

### Comparison of the Formation Pattern of PCDD/F and Related Compounds on Fly Ashes from an Iron Ore Reprocessing Plant and MSWI

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#### Introduction

Polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) are formed as undesired byproducts in thermal industrial processes e.g. municipal solid waste incinerators (MSWI), ore/metal scrap reprocessing plants (MRP) etc. Due to environmental regulations modern abatement technologies have been installed in MSWI and led to a continuously decrease of the PCDD/F emissions in the last decade. Presently metal scrap reprocessing plants are the major source for PCDD/F [1,2,3,4].

Recently Buekens et al. [5] reported about the dioxin fingerprints of gaseous emissions from industrial metallurgical processes. They found some similarities in the PCDF - but also differences in the PCDD homologue pattern compared to those of MSWI. The regenerated formation of PCDD/F in the boiler section in a second copper smelter, the increase of PCDD/F after annealing of the boiler ash of this plant [4] and the forty-fold higher concentrations of PCDD/F on the dust in the cooling section (100-200 °C) compared with PCDD/F concentrations in the furnace (800 °C) of an aluminum recycling plant [3] suggest a de-novo synthesis of PCDD/F as observed for MSWI fly ashes by Stieglitz [6].

In this paper, we describe the investigation of the isomer pattern of polychlorinated benzenes (PCBz), phenols (PCPh) and PCDD/F in the de-novo synthesis on this fly ash and two fly ashes from MSWI. A detailed analysis of the isomers of these compound classes and comparison with the isomer distribution of MSWI can be revealing for a study of the reaction mechanism of PCDD/F.

#### Experimental and Analytical Methods

We performed thermal experiments with two fly ashes from an IRP and with two fly ashes from different MSWI. The IRP fly ash was collected underneath a sintering assembly line while the fly ashes from the MSWI stem from electrostatic precipitators. The two fly ashes from the IRP (IRP-1a and IRP-1b) differ in the date of sampling. MSWI-1 stems from a MSWI in Germany, while MSWI-2 was obtained from the Environmental Protection Agency, USA. The major components of the IRP fly ash are iron (16 %) and chlorine (24 %); the carbon concentration in the IRP material amounts to 3.7 %, that of the MSWI samples ranging between 1.75 % (MSWI-2) and 4.2 % (MSWI-1).

For homogenization the fly ashes were ground to a particle size smaller than 300 µm and used without further treatment. The thermal experiments were performed at 300 °C with a reaction time of 2 hours and with an apparatus described earlier by Stieglitz [7]. As gas phase we used synthetic air (flow: 50 mL/min) containing 150 mg watervapor/L. The volatile compounds were collected in a toluene trap.

After spiking the solution of the impinger and the fly ashes with <sup>13</sup>C-labeled internal standards, the fly ash samples were extracted in a toluene-methanol mixture with an extraction technique recently developed: the dynamic high-pressure solvent extraction (DHPSE) [8].

The solution of the impinger and the DHPSE extract were cleaned-up separately. PCPh and PCBz were analyzed by HRGC-LRMS on a 30 m DB-5 column and the PCDD/F by HRGC-HRMS (HP5890 - Fisons Autospec) on a 60 m DB-Dioxin column.

**Results and Discussion**

The first very distinct behavior in the de-novo synthesis of fly ashes from this IRP compared with MSWI fly ashes is the distribution of the products of incomplete combustion (PIC) between the gas phase and solid phase already at 300 °C. The values for PCPh, PCBz and PCDD/F are depicted in Table 1.

Table 1. Distribution [%] of the PCPh, PCBz and PCDD/F between the solid phase (SP) and gas phase (GP) for the de-novo synthesis on an IRP and MSWI fly ashes at 300 °C

	IRP-1a		IRP-1b		MSWI-1		MSWI-2	
	SP	GP	SP	GP	SP	GP	SP	GP
PCPh	3.7	96.3	7.2	98.2	100.0	0.0	97.5	2.5
PCBz	1.1	98.9	1.0	99.0	72.6	27.4	29.4	70.6
PCDD	0.2	99.8	3.7	94.3	94.9	5.1	99.9	0.1
PCDF	0.2	99.8	3.2	96.8	95.1	4.9	99.8	0.2

While in MSWI fly ashes more than 94 % of the PCPh and PCDD/F remain adsorbed on the fly ash surface, more than 94 % of the products are found in the gas phase on fly ashes from the IRP. Responsible for this reaction behavior might be the coke additive in the reprocessing facility or the high metal content of this ash, which might change the surface properties of the fly ash particles. This reaction behavior might also influence the homologue and isomer pattern.

As these fly ashes do hardly retain the PIC and show a very high PCDD/F generation potential it is very important to study the TEQ values. In our experiments the TEQ values of the gas phase of IRP fly ashes are two to four orders of magnitude higher than in experiments with the MSWI fly ashes. The total TEQ values (fly ash and gas phase) are depicted in Table 2.

Table 2. Contribution of the PCDD and PCDF [ng/g] to the total TEQ value

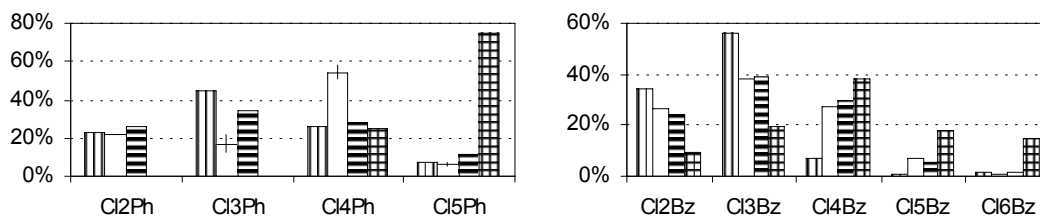
	IRP-1a	IRP-1b	MSWI-1	MSWI-2
PCDD	300	230	92	10
PCDF	1050	1230	183	5

The homologue profile for the PCPh, PCBz and PCDD/F are presented in Figure 1. For the calculation of the distribution of the PCDD and PCDF homologues the data were normalized to the total sum of PCDD/F. The experiments with IRP-1b are performed in duplicate. The error bars represent the standard deviation of the average percentage for these two experiments. The standard deviation of the PCDD/F concentrations of the duplicate de novo runs ranges between 2 and 9 % with an average of 5 %; that for IRP-1a and IRP-1b between 1 and 31 % with an average of 17 %. The PCDD/PCDF ratio of these fly ashes is 0.25, similar to that of MSWI-1. The PCDD/PCDF ratio of MSWI-2 differs with a value of 2.2. Regarding the product ratio the share of the PCPh and PCDD/F is increased on the IRP fly ash, while that of the PCBz is lower compared to the MSWI samples.

Among the PCDD homologues high concentrations were obtained for Cl5DD on the IRP samples and MSWI-1, while for MSWI-2 Cl7DD are formed in the highest concentration. For the IRP fly ashes and MSWI-1 the maximum of the PCDF is located at Cl4DF and for MSWI-2 at Cl6DF. Similar observations for gaseous emissions of different MRP were reported by Buekens et al.[5] with the exception that they observed a maximum for the PCDD at Cl4DD and for the PCDF at Cl5DF.

In all samples all PCPh, PCBz and PCDD/F congeners were formed. Although the samples of the IRP and MSWI-1 show similar homologue patterns for these compound classes, the isomer patterns of the PCPh and PCDD/F of MSWI-1 differ more strongly than those of MSWI-2 from the IRP samples. Predominant congeners among the PCPh for the IRP are 2,5/2,4- and 2,3-Cl2Ph, 2,4,6- and 2,4,5-Cl3Ph and 2,3,4,6-Cl4Ph. On MSWI-1 the formation of 2,5/2,4- and 3,4-Cl2Ph, 2,4,5- and 3,4,5-Cl3Ph, 2,3,4,6- and 2,3,4,5-Cl4Ph is favored. The congener pattern of the PCBz is in very good agreement for all samples with following dominating isomers: 1,2-Cl2Bz, and among the Cl3Bz: 1,2,4- and 1,2,3-Cl3Bz in similar amounts. Exemplary, for the PCDD and PCDF the isomer patterns of the Cl4DD and Cl4DF are presented in Figures 2 and 3. For the Cl5- to Cl7DD/F similar small shifts are observed between the IRP and the two MSWI samples. The higher difference between the PCDD isomer pattern of the IRP samples and MSWI-1 might be attributed to the different PCPh isomer pattern. In sum, the homologue profiles of PCPh, PCBz and PCDD/F between the IRP and MSWI-1 fly ashes are very similar, but the isomer pattern of the PCPh and PCDD show some differences, suggesting the intermediately formed de-novo PCPh are serving as precursors for the PCDD. The differences between the isomer pattern of the PCDD/F in the MSWI fly ashes are in the same order of magnitude as between the IRP and MSWI fly ashes, which supports the theory that the de-novo reactions forming PCDD/F are similar on both matrices.

Furthermore, the very different composition of the IRP and MSWI fly ashes and the different distribution of the products between the solid phase and gas phase seems to have only little influence on the isomer patterns.



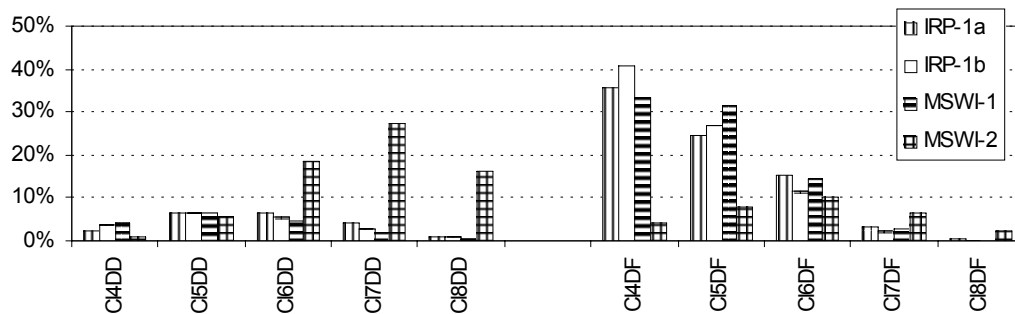


Figure 1. PCPh, PCBz and PCDD/F homologue profiles for the de-novo synthesis on fly ashes from an iron reprocessing plant and municipal solid waste incinerators

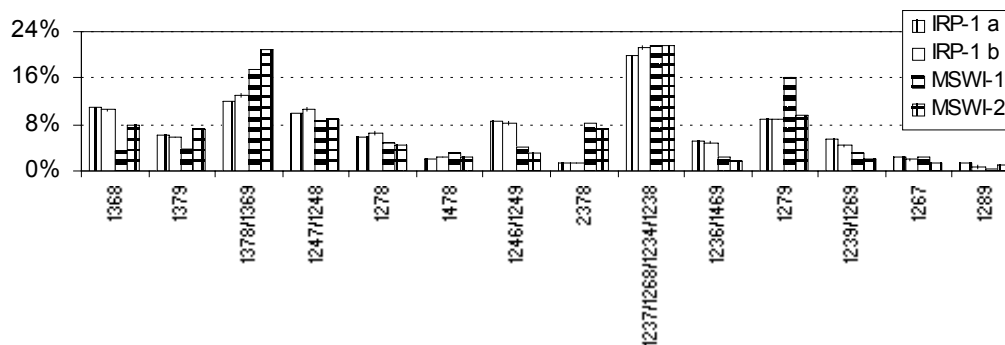


Figure 2. C14DD isomer distribution for the de-novo synthesis on fly ashes from an IRP and MSWI

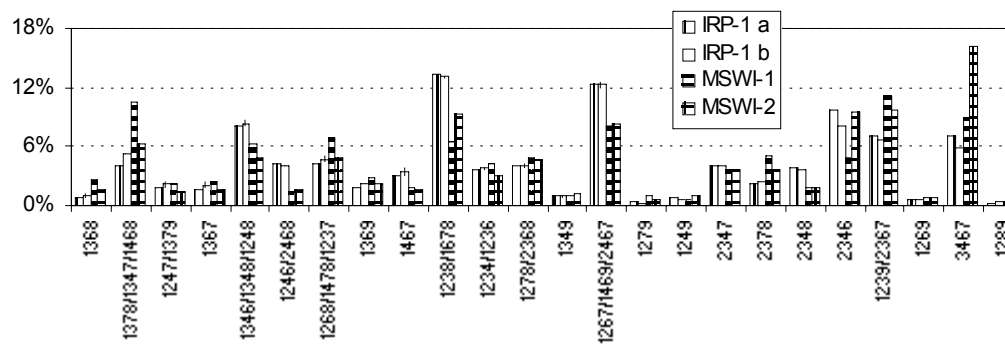


Figure 3. C14DF isomer distribution for the de-novo synthesis on fly ashes from an IRP and MSWI

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