

# PROFILES OF PCDD/F CONGENERS IN VARIOUS MATRICES DERIVED FROM CHARCOAL PRODUCTION FACILITIES WITH RUDIMENTARY KILNS

Siqueira LCG<sup>1</sup>, De Assunção JVA<sup>2</sup>, Tominaga MY<sup>1</sup>, Lemos MMG<sup>1</sup>

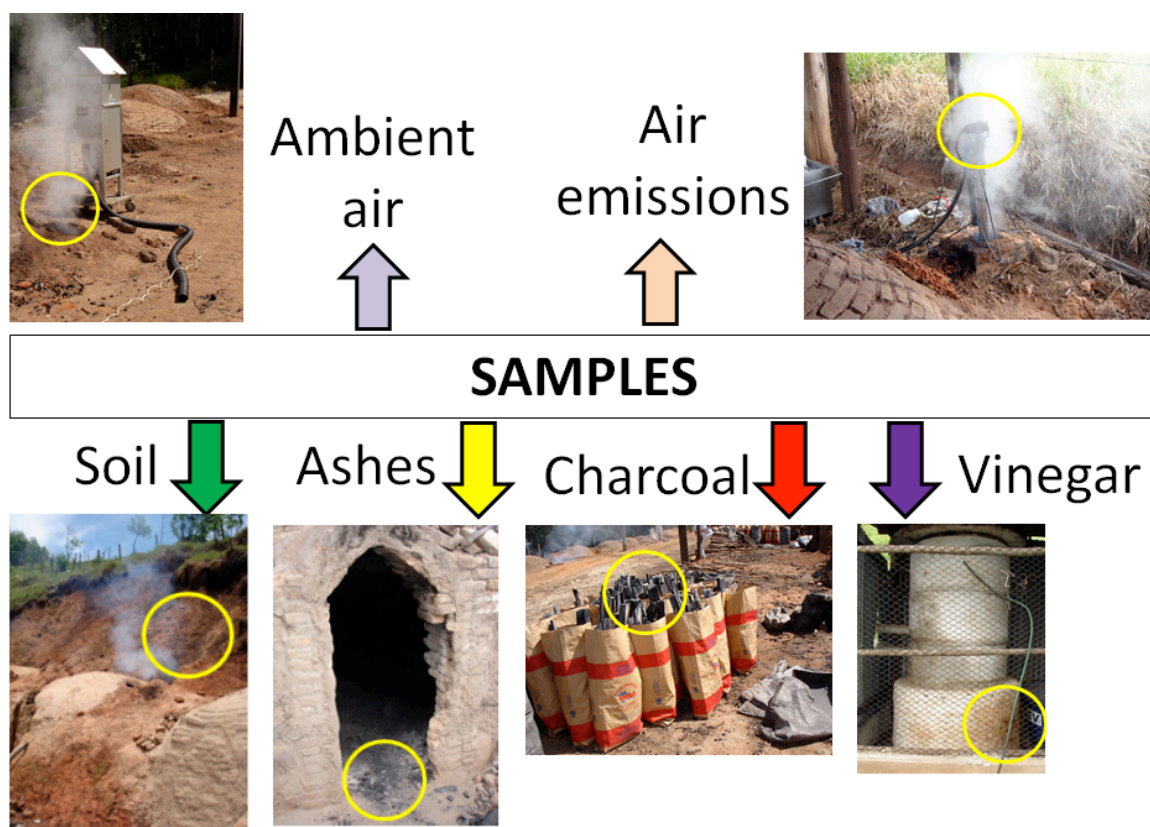
<sup>1</sup>CETESB – Environmental Company of the State of São Paulo - Brazil, Avenida Professor Frederico Hermann Junior, 345, São Paulo, Brazil. ZIP CODE 05459-900

<sup>2</sup>School of Public Health, University of São Paulo, Avenida Doutor Arnaldo, 715, São Paulo - Brazil. ZIP CODE 01246.904

## Introduction

Charcoal production in rudimentary kilns may cause local contamination of air and soil mainly due to the smoke released to the atmosphere. Usually emissions have no control in most of the plants. Carbonization of biomass (pyrolysis) generates toxic substances like PAHs and small amount of PCDD/Fs. In this study, PCDD/F congener data from samples of industrial ambient air, air emissions, charcoal, bottom ashes, soil affected by smoke plume, and vinegar (pyroligneous acid) from condensed smoke were analyzed with respect to congener profile and to discuss similarities and dissimilarities on these several matrices. Points of sample collection on a charcoal production plant that uses rudimentary kilns are shown in Figure 1.

Figure 1 – Origin of samples analyzed in this study



## Materials and Methods

Collection and analysis of PCDD/F in air samples, charcoal and ashes are described in details by De Assuncao et al<sup>1</sup>.

Samples of vinegar (pyroligneous acid) were taken from the reservoir that stored the resulting liquid from carbonization process. PCDD/Fs were analyzed according to method US EPA 8290 A<sup>2</sup>, as described in details by Siqueira et al<sup>3</sup>.

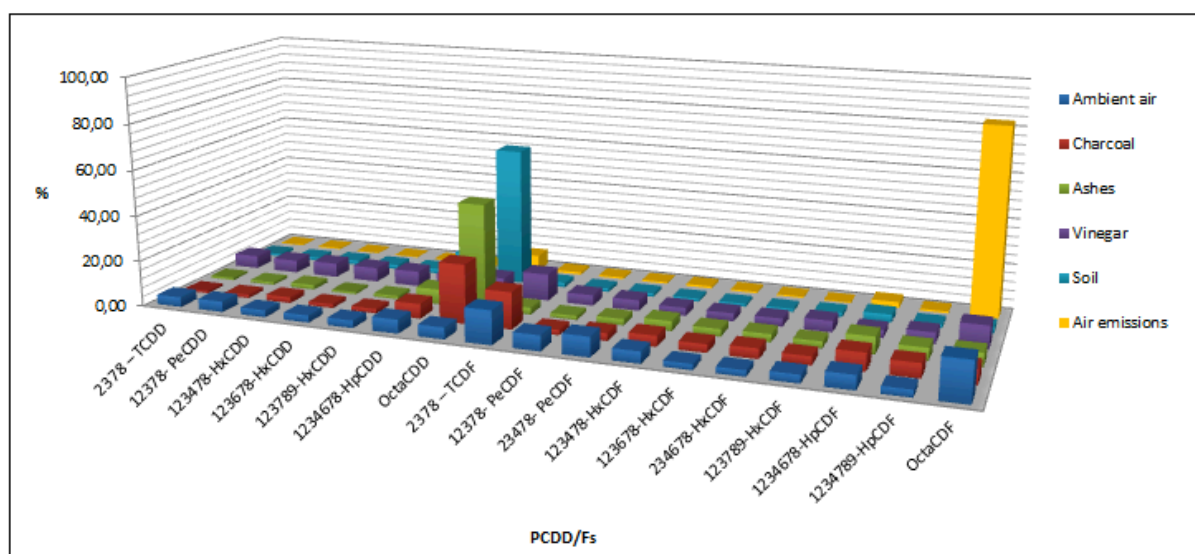
Composite soil samples were collected at a depth of 0 to 2 cm, in the vicinity of emission near the kiln. PCDD/F in soil samples were analyzed according to the method US EPA 8290A<sup>2</sup>. The samples were spiked with <sup>13</sup>C<sub>12</sub>-PCDD/F surrogate standards (Wellington Laboratories) and extracted for 24 hours in a Soxhlet extractor with toluene:acetone (9:1). The extracts were purified in an acid silica column (40% H<sub>2</sub>SO<sub>4</sub> and 10% AgNO<sub>3</sub>) and then in an Alumina column. The final extracts were concentrated to dryness and resuspended with 10μL of internal standards (<sup>13</sup>C<sub>12</sub>-1234-TCDD and <sup>13</sup>C<sub>12</sub>-123789-HxCDD). The final extracts were analyzed in a Agilent 6890 model high resolution gas chromatography coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS), operating with electron impact ionization of 35eV at a mass resolution of 10.000. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25 μm film thickness). The PCDD/F analysis in soil samples was performed by an ISO 17025 accredited laboratory at CETESB in São Paulo, Brazil.

Air emission samples were withdrawn from the gas stream by a sampling probe, and collected on a glass fiber filter, followed by a packed column of adsorbent material (XAD-2), according to US EPA Method 23<sup>5</sup>, with Sampling Train assembled by AIRSERVICES and certified by CETESB. The sample was performed in carbonization phase of white smoke plume. Average sampling flowrate was 21.73 Nm<sup>3</sup>.h<sup>-1</sup>. The sample could not be separated into a particle and vapor fraction. The XAD-2 resin and filter samples were extracted and analyzed separately according to the method US EPA 8290A<sup>3</sup>. The samples were spiked with <sup>13</sup>C<sub>12</sub>-PCDD/F surrogate standards (Wellington Laboratories) and extracted for 16 hours in a Soxhlet extractor with toluene. The extracts were purified an acid silica column (60% H<sub>2</sub>SO<sub>4</sub> and 40% silica gel) and a Florisil column. The final extracts were concentrated to dryness and resuspended with 10μl of internal standards (<sup>13</sup>C<sub>12</sub>-1, 2,3,4-TCDD and <sup>13</sup>C<sub>12</sub>-1,2,3,7,8,9-HxCDD). The final extracts were analyzed in a GC Agilent 6890 coupled to a Micromass high resolution mass spectrometer (HRGC/HRMS), operating with electron impact ionization of 35eV at a mass resolution of 10.000. The GC was fitted with a DB5-MS capillary column (60m x 0.25 mm id x 0.25 μm film thickness). The PCDD/F analysis in air samples was performed by an ISO 17025 accredited laboratory (CRONOLAB, Rio de Janeiro, Brazil).

## Results and discussion

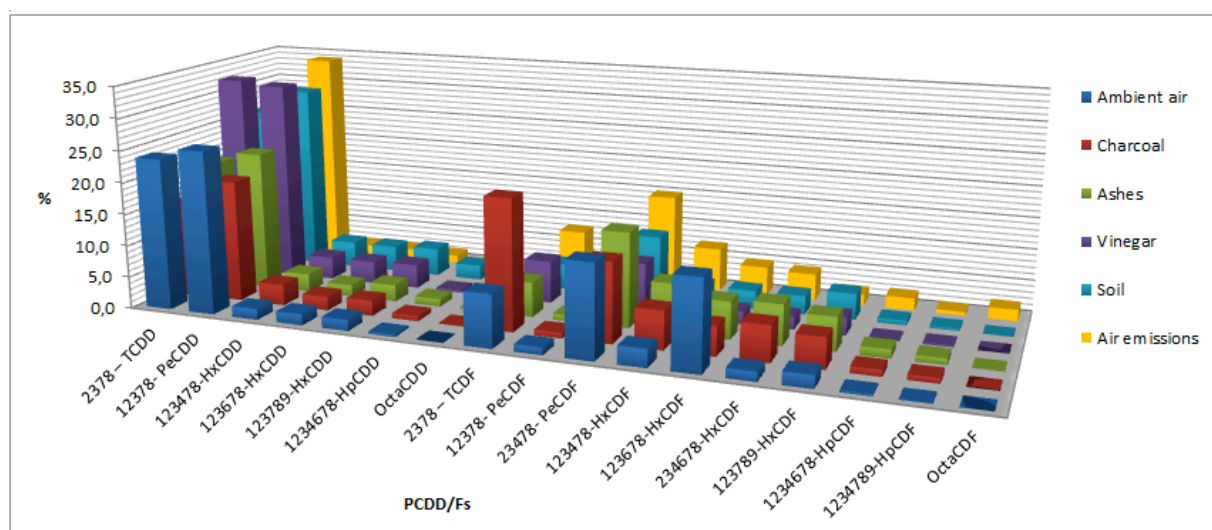
Profiles of PCDD/F congeners distribution in the matrices considered for the original mass concentration are shown in Figure 2. In ambient air and in air emissions the predominance was from Octa-CDF. In charcoal, ashes and soil the predominance was from OctaCDD congener and in vinegar the predominance was from 2378-TCDF congener.

**Figure 2 – PCDD/F congener contribution (%) by type of matrix, for the original mass concentration**



Profiles of PCDD/F congeners of all these matrices, in Toxic Equivalency Toxicity (TEQ) are shown in Figure 3. In ambient air, soil, ashes and air emissions 12378-PeCDD congener predominated, and it was followed by 2378-TCDD congener and 23478-PeCDF congener. The result is an indication that all these matrices have the same influence of the carbonization process in order to generate similar PCDD/Fs congener profile. In vinegar predominated 2378-TCDD congener, followed by 12378-PeCDD congener and 23478-PeCDF congener. In charcoal 2378-TCDF congener was predominant and it was followed by 12378-PeCDD and 2378-TCDD congeners. In this case, it seems that the influence on the formation of PCDD/Fs congeners is more closely linked to burned wood emission.

**Figure 3 – PCDD/F congener contribution (%) by type of matrix, in TEQ.**



Results of PCDD/F concentration in the samples of all matrices considered are presented in Table 1.

The results for charcoal, ashes and in vinegar indicated very low PCDD/F concentrations, close to the Limit of Detection. Results for ambient air ( $137 \text{ fg-TEQ/m}^3$ ), showed values close to ambient air concentration in urban areas like central area of Sao Paulo city<sup>1</sup>. PCDD/F concentrations in the soil samples were very low and there is no indication that they can contribute significantly to soil contamination. PCDD/F concentrations in emissions from kiln are also low if compared with the national emission standard set by CONAMA<sup>4</sup> for incineration of hazardous waste ( $0,50 \text{ ng TEQ.Nm}^{-3}$ ) and by CETESB<sup>6</sup> for incineration of medical waste ( $0.14 \text{ ng TEQ.Nm}^{-3}$ ).

PCDD congener concentrations were higher than PCDF congener concentration for all samples. Among congeners 12378-PeCDD was predominant in ambient air, ashes, soil and air emissions followed by 2378-TCDD, except for vinegar, where 2378-TCDD and 12378-PeCDD presented almost the same concentration and for charcoal that predominated 2376 TCDF followed by 12378-PeCDD. Besides that, the concentrations resulted very low in all matrices.

**Table 1 Results for PCDD/F concentration in TEQ, in the samples of ambient air, charcoal, ashes, vinegar, soil and air emissions.**

PCDD/F	Ambient air	Charcoal	Ashes	Vinegar	Soil	Air emissions
	(pgTEQ.m <sup>-3</sup> )	(pgTEQ.g <sup>-1</sup> )	(pgTEQ.g <sup>-1</sup> )	(pg-TEQ.ml <sup>-1</sup> )	(pg-TEQ.g <sup>-1</sup> )	(pgTEQ.m <sup>-3</sup> )
2378 – TCDD	0.03762	0.022	0.022	0.0053	0.32	1.02
12378- PeCDD	0.04049	0.028	0.024	0.0052	0.37	2.25
123478-HxCDD	0.00269	0.0048	0.0031	0.00058	0.0515	0.105
123678-HxCDD	0.00279	0.0032	0.002	0.00058	0.0515	0.105
123789-HxCDD	0.00279	0.0035	0.0029	0.00062	0.0555	0.085
1234678-HpCDD	0.00058	0.0012	0.0013	0.000061	0.0292	0.03
OctaCDD	0.00001	0.000144	0.000273	0.00000219	0.004725	0.01
2378 – TCDF	0.01308	0.030	0.006	0.0011	0.051	0.5
12378- PeCDF	0.00183	0.00126	0.00105	0.000129	0.0126	0.105
23478- PeCDF	0.02297	0.0183	0.0162	0.00129	0.126	0.98
123478-HxCDF	0.00452	0.0088	0.0084	0.00033	0.0365	0.455
123678-HxCDF	0.0221	0.0067	0.0064	0.00032	0.036	0.305
234678-HxCDF	0.00231	0.0082	0.0069	0.00033	0.0365	0.28
123789-HxCDF	0.00317	0.007	0.0058	0.00046	0.051	0.12
1234678-HpCDF	0.00048	0.00146	0.00148	0.000031	0.0091	0.13
1234789-HpCDF	0.00019	0.00116	0.00105	0.000045	0.0046	0.04
OctaCDF	0.00005	0.0000372	0.0000345	0.00000095	0.0002115	0.12
Total PCDD/PCDF	0.14	0.15	0.11	0.017	1.25	6.64

#### Acknowledgements:

We want to express our gratitude to people and organizations who contributed to this study, and to CETESB, especially Office of Atibaia, and to the charcoal production industry that allowed us to work there.

#### References:

1. De Assuncao J.V., Siqueira L.C.G., Tominaga M.Y., Meneses L.V.T., Soares N.S., Almeida S.A.C. (2013). *Organ Comp* 75: 849-852
2. [US.EPA] United States Environmental Protection Agency, (2007). Method 8290A. Washington, DC., USA
3. Siqueira L.C.G., De Assunção J.V., Tominaga M.Y., Meneses L.V.T., Soares N.S., Almeida S.A.C. (2014). In *SHEWC 2014* (ISSN 2317-3173). Vol. 14, 222-227.
4. [CONAMA] Conselho Nacional de Meio Ambiente, (2002). Resolução 316. Brasil.
5. [US.EPA] United States Environmental Protection Agency, (1991). Method 23. Washington, DC., USA
6. [CETESB]. Companhia Ambiental do Estado de São Paulo, (1997). Norma Técnica E-15011. São Paulo, Brasil.