Ca(OH)<sub>2</sub>) for semi-dry removal of acidic gases and carbon spray for removal of PCDD/F was applied. Bagfilters (BF) guaranteed a high removal efficiency for particles. For destruction of NO<sub>x</sub> a SCR honey comb catalysts was operated in the temperature range of 210-230°C.

**Sampling and analysis:** 33 fly ash from bagfilters were sampled in a FBI during a 4 week measurement effort. The fly ashes were sampled directly after pulse. Sampling and quantification for PCDD/F gas samples were carried out according to the procedure of the Japanese Waste Research Foundation<sup>9</sup> and concentrations were normalised to 12% oxygen. The extraction and clean-up procedures are described elsewhere<sup>10,11</sup>. The GC/MS analysis for the fly ash samples was

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carried out on a HP 6890 gas chromatograph coupled to a HP 5973 mass selective detector. The analysis of the gas samples were performed on a Micromass Autospec Ultima with a HP 6980 gas chromatograph.

## Results and discussion

The CO values for the normal (stable) combustion condition and an unstable combustion are shown in Figure 1 and 2, respectively. The difference of these two conditions result from the control of the first and second furnace.

The fluidized bed incinerator was equipped with carbon spray. The use of carbon spray for the removal of PCDD/F at BF temperatures of 160°C resulted in BF-out values considerably below 0.1 ng TEQ/Nm<sup>3</sup> (in average 0.02 ng TEQ/Nm<sup>3</sup>). In MSWI using active carbon spray for PCDD/F removal and semi-dry system for removal of acid gases at low BF temperature - a common combination in Japanese incinerators - more than 99% of the PCDD/F remain adsorbed on the fly ash. Therefore we chose fly ash as indicator for total PCDD/F concentration. All fly ashes analysed during the study were included for the correlations in this study.

The PCDD/F values of the 33 fly ashes sampled during the 4 week measurement project ranged between 0.6 to 4.9 ng TEQ/g. The intervals for bagfilter pulses were about 15 minutes. Therefore the fly ash PCDD/F content after each pulse represent the PCDD/F adsorbed during this time span. Figure 3A shows the correlation of PCDD/F values in the fly ashes versus the average CO value emitted during the respective 15 minutes adsorption time. We find a general trend of increasing PCDD/F concentrations with increasing CO values. However, there were significant outliers (Figure 3A):

- high PCDD/F values (4.3-4.8 ng TEQ/g) at low CO values (20-40 ppm)
- and several PCDD/F values of less than 2 ng TEQ/g at the highest CO levels (80-130 ppm).

The measured PCDD/F found in the BF do not necessarily reflect the PCDD/F formed in the incinerator during this 15 minutes "sampling" time. Memory effects in the cooling section (boiler, economiser and flue gas duct) may result in a "delay" of the PCDD/F in the bagfilter. Memory effects of PCDD/F in waste incineration plants are known for wet scrubbers and can cause elevated PCDD/F emission for weeks and months after contamination<sup>12</sup>. Recently it was reported that memory effects were found for PCDD/F and PAH in the high temperature area/cooling section of an incineration plant lasting for hours after disturbed combustion conditions<sup>13</sup>.

Therefore we compared the PCDD/F fly ash values and the average CO during 2 hours and 4 hours before the actual sampling pulse (Figure 3B and 3C). This resulted in a considerably stronger correlation of PCDD/F concentrations to CO output. Since PCDD/F versus CO correlations still showed a variability, other parameters (e.g. oxygen concentration, HCl concentration etc.) seem to have additional and significant effects on the amount of PCDD/F formed. However, according to the correlation of PCDD/F and CO values, the quality of combustion in the waste incinerator is a main factor for PCDD/F formation which can be influenced considerably by operation parameters of the furnace.

*A challenging question is how combustion conditions can influence the PCDD/F emission several hours later. Considerations of PCDD/F formation processes may provide more information on this issue.. In FBI, the mayor part of PCDD/F are formed via *de novo* synthesis during fly ash catalysed*

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degradation of unburned carbon (soot, PAH etc.). The CO values correlate with the combustion conditions and reflect therefore the amount of unburned carbon emitted from the furnace. However, the degradation rate of unburned carbon in the temperature area of 600°C to 200°C is difficult to estimate. A time frame of several minutes to hours for the degradation of the carbon load and resulting de novo formation of PCDD/F may explain our finding that the CO value (the combustion conditions) several hours before sampling has an impact on the PCDD/F amount in the BF. Furthermore, it is in agreement with the finding of Zimmermann et al. that elevated PCDD/F emission lasted for hours after disturbed combustion<sup>13</sup>. These memory effects were also not related with CO emission<sup>13</sup>.

Another (more speculative) explanation may be derived by assuming a rapid formation of PCDD/F on fly ash particles (in-flight formation<sup>14,15</sup>). Adsorption of rapidly formed PCDD/F in the high temperature/cooling section may result in a memory effect by a subsequent slow desorption and/or slow migration finally reaching the bagfilter within the time frame of several minutes to hours. More research effort is necessary to distinguish between these two potential types of memory effects.

## Acknowledgments

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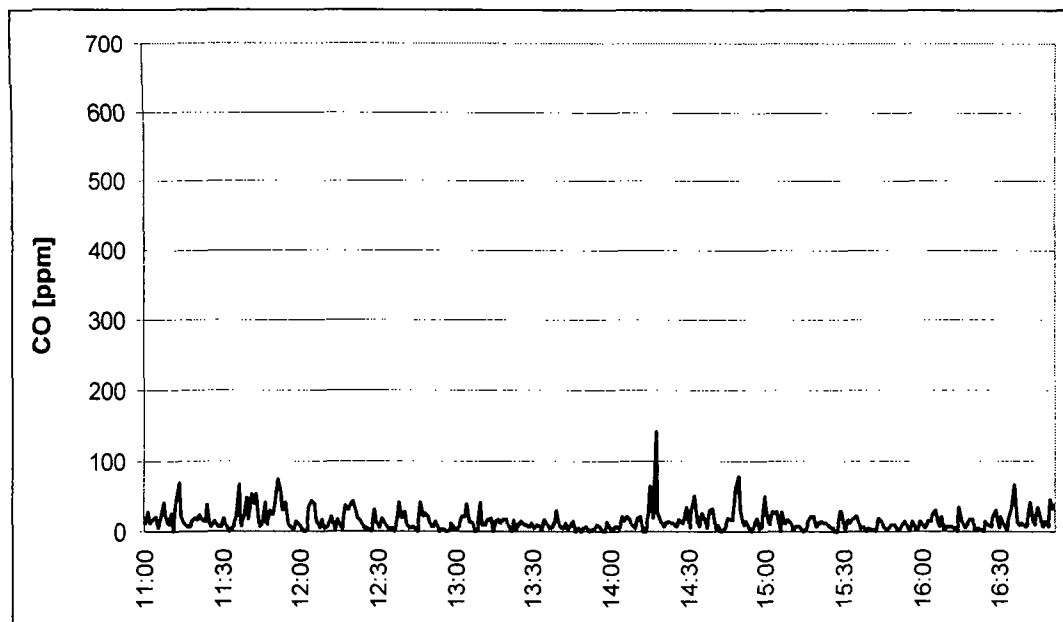


Figure 1: CO emission during normal combustion condition.

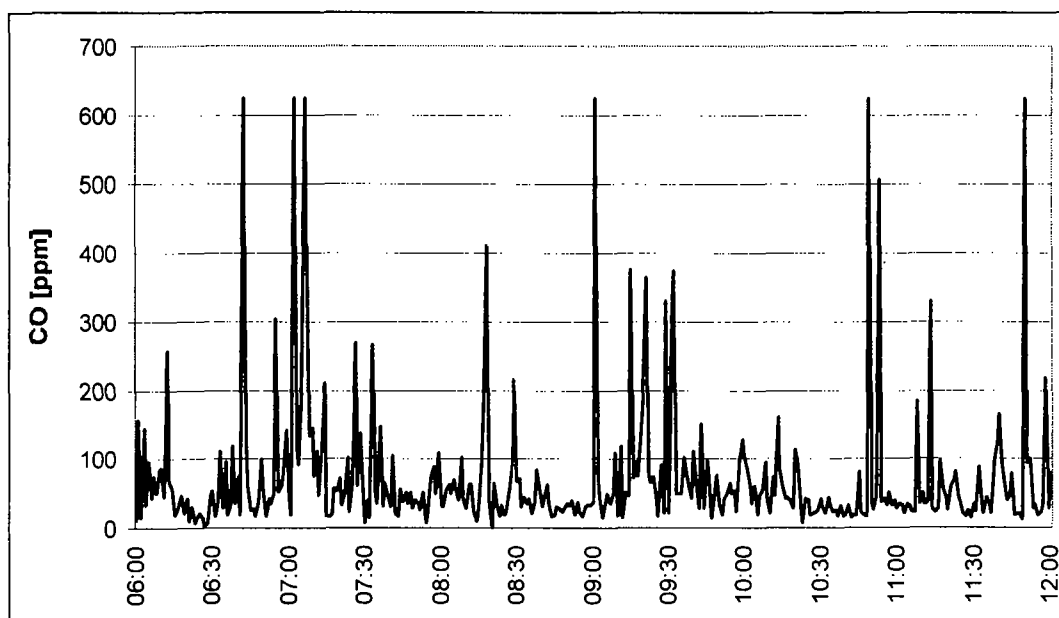


Figure 2: CO emission during unstable combustion conditions.

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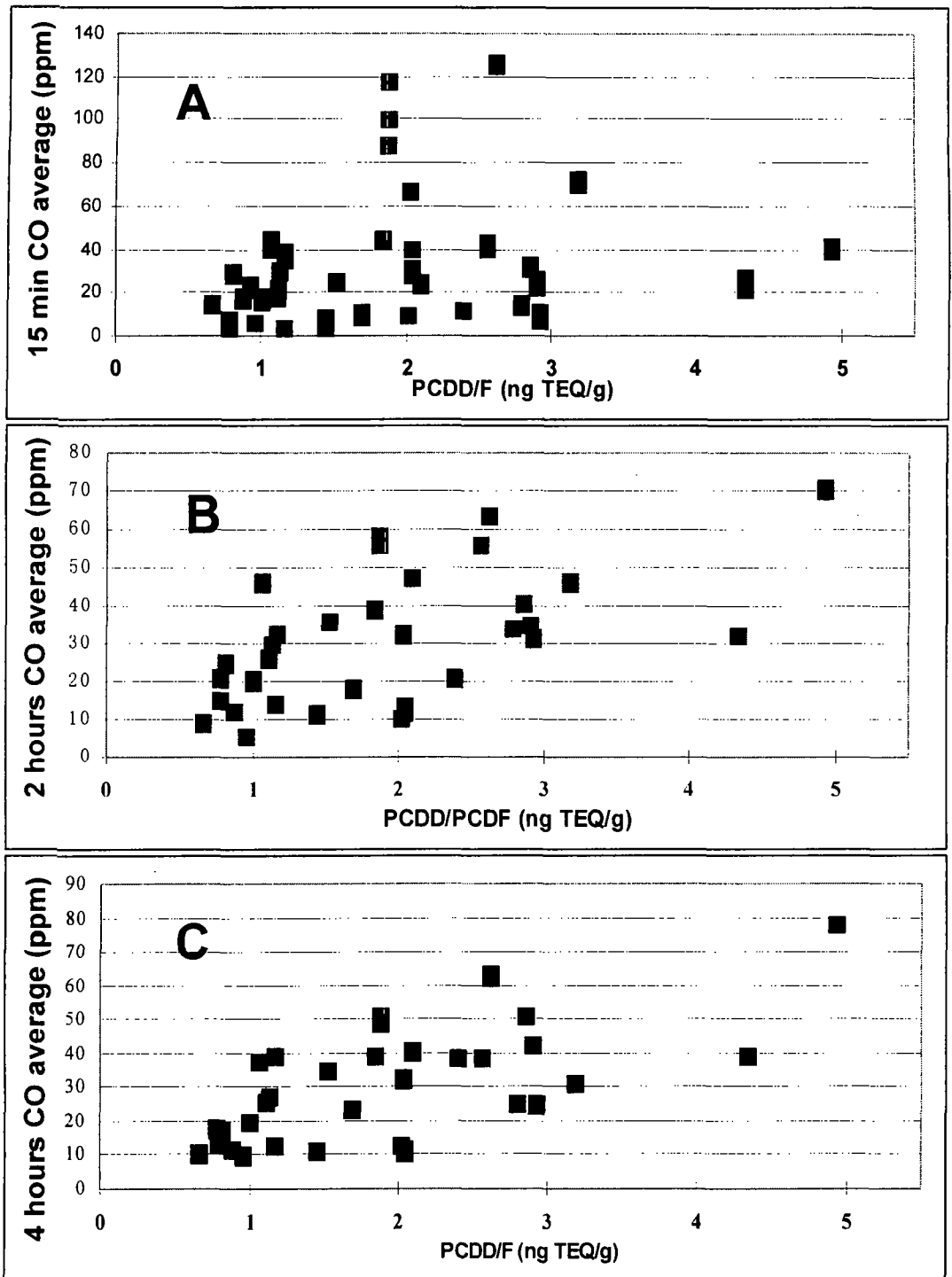


Figure 3: Correlation of PCDD/F amount in fly ash (ng TEQ/g) and average CO (ppm) during 15 minutes (A), 2 hours (B) and 4 hours (C) before respective sampling (bagfilter pulse).

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