# PCDD/F EMISSION FACTOR FOR CHARCOAL PRODUCTION IN RUDIMENTARY KILNS

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## Introduction

No data are available in the literature for releases of dioxins and furans from charcoal production. UNEP's Toolkit[1] suggests the use of the emission factor of Class 1 of coke production, to estimate these emissions, which may be overestimated for charcoal production in rudimentary kilns, since raw material and the production process differ. The aim of this study was the determination of preliminary PCDD/F emission factors for this type of kilns largely used in developing countries. For this study a modified stack sampling method based on US EPA Method 23[2] was applied since the rudimentary kilns do not have stack and the draft is natural. Raw material used was eucalypitus with bark. Description of the production process and statistics about charcoal production in Brazil and around the World is given by De Assuncao et al[3].

## Materials and methods

Samples were withdrawn from the gas stream by a sampling probe, and collected on a glass fiber filter, followed by a packed column of adsorbent material (XAD2), according to US EPA Method 23[2], with Sampling Train assembled by Airservices and certified by CETESB (CIPA CP-10). (Figure 1). The sample was performed in carbonization phase of white smoke. Average sampling flowrate was 21.73 $Nm^3.h^{-1}$. The sample cannot be separated into a particle vapor fraction. PCDDs and PCDFs were extracted from the sample, and then separated by high resolution gas chromatography, and measured by high resolution mass spectrometry. The XAD2 resin and filter samples were extracted and analysed separately according to the method US EPA 8290A[4].

**Figure 1** – Sampling system for PCDD/Fs

The samples were spiked with $^{13}C_{12}$-PCDD/F internal standards (Wellington Laboratories) and extracted for 16 hours in a Soxhlet extractor with toluene. The extracts were purified an acid silica column (60% $H_2SO_4$ and 40% silica gel) and a Florisil column. The final extracts were concentrated to dryness and ressuspended with 10µl of internal standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD). The final extracts were analyzed in a GC Agilent 6890 with high resolution mass spectrometer (HRGC/HRMS) of Micromass, 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 Referencia em Analises Quimicas e Ambientais Ltda, in Rio de Janeiro, Brazil). A field blank was used and its results were subtracted from results in samples.

## Results and discussion

Results are showed in Table 1. PCDDs presented total concentration slightly higher than PCDFs in both samples, showing that dioxin emissions predominate during carbonization of biomass in rudimentary kilns. Although the concentrations found can be considered low, they are not negligible.

**Table 1 – Results of of PCDD/F sampling in emissions from charcoal production in rudimentary kilns**

| Congners | Sample | | | |
|---|---|---|---|---|
| | Sample 1 | | Sample 2 | |
| | Concentration ($ngTEQ.Nm^{-3}$) ($^{1,2,3,4}$) | Emission Rate ($\mu gTEQ.h^{-1}$) | Concentration ($ngTEQ.Nm^{-3}$) ($^{1,2,3,4}$) | Emission Rate ($\mu gTEQ.h^{-1}$) |
| **DIOXINS** | | | | |
| 2,3,7,8 –TCDD | 0.00144 | 0.00003 | 0.00060 | 0.00001 |
| 1,2,3,7,8 – PeCDD | 0.00275 | 0.00006 | 0.00175 | 0.00004 |
| 1,2,3,4,7,8 – HxCDD | 0.00010 | 0.000002 | **0.00011** | **0.000002** |
| 1,2,3,6,7,8 – HxCDD | 0.00014 | 0.000003 | 0.00007 | 0.000001 |
| 1,2,3,7,8,9 – HxCDD | 0.00009 | 0.000002 | **0.00008** | **0.000002** |
| 1,2,3,4,6,7,8 - HpCDD | 0.00003 | 0.000001 | 0.00003 | 0.000001 |
| OCDD | **0.00001** | **0.0000001** | **0.00001** | **0.0000001** |
| Total Dioxins | 0.00456 | 0.0000981 | 0.00265 | 0.0000561 |
| **FURANS** | | | | |
| 2,3,7,8–TCDF | 0.00068 | 0.000015 | 0.00032 | 0.00001 |
| 1,2,3,7,8–PeCDF | 0.00014 | 0.000003 | 0.00007 | 0.000001 |
| 2,3,4,7,8–PeCDF | 0.00134 | 0.000030 | 0.00062 | 0.00001 |
| 1,2,3,4,7,8–HxCDF | 0.00051 | 0.000011 | 0.00040 | 0.00001 |
| 1,2,3,6,7,8–HxCDF | 0.00035 | 0.000008 | 0.00026 | 0.00001 |
| 1,2,3,7,8,9–HxCDF | 0.00031 | 0.000007 | 0.00025 | 0.00001 |
| 2,3,4,6,7,8–HxCDF | 0.00012 | 0.000003 | 0.00012 | 0.000003 |
| 1,2,3,4,6,7,8–HpCDF | 0.00006 | 0.000001 | 0.00020 | 0.000004 |
| 1,2,3,4,7,8,9-HpCDF | 0.00002 | 0.0000004 | 0.00006 | 0.000001 |
| OCDF | **0.00001** | **0.0000001** | 0.00023 | 0.000005 |
| Total Furans | 0.00354 | 0.0000785 | 0.00253 | 0.000064 |
| **SUM OF 17 DIOXINS AND FURANS 2,3,7,8-SUBSTITUTED** | | | | |
| Total PCDD/Fs | 0.00810 | 0.00018 | 0.00518 | 0.00012 |

(1) Expressed in Equivalent Toxicity to 2,3,7,8 Tetrachlorodibenzo p-Dioxin (TEQ-WHO 2005)
(2) Calculated based on the Limit of Detection (LOD)
(3) Results above LOD are highlighted in bold
(4) Normal conditions: 0°C, 1 atm

Among congeners of dioxins the predominance was of 1,2,3,7,8 – PeCDD followed by the 2,3,7,8 –TCDD, the most toxic one, in both samples. Among congeners of furans the predominance was of 2,3,4,7,8–PeCDF in both samples, followed by 2,3,7,8–TCDF in sample 1 and by the 1,2,3,4,7,8–HxCDF, in sample 2.

Figure 2 – PCDD Congeners distribution in emissions from charcoal production in rudimentary kilns

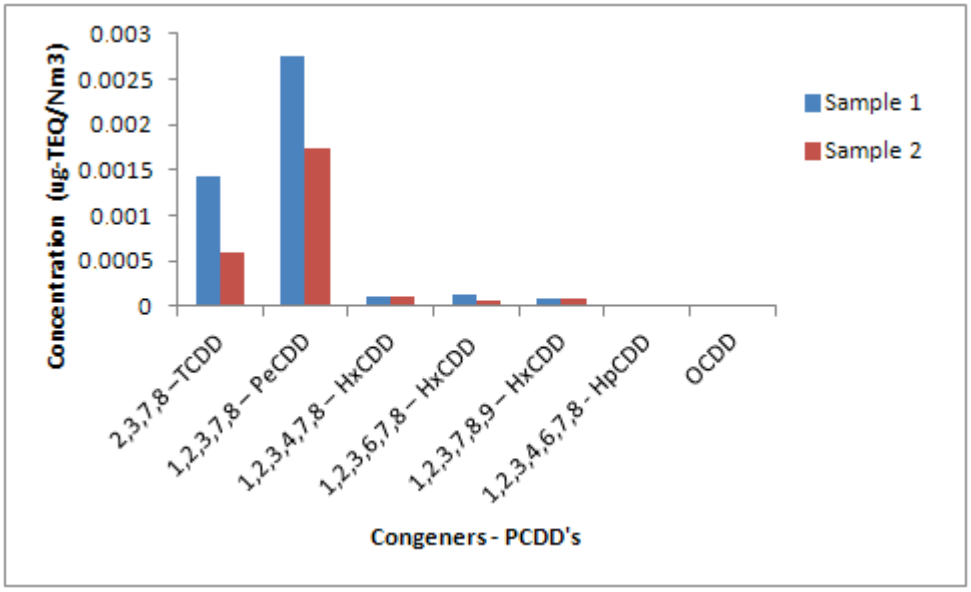
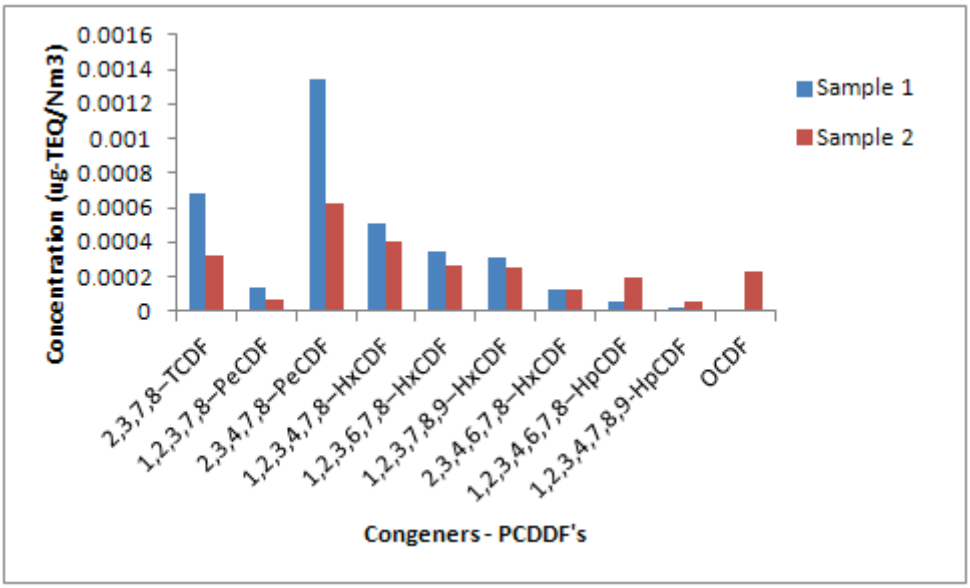



Figure 3 – PCDF Congeners distribution in emissions from charcoal production in rudimentary kilns




**Emission Factor Calculation**

To determine emission factor (EF) it was adopted the following:

a) Mass emission in equivalent toxicity (TEQ).

b) Kiln production: and average of 0.375 Mt (metric tons) of charcoal per batch.

c) Carbonization time: it was used of 43 hours[5] , during which white smoke were visible

Emission factor was obtained as the product of mass emission and operating time divided by the amount of production in one batch. Results are showed in Table 2. The average Emission Factor resulted in 0.056 µg-TEQ/Mt.

**Table 2 – PCDD/F Emission factor**

| Sample | Mass Emission (µg-TEQ/h) | Charcoal Production in one batch (Mt) | Carbonization Time (h) | Emission Factor (µg-TEQ/Mt of charcoal) |
|---|---|---|---|---|
| 1 | 0.00018 | 0.375 | 43 | 0.021 |
| 2 | 0.00011 | 0.375 | 43 | 0.013 |
| Average | | | | 0.017 |

Note: Mt means metric tons

In conclusion: the Emission Factor obtained in this study confirms that UNEP's recommendation[1] of using class 1 of coke production (3 µg-TEQ/t) as a value for charcoal production (simple plants) overestimates the emission from this type of emission source. Emission Factor of Class 2 of UNEP's Toolkit[1] for coke production (0.03 µg-TEQ/t) is closer to the results of this study.

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**References:**

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