

# Emission of PCDD/F, PCB, and HCB from Combustion of Firewood and Pellets in Residential Stoves and Boilers

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To assess potential emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) from residential combustion of biofuels, experiments were performed in which various types of pellets and firewood were combusted in four types of stoves and boilers, with both full and reduced rates of air supply. Intermittent combustion of wood pellets resulted in emissions of 11 ng (WHO-TEQ)/kg combusted fuel (dry weight). A modern, environmentally certified boiler yielded somewhat lower emissions of PCDD/F and PCB than a wood stove. Both gave <0.1 ng (WHO-TEQ)/m<sup>3</sup><sub>n</sub> (1.3–6.5 ng (WHO-TEQ)/kg) and considerably lower emissions than an old boiler (7.0–13 ng (WHO-TEQ)/kg). No positive effect on emissions could be observed in full air combustion (simulating the use of a heat storage tank) compared to combustion with reduced air. Two of the wood combustion experiments included paper and plastic waste fuels. Chlorine-containing plastic waste gave rise to high emissions: ca. 310 ng (WHO-TEQ)/kg over the whole combustion cycle. The homologue profiles of PCDD/Fs show characteristic differences between ashes and flue gas from combustions with different levels of air supply. These differences do not, however, seem to have any correlation to the relative amount of toxic congeners.

## Introduction

Incomplete combustion of organic material in the presence of chlorine causes the formation of chlorinated organic byproducts, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB). Municipal waste combustion in large plants used to be a major contributor of these compounds to the environment, but following the introduction of various regulations, intensive monitoring and improvements in combustion technology and emission cleaning techniques, it is now generally considered to have a low impact on the total emissions to air. However, there are large uncertainties regarding the scale

of emissions from small-scale combustion. Therefore, a national survey of unintentionally produced persistent organic pollutants (POPs) was initiated by the Swedish government (1), including the study of small-scale domestic combustion of biofuels reported here.

Concentrations of dioxins (PCDD and PCDDF) often are reported in terms of toxic equivalents, using estimated toxicity of the individual isomers to give a weighted average dioxin concentration. Two of the most commonly reported toxic equivalent methods are the I-TEQ (2) and WHO-TEQ (3) scales. The latter scale also includes PCBs with dioxin-like toxicity. Because of higher weighting of some isomers, the resulting value of merely PCDD/F also may be approximately 10–20% higher in this scale. When the weighting method is not clearly stated (as in some literature references), the denomination “TEQ” is used.

In comparison to emissions of POPs from municipal waste combustion, literature reports on emissions from small-scale biofuel combustion are scarce. In an extensive review of dioxin emissions from wood combustion, Lavric et al. (4) reported that residential boilers and stoves emitted 0.002–0.7 ng (I-TEQ)/m<sup>3</sup><sub>n</sub> (emission factors: 0.2–5.1 ng (I-TEQ)/kg) from uncontaminated wood. Levels from contaminated wood (waste wood) were often considerably higher. In addition, in a series of field studies of domestic heating appliances, Hübner et al. (5) found emission levels of 0.002–2.6 ng (TEQ)/MJ and 0.023–4.5 ng (TEQ)/MJ from combustions of wood, woodchips, and pellets in boilers and stoves, respectively. Assuming a heating value of 18 MJ/kg (5) these figures are equivalent to 0.04–47 ng (TEQ)/kg and 0.4–81 ng (TEQ)/kg, respectively. The cited authors considered these levels to be higher than those presented in previous studies, which were mainly derived from trials on test-stands under laboratory conditions.

In Sweden, approximately 8% of the energy used within the residential and service sectors is supplied through small-scale biofuel combustion (6). Further increases in biofuels, as renewable sources of energy, are being encouraged by subsidies. In recent years developments in furnace technology have increased combustion efficiency and reduced emissions of products of incomplete combustion. The development of pellet burners has offered a convenient means of biofuel combustion and such systems have replaced many old oil burners (6). New boiler technology also offers new approaches for handling wood fires. Using traditional boilers the air supply is often reduced when the fire is well established and has begun to warm the residence satisfactorily, to make the load of fuel last longer. However, it also results in considerable emissions of particles, tar, and various organic compounds. Although this is still a common practice, in cold climates it has been increasingly superseded in residential combustion systems by the use of heat storage tanks (also called “heat accumulators”), which allow the wood to be combusted quickly, with a full air supply. The heat evolved is absorbed in the heat storage tank and can be stored for an extended period. Heat storage tanks are usually water tanks that are linked to the central heating system, and for single-family residences their volume may be 1–2 m<sup>3</sup>. It has been estimated that such tanks were connected to about 30% of the residential biofuel boilers in Sweden in 2001, of which almost 90% were modern, environmentally approved boilers. 12–13% of the biofuel boilers combusted pellets and the remaining ca. 57% were old boilers without a heat storage tank (7).

Compared to earlier practices, the technique of retaining the heat released by combustion in storage tanks is more energy efficient and results in substantial reductions in

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**TABLE 1. Experimental Plan**

exp	equipment	fuel	performance
1.1	pellet boiler	wood pellets	intermittent
1.2	pellet boiler	wood pellets	continuous
1.3	pellet boiler	straw pellets	continuous
2.1a	old boiler	birchwood	start up + full air
2.1b	old boiler	birchwood	reduced air, smoldering
2.2a	old boiler	coniferous wood	start up + full air
2.2b	old boiler	coniferous wood	reduced air, smoldering
2.3a	old boiler	birchwood+paper	start up + full air
2.3b	old boiler	birchwood+paper	reduced air, smoldering
2.4a	old boiler	birchwood+paper+plastic	start up + full air
2.4.b	old boiler	birchwood+paper+plastic	reduced air, smoldering
3.1	modern boiler	birchwood	full air supply
3.2a	modern boiler	birchwood	start up + full air
3.2b	modern boiler	birchwood	reduced air, smoldering
3.3a	modern boiler	coniferous wood	start up + full air
3.3b	modern boiler	coniferous wood	reduced air, smoldering
4.1	stove	birchwood	normal air supply
4.2	stove	birchwood	reduced air supply

emissions of pollutants, e.g., 80%–95% reductions in PAH, CH<sub>4</sub>, and particle emissions when connected to old boilers (and further substantial reductions with modern boilers) (7), but their influence on emissions of PCDD/F, PCB and HCB has not, to our knowledge, been reported previously.

The objective of this study was to acquire a general understanding of potential emissions of PCDD/Fs, PCBs, and HCB from the residential combustion of biofuels. An attempt was made to cover the most commonly used fuels, types of stoves and boilers, and modes of combustion in Sweden in the experiments.

### Experimental Section

The experiments (Table 1) were performed with four types of stoves and boilers, fueled with pellets or firewood in several modes of combustion. Two of the combustion experiments included paper and plastic waste fuels.

**Fuels.** The pelletized fuels used were made of wood and wheat straw. The wood pellets were commercially available, and made of byproducts, mainly coniferous, from wood processing industries, whereas the straw pellets were manufactured at the Biofuel Technology Center (BTC) of the Swedish Agricultural University (SLU). Analysis showed that the moisture, ash, and chlorine contents of the wood pellets were 6%, 0.03%, and <0.01%, respectively, and the corresponding levels in the straw pellets were 8.1%, 5.9%, and 0.19%. Firewood from three species—birch (*Betula verrucosa* and *Betula pubescens* L.), spruce (*Picea abies* L.), and pine (*Pinus silvestris* L.)—was used. In each case, the wood was cut into pieces of 0.3–0.5 m length, depending on the size of the combustion chamber, and split into halves or quarters (approximately 1 dm across). The wood was stored in a conventional way in an outdoor woodshed prior to combustion, and its moisture content ranged between 16 and 18% on wet basis. In two experiments (exps 2.3 and 2.4, Table 1) paper and plastic wastes were also added. The paper consisted of newspaper, advertising leaflets, magazines, and paper packages. The plastics consisted of three fractions (soft plastic packages, hard plastic packages, and other plastics) obtained from a sorting analysis in a previous work (8), and were shredded into less than 1 cm pieces. These fractions were mixed in equal parts, giving a chlorine content of 4.6% in the combined plastic fraction.

**Boilers and Stoves.** The combustion systems consisted of the following:

(1) An Albin Biotec boiler (Albinpannan AB) constructed for the combustion of pelletized fuel or oil, or electric heating, equipped with a Thermia BeQuem 15 pellet burner (Thermia

Värme AB), including systems for automatically feeding pellets to an under-fed type burner pot, regulated by a thermostat in the boiler, and automatic electric ignition after combustion breaks. The nominal output for the combustion of wood pellets was 15 kW. The double-walled boiler contained 160 L of water and was connected to a circulating system with a radiator and an expansion tank. It also contained an internal 90 L water heater with an inlet for cold water and an outlet. The flue gas was led through a 50 mm channel and the flow was maintained at a continuous level of approximately 25 m<sup>3</sup>/h with a fan.

(2) An approximately 30-year-old CTC 265 K boiler, (CTC AB, presently Bentone), with two separate fireplaces, one for oil and one for solid fuels such as wood or coke. The boiler could also be adapted for use with electric heaters. The nominal output for wood was 12 kW. The primary air was supplied through a draft-regulating damper in the ash pit door below the wood fireplace. The boiler was double-walled with an internal water tank connected to an external heat exchanging system. The flue gas was connected to a dilution system as described below.

(3) A modern eco-labeled (environmentally approved) Solo Innova 30 wood boiler (Baxi AB) with a ceramic grate and downdraft combustion chamber. Supplies of primary and secondary air were regulated with a suction fan connected to the boiler thermostat. The nominal output was 30 kW. The double-walled boiler was connected to an external heat exchanging system. The flue gas was connected to a dilution system as described below.

(4) A modern wood stove, Handöl 10 T (Nibe Stoves), certified according to European standard EN-13240, class 1, with a nominal output of 9 kW and heat storage unit made of olivine and soapstone. The air supply could be regulated by rotating the fire grate. The flue gas was connected to a dilution system as described below.

**Combustion Experiments.** (1) *Pellet Combustion.* Sampling of organic compounds in the pellet combustions started when the temperature recorded by the boiler thermometer was close to the preset temperature (80 °C). In the intermittent experiments (exp 1.1, Table 1) the boiler temperature was allowed to reach the preset temperature, after which the fuel feeding was automatically interrupted. Combustion was restarted by running cold water through the water tank, cooling the boiler and thereby switching on the thermostat-regulated fuel feeding. This was done repeatedly, resulting in combustion cycles of approximately 1 h. Changes in relative levels of furnace temperature and some of the logged emissions over the course of the combustion cycles are

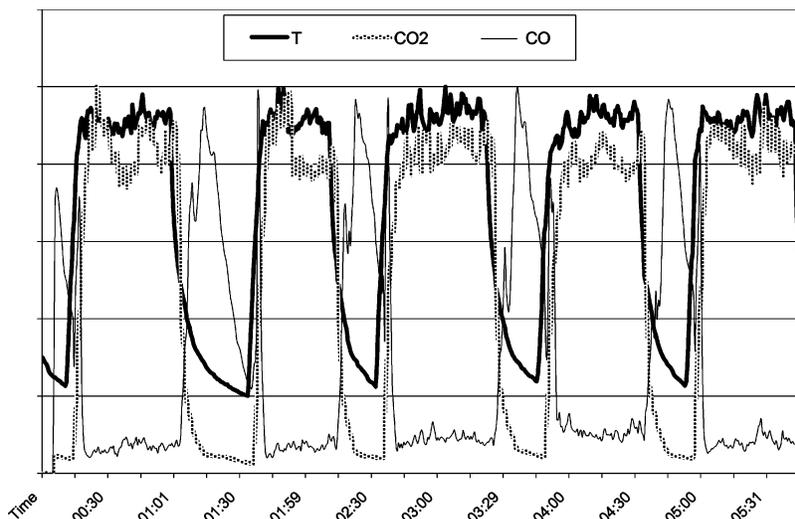


FIGURE 1. Relative levels of temperature in furnace, near burner pot, and emissions during intermittent pellet combustion (exp 1.1).

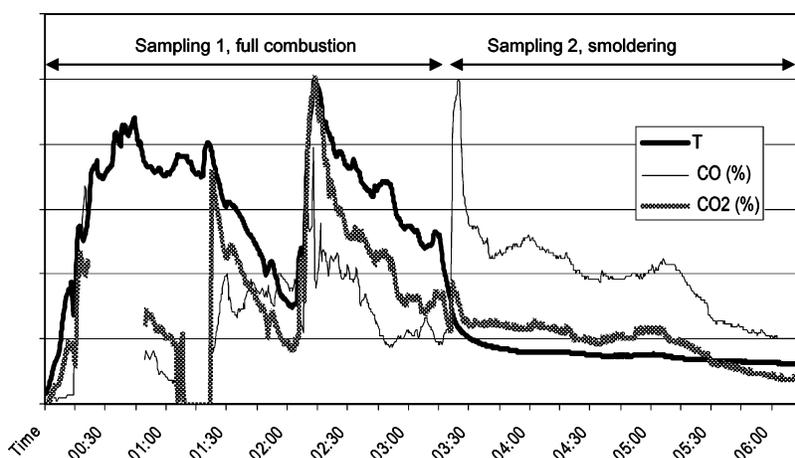


FIGURE 2. Relative levels of temperature in the flue, just above the boiler, and emissions during the combustion of birch in the old boiler (exp 2.1).

illustrated in Figure 1 and more logged emissions are found in the supporting information (Figure S1). In the continuous pellet combustions (exps 1.2 and 1.3) a continuous flow of cold water, at low rates, through the water heater prevented the boiler water from reaching the preset temperature so the burner could work continuously. Nevertheless, two short breaks occurred accidentally in exp 1.2 (distributed on separate duplicates). In all three pellet experiments duplicate samples were taken throughout the course of combustion. The intermittent samplings lasted about 6 h (duplicates on different days) and the others lasted between 3 and 4 h (duplicates on the same day).

(2) *Combustion in the Old Boiler.* The combustions in the old boiler (exps 2.1–2.4, Table 1), all started with the ignition of starting fuel consisting of approximately 1 kg of finely cut wood of the type selected for the respective experiment and a few g of birch-bark. The first load of approximately 10 kg of the fuel specific for the experiment was added after a quarter of an hour and in the birch combusting trials a second load was added between 2 and 2.5 hours. In the coniferous combustion (exp 2.2) the second load was added after 1 h 50 min and a third load was added after 2 h 50 min. The proportions were approximately  $\frac{2}{3}$  pine and  $\frac{1}{3}$  spruce. In exp 2.3, 1.4 kg of paper was included in the fuel and in exp 2.4, 1.1 kg of paper and 0.5 kg of plastic was included. The shredded plastic (see fuel descriptions above) was packed in 0.5–1 L empty beverage packages of laminated paper. The chlorine content of the fuel that included paper and plastic

was calculated to be approximately 0.2%. The total loads of fuels for experiments 2.1–2.4 were 15.5–20 kg.

Two parallel, duplicate series of organic compound samples were taken for each combustion cycle (each consisting of a full combustion and a smoldering combustion phase), by two probes mounted with a center-to-center distance of 20 mm in the dilution channel. The samplings all started simultaneously with the start fire. The first of duplicate samplings was taken under full combustion conditions realized by maintaining a good air supply through an open damper and removing heat from the boiler by circulating hot water through the external heat exchanging system. It was terminated about 1 h after the final load of wood was added. Altogether, the first samplings lasted around 3 h. The damper was then closed, thereby reducing the air supply and within half an hour the second duplicate samplings of the combustion cycle started on the remaining wood. These samplings under smoldering conditions lasted 2 h 30 min to 3 h 30 min (4 h 20 min for coniferous combustion). Changes in the relative levels of temperature and emissions of CO and CO<sub>2</sub> during the combustion of birch (exp 2.1) in the old boiler are illustrated in Figure 2 (and Figure S2 in the Supporting Information). The wood loadings are reflected in the rise of CO<sub>2</sub> levels, and the closing of the damper is seen as a sudden rise of CO level.

(3) *Combustion in the Modern Boiler.* The combustions in the modern boiler (exps 3.1–3.3, Table 1) all started with the ignition of starting fuel consisting of approximately 4 kg

of finely cut wood of the type selected for the respective experiment and a few g of birch bark. For all experiments, a load of 32–33 kg of wood was added after 30–40 min, and for experiment 3.1, a second load of 16 kg was added after 4 h 40 min. The boiler heat was continuously removed through the external heat exchanging system.

Parallel duplicate samplings of organic compounds in expt 3.1 started 1 h after the initial ignition, when the combustion reached stable conditions and lasted about 4 h 50 min under a full supply of air. The first samplings in experiments 3.2a and 3.3a started simultaneously with the start fire and lasted about 2 h 45 min. Simultaneously with the completion of the first samplings, the supply of air was reduced by switching off the suction fan and the second duplicate samplings (exps 3.2b and 3.3b) started half an hour later. These samplings under smoldering conditions lasted about 4 h. Changes in the relative levels of temperature and emissions of CO and CO<sub>2</sub> during the combustion of birch are illustrated in Figure S3 in the Supporting Information (exp 3.2).

(4) *Combustion in the Stove.* The combustions in the stove (exps 4.1 and 4.2, Table 1) started with the ignition of starting fuel consisting of approximately 3.5 kg of finely cut birch wood and a few g of birch bark. In exp. 4.1, in which a good air supply was maintained through an open damper (rotating fire grate), a first load of birch wood (2.8 kg) was added after 37 min, a second load (3.0 kg) was added after 1 h 13 min, and a third load (3.0 kg) was added after 2 h. In exp 4.2, in which a reduced air supply was maintained through a reduced opening in the damper, a first load of birch wood (2.7 kg) was added after 53 min and a second load (2.7 kg) was added after 2 h 10 min. Duplicate samples were taken in parallel, starting simultaneously with the start fire, lasting 3 h 20 min for exp 4.1 and 4 h 35 min for exp 4.2. Figure S4 in the Supporting Information shows the differences in flue gas temperature and CO<sub>2</sub> emissions between the two experiments.

**Logging and Sampling of Flue Gas and Ash.** The temperatures of the flue gas from pellet combustion were continuously logged by thermocouples. One was located in the furnace near the burner pot, and others were at various points along the flue (including one close to the sampling port for organic compounds). Levels of inorganic gases (CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>2</sub>, NO, N<sub>2</sub>O, HCl, NH<sub>3</sub>, and CH<sub>4</sub>) were continuously measured and logged by an FTIR instrument (Bomem 9100)

Combustion systems 2, 3, and 4 (see above) were all connected to a constant volume sampling system (CVS). The flue gas outlets were led into a 160 mm dilution channel that enabled a constant flow to be maintained through regulated dilution of the flue gas and facilitated isokinetic sampling of particles and flue gas in near-ambient temperatures. The system is described in detail by Boman et al. (9). Temperatures were continuously logged by thermocouples located at various points along the flue (including one close to the sampling port for organic compounds). Differential pressures were also logged, thus enabling the flow rate to be calculated. To enable calculation of dilution factors, both undiluted and diluted gases were measured. A Multi Gas Analyzer (Electra Control) was connected to a probe in the undiluted hot flue gases from the combustion appliances for continuously measuring and logging CO<sub>2</sub> and CO by means of infrared detectors and O<sub>2</sub> by means of an electrochemical cell. An FTIR instrument (Bomem 9100) was connected to the diluted flue gas for continuously measuring and logging CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>2</sub>, NO, N<sub>2</sub>O, HCl, NH<sub>3</sub>, and CH<sub>4</sub>.

Organic compounds in the flue gas were isokinetically sampled with a cooled probe and sampling train according to European standard method EN 1948 (8), except that the sampling duration (and hence volume) was adjusted to the

length of the combustion phases and the supply of fuel, and thus sometimes reduced. Temperatures in the sampling port varied between 120 and 180 °C in the pellet combustions. In wood combustion the sampling temperatures varied between 100 and 200 °C during the full combustion phases, whereas during the smoldering combustion phases they decreased toward 50 °C. Ash collected for analysis of organic compounds was separated from unburned solid residues.

PCDD/Fs, PCBs with dioxin like toxicity according to WHO (3), and HCB were analyzed by the Institute of Public Health, Ostrava, Czech Republic, according to European standard methods (10). Because of problems with analysis, all HCB was not analyzed.

**Calculations.** In the calculation of TEQ values, congeners below the detection limit were assigned half of the detection limit. Emission factors of organic pollutants were calculated by dividing the sampled mass by the dry weight of the fuel being combusted. In cases where samples were taken from consecutive combustion phases, the combusted mass of fuel for each phase was calculated by multiplying the total mass of the fuel by the fraction of total emitted carbon (as CO<sub>2</sub> and CO) emitted during each sampling, compensating for the dilution in the CVS by means of the different levels of CO<sub>2</sub> in the undiluted and diluted flue gases.

PCA (principal component analysis) was used to distinguish between profiles of dioxin homologues emitted in different experiments and to detect possible relations to the WHO-TEQ values of PCDD/F. PCA is a method for extracting information from large data matrices, especially when dealing with many variables. Every observation is represented by a point in a multidimensional space with as many coordinates as the number of variables. These points are then projected onto planes of lower dimensions, giving orthogonal principal components (PCs) describing most of the variation in the dataset, and are visualized in score-plots. The first PC, PC1, describes the largest contribution to the variation in the data and so on. The corresponding loading-plots show the variables that have the strongest influence on the distribution of the observations.

The dioxin homologues and the WHO-TEQ values used in the model were normalized by dividing the absolute values by  $\Sigma$ PCDD/F. The models were mean-centered but not further scaled.

## Results and Discussion

The combustion appliances used in these experiments can be regarded as typical of residential biofuel combustion systems in Sweden and the fuels combusted were, except for the straw pellets, probably the most commonly used. Straw pellets were included to assess the influence of high chlorine levels on dioxin emissions. The current extent of waste combustion in residential stoves and boilers is not known, but it is a convenience that has probably decreased due to increased environmental awareness and the introduction of recycling facilities. In the present experiments, the waste added amounted to around 10% of the total fuel, which was considered to be a realistic reflection of the amounts added in those cases where waste is burned in practice. The chlorine contents of the fuels with added plastics (exp 2.4) were within the range of contents in source-sorted combustible waste used in a previous study (8). The use of heat storage tanks was simulated in the wood boiler experiments with heat exchangers.

The values presented in Tables 2 and 3 are averages of duplicate samplings. Additional tables are found in the Supporting Information (Table S1, extended table on normalized emission of inorganic gases; Table S2, emission factors of inorganic gases; and Table S3, emission factors of emitted POPs in flue gas relative to the energy content).

**TABLE 2. Normalized Emissions (273.15 K, 101,325 kPa, 10% CO<sub>2</sub>) of Inorganic Gases and POPs during the Combustions, and Levels of POPs in the Ash<sup>a</sup>**

exp	Continuous measuring by FTIR, geometric means						POPs in flue gas, averages and standard deviations					POPs in ash			
	CO <sub>2</sub> vol %	CO g/m <sup>3</sup> <sub>n</sub>	NO mg/m <sup>3</sup> <sub>n</sub>	NO <sub>2</sub> mg/m <sup>3</sup> <sub>n</sub>	SO <sub>2</sub> mg/m <sup>3</sup> <sub>n</sub>	HCl mg/m <sup>3</sup> <sub>n</sub>	∑ PCDD/F ng/m <sup>3</sup> <sub>n</sub>	PCDD/F (WHO-TEQ) pg/m <sup>3</sup> <sub>n</sub>	PCB (WHO-TEQ) pg/m <sup>3</sup> <sub>n</sub>	HCB pg/m <sup>3</sup> <sub>n</sub>	∑ PCDD/F pg/g	PCDD/F (WHO-TEQ) pg/g	PCB (WHO-TEQ) pg/g	HCB ng/g	
1.1	2.8	0.8	33	2.8	0.6	5.0	200 114	3.2 × 10 <sup>3</sup> 1.8 × 10 <sup>3</sup>	120 15	200 132	4.2 × 10 <sup>3</sup>	83	4.9	1.0	
1.2	6.4	0.2	84	0.4	0.06	1.3	24 16	370 190	22 12	130 160	1.2 × 10 <sup>3</sup>	33	1.6	0.6	
1.3	4.9	4.7	270	40	190	24	44 4.4	1.1 × 10 <sup>3</sup> 70	71 2.3		9.2 × 10 <sup>3</sup>	71	2.2	n.a	
2.1a	5.1	6.1	99	12	0.1	3.9	14 6.6	240 130	24 10	14 4.0					
2.1b	0.6	23	10	10	1.1 × 10 <sup>3</sup>	0.3	5.4 3.5	110 41	21 12	31 5.5	<440	<8.2	0.3	n.a	
2.2a	4.8	6.1	60	20	0.1	7.5	7.3 0.5	140 6.1	16 0.8	12 2.7					
2.2b	0.5	31	1.6	90	200	0.4	<2.6	<51	4.1	34	1.7 × 10 <sup>3</sup>	35	0.9	n.a	
2.3a	3.5	6.7	110	17	0.1	1.2	5.7 0.3	99 1.8	13 0.8	9.0 0.2					
2.3b	0.5	21	2	35	950	0.4	11 8.9	120 81	16 5.4	n.a	<91	<2.9 <sup>b</sup>	<0.3 <sup>b</sup>	n.a	
2.4a	2.5	7.6	130	31	0.1	44	380 7.1	6.9 × 10 <sup>3</sup> 690	680 60	n.a					
2.4b	0.5	26	40	130	1.7 × 10 <sup>3</sup>	130	1.3 × 10 <sup>3</sup> 45	24 × 10 <sup>3</sup> 1.4 × 10 <sup>3</sup>	1.1 × 10 <sup>3</sup> 120	n.a	26 × 10 <sup>3</sup>	680	49	n.a	
3.1	11	0.6	140	4.7	0.5	0.2	2.7 0.1	44 5.9	4.0 0.2	n.a	<10 <sup>b</sup>	<0.9 <sup>b</sup>	<0.1 <sup>b</sup>	n.a	
3.2a	6.6	2.5	98	8.5	0.1	3.5	1.7 0.01	26 2.4	2.0 1.2	n.a					
3.2b	1.1	18	0.2	0.3	160	5.5	0.6 0.1	25 3.1	3.0 2.0	n.a	39 <sup>b</sup>	3.6 <sup>b</sup>	0.6	n.a	
3.3a	5.8	2.5	49	18	0.1	1.9	0.9 0.1	18 1.0	2.2 0.3	n.a					
3.3b	1.8	27	0.1	53	1.4	1.0	1.4 0.2	36 15	4.0 2.5	n.a	20 <sup>b</sup>	1.8 <sup>b</sup>	0.1 <sup>b</sup>	n.a	
4.1	3.5	3.4	65	15	0.8	1.1	2.4 0.2	48 13	4.8 2.6	n.a	20 <sup>b</sup>	1.5 <sup>b</sup>	0.1 <sup>b</sup>	n.a	
4.2	1.8	5.3	75	15	0.8	1.2	4.5 3.8	80 66	8.4 6.3	n.a	21 <sup>b</sup>	1.9 <sup>b</sup>	0.1 <sup>b</sup>	n.a	

<sup>a</sup> n.a = Not analyzed. <sup>b</sup> Values not significantly different from blank values.

The standard deviations of parallel samplings of POPs from full combustions were generally less than 10% (relative to the average), except in exps 2.1a and 4.2, for which they were ca. 50% and ca. 80%, respectively, possibly due to sampling error. The samplings from smoldering combustions, for which emission levels were generally lower, also generally had higher standard deviations (ca. 10–80%). The consecutive samplings from pellet combustions under similar, although not identical, conditions had standard deviations of ca. 50–60% for the wood pellets (exps 1.1 and 1.2) and ca. 10% for the straw pellets (exp 1.3).

**Emissions from Pellet Combustion.** The intermittent combustion of pellets yielded unexpectedly high levels of PCDD/Fs, PCBs, and HCB (Table 2). The levels of PCDD/Fs in terms of TEQ values greatly exceeded the regulated maximum of 100 pg I-TEQ/m<sup>3</sup><sub>n</sub> for the combustion of municipal waste. The levels in the ashes were also high, although not as high in comparison to other types of ashes, as the levels in the flue gas. During the recurrent breaks in the combustion, temperatures decreased and so did levels of CO<sub>2</sub>, NO<sub>2</sub>, and HCl, whereas levels of CO, CH<sub>4</sub>, and SO<sub>2</sub> strongly increased (Figure 1 and a more complete version in Figure S1). Chlorine levels in the wood pellets were low. The average HCl level was higher than in the continuous combustion, maybe due to contamination of the fuel, but HCl levels were not remarkably high compared to those found

in other biofuel combustions. Although dioxin levels in emissions are considered to some extent to be dependent on the chlorine levels of the fuel, it has usually proved difficult to establish correlations between these variables (11). This is because dioxin formation is a complex process that is influenced by many other factors, such as temperatures, oxygen levels, and the presence of particles and potential catalysts (11, 12). Stoichiometrically, very low chlorine levels are needed for producing significant levels of dioxins if the conditions are favorable. In the break and start up of combustion in each cycle the temperatures fall and rise, respectively, through the ranges that are considered to be favorable for dioxin production; 800–500 °C (gas-phase reactions) and 400–200 °C (solid-phase reactions) (12). The temperature within the pot was not registered, but in temperature loggings of other intermittent combustions of wood pellets in underfed pellet-burners, temperatures in the hottest region, just above the fuel bed, have varied between low values of 120–150 °C and high values of 1000–1100 °C (13). The experimental arrangements of the present trials, in which a steady flow of air through the boiler furnace was maintained by a fan, may have caused combustion (glowing) to be maintained at a higher level during the breaks of fuel feeding, thus increasing the release of products of incomplete combustion. In common residential arrangements with drafts

**TABLE 3. Emission Factors: Emitted POPs in Flue Gas Relative to the Mass of Combusted Fuel and POPs in Ash Relative to the Mass of Combusted Fuel (dry weight)<sup>a</sup>**

Emission factors (ng/kg), comb. phases					Emission factors (ng/kg), whole comb. cycle					Ash (pg/kg)		
exp	∑ PCDD/F	PCDD/F (WHO-TEQ)	PCB (WHO-TEQ)	HCB	exp	∑ PCDD/F	PCDD/F (WHO-TEQ)	PCB (WHO-TEQ)	HCB	∑ PCDD/F	PCDD/F (WHO-TEQ)	PCB (WHO-TEQ)
1.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.1	690	11	0.4	0.7	n.a	n.a	n.a
1.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.2	130	2.0	0.1	0.7	n.a	n.a	n.a
1.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	1.3	240	6.0	0.4	n.a	n.a	n.a	n.a
2.1a	850	15	1.5	0.9								
2.1b	120	2.5	0.5	0.7	2.1	670	12	1.3	0.8	3.3	61	2.1
2.2a	420	7.9	1.0	0.7								
2.2b	67	1.3	0.1	0.9	2.2	340	6.3	0.7	0.7	9.3	190	4.9
2.3a	360	6.2	0.8	0.6								
2.3b	210	2.4	0.3	n.a	2.3	310	5.0	0.7	n.a	2.1	66	3.6
2.4a	15 × 10 <sup>3</sup>	280	27	n.a								
2.4.b	17 × 10 <sup>3</sup>	310	14	n.a	2.4	15 × 10 <sup>3</sup>	290	23	n.a	460	12 × 10 <sup>3</sup>	870
3.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	3.1	170	2.8	0.2	n.a	24	2.3 × 10 <sup>3</sup>	310
3.2a	120	1.8	0.1	n.a								
3.2b	14	0.6	0.1	n.a	3.2	70	1.2	0.1	n.a	270	25 × 10 <sup>3</sup>	4.2 × 10 <sup>3</sup>
3.3a	71	1.4	0.2	n.a								
3.3b	37	0.9	0.1	n.a	3.3	52	1.2	0.1	n.a	43	3.8 × 10 <sup>3</sup>	230
4.1	<i>b</i>	<i>b</i>	<i>b</i>	n.a	4.1	170	3.5	0.4	n.a	601	45 × 10 <sup>3</sup>	3.6 × 10 <sup>3</sup>
4.2	<i>b</i>	<i>b</i>	<i>b</i>	n.a	4.2	330	5.9	0.6	n.a	n.a	n.a	n.a

<sup>a</sup> n.a = Not analyzed. <sup>b</sup> Emission samplings are not separated in combustion phases.

maintained through a stack, the combustion will usually die out at an earlier stage.

Much lower levels of emitted dioxins were found in both a recent test on intermittent pellet combustion (14) and the few other reported trials on pellet combustion (5, 15). The differences between the duplicates of the sampled POPs from intermittent combustions in the present work show a high degree of uncertainty. However, there are still significant and considerable differences between them and the continuous combustion, the causes of which should be further examined. Pellet burners are available with diverse designs, with differing mechanisms for feeding fuel, supplying air, ignition after combustion breaks, etc., leading to major differences in the variables affecting the formation of these compounds.

In addition, the continuous combustion of straw pellets yielded high levels of POPs. Combustion of this type of fuel raised some difficulties. No attempt was made to burn them intermittently, because they were unable to heat the boiler sufficiently and the ash in the burner pot sintered toward the end of the second duplicate experiment. Pellet burners for residential use are not usually adapted for pellets that generate ash levels as high as those of straw pellets (16, 17).

The emissions of POPs from the continuous combustion of wood pellets were considerably lower in the second sampling than the first. This is possibly due to improved combustion conditions when the internal surfaces of the furnace and flue are heated. Since the accidental breaks of combustion were distributed each on one of the two duplicates, the resulting effect is difficult to evaluate. They may however have contributed to a higher level of POPs than otherwise expected.

In contrast to the wood pellets combustion, the emission levels detected in the second straw combustion sampling series were somewhat higher than those of the first. This may have been due to impaired combustion conditions toward the end arising from the sintering process.

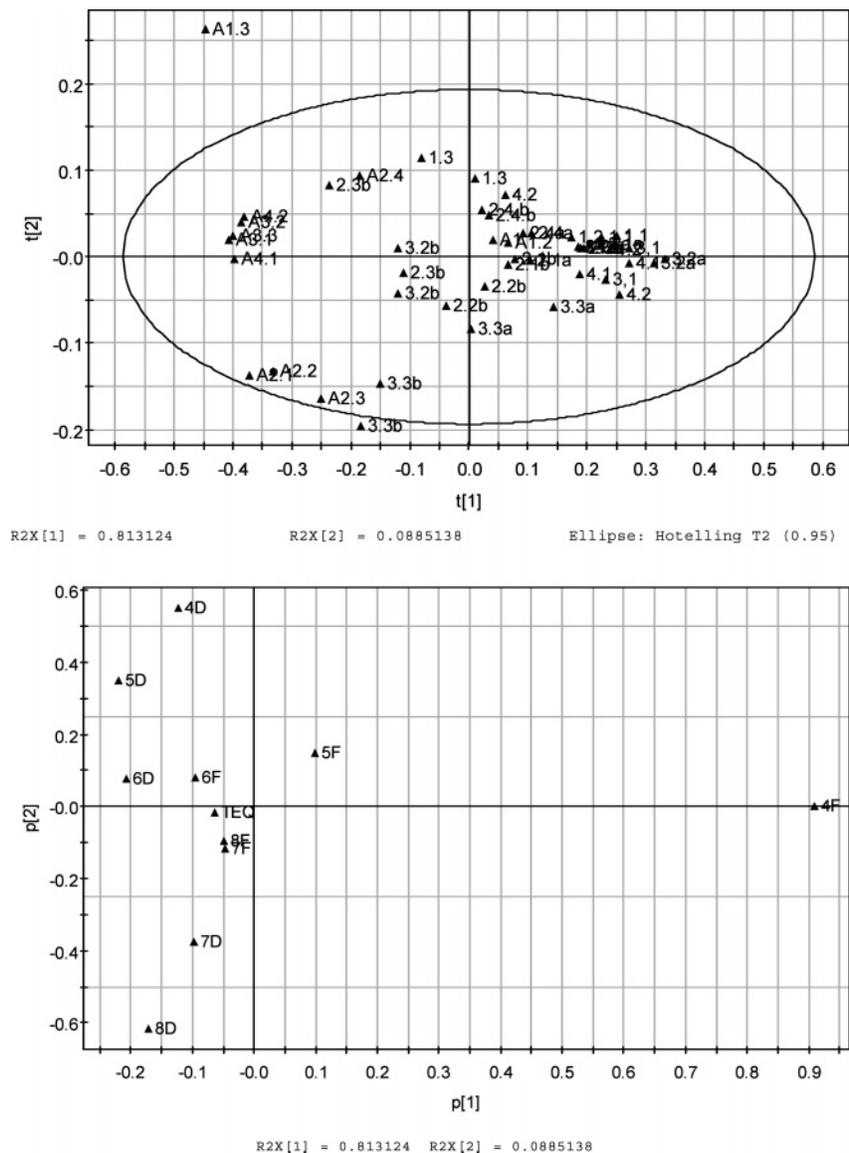
**Emissions from Wood Combustion.** There were considerable differences between the emissions from the old boiler and those from the modern eco-labeled boiler and the stove. The modern boiler gave particularly low emissions of PCDD/F and PCB, slightly lower than the stove; however both emitted less than 100 pg(WHO-TEQ)/m<sup>3</sup><sub>n</sub> (and also lower than the limit value 100 pg/m<sup>3</sup><sub>n</sub> expressed as 1-TEQ). The

same sequence (modern boiler < stove < old boiler) also applies to the emissions factors. Emissions of dioxins from the combustion of coniferous wood were roughly half as high as those from birch combustion, expressed as levels in normalized flue gas volumes (except in the smoldering combustion in the modern boiler). For the old boiler this also applies to the emission factors (Table 3), whereas the emission factors for the combustion of the different woods in the modern boiler were quite similar. Addition of paper waste in the combustion of the old boiler did not lead to any significantly elevated levels of PCDD/F and PCB, but addition of plastic increased the levels by a couple of orders of magnitude (Table 2). In the two combustion phases the levels of PCDD/F as toxic equivalents were approximately 70–240 times higher than the legislative limit for combustion of municipal waste. Since quite moderate levels of chlorine caused this effect, this indicates that the practice of burning these kinds of waste in residential boilers should be avoided.

No general trends in the differences between emission levels in combustion with full air supply and reduced air could be seen, neither with respect to flue gas volumes nor emission factors. Thus, the positive effect on unwanted emissions (as emission factors) attributed to combustion in boilers connected to heat storage tanks (7) could not be observed on the compounds sampled in the present experiments.

PCB and HCB levels generally correlated with the PCDD/F levels, but the proportions appeared to be lower in the combustions with the highest PCDD/F levels, such as the intermittent pellet combustion and plastic waste combustion, indicating that conditions in these combustions may have specifically favored dioxin formation rather than general POP formation. The PCBs generally contribute approximately 10% to the TEQ-values.

**Homologue Profiles.** The projection methods of PCA, illustrated by the score and loading plots, enabled a comprehensive overview of the variations of PCDD/F homologue profiles (levels relative to ∑PCDD/F) and their connections to the different origins: flue gas from full air and smoldering combustions and ashes. One intention was to collect more data on conditions under which formation of certain species occur, which may also give hints of how to avoid formation of the most toxic species.



**FIGURE 3.** Plot of PCDD/F homologue profiles and WHO-TEQ values of PCDD/F relative to  $\Sigma$ PCDD/F. Top panel: score plot. For the designations of the observations see the experimental plan (Table 1). A = Ash. Bottom panel: loading plot. 4F = tetrachlorodibenzofurans etc.

The plots in Figure 3 show distinctive, albeit somewhat overlapping, distributions. Ashes (designated with capital A) are distributed mostly to the far left in the score plot, although some are located in the center. Smoldering combustions (designated b) are distributed in the center-left, whereas the combustions under a full air supply are distributed mostly to the right, especially the full air birch-wood combustion in the modern boiler (exp 3.2). According to the loading plot, this distribution is mainly influenced by the level of tetrachlorodibenzofuran (TCDF, designated 4F in the figure). Although this distribution seems to reflect combustion efficiency (with ashes as residues after smoldering phases), it can be noted that the profiles from both the intermittent pellet combustions (exp 1.1) and the reduced air combustion in the wood stove (exp 4.2) are located among the full air combustions. The distribution along the second principal component is influenced by the difference in levels between lowly and highly chlorinated dioxins. The position of tetra- and penta-chlorinated dioxins (4D and 5D) at the top in the loading plot is mainly due to ash from the straw pellet combustion (A1.3). This observation may however be regarded as an outlier, and an exclusion from the model will instead move the pentachlorinated furan (5F) to the top while

leaving the rest of the model rather unaffected. At the bottom, where the hepta- and octa-chlorinated dioxins are located, there is a connection with the ashes from combustion of wood (A2.1, A2.2) and wood + paper (A2.3) in the old boiler, whereas the ash from the combustion of plastic in the same boiler (A2.4) has a relatively high location. In addition, the emissions from reduced air combustion of coniferous wood in the modern boiler (3.3b) are connected to the highly chlorinated dioxins.

The loading of WHO-TEQ-values of PCDD/F (relative to  $\Sigma$ PCDD/F) are located in the center of the plot, which means that it has insignificant influence of the model and shows little connection to the distribution of homologues.

Conclusively, the homologue profiles of PCDD/Fs show characteristic differences, especially in the relative levels of TCDF, between ashes and flue gas from combustions with different levels of air supply. However, the variation of profiles from different sources does not seem to correlate significantly to the relative amount of toxic congeners.

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### Supporting Information Available

Figures of relative temperatures and emissions, table of normalized emission of gases, and emissions factors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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