Effects of a catalytic converter on PCDD/F, chlorophenol and PAH emissions in residential wood combustion

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ABSTRACT

Catalytic converters can be used to decrease carbon monoxide, organic compounds and soot from small-scale wood-fired appliances. The reduction is based on the oxidation of gaseous and particulate pollutants promoted by catalytic transition metal surfaces. However, many transition metals have also strong catalytic effect on PCDD/F formation.

In this study birch logs were burned in a wood-fired stove (18 kW) with and without a catalytic converter with palladium and platinum as catalysts. PCDD/F, chlorophenol and PAH concentrations were analyzed from three phases of combustion (ignition, pyrolysis and burnout) and from the whole combustion cycle.

PCDD/F emissions without the catalytic converter were at a level previously measured for wood combustion ($0.15–0.74 \ \mathrm{ng \ Nm^{-3}}$). PAH emissions without the catalytic converter were high ($47–85 \ \mathrm{mg \ Nm^{-3}}$) which is typical for batch combustion of wood logs.

Total PAH concentrations were lower (on average 0.8-fold), and chlorophenol and PCDD/F levels were substantially higher (4.3-fold and 8.7-fold, respectively) when the catalytic converter was used. Increase in the chlorophenol and PCDD/F concentrations was most likely due to the catalytic effect of the platinum and palladium. Platinum and palladium may catalyze chlorination of PCDD/Fs via the Deacon reaction or an oxidation process.

The influence of emissions from wood combustion to human health and the environment is a sum of effects caused by different compounds formed in the combustion. Therefore, the usage of platinum and palladium based catalytic converters to reduce emissions from residential wood combustion should be critically evaluated before wide-range utilization of the technology.

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1. Introduction

A large number of residential wood combustion (RWC) appliances such as masonry heaters, boilers and stoves are used for heat production in many countries. RWC will increase even more in the future because biomass combustion is considered to be greenhouse gas neutral energy source. However, RWC is known to be an important source of pollutants such as fine particles (e.g. Boman et al., 2003; Sippula et al., 2007; Karvosenoja et al., 2008; Tissari et al., 2008, 2009), polycyclic aromatic hydrocarbons (PAHs) (e.g. McDonald et al., 2000; Hellén et al., 2008) and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) (e.g. Quaß

et al., 2004). These pollutants impair local and regional air quality and cause adverse health effects (van den Berg, 1994; Boström et al., 2002; Pope et al., 2002; Kappos et al., 2004; Kettunen et al., 2007).

PCDD/Fs constitute a group of persistent organic pollutants which can be unintentionally formed and released from combustion and other thermal processes when there is chlorine, oxygen and carbon available (Shaub et al., 1983; Anderson et al., 2002). Research of PCDD/F emissions started with municipal solid waste (MSW) incinerators where fuel is heterogeneous and contains chlorine and metals such as iron, copper, aluminum and tin. Although chlorine content of wood is much lower than that of MSW, all the requirements of PCDD/Fs formation are filled also in RWC. PCDD/F formation is a complex process which is studied widely but still not completely understood. Three routes have been presented to explain PCDD/F formation in combustion (Shaub et al., 1983; Dickson et al., 1992; Gullett et al., 1992; Tuppurainen et al., 1998, 2000). The homogeneous pathway covers formation

from structurally related compounds such as chlorophenols (CPhs) at high temperatures (400–800 °C). The heterogeneous pathway is divided in two different routes: the *de novo* mechanism and the catalytic-assisted coupling of precursors, both at temperatures between 200 °C and 400 °C. These temperatures are typical in RWC appliances. PAHs are formed from incomplete combustion of pyrolysis gases or from light organic compounds (Tissari, 2008).

Iron ore sintering plants and MSW incinerators are the most important PCDD/F emission sources in Europe (Quaß et al., 2004). PCDD/F emissions from solid fuel (wood and coal) combustion constitute more than 60% of all non-industrial sources (Quaß et al., 2004). Reductions of PCDD/F emissions in waste incineration and iron ore sintering increase more and more the importance of PCDD/F emissions from RWC (Tame et al., 2009). PAH emissions from residential combustion in Finland were estimated to constitute 64% of the total emissions of four genotoxic PAHs (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene) in 2003 (Koskinen et al., 2005).

Because of the health effects of RWC emissions and the influence of the emissions on the air quality there is a need for emission abatement. Improvements in combustion technique aim to decrease the formation of emissions. However, conventional combustion appliances with high emission factors are still widely used. Secondary reduction techniques such as fabric filters, electrostatic precipitators (ESPs), scrubbers and catalytic converters are used to reduce the emissions. However, because of the high price and technical issues, most of these techniques are not applicable for small-scale combustion appliances (<5 MW) (Hytönen and Jokiniemi, 2007). Catalytic converters offer low cost opportunity for emission reduction for combustion appliances with a conventional combustion technique. The reduction is based on the oxidation of pollutants from incomplete combustion such as CO into CO_2 by means of a catalyst. Although catalytic converters are widely used in many countries e.g. the USA where there are emission factor regulations for catalytic wood stoves (US EPA, 1995), the research in this area is scarce. The effects of catalytic converters on the emissions are still not well known.

Usually in catalytic converters noble metals are used as active catalysts. Supported palladium and platinum are among the most widely used catalysts (Carnö et al., 1997). It is known that transition-metal species, especially copper, catalyze PCDD/F formation via heterogeneous routes (Tuppurainen et al., 1998; Altarawneh et al., 2009). There are a few studies conducted where PCDD/Fs have been found to decompose by the catalytic effect of platinum and palladium (Ukisu and Miyadera, 2002, 2004). However, there are also studies where the amount of PCDD/Fs has been increased in consequence of platinum and palladium (Hart, 2004, 2008). Thus, the effect of a catalytic converter on the emissions of organic chlorocompounds such as CPhs and PCDD/Fs needs to be studied further.

The main aim of this study was to find out if the catalytic converter increases the amount of PCDD/Fs and CPhs, while decreasing the PAH emissions. An additional aim was to find out the emission levels of PCDD/Fs, CPhs and PAHs in different combustion phases without the catalytic converter. Combustion measurements were performed in laboratory conditions using a sauna stove as a combustion appliance. PCDD/Fs, CPhs and PAHs were analyzed from flue gas samples which were collected during combustions with and without the catalytic converter. In addition, samples were taken and analyzed from different combustion phases.

2. Experimental set-up

The experiments were carried out in the combustion and emission research laboratory of the University of Eastern Finland.

2.1. Stove

A sauna stove with heat output of 18 kW was used as the combustion appliance. It was chosen for this experiment due to the high flue gas outlet temperature which provides sufficient conditions for the operation of the catalyst. In addition, the appliance type is widely used in Finland and has very high emissions. Thus there is an urgent need for emission reduction for this particular appliance. Typically sauna stoves are light steel-built combustion appliances which are not intended to reserve the produced heat (Tissari et al., 2009). Sauna stoves are operated with high combustion rate because the need for heat in the sauna is temporarily high. The firebox is small and there is no secondary combustion. Therefore the efficiency is low and the flue gas temperature high. In addition, in typical sauna stove operation the fuel gasification is fast and the supply of air is clearly insufficient causing incomplete combustion. Thus due to the conventional combustion technique carbon monoxide, OGC (organic gaseous compounds), particle and PAH emissions from sauna stoves have been observed to be high (Tissari et al., 2007; Lamberg et al., 2011).

2.2. Fuel and operation

The fuel used was seasoned birch logs which are commonly used in Finland. The logs were 35 cm in length. The moisture content of the logs was low, from 6% to 6.5%, because the wood had been stored inside the laboratory. The ash content of the fuel, according to ignition residue analysis at 550 °C, was 0.4% by dry weight which is typical for birch wood (Sippula et al., 2007). The net heating value of the fuel used was 18.7 MJ kg^{-1}. In addition, the main ash-forming elements were determined from the fuel. The elemental analysis revealed potassium and calcium to be the main elements of the fuel with concentrations of 440 and 280 mg kg^{-1}, respectively. P, Mn, Zn, S, and Mg concentrations were 103, 69, 52, 46, and 29 mg kg^{-1}, respectively. Na, Cu, Al, Cr, and Ni were found only in trace amounts and Fe was not detected (detection limit was 200 mg kg^{-1}). Chlorine concentration of the fuel was not analyzed but typically chlorine content of birch wood is from 0.007% to 0.03% (Werkelin et al., 2005; Sippula et al., 2007).

The experiments were performed with the typical operational practice for a sauna stove as presented by Lamberg et al. (2011). The sauna stove was loaded in batches. The combustion procedure started with a kindling batch which consisted of 5–7 logs and 150 g of wood sticks with a minor amount of birch bark. The kindling batch was 1.7 kg for total weight. Fifteen minutes after ignition the kindling batch was followed by two batch additions, each 3.2 kg in weight. The second batch consisted of 6 logs 530 g each and the third batch of 5 logs 640 g each. The second and the third batches lasted for 25 and 32–35 min, respectively. The whole combustion experiment lasted for 72–75 min. Batch additions are presented in Fig. 1. The average levels of excess oxygen in the flue gas were between 7.8–8.1% and 9.7–10.5% during whole combustion cycle with and without the catalytic converter, respectively. The time variation of the flue gas oxygen is shown in Fig. 1.

2.3. Catalytic converter

A commercially available catalytic converter (manufactured by NVI) was used in this study. It was composed of a pack of nets which was covered with the active catalysts, platinum and palladium. The catalytic converter was placed in the stack 80 cm above the sauna stove. The catalytic converter was not used during ignition because it requires relatively high flue gas temperature to function.
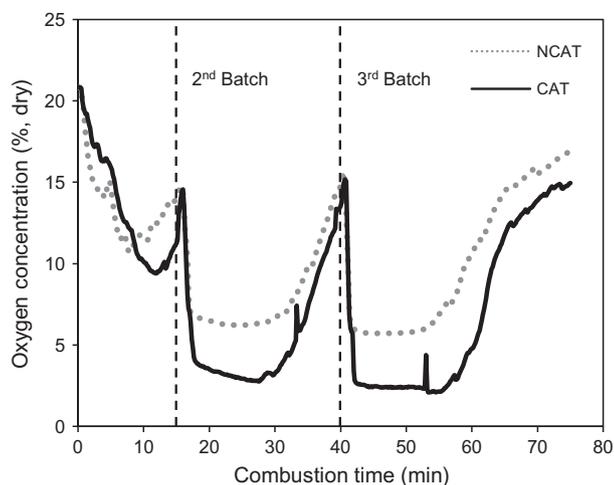
Fig. 1. Batch additions and oxygen concentrations in catalytic and non-catalytic combustion.

2.4. Dilution and continuous measurements

As shown in Fig. 2, the flue gas was led through a stack and diluted with a hood. The draught was adjusted with a flue gas fan and with the distance between the hood and the stack. The draught was measured with a manometer (Alnor AXD model 5691, Alnor Instruments). Flow rates are presented in Fig. 2. Calculation of the flow rates was based on fuel consumption, flue gas excess O_2 and measured dilution ratios in the hood. Temperature was measured continuously with k-type thermocouples near the surface of the catalytic converter and 20 cm above the catalytic converter. Temperature was measured also within the diluted flue gas. CO, CO_2, and O_2 were measured continuously from undiluted flue gas with a combination of gas analyzers (ABB Cemas gas-analyzing rack). OGC emissions were analyzed with a flame ionization detector.

2.5. Sampling

Descriptions of sample phases, collection times and batches are shown in Table 1. Samples were taken from different combustion phases without the catalytic converter and from whole combustion cycle with (CAT) and without (NCAT) the catalytic converter. Three parallel NCAT samples and two parallel CAT samples were taken. The ignition sample represents the initial stage of combustion when the ignition batch is fired. The pyrolysis sample describes the phase where the fuel gasifies and the pyrolysis gases oxidize.
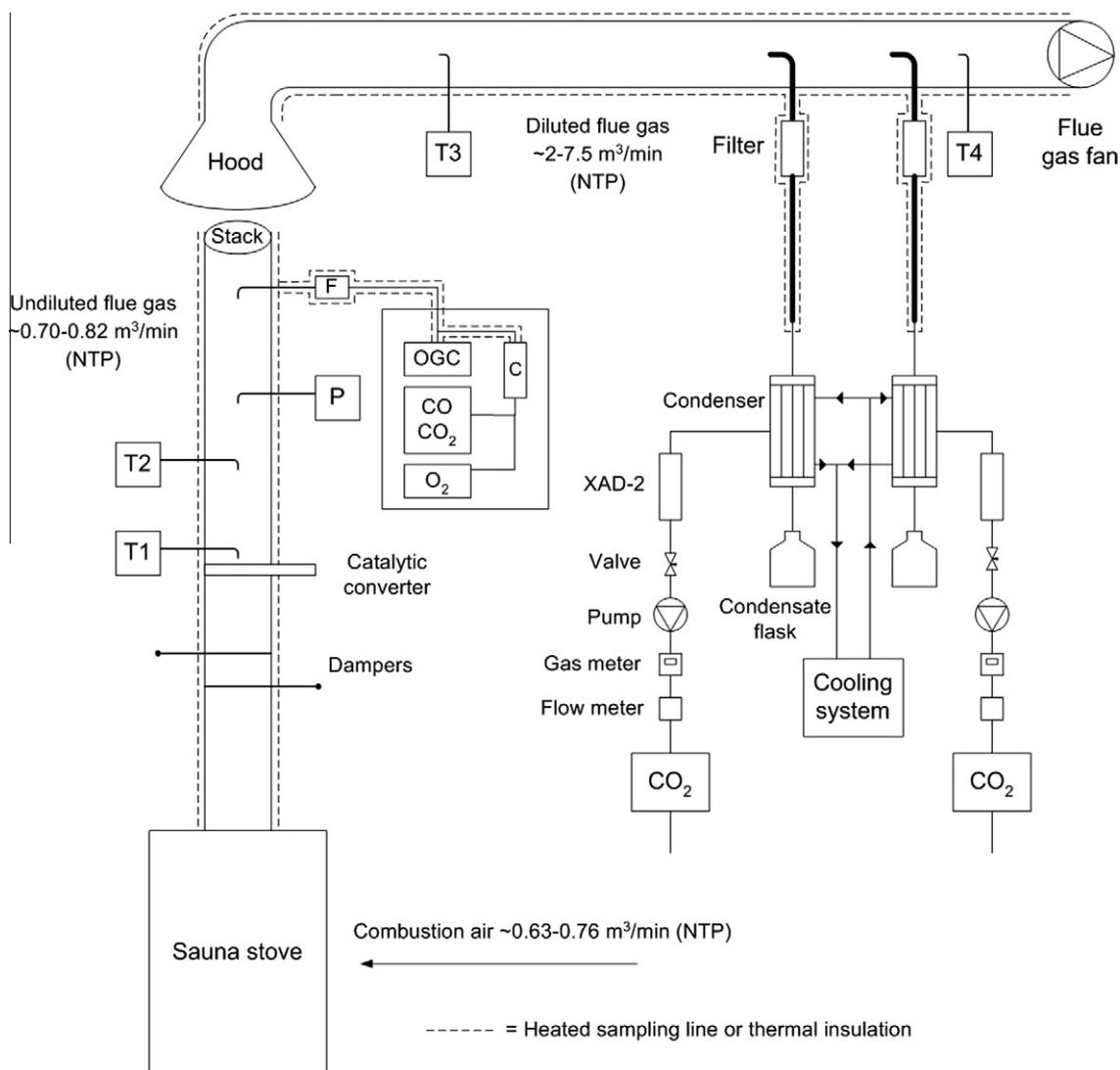

Fig. 2. Experimental set-up and flow rates: T, thermocouple; P, pressure sensor; F, filter; XAD-2, absorption material; C, condenser.

Sample name	Sampling phase	Collection time (min)
Ignition	From the beginning of the ignition batch	15
Pyrolysis	From the beginning of the 3. batch	10
Burnout	20 min after adding the 3. batch	15
NCAT	Whole combustion cycle	72–75
CAT	Whole combustion cycle[a]	75

[a] Catalytic converter was not used during ignition.
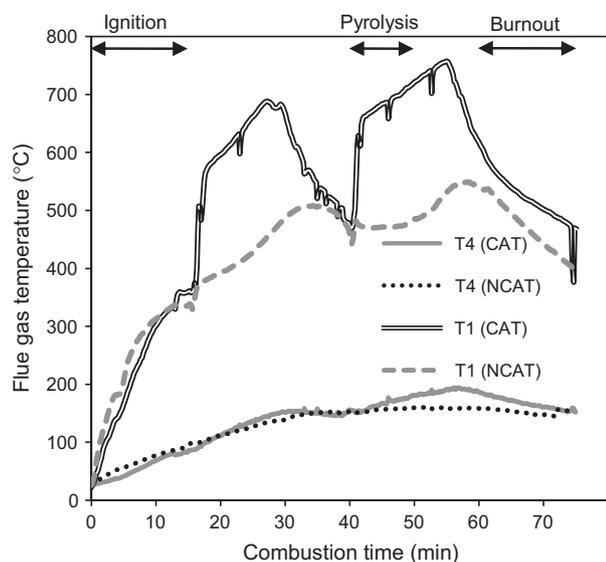
Fig. 3. Sampling phases and flue gas temperatures for catalytic and non-catalytic combustion. T1, temperature near the surface of a catalytic combustor; T4, temperature of the sample.

The burnout sample represents the final stage of the combustion cycle. The sample phases are indicated in Fig. 3.

Sampling of PCDD/Fs, CPhs and PAHs was based on SFS-EN 1948-1 standard with the exception that $^{13}C_{12}$-labeled PCDD/Fs were not used in sampling procedure. Instead of that, internal standard solutions were used in the analysis. The sampling system consisted of a heated glass probe, a filter holder, a cup-shaped filter, a condenser and a condensation flask (Fig. 2). The samples were collected isokinetically from the diluted flue gas which was led through the heated probe. A filter for collecting the particulate compounds was placed inside the probe but outside the stack. After the particle collection the sample flow was cooled with the condenser. The temperature of the cooling water circulation was set to 8 °C. The condensed flue gas flowed to the condensate flask. The flue gas stream continued to a pump through XAD-2 adsorbent (Supelco) which collected the gaseous compounds. The suction air volume was controlled with a valve and measured with a gas meter and a flow meter. Blank samples were taken for quality assurance but no detectable amounts of PCDD/Fs, CPhs or PAHs were detected.

2.6. Sample handling and analysis

Gaseous phase and particulate phase were analyzed separately. A set of standards, 1 mL of PCDD/F internal standard (Wellington/Campro, 16 ^{13}C-labeled isomers with concentration of 1 μg mL^{-1}), 1 mL of PAH internal standard (D8-naphtalene, D10-acenaphtene, D10-phenanthrene, D12-chrysene and D12-perylene with total

concentration of 1 μg mL^{-1}) and 0.75 mL of CPh internal standard (2,4,6-TBrP with concentration of 0.75 μg mL^{-1}), were added to each sample. The samples were eluted with toluene (super purity) in a Soxhlet apparatus for 20 h (Ruokojärvi et al., 1995a, 1995b). After the elution the samples were eluted with potassium carbonate, acetylated with acetic anhydride and dissolved with hexane (HPLC-grade), and the solution analyzed for CPhs. Then, nonane (>99%, Fluka) was added to the samples and the toluene was evaporated. The extraction was dissolved in hexane. The samples were purified by adsorption column chromatography (ICB Alumina B, Al$_2$O$_3$). For the PAH analysis a portion of the sample was dissolved to dichloromethane (Merck) and concentrated with nitrogen. For the PCDD/F analysis a portion of the sample was purified with sulfuric acid (95–97%, Riedel de Haen) and with multistep columns (silicagel, carbon and alumina).

CPhs and PAHs were analyzed with a gas chromatograph and a mass selective detector (6890N GC-5973 INERT MSD, Agilent Technologies). The quantification limit of the method is 0.1 ng mg^{-1}. PCDD/Fs were quantified using a high-resolution gas chromatograph and high-resolution mass spectrometer (VG 70 250 SE). The resolution of the equipment used in PCDD/F analysis was 10,000. Detailed information about the analytical measurements can be found as a Supplementary material.

2.7. Calculations

Emissions measured from diluted flue gas were corrected with the dilution ratio (DR). DR was calculated from the CO_2 concentrations of the undiluted and diluted flue gas as described by Sippula et al. (2009). Emission concentrations were normalized to dry flue gas at NTP and 13% of oxygen. PCDD/F concentrations were converted to toxic equivalents (TEQs) with international toxic equivalency factors (I-TEFs) (NATO/CCMS, 1988). The nominal emission value calculation was based on SFS 5624 (1990) standard. The nominal emission values per unit mass of fuel used was calculated by multiplying the nominal emission value (mg MJ^{-1}) with the fuel net heating value. The emission conversion factors are presented in Table 2.

3. Results and discussion

The measured CPh, PCDD/F and PAH emissions are shown in Table 2. The results are presented as a sum of the gas and particulate phase concentrations. Even though measurements have been conducted with a sauna stove, which is a rather untypical appliance outside of Finland, the results are applicable to other batch-wise operated wood log appliances where the combustion process is not optimal and the emissions of incomplete combustion are high.

3.1. Emissions during different combustion phases without a catalytic converter

CPh concentrations in different combustion phases varied from 730 ng Nm^{-3} to 7470 ng Nm^{-3} (Table 2). CPh emissions from native wood combustion have not been studied much even though CPhs are known to be among the most abundant PCDD/F precursors in combustion processes (Tuppurainen et al., 2000). The highest CPh concentration was found in the pyrolysis sample. Samples composed of only three monochlorophenols: 2-CPh, 3-CPh and 4-CPh. This result is consistent with earlier finding that the most common CPhs in combustion processes are mono-CPhs (Jansson et al., 2009). CPhs existed in the gas phase of the samples, except during the burnout phase.

Table 2
CO, OGC, CPh, PCDD/F and PAH concentrations and emission values for combustion events with and without the catalytic converter.

Concentrations in flue gas (reduced to 13% of O_2)					
	Non-catalytic				Catalytic
	Ignition	Pyrolysis	Burnout	Whole combustion cycle (NCAT)	Whole combustion cycle (CAT)
CO (mg Nm^{-3})	1020	28900	8430	9240–11,600	7660–8110
OGC (mg Nm^{-3})	84	6380	125	1740–2260	1520–1590
CPhs (ng Nm^{-3})[a]					
2-CPh	382	3660	2320	1650–1980	9080–10,900
3-CPh	243	2130	758	1010–1340	3900
4-CPh	104	1680	634	561–676	1860–2000
2,6-DCPh	n.d.	n.d.	n.d.	n.d.	38–54
2,4 + 2,5-DCPh	n.d.	n.d.	n.d.	0–98	0–314
2,3-DCPh	n.d.	n.d.	n.d.	n.d.	92–151
3,5-DCPh	n.d.	n.d.	n.d.	n.d.	101–110
2,4,6-TCPh	n.d.	n.d.	n.d.	n.d.	48–64
Sum of CPhs	730	7470	3710	3220–4100	15,500–17,100
PCDD/Fs (ng Nm^{-3})[a]					
2,3,7,8-TCDD	n.d.	n.d.	n.d.	0–0.04	n.d.
1,2,3,7,8-PeCDD	n.d.	n.d.	n.d.	0–0.02	n.d.
1,2,3,4,7,8-HxCDD	n.d.	n.d.	n.d.	n.d.	0–0.04
1,2,3,6,7,8-HxCDD	n.d.	n.d.	n.d.	n.d.	0.02–0.04
1,2,3,7,8,9-HxCDD	n.d.	n.d.	n.d.	n.d.	0.03–0.04
1,2,3,4,6,7,8-HpCDD	n.d.	n.d.	n.d.	0–0.12	0.1–0.32
OCDD	n.d.	n.d.	n.d.	n.d	0.05–0.22
2,3,7,8-TCDF	n.d.	n.d.	n.d.	0.03–0.13	0.29[b]
1,2,3,7,8-PeCDF	n.d.	n.d.	n.d.	0–0.05	0.03
2,3,4,7,8-PeCDF	n.d.	n.d.	0.007	0–0.13	0.08–0.11
1,2,3,4,7,8-HxCDF	n.d.	0.157	0.002	0.03–0.12	0.2–0.26
1,2,3,6,7,8-HxCDF	0.139	0.112	n.d.	0–0.03	0.18–0.25
2,3,4,6,7,8-HxCDF	n.d.	n.d.	0.005	0–0.12	0.26–0.6
1,2,3,4,6,7,8-HpCDF	n.d.	0.471	0.012	0–0.08	0.76–1.9
1,2,3,4,7,8,9-HpCDF	n.d.	n.d.	n.d.	n.d.	0.03–0.12
OCDF	0.765	n.d.	n.d.	n.d.	0.07–0.27
Sum of PCDD/Fs	0.904	0.741	0.026	0.15–0.74	2.1–4.5
Sum of PCDD/Fs (ng I-TEQ Nm^{-3})	0.015	0.032	0.004	0.009–0.161	0.15–0.23
PAHs (mg Nm^{-3})					
Acenaphthylene (Acy)	1.3	22	0.12	20–38	19–22
Acenaphthene (Ace)	n.d.	0.95	0.21	0.65–1.3	0.87–1.4
Fluorene (Fle)	n.d.	5.8	0.05	4.9–9.2	4.7–5.5
Phenanthrene (Phe)	n.d.	10	0.60	0.34–4.6	0.093–0.15
Anthracene (Ant)	1.8	4.8	0.15	0.8–8	5.7–6.3
Fluoranthene (Fla)	n.d.	5.1	0.19	1.7–9.1	5.6–6.6
Pyrene (Pyr)	1.2	8.6	0.22	1.9–11	6.1–7.2
Benzo[a]anthracene (B(a)a)	n.d.	1.0	0.029	1.3–3.7	0.62–0.82
Chrysene (Cry)	n.d.	1.3	0.025	1.8–3.9	1.4–1.6
Benzo[b]fluoranthene (B(b)f)	n.d.	4.4	0.039	1.9–5.3	1.1–1.4
Benzo[k]fluoranthene (B(k)f)	n.d.	0.87	0.084	0–1.3	0.30–0.31
Benzo[a]pyrene (B(a)p)	n.d.	1.9	0.075	0.59–2.6	0.71–1
Indeno[1,2,3-cd]pyrene (I(123 cd)p)	n.d.	1.2	0.039	0.55–2	0.43–1
Dibenzo[a,h]anthracene (D(ah)a)	n.d.	n.d.	0.0038	n.d.	n.d.
Benzo[g,h,i] perylene (B(ghi)p)	n.d.	1.5	0.039	1–2.3	0.54–1.3
Sum of PAHs	4.3	69	1.9	47–85	47–57
m^{3}MJ^{-1}emission conversion factors	0.87	0.43	0.98	0.56–0.61	0.5–0.65
m^{3}kg^{-1} emission conversion factors	16.42	8.15	18.6	10.54–11.65	9.46–12.25

[a] 3,4-DCPh, 2,3,6-TCPh, 2,3,5-TCPh, 2,4,5-TCPh, 2,3,4-TCPh, 3,4,5-TCPh, 2,3,5,6-TeCPh, 2,3,4,6-TeCPh, PeCPh and 1,2,3,7,8,9-HxCDF were not found in detectable limit.
[b] Result of one sample.

Total PCDD/F concentrations in different combustion phases varied from 0.026 ng Nm^{-3} to 0.904 ng Nm^{-3} (Table 2). The highest PCDD/F level was found in the ignition phase sample and it contained 1,2,3,6,7,8-HxCDF and OCDF. No PCDD compounds were found from the ignition, pyrolysis or burnout samples (Table 2). This finding is congruent with the statement reported previously that the PCDD/Fs formed in wood combustion are mainly PCDF compounds (Tame et al., 2009). PCDD/Fs were mainly found in the particulate phase of the samples, except during the ignition phase.

Although the highest PCDD/F concentration was found in the ignition phase sample, the highest TEQ level was obtained for the pyrolysis phase. The ignition sample contained two mildly toxic congeners whereas the pyrolysis sample contained also more toxic congeners. The total PCDD/F TEQ concentrations in different combustion phases varied from 0.004 ng I-TEQ Nm^{-3} to 0.032 ng I-TEQ Nm^{-3}. These results are very similar to previous studies conducted with typical RWC appliances (Launhardt et al., 1998; Pfeiffer et al., 2000) Emissions from the combustion phases without the catalytic converter are also clearly below the current emission limit in Europe for MSW incinerators, which is 0.1 ng I-TEQ Nm^{-3}.

The PAH concentrations in different combustion phases varied between 4.3 mg Nm^{-3} and 69 mg Nm^{-3} (Table 2). The PAH emission (sum of Fle, Phe, Ant, Fla, Pyr, B(a)a, Chr, B(b)f, B(a)p, I(123-cd)p and B(ghi)p) from the whole combustion cycle without

the catalytic converter was 545 mg kg^{-1} wood which is higher than that measured in previous studies (Hedberg et al., 2002; Tissari et al., 2007) The highest PAH level was obtained for the pyrolysis phase. PAH profiles varied between the different samples. In every sample pyrene was among the three most common PAH compounds. Acenaphtylene and anthracene were dominant compounds during the ignition; acenaphtylene, phenanthrene, fluorine, fluoranthene and anthracene during the pyrolysis; and acenaphtene, phenantrene, fluoranthene, anthracene, and acenaphtylene during the burnout phase. These compounds contributed from 80% to 100% of the total PAHs in the combustion without the catalytic converter. Most of these compounds were among the most dominant PAHs also in previous studies of birch combustion (Hedberg et al., 2002; Tissari et al., 2007). Besides the ignition phase, PAHs were found mainly in the gas phase of the samples.

The highest CPh and PAH emissions during the pyrolysis phase were due to a high gasification rate of the fuel while there is also insufficient air supply or poor mixing of the pyrolysis gases and the combustion air. However, the highest PCDD/F concentration was measured during the ignition phase. It should be noted though that this result represents only one sample from the ignition phase. In general, several factors such as batch size, log size, appliance type and operational practice influence the emissions of RWC (Tissari et al., 2008, 2009).

3.2. Effect of catalytic converter on emissions

During the combustion experiments with the catalytic converter the amount of CO and OCG were clearly lower, as can be expected. In addition, the flue gas temperature was higher (Fig. 3) which is partially due to the catalytic oxidation of the emissions taking place at the catalytic converter but may be also influenced by slightly lower air-to-fuel ratios in the combustion experiments with the catalyst. It is known that PCDD/Fs formed at high temperatures (760–800 °C) are more stable in the atmosphere than those formed at lower temperatures (350–380 °C) (Pennise and Kamens, 1996).

Both the CPh and PCDD/F emissions were substantially higher with the catalytic converter than without it. The CPh and PCDD/F concentrations in CAT compared to those in NCAT were on average 4.5-fold and 8.5-fold, respectively. PCDD/F emissions with the catalytic converter also clearly exceeded the current emission limit in Europe for MSW incinerators. There were differences in both PCDD/F and CPh profiles between CAT and NCAT. Mono-CPhs were the main components also in CAT as in ignition, pyrolysis and burnout phases without catalytic converter, and in NCAT. In addition, all analyzed di- and tri-CPhs were found in CAT. It has been observed that the higher the chlorination degree of the precursor is the easier is the condensation via Ullmann reactions for the precursor (Tuppurainen et al., 1998). Since PCDD/Fs can be formed through the condensation of the chlorophenols the increase of highly chlorinated chlorophenols may increase PCDD/Fs. CAT contained all of the analyzed PCDF compounds while NCAT contained all except 1,2,3,4,7,8,9-HpCDF and OCDF. Also more PCDDs were found in CAT than in NCAT.

The increase in the concentrations of CPhs and PCDD/Fs with the catalytic converter is most likely due to the catalytic effect of platinum and palladium. A possible explanation for this is that platinum and palladium could catalyze the Deacon reaction. Many metals have been proposed to catalyze Deacon reaction (Eq. (1)) but so far it has been proven only for copper and ruthenium (Gullett et al., 1990; Hisham and Benson, 1995; López et al., 2008).

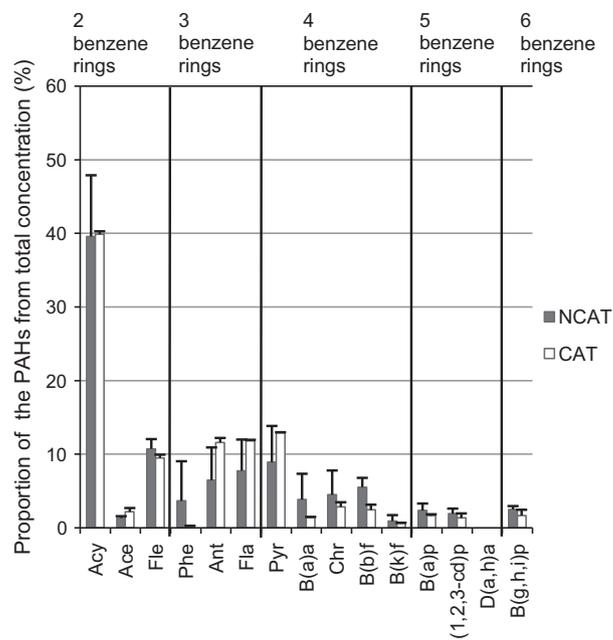$$2HCl + 1/2O_2 = H_2O + Cl_2 \qquad (1)$$

Fig. 4. Proportions of different PAH compounds in the total concentration of 14 PAHs.

Overall, the Deacon reaction is a catalytic cycle which can be divided into two steps. In the first step a metal oxide absorbs HCl to form a metal chloride and water. In the second step chloride oxidizes, and metal oxide and Cl_2 are formed (Suleiman et al., 2011). It is known that chlorine in the fuel is first converted to HCl and metal chlorides (van Lith et al., 2006). Thereafter HCl can be transformed to Cl_2 via the Deacon reaction. HCl is known to be a less effective chlorinating agent than Cl_2 which more likely undergoes substitution reactions to produce PCDD/Fs or their precursors (Ruokojärvi et al., 1998). Since the chlorination of carbon may be the limiting step in PCDD/F formation during wood combustion, HCl conversion to Cl_2 could increase the PCDD/F formation (Tame et al., 2007). Furthermore, platinum and palladium could also catalyze the oxidation of the precursors of PCDD/Fs and thus promote the formation of PCDD/Fs. The catalysis of the oxidation process of PCDD/Fs precursors has been proven for copper oxides (Lomnicki and Dellinger, 2002). In the lack of oxygen in the gas phase the surface of a metal oxide serves as a source of oxygen in the oxidation process. As a consequence platinum and palladium may promote PCDD/F formation in two ways: the oxidation process and the chlorination process.

The total PAH concentration was 24% lower in CAT than in NCAT. The reduction of PAHs was equal to the reduction of OGC. The reduction of PAHs was most likely due to the higher overall combustion efficiency and thus higher oxidation of PAH compounds. Only for Ace, Ant, Fla, and Pyr the concentration was increased. Although the total PAH concentration was lower, the proportion of gaseous PAHs in the total PAHs increased by 10% units with the catalytic converter.

The carcinogenicity of PAHs increases with the amount of benzene rings in the structure (Boström et al., 2002). As can be seen from Fig. 4 catalytic converter decreased the amount of heavier PAH compounds which have 4–6 benzene rings. In addition, the amount of genotoxic PAHs was smaller in CAT than in NCAT. Genotoxic PAHs are reported in WHO/IPCS criteria (WHO, 1998). Thus, it seems that PAH emissions from the combustion with the catalytic converter may be less carcinogenic and genotoxic than those from the combustion without the catalytic converter.

4. Conclusions

The highest CPh and PAH emissions were found in the pyrolysis phase. The PCDD/F emissions without the catalytic converter were at the same level as has been previously measured for wood combustion ranging from 0.15 ng Nm^{-3} to 0.74 ng Nm^{-3} during whole combustion cycle. The PAH emissions without the catalytic converter were high (47–85 mg Nm^{-3} during whole combustion cycle) which is typical for batch combustion of wood logs.

The total PAH concentrations were lower, and the chlorophenol and PCDD/F levels were substantially higher with the catalytic converter than without it. The PCDD/F level exceeded the emission limit in Europe for MSW incinerators. The increase in the levels of organic chlorocompounds was most likely due to the catalytic effect of platinum and palladium. Platinum and palladium may catalyze the chlorination of PCDD/Fs via the Deacon reaction or the oxidation process of PCDD/Fs.

The usage of catalytic converters in RWC is controversial. As was shown, a catalytic converter reduced the adverse products of incomplete combustion such as CO, OGC and PAHs on average 26%, 24%, and 24%, respectively. On the other hand, there was a clear increase in the concentrations of CPhs and PCDD/Fs (4.3-fold and 8.7-fold, respectively) when the catalytic converter was used. The influence of the emissions on human health and the environment is a sum of various effects of different compounds formed in the combustion. In order to estimate the total impact and health effects of catalytic converters further toxicological studies need to be done. Based on this study the usage of platinum and palladium based catalytic converters to reduce emissions from RWC should be critically evaluated before wide-range utilization of the technology.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2012.02.027.

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