PCB AND PAH CONTENT IN CHARCOAL AND IN ASHES FROM CHARCOAL PRODUCTION IN RUDIMENTARY KILNS

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Introduction

The wood carbonization process, also called wood pyrolysis occurs in a kiln with very low oxygen level. In the first phase of the process, evaporation of water occurs (100 to 110 °C). At 270 °C starts the pre-carbonization phase. After that, temperature increases to approximately 450°C, usually for several days, to complete the carbonization process.[1]

Besides charcoal, there are by-products from wood carbonization in gaseous phase, and part of it can condense easily in two fractions: pyro ligneous oil and tar. The amount of non-condensable gases depends on the type of wood, moisture content of wood and the maximum temperature of the process. The fraction of non-condensable gases has relatively low heating content, but they still can be burned and be used in the carbonization process. However, in practice most of the charcoal production plants that use rudimentary kilns send emissions directly to the atmosphere, without treatment or collection of byproducts.

The carbonization process of wood results in the emission of a lot organic compounds, such as carbonyl compounds (CC), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). Studies have identified the presence of significant fractions of carbonyl compounds in different stages of carbonization[2]. No information is available in the literature on the content of dioxin-like PCBs (dl-PCBs), non dioxin-like PCBs (ndl-PCBs) and PAHs in charcoal and in ashes from charcoal production in rudimentary kilns. Results of measurements of PCDD/PCDF in charcoal and in ashes from charcoal production in rudimentary kilns and results for total PCDD/PCDF were reported[3] and were close to the limit of detection (LOD) of the method (ID-GC/MS-MS).

In this work dl-PCBs, ndl-PCBs and HPAs were measured in charcoal and in ashes from pyrolysis of Eucalyptus type of wood, with bark, in rudimentary kilns.

Materials and methods

Samples of commercial charcoal and ashes were taken from a typical kiln (Figure 1) and sent to the Laboratory for Trace Organic Analysis of Cracow University of Technology, Cracow – Poland.

At the laboratory 10g of charcoal and 10 g of ash were spiked with ^{13}C-labelled dl-PCB and ^{2}D-PAHs standards (Cambridge Isotope Laboratories). All standards contained their natural compounds analogues. Spiked samples were freeze-dried and extracted 24h in a Soxhlet extractor with toluene. Toluene extract was rotary evaporated to 10 ml. For dl-PCBs determination 5 ml of the toluene extract was placed in polyethylene semipermeable membrane tube of 80 µm wall thickness and cleaned up with 100 ml hexane (the outer solvent) overnight. The hexane dialysate was cleaned up on a silica gel column coated with 44% sulphuric acid and alumina accordingly to EPA 1613 standard. Final extract was spiked with 20 µl of precision and recovery solution prepared in nonane and evaporated to ca. 20 µl in a gentle stream of nitrogen.

Figure 1 – Charcoal and ashes inside kiln

For PAHs 5 ml of raw toluene extract was evaporated near to dryness and dissolved in 1 ml of hexane and the cleaned-up using polyethylene semipermeable membrane as for dl-PCB. Hexane dialysate was cleaned using 5g of silica gel placed in chromatographic column. A fraction containing all 16 PAHs was collected with assistance of UV lamp.

Determination of dl-PCBs as well as PAHs was performed by isotope dilution gas chromatography - tandem mass spectrometry (ID-GC/MS-MS) on a Thermo Scientific GCQ-1100/Trace2000 system equipped with Xcalibur data acquisition and analysis software. Separation was performed on a 30 m x 0.25 mm i.d. DB5MS J&W capillary column of 25-µm film. Samples of 2 µl volume were injected into SSL injector at 260°C. For dl-PCBs GC oven was programmed as follows: 100°C held for 3 minutes. Then 50°C/minute to 150°C. Then 5°C/minute to 300°C and held for 10 minutes. For PAHs 100°C held for 2 minutes. Then 10°C/minute to 160°C. then 5°C/minute to 280°C and held for 10 minutes. Result uncertainty is expressed as extended measurement uncertainty for k = 2 at confidence level of 95%.

Results and discussion

Table 1 summarizes the results for dl-PCB. Charcoal showed the highest total content of dl-PCBs (0.20 pg TEQ/g) with an order of magnitude higher than in ashes (0.019 pg TEQ/g). Limit of detection (LOD) was 0.00863 ng TEQ/g for charcoal samples and 0.00726 ng TEQ/g for ash samples. The highest levels of these compounds in charcoal were for PCB-126 (90.74%), followed by PCB-118 (4.9%). All other individual dl-PCBs were below 1%.

In ashes the highest content were also of PCB-126 (82.9%), followed by PCB-169 (8.5%), PCB-118 (4.5%), and PCB-77 (2.1%). All other ndl-PCBs in ashes were below 1% content. In charcoal, only PCB-169 was below LOD. In ashes PCB-169 and PCB-189 were below LOD. Results showed that total dl-PCB level in charcoal as well as in ashes is far above LOD.

Compared to total PCDD/PCDF content, expressed in TEQ, given by De ASSUNCAO et al. (2013)[3], total dl-PCBs content, also in TEQ, in charcoal is just a little above total PCDD/PCDF, and, in ashes, total dl-PCB is one fifty of the level of total PCDD/PCDF, both expressed in TEQ.

Table 1 - Levels of dl-PCBs in charcoal and in ashes

dl-PCB	Charcoal (pg TEQ/g)	Ashes (pg TEQ/g)
77	0.00142	0.00039
81	0.000096	0.000054
126	0.187	0.0157
169	**0.0018**	**0.00162**
105	0.00135	0.000141
114	0.0000825	0.0000162
118	0.0101	0.000885
123	0.000615	0.000069
156	0.00135	0.0000381
157	0.000125	0.0000054
167	0.000729	0.000028
189	0.00142	**0.0000023**
Total dl-PCBs	0.20±0,045	0.019±0,0042

Note: Levels below LOD are highlighted in bold

For ndl-PCBs. the highest levels were of PCB-153 (2.02 ng/g in charcoal and 0.16 ng/g in ashes), followed by PCB-138 (0.92 ng/g in charcoal) and PCB-101 (0.91 ng/g in charcoal and 0.15 ng/g in ashes). The content of other ndl-PCBs was well below 0.15 ng/g in charcoal and equal or below 0.055 ng/g in ashes, as shown in Figure

2. Total content of ndl-PCBs was 4.3 ± 0.93 ng/g in charcoal, and 0.44±0.10 ng/g in ashes, and again one order of magnitude below the level in charcoal. LOD for ndl-PCBs in charcoal was 0.00041 ng/g, and 0.00035 ng/g in ashes, what shows that results are far above LOD.

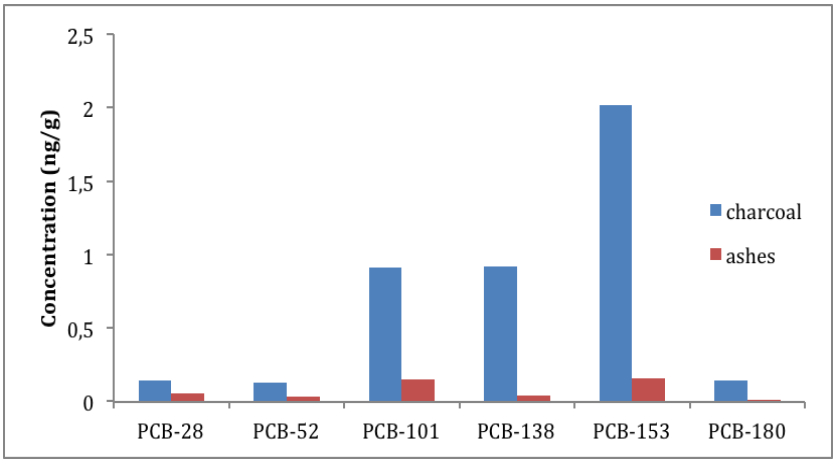

Figure 2 - Levels of ndl-PCBs in charcoal and in ashes from charcoal production in rudimentary kilns

Regarding PAHs, Table 2 presents the results in mass concentration, and Figure 3 presents the results in equivalent toxicity (TEQ). To calculate TEQ it was adopted TEF values from NISBET & LAGOY (1992)[4] and US.EPA (1993)[5]. All 16 compounds of interest were detected in charcoal as well as in ashes, unless naphthalene in charcoal, and naphthalene and acenaphthylene in ashes. Total 16 PAH content in ashes was half of the content in charcoal. The compound with the highest concentration in charcoal was benz(a)anthracene (0.56 ng TEQ/g), followed by anthracene (0.40 ng TEQ/g) and benzo(a)pyrene (0.30 ng TEQ/g), what is very close to content of fluorene (0.28 ng TEQ/g). In ashes Naphthalene was the compound that presented the highest concentration (0.2 ng TEQ/g), followed by benz(a)pyrene (0.2 ng TEQ/g), benzo(b)fluoranthene (0.14 ng TEQ/g) and benz(a)anthracene (0.11 ng TEQ/g).

Table 2 - Levels of PAHs in charcoal and ashes (µg/g)

PAH	Charcoal	Ashes
Naphtalene	**0.2**	**0.2**
Acenaphthylene	0.071	**0.1**
Acenaphtene	0.05	0.022
Fluorene	0.28	0.028
Phenanthrene	0.18	0.032
Anthracene	0.04	0.0079
Fluoranthene	0.12	0.081
Pyrene	0.11	0.077
Benz(a)anthracene	0.0056	0.0011
Chrysene	0.0093	0.0027
Benzo(b)fluoranthene	0.0022	0.0014
Benzo(k)fluoranthene	0.0016	0.0006
Benzo(a)pyrene	0.0003	0.0002
Indeno(1,2,3-cd)pyrene	0.0004	0.0002
Dibenzo(ah)anthracene	0.0002	0.0001
Benzo(ghi)perylene	0.0003	0.0002
Total	1.1±0.22	0.55±0.11

Note: Levels below LOD are highlighted in bold

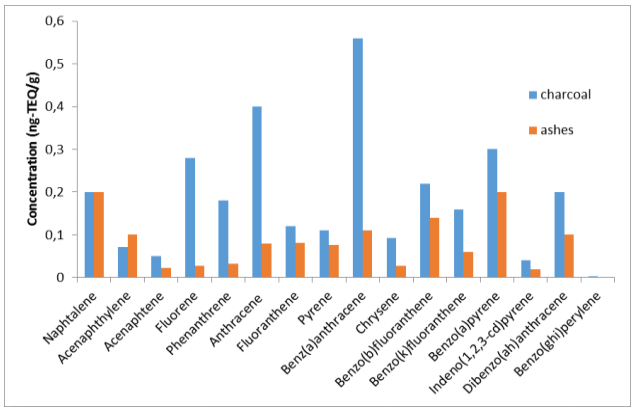

Figure 3 - Levels of HPAs in charcoal and in the ashes from rudimentary kilns. (ng TEQ/g)

References

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