EMISSION OF PCDD/Fs FROM COMBUSTION OF PINE NEEDLES AND PINE CONES IN A RESIDENTIAL STOVE

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Abstract
Combustion of pine needles and pine cones in a residential stove was performed to assess potential emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from house fires and forest fires. In order to know the level of pollutants in the samples themselves, analyses of PCDD/Fs in the materials used were made. The PCDD/F content found in pine needles was 0.66 ng I-TEQ/kg, while for pine cones a lower value of 0.33 ng I-TEQ/kg was obtained.

In the combustion experiment a high value of dioxins and furans was obtained, 196 ng I-TEQ/kg material burnt. The homologue profiles of PCDD/Fs showed differences between the materials and the flue gas emissions. The results obtained show that this kind of uncontrolled combustion is an important source of dioxins and furans.

Introduction
Dioxin emissions from stationary sources are stringently regulated and controlled. Inadvertent and uncontrolled combustion, including that from forest fires, house fires and backyard household waste combustion, has been identified as a large potential source of PCDD/Fs.[1]

In an extensive review of dioxin emissions from wood combustion, Lavric et al. reported that residential boilers and stoves emitted 0.2 – 5.1 ng I-TEQ/kg from uncontaminated wood.[1] In comparison with emissions of persistent organic pollutants (POPs) from municipal waste combustion, literature reports on emissions from small-scale biofuel combustion are scarce.

Pinus halepensis is one of the most important forest species in the Mediterranean region. The study of the *pinus halepensis* pine needles and pine cones combustion can provide information about the composition of the volatile products evolved during a forest fire.[2] On the other hand, pine needles are considered as very suitable passive indicators for monitoring of long-term troposphere concentrations of semivolatile compounds.[3]

The present work is mainly focused on analyzing the dioxins and furans emitted in a bad combustion of pine needles and pine cones.

Materials and Methods
Pinus halepensis pine needles and pine cones collected from the campus of the university of Alicante were employed in a combustion experiment. Table 1 shows some characteristics of the pine needles. Ultimate CHNS analysis was carried out in a Perkin-Elmer 2400 (Perkin-Elmer, U. K.). The moisture was determined by weight loss at 105 ºC for 12 h, obtaining a value of nearly 12 %. Ash content was obtained by calcination at 850 ºC.

Table 1. Characteristics of the pine needles.

C (wt %)	H (wt %)	S (wt %)	N (wt %)	O by difference (wt %)
50.4	6.5	0.01	0.8	37.9
Ash content (wt %)		4.5		

Table 2 shows the results obtained by X-ray fluorescence for pine needles and pine cones.

Table 2. Analysis by X-ray fluorescence of the materials employed.

	Pine needles (wt %)	Pine cones (wt %)		Pine needles (wt %)	Pine cones (wt %)
Ca	5.28	1.95	P	0.17	0.16
Si	0.95	0.66	Ti	0.05	-
K	0.77	0.64	Sr	0.04	0.01
Fe	0.39	0.24	Zn	0.01	0.06
Al	0.24	0.24	Br	0.01	0.02
Cl	0.22	0.17	Cu	-	0.03
S	0.22	0.21	Sr	-	0.01
Mg	0.18	0.06			

In order to study the emission of PCDD/Fs from combustion of these materials in a residential stove the scheme showed in Figure 1 was used. Isokinetic flue gas sampling was carried out using *EPA: Method 0023A – Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources* and *European Standard EN 1948-1 – Emisión de Fuentes Estacionarias. Determinación de la Concentración Másica de PCDD/PCDFs.*

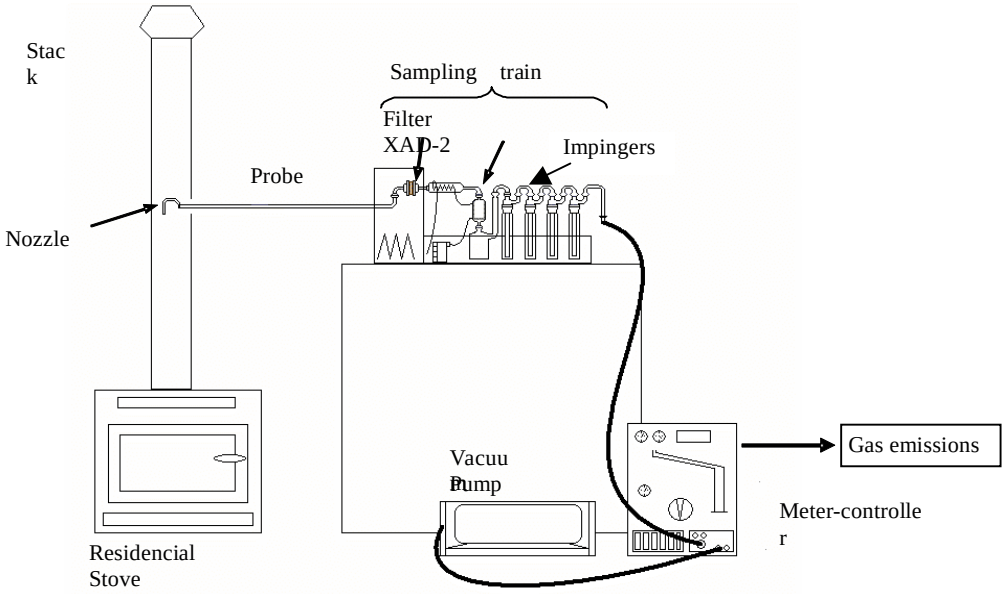

Figure 1. Diagram of isokinetic sampling method for PCDD/Fs in flue gas.

One experiment was carried out with 5704 g of pine needles and 808 g of pine cones, these materials were jointly combusted during 45 minutes and using the residential stove. 0.376 Nm^3 of gas were sampled and a value of 0.12 kg material burnt/ Nm^3 gas emitted was calculated. PCDD/F content in the flue gas was obtained analyzing the PCDD/Fs retained in the glass fiber filter and those adsorbed in the XAD-2 resin. The analysis of dioxins and furans was performed following US EPA method 1613.

Results and Discussion

Pine needles and pine cones were analyzed to determine PCDD/F content, in order to establish the level of pollutants in the samples themselves (Figures 2a and 2b), and 0.66 and 0.33 ng I-TEQ/kg were obtained, respectively. The yield of PCDD/Fs found in pine needles was 98 ng/kg, while for pine cones a lower value of 26 ng/kg was obtained.

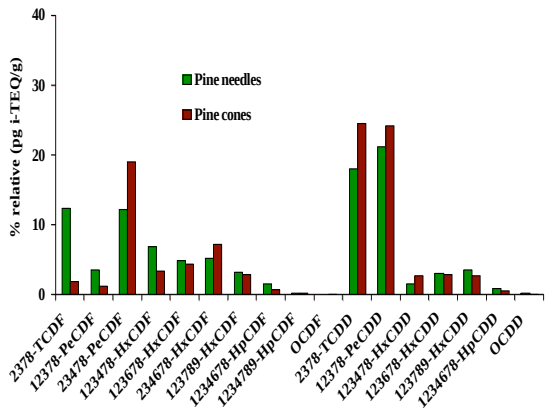

Figure 2a

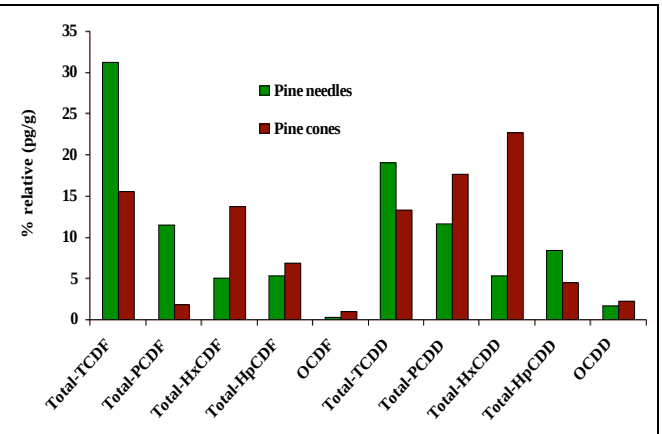

Figure 2b

Figure 2a. Congener specific 2,3,7,8-PCDD/F distribution of pine needles and pine cones. Figure 2b. PCDD/F homologue profile of the samples.

Pine needles and pine cones present a similar congener profile for the 2,3,7,8-PCDD, whereas for the toxic furans these materials present different profiles, being the main difference the high concentration of 2,3,7,8-TCDF in the pine needles. Similar congener profile that the one presented for the pine needles was obtained in an inmission study carried out in ambient air of the university of Alicante, so this proves that pine needles are probably suitable passive indicators for air monitoring.[4] PCDD/Fs obtained in the XAD-2 resin and the filter for the combustion experiment are shown in Table 3.

Table 3. Concentration of PCDD/Fs obtained in the combustion of pine needles and pine cones.

	ng I-TEQ/Nm^3	ng I-TEQ/Nm^3	ng I-TEQ/Nm^3	ng I-TEQ/kg solid	ng I-TEQ/kg solid	ng I-TEQ/kg solid
	XAD-2 resin	**Filter**	**XAD-2 + Filter**	**XAD-2 resin**	**Filter**	**XAD-2 + Filter**
2378-TCDF	4.172	0.066	4.238	35.114	0.559	35.673
12378-PeCDF	0.878	0.014	0.892	7.393	0.115	7.508
23478-PeCDF	9.441	0.184	9.625	79.468	1.552	81.020
123478-HxCDF	0.644	0.017	0.661	5.423	0.145	5.567
123678-HxCDF	0.615	0.016	0.632	5.180	0.137	5.317
234678-HxCDF	0.453	0.014	0.466	3.812	0.114	3.925
123789-HxCDF	0.169	0.007	0.176	1.424	0.054	1.478
1234678-HpCDF	0.045	0.003	0.052	0.419	0.021	0.441
1234789-HpCDF	0.009	0.0006	0.009	0.073	0.005	0.078
OCDF	0.0007	0.0001	0.0008	0.006	0.0009	0.006
2378-TCDD	4.453	0.087	4.539	37.480	0.730	38.210
12378-PeCDD	1.681	0.056	1.737	14.153	0.469	14.622
123478-HxCDD	0.071	0.006	0.076	0.594	0.049	0.642
123678-HxCDD	0.067	0.006	0.073	0.565	0.050	0.616
123789-HxCDD	0.084	0.005	0.089	0.705	0.044	0.749
1234678-HpCDD	0.010	0.0006	0.010	0.080	0.005	0.085
OCDD	0.0005	0.0001	0.0005	0.0040	0.0005	0.005
ng i-TEQ/Nm^3	22.80	0.48	23.28	191.89	4.05	195.94

These values are higher than those obtained by Schatowitz et al.[5] in the combustion of natural wood sticks (0.019

to 0.064 ng I-TEQ/Nm^3) in residential wood burners. However, in stack emissions from an industrial wood-burning furnace with 50 % excess air an average emission factor for PCDD/Fs of 17.1 ng I-TEQ/kg of wood burned was obtained.[6] Figures 3a and 3b show congener specific 2,3,7,8-PCDD/F distribution and PCDD/F homologue profile, respectively, obtained in the combustion of mixed pine needles and pine cones.

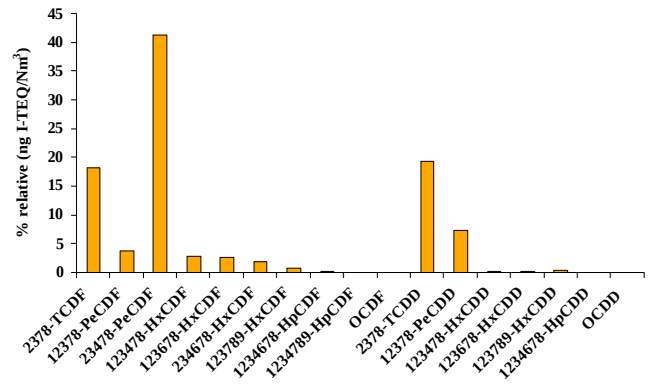

Figure 3a

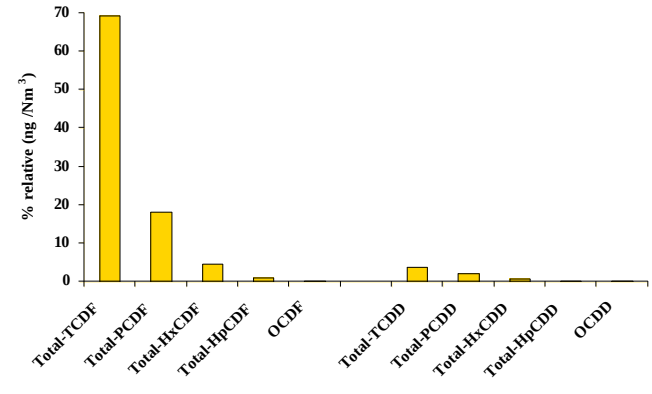

Figure 3b

Figure 3a. Congener specific 2,3,7,8-PCDD/F distribution obtained in the simultaneous combustion of the materials. Figure 3b. PCDD/F homologue profile of the combustion.

It can be concluded that the combustion of pine needles and pine cones produces a change in the homologue profile due to the high production of lower chlorinated homologues, increasing in this way the toxicity of the flue gas in comparison with the original materials.

Acknowledgements

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