

## ISOKINETIC SAMPLING OF PCDD/F AND PCB DURING COMBUSTION OF WOOD AND HOSPITAL WASTE. INFLUENCE OF $(\text{NH}_4)_2\text{SO}_4$ AS ADDITIVE ON PCDD/F AND PCB EMISSIONS

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### Introduction

Incineration is an important method for the treatment and decontamination of biomedical and health-care waste. This process of high-temperature (850°C to 1100°C) dry oxidation may successfully reduce organic and combustible waste to inorganic, incombustible matter and results in a very significant reduction of waste volume and weight. Furthermore, incineration is certainly capable to destroy the bacteria and viruses and the material of attached pathogens: the paper, plastic, glass and metal. Consequently, acidic gases are generated from the chlorinated organic plastics present; toxic metals are liberated from the pigments and the additives of the paper and plastic products as well as discarded thermometers; and dioxins and furans are formed from the chlorine in the waste<sup>1</sup>. Unfortunately, incineration is not a clean process<sup>2</sup>. In 2001, emissions from hospital waste incinerators in the European Union were estimated in 200-400g I-TEQ year<sup>-1</sup>, accounting for 25% of the total polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/F) emissions<sup>3</sup>. Currently, two major options of primary and secondary measure are known to comply with the limit value of 0.1 ng/m<sup>3</sup> TEQ PCDD/F, which was demanded by the European directive 2000/76/EC. Compared to the primary measures, the installation and operation costs of secondary measures such as air pollution control systems are much more expensive and cannot be considered for small hospital waste facilities. Primary measures include adjustment of operation conditions (temperature, turbulence, air flow, residence time) and focus on mechanism of inhibition of selective compounds or inhibitors, which can inhibit the formation of PCDD/F substantially<sup>4</sup>. In the recent years the usage in a laboratory scale experiment of some sulfur and nitrogen compounds such as hydroxylamine-O-sulfonic acid ( $\text{H}_2\text{NSO}_4\text{H}$ ); amidosulfonic acid ( $\text{H}_2\text{NSO}_3\text{H}$ ); sulfamide ( $\text{H}_2\text{NSO}_2\text{NH}_2$ ); ammoniumthiosulfat ( $(\text{NH}_4)_2\text{S}_2\text{O}_3$ ); urea+sulfur ( $(\text{NH}_2)_2\text{CO}+\text{S}$ ) (1:1); ammoniumsulfat ( $(\text{NH}_4)_2\text{SO}_4$ ) become beneficial into prevention of PCDD/F and PCB emissions<sup>5</sup>. Especially successful concerning the abatement of organic toxic pollutants in flue gas was the addition of only 5%  $(\text{NH}_4)_2\text{SO}_4$  to the coal/PVC-containing solid waste fuel<sup>6</sup>. The objectives of this work were to investigate and determine the PCDD/F and PCB emissions during the co-combustion of wood and hospital waste, operated in a pilot scale plant, and to study the effect of  $(\text{NH}_4)_2\text{SO}_4$  as potential inhibitor on PCDD/F and PCB emissions.

### Material and Methods

The pilot application was performed on an existing domestic grid-stove in a small-technical scale. A combustion scheme to generate PCDD/F and PCB was designed and constructed. The system consisted of two chambers. A small domestic stove was installed a room where the emission sampling was executed.

Wood, hospital waste and  $(\text{NH}_4)_2\text{SO}_4$  with different proportions were used for combustion to produce or prevent exhaust gas containing PCDD/F and PCB. Five combustion experiments of 100% wood, case (a); 75% wood / 25% hospital waste, case (b); 75% wood / 25% hospital waste, case (c); 71% wood / 24% hospital waste / 5%  $(\text{NH}_4)_2\text{SO}_4$ , case (d) and 71% wood / 24% hospital waste / 5%  $(\text{NH}_4)_2\text{SO}_4$ , case (e) were performed. The prepared fuel mixtures were combusted in batches. The basic fuel in all cases was eco-farm wood briquettes (BIO-Brennstoff-Vertrieb-GmbH). Wood combustion is known to be an important source of PAH and is also considered to be responsible for a significant percentage of the PCDD/F emissions. Chlorine addition to the fuel mixtures (b), (c), (d) and (e) was in the form of PVC-containing hospital materials such as hoses and blood bags (Sarstedt AG & Co). Further various non-chlorine containing hospital materials were also included in the fuels such as syringes, needles, swabs (all from NeoLab Migge Laborbedarf-Vertriebs GmbH), gloves and sticking plaster (Söhngen GmbH). The pooling of the hospital waste was estimated so that the PVC-containing materials

prevail two times the non-chlorine containing ones. Additionally, in case (d) and (e) the inhibitory effect of  $(\text{NH}_4)_2\text{SO}_4$  was examined inhibit the emissions of PCDD/F and PCB. The amount of the tested N-and S-containing compound was adjusted based on our previous studies to correspond to 5% of the total fuel mixture enforcing successful inhibition results <sup>6</sup>. The weight, fuel composition and provided brands used for the five pilot plant experiments are shown on Table 1.

Table 1.  
Fuel test matrix of the co-combustion experiments at the pilot plant

Fuel	Material	Incineration experiment, weight (g)				
		a	b	c	d	e
eco-farm wood		1700	1275	1275	1210	1210
blood bag	PVC	-	183.1	183.2	138.7	170.3
hoses	PVC	-	71.8	71.8	103.5	71.85
swab		-	22.9	-	30.3	-
syringes E-1505	Polypropylen	-	58.7	62.5	47.9	51.5
needles	Polypropylen	-	16.2	16.1	15.1	16.2
sticking plaster		-	8.3	-	6.1	-
gloves	vinyl	-	10.4	48.6	31.7	54.6
hear saved cap	Polypropylen		12	12	7	7
package	paper and nylon		41.6	30.8	40.4	34.6
$(\text{NH}_4)_2\text{SO}_4$		-	-	-	85	85
% wood		100	75	75	71	71
% PVC waste		-	15	15	14	14
% non-PVC waste		-	10	10	10	10
% $(\text{NH}_4)_2\text{SO}_4$		-	-	-	5	5
%wood/hospital waste/ $(\text{NH}_4)_2\text{SO}_4$		100/0/0	75/25/0	75/25/0	71/24/5	71/24/5

Emissions of PCDD/F and PCB were sampled isokinetically by employing an automatic sampling system MRU 4000 (GSM, Neuss, Germany). The sampling was performed according to DIN EN 1948-1 and the cooled probe method was applied <sup>7</sup>. The volumetric contents of the gas components (Table 2) were measured on-line with a gas analyser TESTO 350 (Lenzkirch, Germany).

Table 2.  
Operation conditions of the pilot incineration plant

	T [°C]	pdyn [hPa]	O <sub>2</sub> [Vol %]	CO [Vol %]	CO <sub>2</sub> [Vol %]	Sampled gas [Nm <sup>3</sup> ]	Exhaust gas velocity [m/s]
a	301.9	0.05	18.21	0.03	2.7	0.20	4.17
b	289.7	0.09	17.5	1	3.4	0.30	5.53
c	302.5	0.1	16.8	1	4.1	0.32	5.89
d	300.8	0.09	17.7	0.8	3.7	0.31	5.58
e	308.2	0.09	16.8	0.7	4.1	0.32	5.61

The soot particles were filtered by a glass cartridge filled with glass wool. The gaseous PCDD/F and PCB were absorbed by using a cartridge filled with Supelpak 2 (cleaned XAD resin from Supelco). Prior sampling the cartridge was spiked with <sup>13</sup>C-labeled sampling standards. After each sampling the water of the condensate flask was poured over the XAD resin and then discarded. The probe and all glassware were rinsed first with n-hexane and afterwards with toluene. The rinsing solutions were kept and used for Soxhlet extraction later.

The sample preparation, instrumental analysis, and quantitation were performed according to DIN EN 1948 part 2 and 3 <sup>8,9</sup>. The XAD resin was extracted in a Soxhlet apparatus with toluene for 24 h. Prior extraction <sup>13</sup>C-labeled standards were spiked onto the cartridge. The clean-up of the extracts and instrumental analysis were performed as described elsewhere <sup>10</sup>. The instrumental analyses were performed by HRGC/HRMS.

## Results and Discussion

Low PCDD/F and PCB concentrations were measured during wood combustion (case (a), Table 3). Due to higher chlorine contents of the hospital waste the dioxins emissions are sufficiently increased during the next two experiments of wood and hospital waste, case (b) and (c). However, in case (d) and (e) where  $(\text{NH}_4)_2\text{SO}_4$  was involved, the reduction of the PCDD/F and PCB concentrations were determined to an average of approximately 50%. Continued experiments of wood/hospital waste fuel without inhibitor and with inhibitor, case (c) and (e) effect the highest and lowest toxic emissions, respectively. Consequently, the results in case (e) compared with case (c) manifest a minimization of 66% for both PCDD/F and PCB emissions.

Table 3

PCDD/F and PCB pg (WHO-TEQ)/Nm<sup>3</sup> concentrations by combustion experiments a, b, c, d and e

	a	b	c	d	e
PCDD/F pg (WHO-TEQ)/Nm <sup>3</sup>	8167	107931	189536	85458	65711
PCB pg (WHO-TEQ)/Nm <sup>3</sup>	192	1810	3691	1366	1260

Furthermore, as shown on Figure 1, furans prevailed over dioxins in all cases with a ratio ranging between 2.5 and 4.5, indicating a relatively constant behavior of PCDD/F formation.

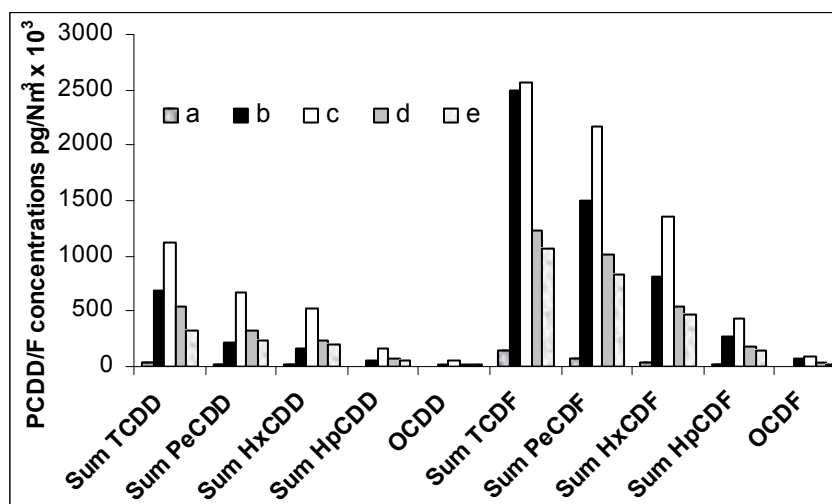


Figure 1

PCDD and PCDF homologue pattern by combustion experiments a, b, c, d and e

This ratio is always more than unity, when precursors are not involved in the formation mechanism, whereas precursor reactions produce very little PCDF<sup>11</sup>. Another study suggest that if the chlorine level in the waste exceeds the threshold (0.8–1.1%), the rates of formation of PCDF increase faster than those of PCDD, probably because the chlorine content in the waste contributes to the deterioration of combustion conditions, and many products of incomplete combustion (PICs) like PAH, will grow to a substantial level. When PCDD/F are formed from PAH, the formation rates of PCDF are higher than those of PCDD<sup>12</sup>. As already concluded from Table 3, PCDF concentrations are higher than the corresponding dioxin concentrations. In addition, as shown from the homologue patterns, the lower chlorinated congeners prevailed over the higher chlorinated ones, in accordance with typical homologue patterns from combustion processes<sup>13</sup>.

Isokinetic sampling of PCDD/F and PCB during combustion of wood and hospital waste was performed in a pilot plant. The influence on toxic emissions of 5%  $(\text{NH}_4)_2\text{SO}_4$  in toxic fuel was further investigated. As a result the lowest PCDD/F and PCB emissions were observed during the combustion of fuel blends containing wood only. In contrast to case (a) the forward four campaigns described with presence of chlorine in the fuel mixture lead to significant toxic emissions.

Consequently, the experiments of wood and hospital waste, case (b) and (c) the higher percentage PVC content results in the higher toxicity. In agreement another study suggested that even 3% PVC in the fuel is able to result increase in PCDD/F concentrations<sup>14</sup>. Several recent publications reported also correlations between chlorine input and the emission of polychlorinated aromatics based on de novo formation of the PCDD/F<sup>15</sup>. The contradictory effect was found for the experiments (d) and (e). Despite presence of PVC content the detected toxic emissions enhance to be lower. The relationship manifests the strong inhibition effect of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by continued combustion of wood and hospital waste such as case (e).

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