Emissions from co-combustion of demolition and construction wood and household waste fuel blends

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ABSTRACT

Four different types of fuel blends containing demolition and construction wood and household waste were combusted in a domestic pellet stove unit to study the effect of their composition on the emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), chlorobenzenes (PCBzs), chlorophenols (PCPhs) and polycyclic aromatic hydrocarbons (PAHs). Two woody materials, commercial stemwood (ST) and demolition and construction wood (DC) were selected because of the differences in their persistent organic pollutants (POPs), ash and metals content. For household waste, we used a municipal solid waste (MSW) and a refuse-derived fuel (RDF) from MSW with 5 – 20 wt.% and up to 5 wt.% food waste content respectively. No clear effect on the formation of pollutants was observed with different food waste content in the fuel blends tested. Combustion of ST-based fuels was very inefficient which led to high PAH emissions (32 ± 3.8 mg/kg_{fuel}). The use of DC clearly increased the total PCDD and PCDF emissions (71 ± 26 µg/kg_{fuel}) and had a clear effect on the formation of toxic congeners (210 ± 87 ng WHO₂₀₀₅-TEQ/kg_{fuel}). The high PCDD and PCDF emissions from DC-based fuels can be attributed to the presence of material contaminants such as small pieces of metals or plastics as well as timber treated with chromated copper arsenate preservatives and pentachlorophenol in the DC source.

KEYWORDS

PCDD; RDF; FOOD WASTE; POPs; DOMESTIC PELLEST STOVE

47 **HIGHLIGHTS**

- 48 - Food waste content between 1 to 4 wt.% has no influence on PAH, PCBz and PCPh formation
- 49 - Replacing MSW with RDF increases POPs emission
- 50 - The use of DC increases the formation of toxic PCDDs, PCDFs and PCBs
- 51 - Pre-treatment of DC is suggested as a way to reduce POPs emission

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INTRODUCTION

Fuels that contain only high-quality biomass, such as stemwood, are generally considered to have low environmental impact but can be very expensive. Moreover, high-quality wood conversion into bio-based chemicals and advanced materials, such as fibre or nanomaterial, is considered by the forestry and bioenergy sector to be a better use of biomass than energy production. The use of low quality and cheap materials, such as municipal solid waste (MSW) or waste wood (WW), in a fuel blend can reduce its price considerably whilst being a method of waste disposal. This is the reason why waste materials are becoming attractive resources for use in fuel production. However, modelling studies have suggested that the use of these materials may reduce the combustion efficiency [1] and lead to an increase in toxic air pollutants. Most of these pollutants are products of incomplete combustion: polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), chlorobenzenes (PCBzs), chlorophenols (PCPhs) and polycyclic aromatic hydrocarbons (PAHs). The main concern with PCDDs, PCDFs, PAHs and PCBs is their toxicity related to carcinogenic effects [2-4], and persistence in the environment. PCBzs and PCPhs are precursors of dioxin formation and PCBzs and PAHs are considered to be PCDD and PCDF indicators [5].

The use of mixed household waste, and in particular food waste, for the production of biofuels, such as biogas, using mechanical biological treatments has gained importance in the current energy and waste management sector. For almost any application, it is important to achieve an effective separation of food waste from the waste source. Separation can be carried out either in households or at waste management facilities using mechanical treatments such as shredding and screening. The outcome of this process is a residual fraction suitable for combustion. The heterogeneity of this fraction makes recycling difficult and co-combustion in waste-to-energy plants is, at present, the best alternative for its destruction [6]. However, some household waste components are a source of chlorine and metals which, together with a carbonaceous matrix, are key elements for the formation of PCDDs and PCDFs under specific conditions [7, 8].

There are many variables involved in the combustion process that influence its efficiency and emissions including combustion technology, air/oxygen supply, temperature, turbulence or presence of catalysts. The chemical composition of the fuel influences the combustion and stack gas concentrations [9]. According to the Stockholm Convention's guidelines [10], chimney deposits from

residential wood-burning and flue gas from MSW incinerations have similar PCDD and PCDF congener profiles. This could be due to the fact that contaminated wood, along with materials such as plastic, may also be combusted in these domestic stoves. Based on this idea, a domestic heating unit could be used in the early stages of a study to assess the organic emissions from burning different fuels, prior to be tested in full-scale facilities. In addition, a domestic pellet stove is very easy to operate, making it a convenient way to carry out combustion experiments.

There is an extensive body of literature concerning MSW and biomass combustion in domestic (< 50 kW) and small boilers (50 kW to 50 MW). Hedman et al. [11, 12] studied the PCDD and PCDF emissions from biofuel and MSW co-combustion in 150 kW and 600 kW biofuel boilers. Maasikmets et al. [13] assessed how changes in the composition of combustible waste over the past 15 years have affected the emissions from domestic heaters; using correlation analysis and modelling, Moran et al. [1] investigated the ratio between biomass and RDF in a fuel blend needed to balance efficiency, low emissions and reasonable price. However, these studies did not evaluate the use of waste wood and municipal solid waste fuel blends and their influence on the emissions of organic pollutants. Furthermore, none of these considered fuel blends with different food waste content. In a previous study [14], we evaluated how the combustion behaviour of fuel blends based on low cost and low-demand materials was affected by their composition. The materials tested were waste wood, MSW, RDF and a combustible fraction obtained after MSW was extruded in a high-pressure press to separate the organic fraction from the combustible fraction of the MSW source. For this study, the main component of the fuel blend, lignocellulosic material (stemwood or demolition and construction wood), was combined with MSW-based materials with varying food waste content. This study explored how the composition of these fuel blends was related to their performance in terms of emissions of organic pollutants. Based on these results, we can suggest the use of DC wood rather than using clean wood and food waste in the MSW to produce a fuel blend which has the lowest emissions possible. This study is a first assessment of the viability of using waste wood and MSW fuels in co-combustion facilities.

MATERIALS AND METHODS

Fuel preparation. Four different materials were used to produce four different fuel blends: commercial stemwood (ST), demolition and construction waste wood (DC), municipal solid waste (MSW) and refuse-derived fuel (RDF) from MSW. ST was selected as a reference wood material because of its low content of persistent organic pollutants (POPs), ash and metals. As was described in a previous study [15], DC is a material with elevated concentrations of chemical and material contaminants and, therefore, is very likely to produce pollutants when combusted. MSW is the household waste fraction remaining after the separate collection of household food waste. MSW comprises plastics, paper, cardboard, textiles but may also contain 5 – 20 wt.% food waste. Different mechanical treatments can be applied to MSW in order to improve its quality as a fuel by changing its composition. Our previous study showed that screening and shredding are efficient methods for removing chlorine from the MSW [14] by reducing the food waste content in the source. The combustible fraction obtained after MSW is shredded and screened is a RDF. It mainly comprises plastics and papers and may contain up to 5 wt.% food waste. DC, MSW and RDF are available in large quantities in Sweden.

The fuel blends were a mixture of 80% woody material (either ST or DC) and 20% household waste (either MSW or RDF) by weight, pelletized (5 mm diameter and 10 – 12 mm length) to improve homogeneity and feed properties. The final food waste content in the fuel blends was up to 4 wt.% for those blends containing MSW and up to 1 wt.% for those with RDF. Hereafter, fuel blends whose main component was ST or DC will be referred as ST fuel blends (ST:MSW and ST:RDF) and DC fuel blends (DC:MSW and DC:RDF). The term household waste refers to both MSW and RDF.

DC was collected at the Dåva facility, the combined heat and power (CHP) plant owned by Umeå Energi AB in Umeå (Sweden). Further details about the origin of the materials, sampling procedure, and fuel preparation can be read in a previous study [14]. Characterisation of the fuels was carried out in accordance with the standard methods described in the Supporting information (SI). Chlorine and metals were analysed in the fuel blends, whilst all the other parameters were analysed in the individual fuels and calculated for the blends. Chemical properties of the individual fuels are shown in Table S1 (SI). Chemical properties and metal content in the fuel blends are shown in Tables 1 and S2 (SI) respectively.

Table 1. Chemical properties and combustion-related parameters of the fuel blends

		ST	ST:MSW	ST:RDF	DC:MSW	DC:RDF				
Moisture Content	% _{ar} ¹	7.9	8.5	7.3	4.6	3.3				
LHV ²	MJ/kg _{ds} ³	19.0	18.8	19.8	18.6	19.7				
Volatile Matter	% _{ds}	87	84	85	82	83				
Ash	% _{ds}	1.7	5.9	5.1	7.5	6.7				
Fixed carbon	% _{ds}	11	10	9.8	10	10				
Cl	% _{ds}	<0.01	0.21	0.10	0.47	0.42				
C	% _{ds}	51	49	52	49	52				
H	% _{ds}	6.3	6.3	6.6	6.3	6.6				
N	% _{ds}	<0.10	<0.26	0.18	0.90	0.82				
O	% _{ds}	42	39	38	35	34				
S	% _{ds}	<0.01	<0.036	<0.024	0.076	0.064				
H/C		0.12	0.13	0.13	0.13	0.13				
Fe	mg/kg _{ds} ³	10	720	302	1770	1400				
Cu	mg/kg _{ds} ³	0.97	91	7.3	108	150				
Density	kg/m ³	2760	1163	1322	1086	1165				
Combustion Parameters										
Replicates		#1	#2	#1	#1	#2	#1	#2	#1	#2
Run order		2	3	4	6	7	8	9	10	11
Feed rate	kg/h	0.55	0.51	0.73	0.8	0.83	0.87	0.96	0.84	0.85
Flue gas sampled	Nm ³	1.3	0.99	1.2	1.2	1.1	1.1	1.2	1.3	1.1
CO ₂	%	1.0	0.87	0.99	1.0	1.1	1.8	1.6	1.4	1.5
CO	ppm	1080	983	879	754	907	219	325	114	416
NO	ppm	3.3	3.5	10	6.8	8.8	64	57	49	59
NOx	ppm	6.7	3.5	11	7.0	9.0	66	69	51	60
SO ₂	ppm	2.4	-	0.60	0.24	0.60	9.4	5.0	5.5	7.6
HCl	mg/Nm ³	0.17	0.32	6.3	6.1	6.7	56	31	22	26
Cl ₂	mg/Nm ³	0.90	4.1	0.53	0.70	0.80	2.7	1.1	2.6	1.5

ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste with 5 to 20 wt.% food waste content; RDF: refuse-derived fuel with up to 5 wt.% of food waste content. ¹ar: as received; ²LHV: low heating value; ³ds: dry sample

Domestic pellet stove description. The pellets described in the previous section were combusted in an EPE-01A (Haverland ®) domestic pellet stove. This stove is rated as an 11 kW heater that can be regulated automatically using room thermostats. There is a detailed schematic of the pellet stove unit described in the Supporting Information, Figure S1. From the integrated pellet storage tank (c.a. 15 kg capacity), a top feed burner supplies pellets continuously to the integrated burner. Feed rates can vary depending on the size and density of the pellets. The ignition of the first pellets is achieved using a resistive heating element. The air enters the stove through the air inlet; the combustion chamber has a number of holes in the bottom and on the sides that provide combustion air to the pellets. The exhaust gas fan pushes the exhaust gases from the combustion chamber into the air outlet pipe and then to the stack. A second fan enables the distribution of heated air into the room. Temperature is monitored in the ambient air, combustion chamber and in the stack.

The fuel feed rate and heated air flow rate can be manually or automatically controlled, in order to achieve the desired ambient temperature. Exhaust gas is released through the air outlet pipe to a stainless steel stack, as described in the manufacturer's specifications. Ash is manually removed from the ash container. For practical reasons, the unit was located outdoors for this experiment. During the combustion runs, the temperature set point was manually changed in order to be always two degrees higher than the ambient temperature. In this way, a continuous fuel feed was achieved and the stove was forced to work in continuous, rather than intermittent, mode.

Combustion runs. A total of four different fuel blends and one reference material (ST) were tested in a total of 9 combustion runs (Table 1). All the runs lasted approximately 90 minutes divided into two stages: (i) Start-up of the pellet stove and reaching steady operating conditions (~30 min); (ii) sampling stage (~60 min). We defined steady operating conditions as temperatures in the combustion chamber varying between 220 – 380 °C, corresponding to a continuous feed of pellets. Temperatures out of that range were related to the starting up or shutting down of the pellet stove. The combustion chamber temperature profile is shown in Figure S2 (SI). The amount of fuel used in each run during the sampling stage ranged from 770 g to 960 g except for ST (550 g). Each run was duplicated. A sampling blank was also carried out by allowing air to pass through the sampling train over 60 minutes without inserting the nozzle of the probe into the stack. The sample collected during run 5 was lost during clean-up and therefore there is no duplicate for ST:MSW.

Sampling and analysis procedure. Sampling of flue gases to determine the POP emissions (PAHs, PCBzs, PCPhs, PCBs, PCDDs and PCDFs) was carried out based on the U.S EPA method 23A [16]. A Model XC-500 Series Sampling System (Apex Instruments, Inc.) was used as the sampling train. The train was modified by adding two impingers containing acidic and alkaline absorbing solutions, respectively, in order to allow for an approximate determination of hydrogen halide and halogen emissions [16, 17]. The measurement point was selected in accordance with the criterion defined in the U.S. EPA Method 1A for small stacks, establishing that it should be located at least 8 stack diameters downstream and 10 diameters upstream from any flow disturbances [18]. The flow gas from the stove is irregular, so isokinetic sampling is very difficult to achieve. Instead of this, a constant flow of gas was sampled over the whole sampling stage. A nozzle was inserted into the stack and flue gas withdrawn and collected in the sampling train, which contained a glass fibre filter and a solid adsorbent (Amberlite® XAD-2 resin) (for a detailed schematic of the experimental set-up, see Figure S3, Supporting Information). Prior to sampling, the solid adsorbent was washed with methanol, dichloromethane and toluene and spiked with isotopically-labelled sampling standards just before the combustion runs. The volume of flue gas sampled ranged from 0.99 to 1.33 Nm³ in each run, equivalent to 16.4 ± 3.7 g of combusted fuel per run. The solid adsorbent and glass fibre filter were spiked with ¹³C-labelled internal standards (IS) before Soxhlet extraction with toluene for 24 hours [19]. The extract was concentrated using a rotary evaporator and divided into three aliquots. A 50% aliquot of the concentrated extract was used for PCDDs, PCDFs and PCBs determination and cleaned using a multilayer silica column followed by an alumina column. It was fractionated using an AX21-carbon column. One 25% aliquot was used for PAHs, PCBzs and PCPhs determination. PCPhs were separated from PAHs and PCBzs using liquid-liquid extraction with 0.5M NaOH, acetylated with acetic anhydride and then extracted with cyclopentene. The organic phase containing the PAHs and PCBzs was washed using a deactivated silica column and eluted with cyclopentene [19, 20]. The second 25% aliquot was saved as a backup. All the samples were concentrated and spiked with ¹³C-labelled recovery standard prior to analysis. PAHs, PCBzs, PCPhs PCBs, PCDDs and PCDFs were analysed with GC/HRMS using a Hewlett-Packard 5890 gas chromatograph (Agilent Technology, Santa Clara, CA, USA) coupled to an Autospec Ultima mass spectrometer (Waters Corporation, Milford, MA). A DB-5ms J&W fused silica capillary column (60m x 0.25mm i.d. x 0.25 µm film thickness) (Agilent Technology, Santa Clara, CA, USA) was used for GC separation. Quantification was carried out using

the isotopic dilution method. Data with recoveries out of the acceptable range (50 – 130%) established by the EN 1948:1-3 standard [21] were not included in the evaluation. CO, CO₂, NO, NO_x and SO₂ were measured with an on-line gas analyser (IMR 2800-P, IM Environmental Equipment Germany Gmb). One sampling blank and one laboratory blank had the same extraction, clean-up and analysis procedure applied as the samples.

Calculations. The emission factors (EF) were calculated by dividing the mass of the compound by the mass of fuel combusted (mass of compound per kg fuel). The amount of fuel combusted was determined by a carbon balance using the total carbon emitted, calculated as the sum of carbon in CO and CO₂ from the on-line measurements, the carbon content in the fuel (Table 1) and the volume of gas sampled (Nm³) in each run.

RESULTS AND DISCUSSION

A total of five different fuel materials (ST and four fuel blends) were tested in the domestic pellet stove (11 kW). The ST-based fuels **produced** three times higher CO concentrations than the DC-based fuel blends (Table 1), indicating less effective combustion when ST is the main component of the fuel blends. Although the **feed** rate was **set to be constant**, there were differences between different fuels which may be attributed to the differences **in their densities (Table 1)**: 8.5 – 9.2 g/min for stemwood pellets in comparison to **12 – 16** g/min for the fuel blends containing household waste. As Moran et al. [1] **stated** in a previous study, it is almost impossible to achieve steady **operating** conditions in small-scale **pellet heating units**, mainly due **to the batch feed** systems which can sometimes supply only one pellet at a time.

PAHs. The ST-based fuel blends had the highest PAH emissions (Figure 1). The total PAH emission factor for ST was 9.6 mg/kg_{fuel} and increased considerably when ST was combined with household waste, 32 ± 3.8 mg/kg_{fuel}. However, the combination of DC and household wastes generated lower PAH emissions, 6.4 ± 1.9 mg/kg_{fuel}, compared to the ST-based fuel blends. The elevated PAH emissions generated by the ST-based fuel blends were in agreement with the observed CO emissions (Table 1), indicating a less efficient combustion when ST is the main component. Out of the 16 EPA PAHs analysed (Table S3, SI), naphthalene represented the main PAH species in all runs, making up

approximately 50% of the total PAH emissions. ST-based fuels generated considerably higher emissions of naphthalene, $20 \pm 2.0 \text{ mg/kg}_{\text{fuel}}$, compared to ST and DC-based fuels, $4.1 \text{ mg/kg}_{\text{fuel}}$ and $3.7 \text{ mg/kg}_{\text{fuel}}$ respectively. Jenkins et al. [22] explained the high naphthalene concentrations from burning biomass as being due to contamination during the sampling and analysis procedure because of the breakdown of the XAD-2 adsorbent. However, our sampling and laboratory blank analysis showed low levels of naphthalene, $0.01 - 0.04 \text{ mg/kg}_{\text{fuel}}$. Many studies have also identified naphthalene as the main PAH emitted from the combustion of woody material [23-25]. Comparison of ST:MSW with ST:RDF and DC:MSW with DC:RDF showed small differences in the PAH emissions, indicating that the use of MSW or RDF did not have a strong effect on the total PAH emissions. Food waste is not a determining factor for the formation of these pollutants.

Figure1. Emission factors ($\text{mg/kg}_{\text{fuel}}$) of naphthalene and PAH with naphthalene excluded for the fuels tested. ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste with 5 – 20 wt.% food waste content; RDF: refuse-derived fuel with up to 5 wt.% food waste content.

PCBzs and PCPhs. PCBz emissions (Figure 2) slightly increased when household waste was added to the ST fuel, rising from 20 to $35 \mu\text{g/kg}_{\text{fuel}}$ when waste was added. When ST was replaced with DC, PCBz emissions increased more than three-fold, up to $142 - 291 \mu\text{g/kg}_{\text{fuel}}$. In addition, the average PCBz emission from the DC:RDF blend ($259 \mu\text{g/g}_{\text{fuel}}$) was higher than from the DC:MSW blend (167

$\mu\text{g}/\text{kg}_{\text{fuel}}$). The combination of household waste with DC led to higher PCBz emissions than household waste combined with ST. Thus, it appears DC greatly affects PCBz formation.

PCPh emissions increased considerably when ST ($20 \mu\text{g}/\text{kg}_{\text{fuel}}$) was combined with MSW and RDF in the fuel blends ($725 \mu\text{g}/\text{kg}_{\text{fuel}}$ and $363 \mu\text{g}/\text{kg}_{\text{fuel}}$ respectively). Replacement of ST by DC in the fuel blends produced an increase in PCPh emissions by 85% in the MSW blends and 233% in the RDF blends. The increases observed in PCPh emissions coincide with the increase of the total chlorine content in the feedstock. As with the PCBzs, the PCPh emissions increased when DC was combined with MSW and RDF, but with no clearly distinguishable differences between MSW and RDF, indicating that the difference in food waste content was not influential to the formation of these pollutants. For instance, the variation in PCPh emissions for the DC-based fuels was relatively limited ($1160 - 1478 \mu\text{g}/\text{kg}_{\text{fuel}}$). Comparing ST to the ST-based blends revealed that the type of household waste was not so influential. This, combined with the observed influence of the DC component on PCPh emissions, leads us to conclude that the wood component is a key factor for the formation of PCPhs in the studied fuel blends.

Figure 2. Total PCBz and PCPh emissions ($\mu\text{g}/\text{kg}_{\text{fuel}}$) for the fuel tested. ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste with 5 – 20 wt.% food waste content; RDF: refuse-derived fuel with up to 5 wt.% food waste content.

Increased levels of chlorine available in the fuel will increase the potential for formation of chlorinated compounds such as PCBzs and PCPhs. The chlorine content in DC was 0.27% but was 0.74% in MSW and 0.36% in RDF (Table S1, SI). The blend ratio 80:20 used when preparing the fuel blends meant that DC was the main source of chlorine in the blends. DC wood comprises considerable amounts of so-called material contaminants such as plastics, pieces of metal, glass or concrete [15]. PVC residues are, by far, the most common plastic in buildings (pipes, windows and wall and floor coverings) and therefore the most important source of organic chlorine in DC [26, 27]. Furthermore, separation of PVC from demolition waste, such as floor covering, for recycling is almost impossible. Timber treated with pentachlorophenol (PCP), extensively used as wood preservative over many years and banned in many countries, may also be an important contribution to the total PCPh emissions. The high PCP content in DC wood, 1696 $\mu\text{g}/\text{kg}_{\text{fuel}}$ (Table S5, Supporting Information), supports the idea that PCP-treated wood was present in the DC used for the production of the fuel blends. Emissions were $57 \pm 17 \mu\text{g}/\text{kg}_{\text{fuel}}$ from DC-based fuels and $3.0 \pm 3.8 \mu\text{g}/\text{kg}_{\text{fuel}}$ in ST-based fuels (Table S5, SI).

PCBs. Total PCB emissions ranged from 5.3 to 13.3 $\mu\text{g}/\text{kg}_{\text{fuel}}$ (Figure 3). ST produced the lowest PCB emissions, 7.2 $\mu\text{g}/\text{kg}_{\text{fuel}}$ on average, whilst DC-based fuel produced the highest, $10.6 \pm 2.4 \mu\text{g}/\text{kg}_{\text{fuel}}$. The TEQ emissions showed that, for the ST-based fuels (ST:MSW and ST:RDF), TEQ_{PCB} varied slightly: $0.28 \pm 0.02 \text{ ng WHO}_{2005}\text{-TEQ}/\text{kg}_{\text{fuel}}$. However, the use of DC in the fuel blends considerably increased the TEQ emissions to $9.6 \pm 4.5 \text{ ng WHO}_{2005}\text{-TEQ}/\text{kg}_{\text{fuel}}$. The amount of food waste in the household waste seemed to have a clear influence on the formation of PCBs. However, the choice of DC instead of ST considerably increased the PCB emissions.

Figure 3. Total emissions ($\mu\text{g}/\text{kg}_{\text{fuel}}$) and TEQ emissions ($\text{ng WHO}_{2005}\text{-TEQ}/\text{kg}_{\text{fuel}}$) for PCBs from the fuel blends. ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste with 5 – 20 wt.% food waste content; RDF: refuse-derived fuel with up to 5 wt.% food waste content

PCDD and PCDFs. The total PCDD and PCDF (mono to octa) emissions observed in this study varied from $2.2 \mu\text{g}/\text{kg}_{\text{fuel}}$ (ST) to $96 \mu\text{g}/\text{kg}_{\text{fuel}}$ (DC:RDF) as shown in Figure 4. The combination of ST and household waste increased the average total emissions from $4.6 \mu\text{g}/\text{kg}_{\text{fuel}}$ (ST) to $7.4 \pm 1.2 \mu\text{g}/\text{kg}_{\text{fuel}}$ (ST:MSW and ST:RDF). Both of the household waste materials, MSW and RDF, seemed to have a similar effect on the formation of PCDDs and PCDFs when combined with ST. However, the combination of DC with household waste materials was even more efficient at promoting formation of PCDD and PCDF, resulting in dramatic increases in emissions. The considerable difference in overall emission between ST-based and DC-based fuels can be explained by the presence of chlorine, copper and iron, which are well-known catalysts for promoting the formation of PCDDs and PCDFs [5, 28], or precursors such as PCP in the DC feedstock [26]. The concentrations of both chlorine and metal species were higher in the DC-based fuels than in the ST-based ones. DC-based fuels had, on average, $1590 \text{ mg}/\text{kg}$ of Fe and $129 \text{ mg}/\text{kg}$ of Cu; whilst ST-based fuels contained $511 \text{ mg}/\text{kg}$ of Fe and $49 \text{ mg}/\text{kg}$ of Cu (Table 1). The copper in DC may come from copper-based preservatives such as CCA (chromated copper arsenate) [15, 26, 29, 30]. Iron potentially originates from small metal scraps, but also from coating and paints [27]. In addition, the dramatic increase in the PCDD and PCDF

emissions from DC-based fuels could also be explained by the presence of chlorinated preservatives such as PCP in the DC feedstock. PCP is a well-known precursor of PCDD and PCDFs, but may also contain these compounds as impurities [26, 31].

When ST is combusted, formation of PCDDs is favoured over PCDFs. Total PCDD and PCDF emissions from DC:RDF were almost twice as high as those from DC:MSW (92 and 50 $\mu\text{g}/\text{kg}_{\text{fuel}}$ respectively), mainly due to emissions of PCDFs.

The TEQ emissions (Figure 4) showed that when ST was combined with household waste, the $\text{TEQ}_{\text{PCDD/F}}$ decreased considerably from 35.3 ng WHO₂₀₀₅-TEQ/ kg_{fuel} to 3.5 ± 1.5 ng WHO₂₀₀₅-TEQ/ kg_{fuel} . The use of DC instead of ST considerably increased the $\text{TEQ}_{\text{PCDD/F}}$ concentration, indicating that DC is a key factor in the formation of the toxic congeners. The same behaviour was observed for PCPhs, as described in the previous section. By contrast, the content of food waste in the MSW-based fuels did not clearly influence the $\text{TEQ}_{\text{PCDD/F}}$ concentration, only the total.

Note that replicates #1 and #2 of DC:MSW produced important differences in PCBs, PCDD and PCDF emissions. This could be related to the observed differences in SO₂, HCl and Cl₂ emissions (Table 1).

Figure 4. Total PCDD and PCDF emissions ($\mu\text{g}/\text{kg}_{\text{fuel}}$) and PCDD and PCDF TEQ emissions (ng WHO₂₀₀₅-TEQ/ kg_{fuel}) from the fuel blends. ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste with 5 – 20 wt.% food waste content; RDF: refuse-derived fuel with up to 5 wt.% food waste content

PCDD/Fs homologue profiles (Figure S5, SI) supported the previous findings that food waste content in household waste materials (MSW and RDF) used for the production of the fuel blends did not exhibit a clear influence on the total PCDD, PCDF and PCB emissions.

CONCLUSIONS

The variation of food waste content (1 to 4 wt.%) in the fuel blends **did not seem** to have a clear influence on the formation of **PAHs**, PCBzs, PCPhs and PCBs and toxic emissions of PCBs, PCDDs and PCDFs. However, differences in total emissions were observed when RDF (up to 5 wt.% food waste content) was used instead of MSW (up to 20 wt.% food waste content) in DC-based fuels. Based on the results obtained, there is not a clear benefit to using MSW or RDF in the fuel blends. Regarding the choice of the woody materials for the fuel blend, ST-based fuel blends exhibited lower combustion efficiency when compared to DC-based fuels, which led to high PAH emissions. The use of DC as a lignocellulosic component in the fuel blend is clearly related to the formation of toxic PCDDs, PCDFs and PCBs congeners. The increase in PCDD and PCDF emissions may be attributed to the presence of metal scraps, plastics, such as PVC, and timber treated with CCA and PCP preservatives in the DC source. It would be advisable to carry out a pre-treatment of the DC source in order to reduce the amount of those materials with a high potential for POPs formation, thus providing some environmental benefits.

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