PCDD/PCDF in Bottom Ashes from Municipal Solid Waste Incinerators in Bavaria, Germany

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Abstract

Bottom ashes from five municipal solid waste incinerators in Bavaria, Germany, were analyzed for PCDD/PCDF. The concentrations ranged from 1.6 to 24 ng I-TEQ/kg and were lower than those reported earlier by German agencies. The decrease in concentration is due to improved combustion technology required to meet the emission limit for flue gases of 0.1 ng I-TEQ/m³. In all 38 samples, the Fine fractions of the bottom ashes (<8 mm) exhibited much higher concentrations than the Coarse fractions (8-32 mm). The patterns of the 2,3,7,8-substituted PCDD/PCDF congeners were very similar in all samples.

Keywords: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, bottom ash, municipal solid waste incinerator, daily variation

1 INTRODUCTION

Combustion processes and especially incineration of municipal solid waste are known to produce polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) as unwanted by-products in trace amounts (1). Whereas in the past and still today due to regulatory requirements, most activities were directed towards the determination of PCDD/PCDF in the stack gases of municipal solid waste incinerators, present interest also deals with the contamination in the solid emissions (2,3). Solid emissions from MSWI are bottom ash (mostly referred to as "slag"), fly ash, and residues from dry sorption devices. Recent German laws require to a) recover precious compounds from residues (*e.g.* metals, mineral salts, *etc.*) or b) detoxify residues to allow for either use as a secondary resource or an environmentally sustainable landfilling (4-6).

Typically, the major emissions from combustion of one ton of municipal solid waste in a modern MSWI are 300 kg of bottom ash, 30-60 kg of residues from flue gas cleaning, and 5,000 m³ of flue gases. Based on these fluxes, bottom ash is a major emission and in addition, as being used *e.g.* in road construction, there is a need for a better characterization of this matrix. So far, there are not many publications to give PCDD/PCDF concentrations in bottom ash. The status report by the German Environmental Agency gave an average concentration

of 50 ng I-TEQ/kg for bottom ash and of 13,000 ng I-TEQ/kg for fly ash (7). In 1992, the Bavarian Department of Environmental Protection published results from Bavarian MSWI in the range from 1 to 100 ng TEQ/kg; two outliers gave 3,570 and 580 ng TEQ/kg, respectively (8). However, advanced technology and an improved burn-out in the combustion chamber should result in lower levels of organic compounds in both, the flue gases and the residues. In a recent publication, Friesel *et al.* (9) reported a PCDD/PCDF concentration of 19 ng I-TEQ/kg from the bottom ash of the new MSWI from Hamburg (Germany).

The goal of a three year project was to describe the influence of the incineration process on the quality of the emission streams. In a first step, we determined the PCDD/PCDF concentrations in bottom ash from five MSWI in Bavaria.

2 EXPERIMENTAL

2.1 Sampling

As bottom ash is a very heterogeneous material, adequate sampling procedures and methods had to be developed to account for spatial and temporal variations within the matrix. Bottom ash was collected from five MSWI (A-E) with traditional grate systems but varying flue gas cleaning technologies. A brief description of the plants is given in Table 1.

Table 1: Characterization of the MSWI (grate systems) and sampling dates
ESP = Electrostatic precipitator; SCR = Selective catalytic reduction.
* SNCR in combustion chamber

Plant	Sampling Year	Sequence of Flue Gas Cleaning Units	Slag Production
A	1996	ESP → Wet scrubber → Wet ESP → SCR → Fabric filter	2 Mg/h
B	1995	ESP → 2-stage scrubber → SCR→ Absorber → Fabric filter	4 Mg/h
C	1997	* → → Spray absorber→ Fabric filter → 2-stage scrubber → Wet ESP	2 Mg/h
D	1995/96	Spray absorber → Fabric filter → SCR-Reactor	4 Mg/h
E	1995	Cyclone → Fluidized-bed reactor → Fabric filter → SCR	3 Mg/h

Bottom ash samples, 60-80 kg per sample, were taken immediately after the wet slag removal unit. Eight samples per day were collected from each plant during five consecutive days. The eight samples were combined to one daily sample. The sample was homogenized manually and 200 kg sub-sampled according to LAGA guideline for sampling of solid wastes (10). The sub-sample was divided into two portions, of which one was stored as the daily sample and the other was used to generate a weekly composite sample collected during the five days. The weekly composite was processed as described for the daily samples. Thus, six bottom ash samples were obtained per plant and week. On-site, ferrous materials were removed manually and by a magnetic device before sieving. The fraction larger than 32 mm was discarded; the fraction of grain size smaller than 8 mm was defined "Fine" and packaged into a PE drum; the fraction 8-32 mm was named "Coarse" and packaged into a second PE drum. The drums were shipped to the laboratory for further processing.

2.2 Analytical

In the laboratory, the bottom ashes were homogenized. A sub-sample (1,000 g) was taken and any metals carefully removed manually or magnetically, respectively. The samples were crushed and grinded until a fine meal was obtained. Clean-up, fractionation, and final separation of the PCDD/PCDF followed standard methods (11,12[13]) using HRGC/HRMS at a resolution of 10,000.

3 RESULTS

The Loss of Ignition (LOI) of the bottom ashes "Fine" ranged 1.0-4.7% whereas the "Coarse" ranged 0.7-3.6%. The PCDD/PCDF concentrations in the Fine and the Coarse fractions from four plants are shown in Table 2. Presently, we have only the analytical result for the weekly composite from Plant A; samples from Plant C were taken early this year; however, the analyses of these samples are not yet finished.

The PCDD/PCDF concentrations range from 1.6 to 24 ng I-TEQ/kg. As can be seen from Table 2, the concentrations in the Coarse fractions are always lower than those in the Fine fractions. In most samples, the concentrations in the Fine fraction is approximately 2-times higher than the concentrations in the respective Coarse fraction. In some cases, however, there is a factor of 4-5 between these two matrices, *e.g.* Plant A - weekly composite and Plant B - Monday. For Plant E, the ratio between the concentrations in the Fine and the Coarse fractions is always higher than in the samples from all other plants.

From Table 2 it can also be seen that there is a daily variation in the PCDD/PCDF concentrations in bottom ash. Although the concentrations as determined by the weekly composite are in the same range as the samples generated daily, there is a difference of approximately 10% between the mean or median concentrations of the daily samples and the respective weekly sample. For the Fine fraction obtained from Plant E, the difference is almost 40% (median of five daily samples = 21 ng I-TEQ/kg, weekly composite = 14 ng I-TEQ/kg). For the Coarse ashes from Plant D, the difference is 26% (median of five daily samples = 8.3 ng I-TEQ/kg, weekly composite = 6.1 ng I-TEQ/kg).

Table 2: PCDD/PCDF concentrations in the bottom ashes. Concentrations in ng I-TEQ/kg

Plant	A		B		D		E	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Monday			12	3.6	14	5.2	31	7.4
Tuesday			16	8.2	19	8.3	21	4.7
Wednesday			12	5.7	24	12	20	6.6
Thursday			9.4	4.7	16	9.2	18	4.9
Friday			17	7.2	12	4.8	24	5.7
Mean			***14***	***5.9***	***17***	***7.8***	***23***	***5.9***
Median			***12***	***5.7***	***16***	***8.3***	***21***	***5.7***
Week	7.8	1.6	12	5.8	17	6.1	14	5.2

4 DISCUSSION

Within this first phase of the project, we were able to develop and apply a sampling method to obtain "representative" samples of bottom ash from five MSWIs in Bavaria. The concentrations obtained from four MSWI were in a very narrow range and lower than those reported earlier (7,8). An explanation for such results may be that all plants under investigation were modern MSWI, either newly built or retrofitted to comply with the emission limit value of 0.1 ng I-TEQ/m³ (14). To achieve this target concentrations, primary measures, such as a good burn-out and good combustion conditions have to be maintained which, as a consequence, will result in lower PCDD/PCDF emissions in all streams (bottom ash, fly ash, residues from flue gas cleaning, flue gas).

The conclusion that the PCDD/PCDF are similar in all bottom ash samples is further underlined by the fact that the profiles of all samples are very similar. Evaluation by hierarchical cluster analysis did not show any difference in the congener pattern between plants or within the sample matrix (Fine *vs.* Coarse).

Figure 1 shows the spectra plot of four samples of bottom ash - Fine and Coarse fractions from Plants B and D taken at the same day - which exhibit the most different patterns. As can be seen, in all four samples the highest contribution to the I-TEQ is due to 2,3,4,7,8-Cl_5DF attributing between 23% and 50% of the TEQ. The two samples from Plants B are different from all other samples - represented here by the samples from Plant D - due to the relatively low contributions (23 and 25%, respectively) from this congener.

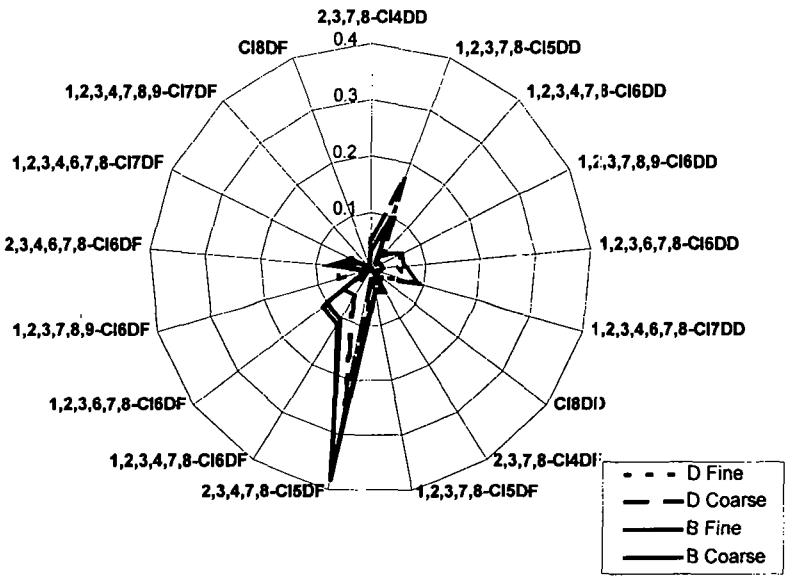

Figure 1: Spectra plot of four bottom ash samples exhibiting the highest dissimilarity on the basis of contribution to the I-TEQ

The next steps include further chemical and physical characterization of the bottom ashes obtained so far. In addition to the traditional grate systems, we have sampled solid emissions from new and innovative thermal treatment systems, *e.g.* from a thermal waste recycling plant (Siemens KWU) and the Thermoselect system. Once these samples will be analyzed, we hope to be able to correlate operational parameters and technology with chemical and physical data along all emission streams. In a final step, we attempt to completely balance a municipal waste incinerator on the basis of PCDD/PCDF fluxes.

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