THE INFLUENCE OF SULFUR ON THE FORMATION OF PCDD/F BEFORE, DURING AND AFTER POOR COMBUSTION OF MUNICIPAL SOLID WASTE

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Abstract
In a laboratory-scale fluidized-bed reactor combusting artificial municipal solid waste the formation of PCDD/F was studied during good combustion, poor combustion and the following memory effects; with and without addition of SO_2. The SO_2:HCl ratio in the flue gas for the different experiments, were 0, 0.1, 0.4 and 1.6. Parallel sampling at the temperatures 400 and 200°C were performed. The results show that sulfur reduces the PCDF formation during and after poor combustion, while PCDD formation increases. The PCDD/PCDF ratio increased with increased SO_2:HCl ratio at 200°C. However, the PCDD/PCDF ratio decreased during poor combustion with no sulfur added. The results imply that there are different pathways involved for the PCDF and PCDD formation.

Introduction
Poor combustion of municipal solid waste is known to increase the PCDD/F formation[1]. This could lead to an I-TEQ concentration above regulation limits, 0.1 ng/Nm^3 and 15µg/kg, both in the flue gas and the residues[2]. A reduced dioxin concentration in the residues makes it possible to use them in construction works instead of deposit on landfills. This can be accomplished by either treatment of the residues or optimization of combustion plants such as temperatures, process parameters and the composition of the flue gas and fuel. Sulfur in the fuel has been seen by other authors to reduce the formation of PCDD/F[3,4]. Recent research found that sulfur can even reduce the PCDD/F during poor combustion periods[5]. The aim of this study was to examine if sulfur reduces the PCDD/F emissions during poor combustion, also to study the formation of PCDD and PCDF before, during and after such condition.

Material and Methods
A laboratory-scale fluidized-bed reactor, 5 kW, combusting an artificial municipal solid waste was used, Figure 1, described in detailed by Wikström et al.[6] and Aurell et al.[7]. A total of seven combustion experiments where performed; three with no addition of SO_2, one with 30 ppm SO_2 in the flue gas, two with 100 ppm SO_2 in the flue gas and one with 500 ppm SO_2 in the flue gas. For each of the combustion experiments the reactor was preheated with propane for two hours, thereafter the solid fuel feed started. The reactor reaches steady state after approximately three hours of solid fuel combustion[7]. The SO_2 gas was injected in I1 (Figure 1), located at the secondary air supply, and preheated with an oven to approximately 240°C. For each combustion experiment four sampling periods were performed:

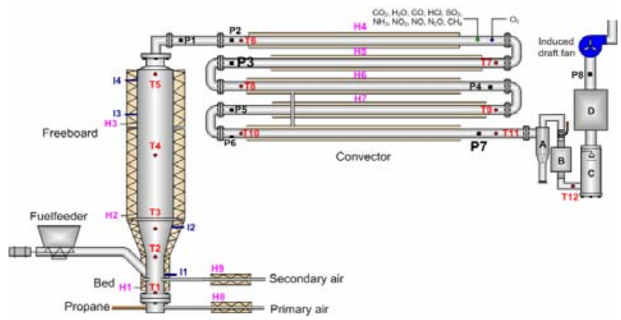

Figure 1. The laboratory-scale fluidized-bed reactor, not in scale. The air pollution control system consist of cyclone, textile filter, wet scrubber and active carbon denoted A, B, C and D, respectively. The sampling was performed in P3 and P7, in the convector section, and SO_2 added in I1, in the bed section.

1. Good combustion, after four hours of solid fuel combustion, this sampling occurred for 45 min.
2. Poor combustion (PC), an increased CO level were made by adding more fuel and reducing the air supply, an increased CO concentration (>3000 ppm) every third minute for one hour, this sampling occurred for 20 min.
3. Memory effects 1, sampling started directly after the poor combustion period and was performed for 30 min.
4. Memory effects 2, sampling started 60 minutes after the poor combustion period and was performed for 30 min.

For one of the three combustion experiments, with no addition of SO_2 and also for one of the 100 ppm SO_2 in the flue gas, only sampling period number 1 (good combustion) was performed. For each of the seven combustion experiments, parallel sampling at 400 and 200°C was performed, ending up in a total of 40 samples. To reduce the memory effects between combustion experiments, the fuel feed continued for 30-60 minutes after the last sampling occasion, and the reactor was thoroughly cleaned after each experiment. Measures of H_2O, CO_2, SO_2, NO_2, CO, NO, HCl, NH_3, N_2O, and CH_4 (30 seconds average) and O_2 (every second) were continuously made. The cooled probe sampling technique was used and performed according to the standard method EN:1948:1-3[8]. The extraction and clean-up procedures are explained elsewhere[9]. The samples were analyzed for PCDD/F 4-8 and PAH (acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, flouranthene, pyrene, chrysene, benzo [*b* and *k*] fluoranthene, benzo [*a*] pyrene, indeno [1,2,3-*cd*] pyrene, dibenzo [*a*,*h*] anthracene and benzo [*ghi*] perylene), with high and low resolution GC/MS respectively.

Results and Discussion

The SO_2:HCl ratio (by mass) in the flue gas for the different experiments, during good combustion, were 0, 0.1, 0.4 and 1.6 respectively. With this small experimental set-up it was rather difficult to reach the same increased CO concentration throughout each experiment and between the different combustion experiments. Since a cumulative sampling method was used, and one interest of this study was to study the formation of PCDD/F before, during and after poor combustion the number and level of CO is exaggerated compared to a malfunction in a full scale plant. Noted is that increased CO level were easier to reach when no SO_2 were added, and the increased CO level returned to the start value faster when SO_2 was added, Figure 2. Addition of SO_2 reduces the NO_2 and NO and increases the HCl and N_2O, at SO_2:HCl 1.6 the CH_4 even increase (this at good combustion). NO, HCl, N_2O, NO_2 reduces and NH_3, CH_4 and SO_2 increases with increased CO concentration.

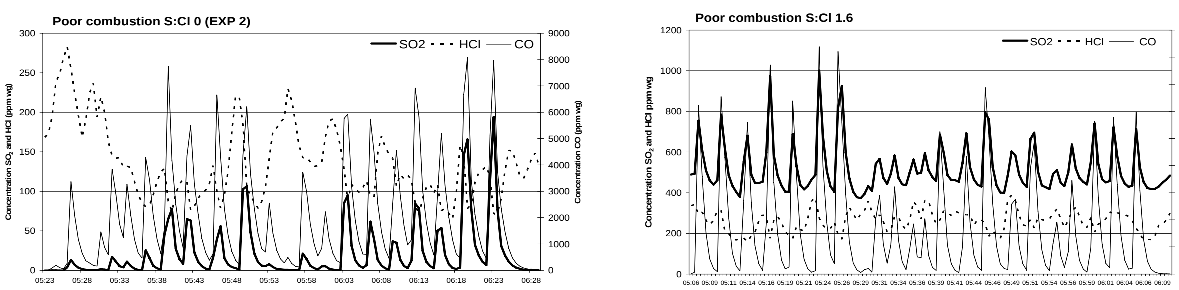

Figure 2. The variation of CO, SO_2 and HCl concentration during poor combustion. The left hand side SO_2:HCl 0 (no sulfur added) and the right hand side SO_2:HCl 1.6. Sampling occurred during the first 20 minutes of the one hour of poor combustion.

It has been suggested that CO concentration do not correlate to PCDD/F[10,11]. The CO has been reported in the literature to be a good indicator for the Sum PAH[12]. In this study the average CO concentration with the Sum PAH are used to confirm that a certain level of poor combustion has been reached, in each of the experiments. A higher soot formation could have occurred in the added SO_2 experiments, since more fuel needed to be added to reach an increased CO level. However, the total amount fuel used during the poor combustion was the same as during the good combustion periods. Figure 3 show an increase of the Sum PAH with increased CO

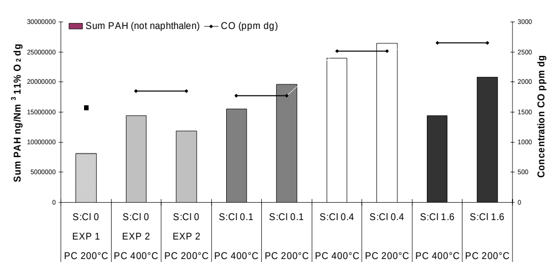

Figure 3. Concentration of the Sum PAH in relation to the average CO concentration during poor combustion.

concentration, for the replicate experiments, without any addition of SO_2. The experiments with addition of SO_2 show no less level of poor combustion.

During good combustion a reduction on the formation of Sum PCDF can be seen for, SO_2:HCl 0.4 and 1.6 at both 400 and 200°C, Figure 4. However, for the Sum PCDD a reduction in the formation can only be seen at 400°C, with SO_2:HCl 0.4 and 1.6. The PCDD formation at 200°C, SO_2:HCl 1.6, can be due to the change in combustion conditions (increased CH_4). The triplicate runs, without addition of SO_2, show an excellent reproducibility for this combustion system. An increase of the PCDD/PCDF ratio occurred with increased SO_2:HCl ratio at 200°C, Table 1.

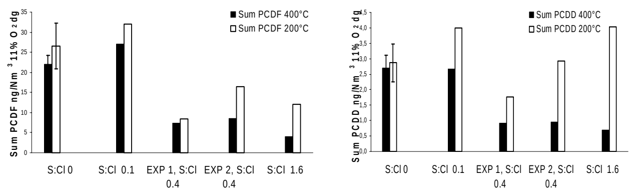

Figure 4. Concentration of Sum PCDF (left hand side) and Sum PCDD (right hand side) during good combustion, with and without addition of SO_2. Error bars represent ±1 standard deviation.

The poor combustion periods show a reduced formation of the Sum PCDF at both 400 and 200°C with addition of sulfur, while for the Sum PCDD it actually show an increased formation, Figure 5. The Sum PCDF formation during the memory effects shows the same trends as during poor combustion. The Sum PCDD formation increase at the second memory effects at 200°C with addition of sulfur, at 400°C it tend to reduce with increased SO_2:HCl ratio. Experiment 1 (only poor combustion) SO_2:HCl 0, 200°C, was sampled for 30 min instead of 20 min, this can be the reason why the memory effects 1 are higher than during the poor combustion for the other experiments. The reduction in formation seen in the experiment SO_2:HCl 0.1 can be due to the enhanced SO_2:HCl ratio, which occur due to the increased CO concentration. These results indicate that sulfur reduces the PCDF formation during and after poor combustion, while PCDD formation increases.

Table 1. PCDD/PCDF ratios, during good combustion, poor combustion and memory effects.

Sampling period	S:Cl 0, EXP 1	S:Cl 0, EXP 2		S:Cl 0.1		S:Cl 0.4		S:Cl 1.6	
	200°C	400°C	200°C	400°C	200°C	400°C	200°C	400°C	200°C
Good combustion	0.10	0.13	0.11	0.10	0.12	0.11	0.18	0.17	0.33
Poor combustion	0.06	0.05	0.06	0.16	0.20	0.29	0.41	0.52	0.77
Memory effects 1	0.15	0.09	0.12	0.28	0.51	0.32	0.87	0.42	0.98
Memory effects 2	0.13	0.11	0.14	0.14	0.72	0.14	1.12	0.21	1.18

The increased PCDD concentration at 200°C for the added sulfur experiments can be due to a higher soot formation, looking at the CO- and Sum PAH concentrations, Figure 3. If so, it again imply that sulfur have a larger impact on the PCDF formation then PCDD and there most probably are different pathways involved for the PCDF and PCDD formation.

Whether or not the CO and PAH are good indicators for PCDD/F formation, the PCDD/PCDF ratio tend to change with increased SO_2:HCl ratio even during and after the poor combustion periods. During poor combustion with no sulfur addition, the PCDD/PCDF ratio decrease compared with good combustion. However, with sulfur addition the ratio increased, compared to good combustion, with increased SO_2:HCl ratio and decreased temperature, Table 1. In full scale plants an increased PCDD/PCDF ratio has been observed during transient conditions[10,13,14], however the SO_2:HCl ratio was not discussed. The result from this study also show that average CO and Sum PAH concentration do not correlate to the PCDD/F concentration, the fuel composition and memory effects is important.

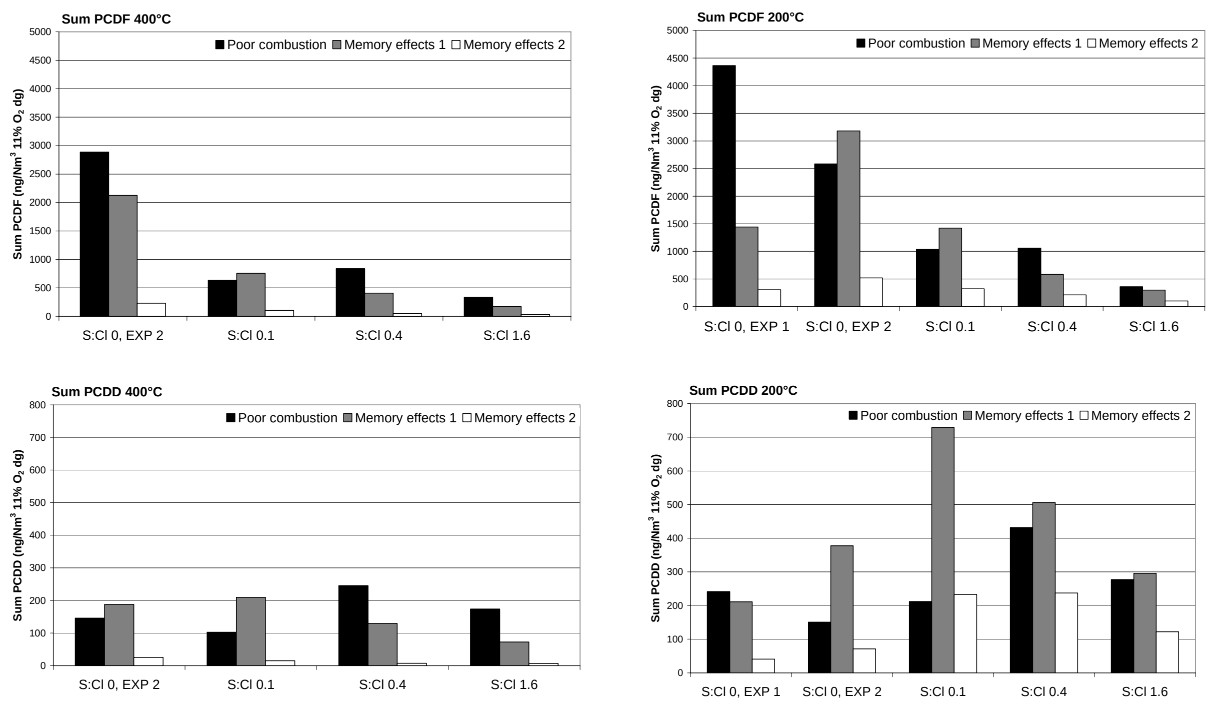

Figure 5. The concentration of Sum PCDF (upper diagrams) and Sum PCDD (lower diagrams) during and after poor combustion, at 400 (left hand side) and 200°C (right hand side). EXP 1 poor combustion with no addition of SO_2, was sampled for 30 minutes instead of 20 minutes as for the other poor combustions sampling occasions.

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