Suspect screening of OH-PAHs and non-target screening of other organic compounds in wood smoke particles using HR-Orbitrap-MS

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HIGHLIGHTS

- Suspect and non-target screening were used to characterize wood smoke particles.
- Suspect screening was done in order to identify OH-PAH isomers.
- 32 peaks corresponding to 12 OH-PAH masses were tentatively identified.
- Non-target screening involved statistical analysis and tentative identification of unknowns.
- Unique compounds for each wood type and burning condition were identified.

ARTICLE INFO

ABSTRACT

Wood combustion has been shown to contribute significantly to emissions of polycyclic aromatic hydrocarbons and hydroxylated polycyclic aromatic hydrocarbons, compounds with toxic and carcinogenic properties. However, only a small number of hydroxylated polycyclic aromatic hydrocarbons have been determined in particles from wood combustion, usually compounds with available reference standards. In this present study, suspect and non-target screening strategies were applied to characterize the wood smoke particles from four different wood types and two combustion conditions with respect to hydroxylated polycyclic aromatic hydrocarbons and other organic compounds. In the suspect screening, 32 peaks corresponding to 12 monohydroxylated masses were tentatively identified by elemental composition assignments and matching of isotopic pattern and fragments. More than one structure was suggested for most of the measured masses. Statistical analysis was performed on the non-target screening data in order to single out significant peaks having intensities that depend on the wood type and/or combustion condition. Significant peaks were found in both negative and positive ionization modes, with unique peaks for each wood type and combustion condition, as well as a combination of both factors. Furthermore, structural elucidation of some peaks was done by comparing the spectra in the samples with spectra found in the spectral databases. Six compounds were tentatively identified in positive ionization mode, and 19 in negative ionization mode. The results in this present study demonstrate that there are significant overall differences in the chemistry of wood smoke particles that depends on both the wood type and the combustion condition used.

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1. Introduction

Residential combustion is one of the main and important sources of particulate matter emissions worldwide and residential wood combustion particles accounted for between 12 and 69% of the PM$_{2.5}$ emissions in the Nordic countries in 2000 (Karvosenoja et al., 2004). The chemical composition of the emitted particles varies significantly and depends on combustion conditions, fuel type, moisture content, etc. (Orasche et al., 2012; Pettersson et al., 2011; Lamberg et al., 2011; McDonald et al., 2000). The chemical composition of the particles has been pointed out as an important factor for the adverse health effects associated with exposure to wood smoke particles and one group of compounds, polycyclic aromatic hydrocarbons (PAHs) are of special concern (Bølling et al., 2009; Rohr and Wyzga, 2012). In Sweden, wood combustion has been shown to contribute significantly to emissions of PAHs and

hydroxylated polycyclic aromatic hydrocarbons (OH-PAHs) (Westerholm et al., 2012; Avagyan et al., 2016). PAHs are environmental contaminants with carcinogenic properties (el-Bayoumy, 2008; Boffetta et al., 1997; Mastrangelo et al., 1996; Rantanen, 1983) mainly formed during different incomplete combustion processes, while OH-PAHs are oxidation products of PAHs, with one or more OH-group(s) attached. Although OH-PAHs have not been studied as extensively as PAHs, they have been shown to have toxic, endocrine disrupting and carcinogenic properties (Hirose et al., 2001; Kazunga et al., 2001; Yu, 2002; Kamiya et al., 2005; Wang et al., 2009a). Combustion particle emissions are considered as a primary source of OH-PAHs in urban air and the environment, however, there are few studies in the literature that have determined OH-PAHs in wood smoke particles (Cochran et al., 2013; Avagyan et al., 2016). Only a small number of OH-PAHs have been determined, usually compounds for which there are reference standards available. The molecular composition of particles from burning of wood or biomass have been characterized in several studies, and compound groups such as PAHs, alkanes, alkenes, aldehydes, ketones, fatty acids, fatty alcohols, methoxyphenols, monosaccharide derivatives, etc. have been determined using gas chromatography mass spectrometry (Rogge et al., 1998; Oros and Simoneit, 2001; Wang et al., 2009b). In recent years, the development of different liquid chromatography mass spectrometry (LC-MS) techniques has enabled determination of non-volatile, thermolabile, polar compounds in environmental matrices. Especially the coupling of LC to high resolution mass spectrometers (LC-HRMS) has been a powerful tool, due to high mass accuracy measurements (Krauss et al., 2010). Furthermore, the new generation of high resolution hybrid orbitrap instruments have been shown to have excellent detection and identification capabilities for low molecular weight compounds in various matrices, providing both better sensitivity in full scan and accurate masses of the product ions (Gosetti et al., 2015) and in a small number of studies LC-HRMS have been used to characterize the polar fraction of wood particle extracts, focusing on oxygenated and nitrogenated organic compounds (Smith et al., 2008; Laskin et al., 2009).

In a study launched by our research group, 11 OH-PAHs were determined in four different wood types (birch, aspen, pine and spruce) and two combustion conditions (Avagyan et al., 2016) showing that emissions of OH-PAHs corresponded on average to 28% of PAH emissions. However, only OH-PAHs with available reference standards were determined, showing a need to further investigate the composition of wood smoke particles. In this present study, a suspect screening strategy was applied in order to characterize the wood smoke particles with respect to OH-PAHs utilizing a liquid chromatograph coupled to a high resolution orbitrap mass spectrometer. The wood smoke particles were further characterized using a non-target screening strategy, involving statistical analysis of the data and tentative identification of some unknown compounds.

2. Materials and methods

2.1. Chemicals and solvents

Detailed information on the seven OH-PAH standards used in this study is presented in Table S1 in the Electronic Supplementary Material (ESM). Acetonitrile (ACN), and methanol, both HPLC-grade, were purchased from Rathburn Chemicals Ltd (UK) and formic acid (98%) from Fluka Analytical (Germany). Water was purified using a Millipore Synergy 185 (Millipore Corp., USA) water purification system equipped with a Millipak 0.22 μm membrane filter (Millipore Corp., USA).

2.2. Wood smoke particles

The combustion experiments and collection of wood smoke particles have been described in detail elsewhere (Avagyan et al., 2015, 2016). Briefly, the combustion experiments were performed in a conventional natural draft wood stove, operated in two modes; nominal burn rate (NB) with "normal" (recommended from the manufacturer) combustion conditions and high burn rate (HB) achieved by slightly overloading the stove with more and smaller logs resulting in high load intensive combustion. Four different wood fuels (birch, aspen, spruce, pine) were used in the combustion experiments.

Sampling of the wood smoke particles was performed during the whole combustion batch and samples were collected during two succeeding fuel batch additions. The particles were sampled 2.5 m from the top of the stove at an approximate flue gas temperature of 250–300 °C. The flue gases were diluted 4 times by a porous tube diluter and the particles were collected on MK360 90 mm micro-quartz fiber filters (Munktell Filter AB, Sweden).

2.3. Sample extraction and instrumental analysis

The collected particles were extracted using an ASE 200 accelerated solvent extraction system (Dionex Corporation, USA) with methanol at 200 °C and 2000 psi in two 10 min extraction cycles, with a pre-heating time of 3 min, equilibration time of 9 min, purge with nitrogen in 1 min and 30% solvent flush. The extracts were then reduced in volume under a gentle stream of nitrogen in a TurboVap® LV evaporator (Zymark Corporation, USA) at 65 °C to a final volume of approximately 0.5 mL. The extraction method has previously been used for the extraction of OH-PAHs in wood smoke particles and soil samples (Avagyan et al., 2015). Similar extraction with methanol as the solvent has also been used in another study for the extraction of nitrated and oxygenated PAHs in air and soot particles (Mirivel et al., 2010).

The instrumental analysis was performed on a Q Exactive HF Hybrid Quadrupole-Orbitrap mass spectrometer (Q-OT-MS) (Thermo Scientific, Bremen, Germany) coupled to Ultimate 3000 Rapid Separation Liquid Chromatography (RSLC) system (Dionex, Germering, Germany) equipped with an online vacuum degasser, quaternary pumps, an autosampler and a thermostated column compartment. The chromatographic separation was performed on a C_{18} column (ACE 3, Ø 2.1 mm × 50 mm, 3 μm particle size, Advanced Chromatography Technologies, Aberdeen, Scotland). For positive ionization mode, the mobile phase A was purified water with 0.10% (v/v) formic acid and mobile phase B was acetonitrile with 0.10% (v/v) formic acid. For negative ionization mode, the mobile phase A and B were purified water and acetonitrile, respectively. The injection volume was 5 μL and the mobile phase flow rate was set to 400 μL/min. The non-target screening gradient program was as follows: 0.0 min 20% B, 18.00 min 95% B, 20.00 min 95% B. The system was equilibrated for 4.9 min with 20% B after each run. The gradient program for suspect screening of OH-PAHs was similar to those previously developed for target screening of OH-PAHs (Avagyan et al., 2015, 2016) and was as follows: 0.1 min 30% B, 2 min 60% B, 4 min 60% B, 6 min 90% B, 7.1 min 30% B and equilibration for 3 min with 30% B after each run. The chromatographic separation used for the suspect screening was a fast separation suited for OH-PAHs, optimized using the available OH-PAH reference standards, shown in Fig. S1 in ESM. The separation for the non-target screening was slower and more general in order to elute and separate as many compounds as possible. The autosampler temperature was set to 15 °C and the column temperature was set to 25 °C.

The heated electrospray ionization (HESI-II) source was