Toxicological characteristics of particulate emissions from biomass combustion

Maija-Riitta Hirvonen, Professor, Vice Dean

1University of Eastern Finland
2National Institute for Health and Welfare

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Particulate air pollution is regarded as one the most important health concerns worldwide.

Dual role of fine particles
- impact on the health of populations
- radiative forcing causing climate change
Particulate air pollution
- an issue of public health

In Europe:
• Up to 350,000 premature deaths annually
  - 8 months loss of statistical life expectancy which is mainly due to life years lost by cardiorespiratory patients (up to 10yrs)

• Large economic impacts
  - due to worsening of symptoms of cardio-respiratory diseases, hospitalizations, loss of working days, etc.

• No obvious threshold value for particle levels below which no adverse health effects occur.

(EU/CAFÉ 2000, Directive 2008/50)
Adverse health effects associated with PM exposure

- Cardiac diseases
  - Arrhythmia, atherosclerosis, unstable plaques, blood pressure -> infarct, stroke
- Respiratory diseases
  - Asthma, COPD
- Lung cancer
- Chronic bronchitis

Most sensitive population groups are cardiorespiratory patients, small children and the elderly
Why worry about biomass combustion emission?

- The use of renewable energy in EU will be increased up to 20% of the total energy consumption by 2020 in order to slow down the climate change.

- This may lead to an increase in adverse effects on human health, because biomass combustion is one of the most important particulate sources.

- Currently only limited scientific data exist on the source-specific harmful characteristics of emissions, which are the actual cause of the health effects.
• Thus, the increase in use of biomass based energy should be done without increasing fine particle emissions and their current extensive annual health impacts.

• In-depth toxicological and physicochemical characterisation of particles, connected to emission studies, is needed in assessing potential health risks of different combustion technologies and fuels as well as to develop clean combustion processes.
Chemical composition of biomass combustion particles is different from fossil fuel combustion.

Health risks may differ from other particles of similar size.
What do we **NOT** know?

- causal compounds behind the health effects and their effective doses
- specific sources of the harmful emissions
- how the atmospheric transformation and other components of the complex ambient mixture affect the potency of the different emissions in the atmosphere
Why the fine particles are so dangerous?

- PM less than 0.1um have the largest reactive surface
- Transition metals and their oxidized forms
- Reactive organic compounds (e.g. uncompleted combustion)
- Age of the particles (fresh PM more harmful than aged)
- Poor water solubility

Activation of wide variety of mechanisms leading to adverse health effects
Mechanisms behind the health effects?

Particulate matter

- Chemistry
- Age

Physicochemical properties

- Shape
- Surface
- Size

Toxicological properties

- Oxidative stress
- Inflammation

Health effects

- DNA damage
- Cell death
- Cancer
- Chronic cardiovascular and respiratory diseases
Multidiciplinary approach

• To define the Chemistry-Toxigology-Health connection, examining the toxicity of the entire PM mixture is important, since interactions between various chemical components may lead to unpredictable responses.

• To gain comparable data, harmonised sampling methods and analysis of physicochemical and toxicological characteristics need to be studied in both in field studies and experimental settings focusing on
  – complex mixture of urban air particulate matter (PM)
  – source specific PM emissions
Efficiency of log wood combustion affects the toxicological and chemical properties of emission particles.

Objective

• To investigate chemical and consequent toxicological characteristics of PM(1) emitted from different phases of batch combustion in four heating appliances.
Particle collection
(University of Eastern Finland, FINE)

• Particle samples were collected to filters with a Dekati Gravimetric Impactor (DGI)
  – sample diluted with porous tube diluter
• DR 13-26
Sample preparation

1. Weighing of filters
2. Methanol extraction (sonication)
3. Evaporation of additional methanol
4. Dispensing the particle suspension to glass tubes on mass basis
5. Drying under nitrogen flow
6. Storing at -20 °C

Before exposure of cells:
6. Dissolving particles to DMSO and water
7. Sonication for 30 minutes
Exposure to particulate matter

**Cell lines:**
- Mouse RAW264.7 macrophages,
- Human BEAS-2B cells

They are target cells in PM induced immunotoxicity

**Particulate doses:** 15, 50, 150 and 300 µg/ml

**Exposure time:** 24 hours

**Detected endpoints:**
- Cell death (acute and programmed)
- Inflammatory mediators (e.g. MIP-2, TNFα)
- DNA damage
Combustion situations, bathes and sampling durations of four different log wood combustion appliances.

Collaboration: Professor Jorma Jokiniemi
University of Eastern Finland

<table>
<thead>
<tr>
<th>Appliance</th>
<th>Combustion situation</th>
<th>Batch</th>
<th>Sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern masonry heater</td>
<td>Improved batch combustion</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; batch 10x0.4 kg, others 4x1 kg</td>
<td>3&lt;sup&gt;rd&lt;/sup&gt; and 4&lt;sup&gt;th&lt;/sup&gt; batches, 50min</td>
</tr>
<tr>
<td>Conventional masonry heater 1</td>
<td>Conventional batch combustion</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; batch 7x0.43 kg, others 4x0.75 kg</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; and 3&lt;sup&gt;rd&lt;/sup&gt; batches, 40min</td>
</tr>
<tr>
<td>Conventional masonry heater 2</td>
<td>Conventional batch combustion</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; batch 3x1 kg, others 3x1.3 kg</td>
<td>Firing phase, beginning of the 2&lt;sup&gt;nd&lt;/sup&gt; batch, 15min</td>
</tr>
<tr>
<td>Sauna stove</td>
<td>Inefficient batch combustion</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; batch 5x0.31 kg, 2&lt;sup&gt;nd&lt;/sup&gt; batch 6x0.53 kg</td>
<td>Ignition batch and 2&lt;sup&gt;nd&lt;/sup&gt; batch, 20-35min</td>
</tr>
</tbody>
</table>
PM$_1$ emissions and their carbon content of four log wood combustion appliances.

<table>
<thead>
<tr>
<th></th>
<th>Modern masonry heater 3,4 batches</th>
<th>Masonry heater 1 2,3 batches</th>
<th>Masonry heater 2 Firing</th>
<th>Sauna stove Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_1$</td>
<td>51±26</td>
<td>52±12</td>
<td>67±7</td>
<td>257±85</td>
</tr>
<tr>
<td>EC</td>
<td>24±7</td>
<td>28±4</td>
<td>49±10</td>
<td>130±23</td>
</tr>
<tr>
<td>OC</td>
<td>4±2</td>
<td>4±2</td>
<td>19±16</td>
<td>160±26</td>
</tr>
</tbody>
</table>
The inefficient batch combustion phase in the sauna stove emitted particles with the strongest genotoxicity and cytotoxicity.

Instead, the cytotoxic effects of more efficient combustion phases in the masonry heaters might be linked to water-soluble metal content of the PM samples.
Conclusions (1)

• All the wood combustion samples exerted high cytotoxicity, but only moderate inflammatory activity.

• The particles emitted from the inefficient phase of batch combustion in the sauna stove induced the most extensive cytotoxic and genotoxic responses.

• PAHs and other organic compounds in samples might have contributed to these effects. Instead, water-soluble metals seemed to participate in the cytotoxic responses triggered by the particles from more efficient batch combustion in the masonry heaters.

• Efficiency of batch combustion plays a significant role in the harmfulness of PM even under incomplete wood combustion processes.
In vitro toxicological characterization of particulate emissions from residential biomass heating systems based on old and new technologies

Pasi I. Jalava a,*, Mikko S. Happo a, Joachim Kelz b, Thomas Brunner b,c,d, Pasi Hakulinen e, Jorma Mäki-Paakkanen e, Annika Hukkanen a, Jorma Jokiniemi a, f, Ingwald Obernberger b,c,d, Maija-Riitta Hirvonen a,e

a University of Eastern Finland, Department of Environmental Science, P.O. Box 1627, FI-70211 Kuopio, Finland
b Bioenergy 2020þ GmbH, Inffeldgasse 21b, A-8010 Graz, Austria
c Institute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 21a, A-8010 Graz, Austria
d BIOS Bioenergiesysteme GmbH, Inffeldgasse 21b, A-8010 Graz, Austria
e Department of Environmental Health, National Institute for Health and Welfare, P.O. Box 95, FI-70701 Kuopio, Finland
f VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland
Toxicological properties of PM samples from seven different small-scale biomass heating systems

Collaboration: Professor Obernberger
Graz University of Technology and BIOENERGY 2020+ GmbH

<table>
<thead>
<tr>
<th>Studied appliances</th>
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</thead>
<tbody>
<tr>
<td><strong>New technology</strong></td>
</tr>
<tr>
<td>1. stove</td>
</tr>
<tr>
<td>2. log wood boiler</td>
</tr>
<tr>
<td>3. tiled stove</td>
</tr>
<tr>
<td>4. pellet boiler</td>
</tr>
<tr>
<td>5. wood chip boiler</td>
</tr>
<tr>
<td><strong>Old technology</strong></td>
</tr>
<tr>
<td>1. stove</td>
</tr>
<tr>
<td>2. log wood boiler</td>
</tr>
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</table>

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Cytotoxicity (MTT test)

Jalava et al. 2012
Cytotoxicity /Cell membrane permeability

![Graph showing cytotoxicity and cell membrane permeability for different technologies and stoves. The y-axis represents % PI positive, and the x-axis includes Stoves, Log wood boilers, Wood chip boiler, Tiled stove, and Pellet boiler. The graph compares New tech and Old tech with doses ranging from 0 to 80% PI positive.

Jalava et al. 2012

150μg/ml

Dose

New tech

Old tech

New tech

Log wood boilers

Wood chip boiler

Tiled stove

Pellet boiler

Jalava et al. 2012
Genotoxicity / Comet assay

Jalava et al. 2012
The PAH composition was in a key role in activated toxicological responses

<table>
<thead>
<tr>
<th>Six criteria PAH (EC/2004)</th>
<th>MTT</th>
<th>TNF-α</th>
<th>MIP-2</th>
<th>PI</th>
<th>SubG1</th>
<th>G1</th>
<th>S/G2M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[a]anthracene</td>
<td>0.354</td>
<td>0.587*</td>
<td>0.697**</td>
<td>0.697**</td>
<td>0.648*</td>
<td>-0.662**</td>
<td>0.116</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>0.323</td>
<td>0.556*</td>
<td>0.705**</td>
<td>0.688**</td>
<td>0.692**</td>
<td>-0.692**</td>
<td>0.130</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>0.214</td>
<td>0.762*</td>
<td>0.619</td>
<td>0.310</td>
<td>0.405</td>
<td>-0.357</td>
<td>-0.286</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>0.341</td>
<td>0.569*</td>
<td>0.714**</td>
<td>0.679**</td>
<td>0.666**</td>
<td>-0.670**</td>
<td>0.103</td>
</tr>
<tr>
<td>Indeno[1.2.3-cd]pyrene</td>
<td>0.204</td>
<td>0.266</td>
<td>0.495</td>
<td>0.530</td>
<td>0.543*</td>
<td>-0.596*</td>
<td>0.358</td>
</tr>
<tr>
<td>Dibenzo[a.h]anthracene</td>
<td>0.049</td>
<td>0.119</td>
<td>0.399</td>
<td>0.448</td>
<td>0.434</td>
<td>-0.594*</td>
<td>0.329</td>
</tr>
</tbody>
</table>

Jalava et al. 2012
Effect of chemical composition on toxicological responses

<table>
<thead>
<tr>
<th></th>
<th>MTT</th>
<th>TNFα</th>
<th>MIP-2</th>
<th>PI</th>
<th>SubG1</th>
<th>G1</th>
<th>S/G2M</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>-0.270</td>
<td>-0.013</td>
<td>0.445</td>
<td>0.451</td>
<td>0.456</td>
<td>-0.454</td>
<td>0.275</td>
</tr>
<tr>
<td>EC</td>
<td>0.440</td>
<td>0.492</td>
<td><strong>0.612</strong></td>
<td>0.382</td>
<td><strong>0.763</strong></td>
<td>-0.527</td>
<td>-0.332</td>
</tr>
<tr>
<td>Ca</td>
<td>-0.244</td>
<td>-0.433</td>
<td><strong>-0.705</strong></td>
<td><strong>-0.749</strong></td>
<td><strong>-0.793</strong></td>
<td><strong>0.833</strong></td>
<td>-0.262</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.165</td>
<td><strong>-0.550</strong></td>
<td><strong>-0.783</strong></td>
<td><strong>-0.759</strong></td>
<td><strong>-0.724</strong></td>
<td><strong>0.772</strong></td>
<td>-0.220</td>
</tr>
<tr>
<td>Mn</td>
<td>-0.285</td>
<td>-0.510</td>
<td><strong>-0.766</strong></td>
<td><strong>-0.659</strong></td>
<td><strong>-0.798</strong></td>
<td><strong>-0.731</strong></td>
<td>0.065</td>
</tr>
<tr>
<td>K</td>
<td>0.051</td>
<td>-0.495</td>
<td><strong>-0.802</strong></td>
<td><strong>-0.670</strong></td>
<td><strong>-0.657</strong></td>
<td>0.666**</td>
<td>-0.138</td>
</tr>
<tr>
<td>Na</td>
<td>-0.033</td>
<td>-0.332</td>
<td><strong>-0.653</strong></td>
<td><strong>-0.705</strong></td>
<td><strong>-0.776</strong></td>
<td><strong>0.824</strong></td>
<td>-0.301</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.077</td>
<td>-0.515</td>
<td><strong>-0.789</strong></td>
<td><strong>-0.725</strong></td>
<td><strong>-0.641</strong></td>
<td><strong>0.969</strong></td>
<td>-0.194</td>
</tr>
<tr>
<td>S</td>
<td>-0.029</td>
<td>-0.455</td>
<td><strong>-0.758</strong></td>
<td><strong>-0.688</strong></td>
<td><strong>-0.622</strong></td>
<td><strong>0.662</strong></td>
<td>-0.152</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.136</td>
<td>-0.493</td>
<td><strong>-0.711</strong></td>
<td><strong>-0.700</strong></td>
<td><strong>-0.587</strong></td>
<td><strong>0.695</strong></td>
<td>-0.163</td>
</tr>
<tr>
<td>Cd</td>
<td>-0.062</td>
<td>-0.251</td>
<td><strong>-0.556</strong></td>
<td><strong>-0.602</strong></td>
<td>-0.507</td>
<td><strong>0.629</strong></td>
<td>-0.389</td>
</tr>
</tbody>
</table>

Jalava et al. 2012
Old technology log wood boiler
- rather high inflammatory response
- high cytotoxicity, especially with PI-method
- genotoxicity is dramatically increased.
- this appliance type may affect all the proposed disease mechanisms.

Old technology stove
- increased genotoxicity
- slightly increased inflammatory responses

New technology stove
- same activated cellular mechanisms as by the PM emissions from old tech stove but response level is lower

Tiled stove, wood chip boiler and new technology log wood boiler
- at least some of the toxicological parameters are increased

Pellet boiler
- most of the toxicological parameters were only slightly increased, and the genotoxic response was negligible.
Conclusions (2)

• Combustion technology largely affects the particulate emissions and their toxic potential this being reflected in substantially larger responses in devices with incomplete combustion.

• These differences become emphasized when the large emission factors from old technology appliances are taken into account.

• The present data also demonstrated clearly that toxicological methods can be applied in the development of new combustion technologies
Growing use of biomass energy should be done without increasing harmful health effects
Acknowledgements

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• Graz University of Technology
  – Ingwald Obernberger, Thomas Brunner, Joachim Kelz
Thank you for your attention!