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Influence of ozone initiated processing on the toxicity of aerosol particles from small scale wood combustion

Erik Z. Nordin [a, *], Oskari Uski [b, c], Robin Nyström [d], Pasi Jalava [c], Axel C. Eriksson [e], Johan Genberg [e], Pontus Roldin [e], Christoffer Bergvall [f], Roger Westerholm [f], Jorma Jokiniemi [c, g], Joakim H. Pagels [a], Christoffer Boman [d], Maija-Riitta Hirvonen [c, b]

[a] Ergonomics and Aerosol Technology, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden
[b] Department of Environmental Health, National Institute for Health and Welfare, P.O. Box 95, FI-707 01 Kuopio, Finland
[c] Department of Environmental Science, University of Eastern Finland, P.O. Box 1627, FI-702 11 Kuopio, Finland
[d] Thermochemical Energy Conversion Laboratory, Dept. of Applied Physics and Electronics, Umeå University, SE-901 87 Umeå, Sweden
[e] Nuclear Physics, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden
[f] Department of Analytical Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden
[g] VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland

HIGHLIGHTS

- The PAH fraction of biomass combustion aerosol decreases due to ozone aging.
- Nominal combustion PM induced less cell death compared to PM from hot air starved combustion.
- Aging alters the toxicological effects of biomass combustion PM.

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ABSTRACT

Black carbon containing emissions from biomass combustion are being transformed in the atmosphere upon processing induced by tropospheric ozone and UV. The knowledge today is very limited on how atmospheric processing affects the toxicological properties of the emissions.

The aim of this study was to investigate the influence of ozone initiated (dark) atmospheric processing on the physicochemical and toxicological properties of particulate emissions from wood combustion.

Emissions from a conventional wood stove operated at two combustion conditions (nominal and hot air starved) were diluted and transferred to a chamber. Particulate matter (PM) was collected before and after ozone addition to the chamber using an impactor. Detailed chemical and physical characterization was performed on chamber air and collected PM. The collected PM was investigated toxicologically *in vitro* with a mouse macrophage model, endpoints included: cell cycle analysis, viability, inflammation and genotoxicity.

The results suggest that changes in the organic fraction, including polycyclic aromatic hydrocarbons (PAHs) are the main driver for differences in obtained toxicological effects. Fresh hot air starved emissions containing a higher organic and PAH mass-fraction affected cell viability stronger than fresh emissions from nominal combustion. The PAH mass fractions decreased upon aging due to chemical degradation. Dark aging increased genotoxicity, reduced viability and reduced release of inflammatory markers. These differences were statistically significant for single doses and typically less pronounced. We hypothesize that the alterations in toxicity upon simulated dark aging in the atmosphere may be caused by reaction products that form when PAHs and other organic compounds react with ozone and nitrate radicals.

* Corresponding author.
E-mail address: erik.nordin@design.lth.se (E.Z. Nordin).

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1. Introduction

Exposure to small scale biomass combustion aerosol is considered a major health issue globally. There is cumulative evidence from both *in vitro* and *in vivo* experiments including controlled human exposure studies, where exposure to fresh biomass combustion particles from incomplete combustion conditions, have been shown to cause adverse health effects. The endpoints include inflammation, cytotoxicity, genotoxicity, oxidative stress and arterial stiffness (Barregard et al., 2006; Jalava et al., 2012; Uski et al., 2012; Happo et al., 2013; Unosson et al., 2013). Polycyclic aromatic hydrocarbons (PAHs) are suspected to be mediators of adverse health effects in exposure to this kind of biomass combustion aerosol (Binkova et al., 2007). Several publications demonstrated that elevated levels of PAHs and soot (black carbon) are emitted from wood stoves operated at hot air starved conditions (Pettersson et al., 2011; Orasche et al., 2013; Eriksson et al., 2014).

The chemical composition of ambient particles is regarded an important factor behind toxicological responses (Rohr and Wyzga, 2012). The composition varies rapidly over time in batch-wise biomass combustion (e.g. wood stoves) and between different combustion systems as the combustion conditions changes (Bolling et al., 2009; Elsasser et al., 2013; Pagels et al., 2013). Recent studies have demonstrated that the combustion conditions and the associated changes in chemical composition of fresh emission particles results in large differences in toxicological responses (Danielsen et al., 2009; Bolling et al., 2012; Jalava et al., 2012).

Upon emission to the atmosphere the particle characteristics changes due to atmospheric processing. Processing initiated by UV radiation, ozone or nitrate radicals leads to formation of additional secondary organic aerosol (SOA), mass and chemical transformation of the primary aerosol can also occur due to surface reactions. There are indications from field studies that atmospheric processing significantly affects the toxicity of ambient particulate matter (Jalava et al., 2006). Since a large proportion of residential biomass combustion is performed at night or in winter time when the UV radiation intensity is low, atmospheric aging initiated by tropospheric ozone becomes highly relevant.

There are only a few studies published on the toxicology of aged biomass combustion aerosol, Kunzi et al. (2013) reported mild effects, typically not statistically significant neither for fresh nor for aged biomass combustion aerosol, on a range of endpoints. The low effects might be due to comparatively low particle doses used to expose cells at the air liquid interface. In real life situations humans are exposed to both fresh and aged aerosols, in different locations and meteorological conditions. Hence, it is important to link combustion condition, aerosol aging processes and concomitant chemistry of PM to the toxicological effects.

The aim of this study was to investigate the influence of dark aging and combustion conditions on the physicochemical and toxicological properties of particulate emissions from small-scale biomass combustion.

2. Materials and methods

A conventional wood stove was used to generate the emissions (Pettersson et al., 2011), the fuel was birch wood. Two combustion modes were defined, “normal” firing procedure at nominal load (NOM) and hot air starved combustion (HAS). Particles were collected for toxicological analysis during two replicate experiments for each combustion mode. In each experiment a fresh and an aged sample was collected. The two replicate samples were pooled to one sample for the toxicological investigation.

2.1. Combustion aerosol generation

The nominal combustion case was defined as a full combustion cycle (from fuel addition on glowing embers until the oxygen concentration reached ~16%), the stove was operated as instructed by the manufacturer. This resulted in comparatively low emissions, with an aerosol dominated by black/elemental carbon. The hot air starved combustion aimed to reflect adverse combustion conditions with a higher OA and PAH fraction. This was achieved by adding small amounts of wood logs, cut in relatively small pieces every 5–6 min to the fire. This procedure generated intermittent periods of 1) high organic aerosol emissions following fuel addition and 2) “overload” hot air starved conditions with very low O_2 concentrations (<5%), resulting in high PAH emissions (Eriksson et al., 2014). A similar combustion mode was also recently used in controlled human exposures in the same laboratory by Unosson et al. (2013). The experiment average concentrations of O_2, CO and NO is shown in Table 1.

2.2. Experimental procedure

The emissions were diluted and sampled to a 15.3 m^3 stainless steel reaction chamber, according to principles further described in the Supporting Information (SI). The emissions were added to the chamber for a period of 30–60 min until a mass concentration of about 3000 μg m^{-3} was achieved. A cascade impactor (DGI, Dekati Ltd, Finland) was used for collection of samples for chemical and toxicological analysis. First fresh aerosol was sampled for about 1 h. After the fresh aerosol sampling period had ended, ozone was added to the chamber at concentrations that corresponded to 1200 ppb in an empty chamber for the hot air starved experiments and 1900 ppb in the nominal combustion experiments due to higher concentration of NO in the latter case. After ozone addition, the aged aerosol was collected on a new filter set until the mass concentration in the reaction chamber was 200–300 μg m^{-3}, or just before the filters in the DGI had become overloaded.

2.3. Aerosol characterization and instrumentation

The mass concentration (PM_1) in the chamber was measured by a tapered element oscillating microbalance (TEOM) at an operating temperature of 30 °C (series 1400, Ruprecht & Patchnik, USA). Filter sampling for organic carbon (OC) and elemental carbon (EC) was carried out and analyzed with a thermal-optical analyzer according to the EUSAAR-2 protocol (Cavalli et al., 2010). OC was converted to organic matter (OM) to include the hydrogen and oxygen bound in the organic compounds. The conversion factor was directly measured with aerosol mass spectrometry. The ozone concentration in the reaction chamber was monitored using a UV spectrophotometer (model 49i, Thermo Scientific, USA). The NO and NO_2 (NO_y–NO) concentration was measured by a NO_x monitor (model CLD-700-AL, Ecophysics, USA).

Separate sampling for particle and gas phase PAHs was performed for fresh emissions in the chamber with an integrated sample unit including polyurethane foam plugs (gas phase) and

Table 1
The experiment average concentration of O_2, CO and NO_x measured in undiluted flue gases.

Experiment	O_2 (%)	CO (mg MJ^{-1})	NO_x (mg MJ^{-1})
HAS#1	11.4	1760	61
HAS#2	9.9	1900	65
NOM#1	10.9	930	64
NOM#2	13.8	1050	73