

### ANALYSIS OF DIOXIN-LIKE COMPOUNDS IN VEGETATION AND SOIL SAMPLES BURNED IN CATALAN FOREST FIRES. COMPARISON WITH THE CORRESPONDENT UNBURNED MATERIAL.

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#### INTRODUCTION

Recently, many countries have undertaken inventories of sources of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) to better identify these sources and to quantify the emitted amounts of PCDD/F. The main source reported in the inventories is municipal solid waste incineration, followed by metal plants and clinical waste incineration [1-3]. However, another type of combustion appears as an important source in these lists (e.g. in the 4<sup>th</sup> place in US inventory [2]): natural (forest) fires. The emissions of PCDD/F from natural fires are estimated in a range from 0.4 g ITEQ/y to 308 g ITEQ/y [1-4]. However, the uncertainty of these numbers is very high because only a few data about the formation of PCDD/F in natural fires are reported in bibliography. In the early 1980s, some authors proposed forest fires as one of the main sources of formation of PCDD/F ("trace chemistries of fire" hypothesis) but they were not based on measurements in real fires [5-7]. However, Tashiro *et al.* [8] measured air, soil and ash samples from prescribed fires and the results obtained were not clear enough to conclude whether or not forest fires were a natural source of PCDD/F.

In this work, a preliminary study about the formation of PCDD/F in forest fires is described. Forest fires are open and uncontrolled processes and, therefore, the sampling (mainly, air sampling) is very difficult. Therefore, in our work, we have measured PCDD/F concentration in vegetation and soil samples burned in several real forest fires happened in Catalonia (Spain) in the summer of 1998. The levels obtained have been compared with those of the corresponding unburned material in order to evaluate the formation of PCDD/F during the fires. Since non-*ortho* and mono-*ortho* polychlorinated biphenyls (PCB) show the same type of toxicity as PCDD/F, they have also been analysed in the samples.

#### EXPERIMENTAL

*Samples:* The samples were collected from four Catalan places where fires occurred in July 1998: Garraf, Aguilar de Segarra, Mataro and Barcelona. The most important fire was located in Aguilar and it involved 26800 Ha of land (17500 Ha of forest). In each place, samples of burned material (vegetation and soils with ash) and unburned material (vegetation and soils from a place near to the fire but not affected) were collected. Wood and bark (the most superficial layer in the tree trunk) of pines and bushes constituted the vegetation samples. The soils were collected with all the

material present on them (in the unburned soils: pine needles, leaves of bushes and trees, etc.; in the burned ones: ash) to better represent the real matrix.

**Analytical method:** The samples were ground and sieved (2 mm) before extraction. Twenty grams of soil or vegetation, spiked with a mixture of  $^{13}\text{C}_{12}$  labelled 2,3,7,8-PCDD/F,  $^{13}\text{C}_{12}$  labelled non-*ortho* PCB (PCB 77, PCB 126 and PCB 169) and  $^{13}\text{C}_{12}$  labelled mono-*ortho* PCB (PCB 105, PCB 114, PCB 118, PCB 156, PCB 157, PCB 167 and PCB 189), were extracted in a Soxhlet apparatus with toluene for 24 h. The burned samples (both vegetation or soil with ash) were digested by sonication with HCl 1 N (T=45°C) for 1 h before Soxhlet extraction. The extracts were cleaned up in a sulphuric silica column and a multilayer silica column (from bottom to top: glass wool, silver nitrate-silica, silica, sodium hydroxide-silica, silica, sulphuric acid-silica, silica, sodium sulphate). Afterwards, a fractionation step of PCB and PCDD/F was carried out on a pyrenyl silica column as described elsewhere [9]. This separation allowed to obtain four fractions: (1) PCB tetra-, tri- and di-*ortho*, (2) PCB mono-*ortho*, (3) PCB non-*ortho*, and (4) PCDD/F. The second, third and fourth fractions were concentrated under nitrogen stream up to 15  $\mu\text{l}$  and the syringe standards ( $^{13}\text{C}_{12}$ -1234-TCDD and  $^{13}\text{C}_{12}$ -123789-HxCDD, for PCDD/F, and  $^{13}\text{C}_{12}$ -PCB 123 for PCB) were added. Finally, the samples were analysed by HRGC-HRMS in a CE 8000 gas chromatograph coupled to an AutoSpec-Ultima (Micromass, Manchester, UK) mass spectrometer, operating in EI ionisation (32 eV) at 10,000 resolving power. The analyses of PCDD/F were carried out in a DB-5 capillary column (60 m x 0.25 mm, 0.25  $\mu\text{m}$ ) and in a DB-DIOXIN (60 m x 0.25 mm, 0.25  $\mu\text{m}$ ) in order to separate those 2,3,7,8-congeners that were not resolved in DB-5 column. Monitored masses were those proposed by EPA 1613 method [10]. The analyses of non-*ortho* and mono-*ortho* PCB were performed in a DB-DIOXIN column. Monitored masses were  $[\text{M}]^+$  and  $[\text{M}+2]^+$  for tetra-PCB and  $[\text{M}+2]^+$  and  $[\text{M}+4]^+$  for penta-, hexa- and hepta-PCB. With each series of samples a complete procedure blank was performed to check the lack of contamination by solvents, lab material, etc.

## RESULTS AND DISCUSSION

The analytical method was applied to 14 samples of burned and unburned vegetation and soils. However, previously to these analyses the reproducibility and the limit of detection of the method were studied by analysing three times the unburned pine bark of Mataro in different series of samples. The results are shown in Table 1.

**Table 1.** Reproducibility and LOD of the analytical method

	Concentration (pg ITEQ/g d.w.)	Reproducibility (RSD, %)	LOD (pg ITEQ/g d.w.)
<b>PCDD/F</b>	0.65	7.0	0.050
<b>Non-<i>ortho</i> PCB</b>	0.42	12	0.006
<b>Mono-<i>ortho</i> PCB</b>	0.03	6.7	0.0001
<b>Total</b>	1.10	8.8	0.054

The variability was lower than 12 % for individual congeners (both PCDD/F and PCB) and the detection limits ranged from 0.02 pg/g d.w. to 0.11 pg/g d.w.

After having checked the good performance of the method, the analyses of the samples were carried out. The results are shown in Table 2 and Table 3.

**Table 2.** Concentration of dioxin-like compounds in vegetation samples (burned and unburned)

	Concentration (pg ITEQ/g d.w.)							
	Aguilar		Garraf		Mataro		Barcelona	
	UB	B	UB	B	UB	B1	B2	B
<b>PCDD/F</b>	0.54	0.10	0.45	0.61	0.65	0.22	0.32	0.66
<b>Non-ortho PCB</b>	0.59	0.07	n.a.	0.25	0.42	0.14	0.17	0.47
<b>Mono-ortho PCB</b>	0.04	0.004	n.a.	0.02	0.03	0.007	0.01	0.03
<b>Total</b>	1.17	0.17	0.45	0.87	1.06	0.36	0.50	1.17

UB: unburned; B: burned; n.a.: not analysed.

**Table 3.** Concentration of dioxin-like compounds in soil samples (burned and unburned)

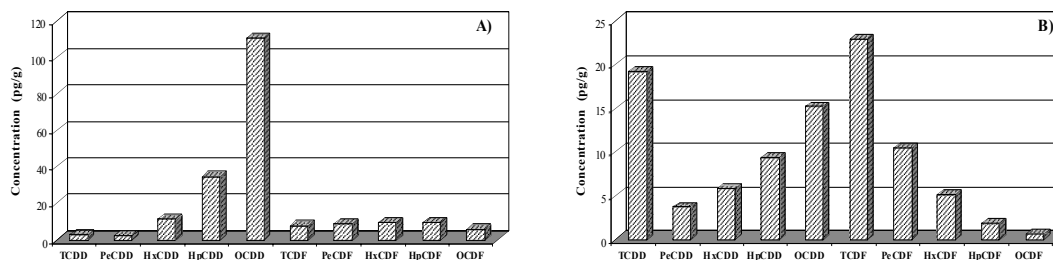
	Concentration (pg ITEQ/g d.w.)					
	Aguilar		Garraf		Mataro	
	UB	B	UB	B	UB	B
<b>PCDD/F</b>	0.95	1.22	1.41	1.67	0.53	3.49
<b>Non-ortho PCB</b>	n.a.	0.37	1.03	0.48	0.68	1.84
<b>Mono-ortho PCB</b>	n.a.	0.02	0.12	0.03	0.04	0.08
<b>Total</b>	0.95	1.61	2.55	2.18	1.25	5.41

UB: unburned; B: burned; n.a.: not analysed.

*Vegetation samples:* The three unburned samples showed very similar concentrations and the most important 2,3,7,8-substituted congeners were the same (OCDD 75, HpCDD 73, HpCDF 131 and OCDF 135). The concentrations in most burned samples were lower than in unburned ones, both in total concentration of PCDD/F and in ITEQ. This could be explained by the fact that the fire would have removed the most superficial layer of the sample (where PCDD/F are usually present by deposition). A change was also observed in the congener profile: TCDF 83 became the third 2,3,7,8-congener after OCDD 75 and HpCDD 73. This fact is in accordance to a proportional increase of TCDF and TCDD homologues in the homologue profile of burned samples. In addition, a proportional increase of TCDF 85 congener was observed in the pattern of all burned samples. The contribution of non-ortho PCB to ITEQ was important in all the samples (from 30% to 50%) while the contribution of mono-ortho PCB was very low (<5% in all the cases). The profiles of PCB congeners in unburned samples remained the same in the burned ones although the total contents were lower, in a similar trend to that showed for PCDD/F.

*Soil samples:* The levels of dioxin-like compounds, expressed in ITEQ, were higher than those obtained for vegetation samples. The contribution of non-ortho PCB to ITEQ was high (22% to 50%) but the contribution of mono-ortho PCB was very low (<5%). The comparison of the burned samples to the correspondent unburned ones revealed a slight increase in PCDD/F ITEQ. However, the total concentration of PCDD/F decreased in Aguilar and Garraf samples and increased in Mataro samples. This different trend between ITEQ and total concentration could be explained by the changes in the congener profile, since a proportional increase in the level of those congeners with lower chlorination degree (especially furans) and higher TEF, like TCDF 83, was detected in the burned samples. This is according to the changes observed in the homologue profile when burned and unburned soils are compared (Figure 1). This profile of burned material is

similar to that reported in bibliography for emission gases of wood combustion [11]. A characteristic homologue profile is not observed in the unburned samples.



**Figure 1.** Homologue profile of PCDD/F in (a) unburned soil and (b) burned soil from Garraf fire. As a summary, in vegetation samples, the concentration of PCDD/F, non-ortho and mono-ortho PCB (in pg/g d.w.) decreased in most burned samples respect of the unburned ones and, in soils, the concentration of these compounds also decreased in two burned samples of the three samples studied. If PCDD/F or dioxin-like PCB formation had happened during the fires, an increase of their concentration in the burned samples should have been detected. However, a proportional increase of TCDF and TCDD homologues have been observed in the burned samples (both vegetation and soils).

Although this work is a preliminary study, the results obtained from burned and unburned material from forest fires does not show a clear trend in concentration of dioxin-like compounds that allow to assure the formation of these compounds in the fires, but changes in profiles are observed.

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