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Biofuel Combustion Emissions -
Chemical and Physical Smoke Properties

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1. Introduction

Biofuels have recently gained much attention, mainly as alternative fuels for applications in energy generation and transportation. The utilization of biofuels in such controlled combustion processes has the great benefit of not further depleting the limited resources of fossil fuels, yet it is associated with emissions of greenhouse gases and smoke particles similar to traditional combustion processes, i.e., those of fossil fuels. On the other hand, a vast amount of biofuels is subject to combustion in small-scale processes, such as for heating and cooking in residential dwellings, as well as in agricultural operations, such as for crop residue removal and land clearing. In addition, large amounts of biomass are consumed annually during forest and savanna fires in many parts of the world. These types of burning processes are typically uncontrolled and unregulated. Consequently, the emissions from such processes may be substantially larger compared to industrial-type operations. Aside from direct effects on human health, especially due to a sizeable fraction of the smoke emissions remaining inside residential homes, the smoke particles and gases released from uncontrolled biofuel combustion impose significant effects on regional and global climate. Estimates have shown the majority of carbonaceous airborne particulate matter to be derived from the combustion of biofuels and biomass. The resulting “clouds” of carbonaceous aerosol particles nowadays span vast areas across the Globe. Aside from the negative health impacts and influence on global climate, these smoke particles affect biogeochemical cycles and regional air quality, which is also associated with severe economic impacts.

Whereas emissions from industrial operations and traffic have been fairly well characterized, smoke released during combustion of biofuels is poorly understood in terms of its chemical composition and physical properties. Biofuel combustion generates smoke particles which are predominantly of carbonaceous nature, consisting of an organic carbon (OC) and an elemental carbon (EC) fraction, the latter of which is at times mistakenly referred to as black carbon (BC) or soot. While the OC and EC fractions can be quantified by various methods, there is a large gap in our knowledge regarding the specific composition of OC in biofuel smoke particles. In fact, OC is composed of thousands of individual organic compounds with a wide range of chemical and physical properties. Recent advances in the
speciation of the OC fraction in smoke aerosol generated from biofuel combustion provide some new insights into the chemical and physical characteristics of such particles. For instance, it is now understood that biomass smoke particles contain a sizeable portion of higher molecular weight substances as well as polar organic compounds. However, much effort is still needed to better characterize emissions from biofuel combustion, which has to include source and near-source emissions measurements as well as better characterization of ambient aerosol influenced by biofuel/biomass smoke. This chapter will give an overview of the current state of knowledge regarding the chemical and physical properties of smoke aerosol released from biofuel combustion, by providing selected key references, and point out future research needs and directions.

2. Biofuel usage in Asia and China

In Asia, biofuel emissions are very substantial and have significant influence on regional air quality. Streets et al. (2003) estimated that the major biofuel emissions in Asia arose from the combustion of woods, animal waste (dung) and agricultural waste, and the high biofuel emission regions were mainly located in central and East China, Southeast Asia, and South Asia by spatial and rural population allocation. The average annual biofuel consumption in Asia was estimated to be 730 Tg from both anthropogenic and natural sources, with 45, 34 and 20% accounted for by forest burning, crop residue open burning and grassland/savanna burning, respectively. When allocated to countries, it was found that China contributed 25%, India 18%, Indonesia 13%, and Myanmar 8% of the total consumption. Regionally, forest fires in Southeast Asia dominated.

Tropical Southeast Asia is an active biofuel emission region as a result of increasing deforestation and agricultural activities (Stott, 1988; Christopher and Kimberly, 1996; Dwyer et al., 1998), including East-Central India and the region comprised by Thailand, Burma, Laos, Cambodia and Vietnam (Christopher and Kimberly, 1996). March and April constitute the intensive burning season in this region (Stott, 1988). The intensive fire activity resulting from burning of agricultural waste and shifting cultivation is clearly reflected by the fire hot spots derived from the Along Track Scanning Radiometer (ATSR) on board of a European Space Agency (ESA) satellite (Figure 1); these fires usually reach their full strength in March or April (Figure 2). The amount of biofuels burned in all tropical Asia is very large, which was estimated at about one-half of the amount burned in tropical America, and about one-third of the amount burned in tropical Africa (Liu et al., 1999).

China has a large rural population whose major energy source has been biofuels (crop residues, fuel woods, etc.) for the last several decades. It is not uncommon to see burning of wood and crop residues in kitchens and stoves in the countryside, and even in the surrounding regions of wealthy areas, such as Guangdong Province and Beijing. In addition, biofuel burning is often used as a convenient way of clearing vegetated areas in China (Figure 3). Based on the crop output data from 2001 to 2005, Yang et al. (2008) estimated that the generated annual average amount of crop residue was 3.04×10^6 t, and about 43% of this was burned in the field. According to the statistics of Guangdong Province, the annual consumption of fuel wood in Guangdong Province is about 5.13-6.00 Tg, and 30%-40% of the produced straws is used as biofuel. PM$_{2.5}$ mass concentrations derived from rice straw combustion can reach as much as 3557 Tg. There have been several literature reports of biofuel/biomass burning contributions to ambient air in China (Zhang et al., 2008; Zhang et al., 2010; Sang et al., 2011).
Fig. 1. The geographical distribution of fire hot spots in the tropics derived from ATSR data

(a) 1997

(b) 1998

(c) 1999

Fig. 2. Monthly variability of fire hot spots in the southeast Asian subcontinent (30°N, 90°E - 5°N, 115°E)
3. Combustion process

Biomass/biofuel burning can be divided into four types: forest fires, savanna or grassland fires, burning of crop residues in the field and domestic biofuel combustion. Here we refer to biofuels mainly in respect to biomass burned in domestic stoves and ovens for cooking and heat generation, in contrast to biomass that is openly burned on a larger scale, such as in wildfires. The main structural components of biomass/biofuels are the biopolymers cellulose (40-50%), hemicelluloses (20-30%) and lignins (15-35%) (Sergejewa, 1959; Petterson, 1984). Cellulose, a linear polymer composed of 7000-12000 D-glucose monomers, is the elementary fibrils and could form larger fiber structures (Sergejewa, 1959). Hemicelluloses, consisting of only about 100-200 sugar monomers, are mixtures of polysaccharides derived from glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid (4-OMGA), and galacturonic acid (Sergejewa, 1959; Pharham and Gray, 1984) and are less structured than cellulose molecules. The biofuel combustion processes could be summarized as the heating, flaming and smoldering phases. At the heating stage, biofuels are being hydrolyzed, oxidized, dehydrated and pyrolyzed to form tarry substances, volatiles and highly reactive carbonaceous char (Roberts, 1970; Shafizaden, 1984). When reaching the required temperature of the volatiles and tarry substance, the flaming combustion phase commences, which could provide enough energy for the gasification of the biofuel substrate, propagation of the fire and char formation until the combustible volatile flux drops below the minimum level required for the propagation of flaming combustion. Then the smoldering process starts and is best described as the gradual oxidation of the reactive char (solid phase combustion). Table 1 shows the characteristics of various combustion processes during the different combustion phases. The gas and particle-phase chemical species contained in the smoke released during biomass/biofuel include a large number of compounds with a wide range of chemical and physical properties, depending on biofuel type and combustion conditions. As it is beyond the scope of this chapter to give a comprehensive overview of the chemical smoke constituents, the reader is referred to some key literature (Andreae and Merlet, 2001; Hays et al., 2002; Christian et al., 2003; Akagi et al., 2010), while we will focus the discussion here on source-specific compounds, i.e., molecular tracers for biomass/biofuel combustion.
Combustion Stage | Process | Process Characteristics
--- | --- | ---
**Flaming Stage**
Solid Phase | Drying/Distilling Process | Water and volatile contents are removed or diffused into the inner layers of the bulk material
 | Pyrolysis Process | Starts at about 400 K Below 450 K the process is endothermic Above 450 K the process is exothermic Dehydrocellulose decomposition takes place
Glowing Combustion | Start at about 800 K if oxygen is present Resulting in char being oxidized
**Gas Phase** | The Flame | The emitted volatiles are converted to combustion products of low-molecular weight
**Smoldering Stage** | Smoldering Process | A low-temperature process Takes place at concentrations of oxygen as low as 5% Can proceed over days under conditions of high moisture

Table 1. Different combustion stages and the characteristics of different combustion processes

4. Molecular tracers for biomass burning processes

During the combustion, the cellulose molecules decompose by two pathways. When the temperature is <300 degrees C, biofuels are depolymerized, fragmented and oxidized to char. During the second pathway, i.e. > 300 degrees C, bond cleavage by transglycosylation, fission and disproportionation reactions give rise to the formation of levoglucosan, accompanied by its stereoisomers, mannosan (Man) and galactosan (Gal). (Simoneit et al., 1999; Schmidl et al., 2008b; Engling et al., 2009; Fabbri et al., 2009). Due to reasonable atmospheric stability with no decay over 10 days in acidic conditions, levoglucosan has been widely used as a molecular marker for biomass burning processes (Fraser and Lakshmanan, 2000), although it could be oxidized when exposed to gas phase hydroxyl radicals (OH) (Hennigan et al., 2010), nitrate (NO$_3$) or sulfate (SO$_4$) radicals (Hoffmann et al., 2010). Combustion of other materials (e.g., fossil fuels) or biodegradation and hydrolysis of cellulose does not produce any levoglucosan.

The typical bulk chemical composition of smoke particles derived from agricultural residues/fuels is shown in Figure 4 by the example of rice straw smoke particles. While OC being the predominant species in the carbonaceous fraction, chloride and potassium are the key components in the ionic fraction of smoke aerosol found in source emissions studies. As such, biomass burning plumes are generally characterized by high water-soluble potassium content, specifically enriched in the fine mode. Thus, potassium has also been used as source tracer to estimate the contributions of biomass burning smoke to the ambient aerosol burden (e.g., Duan et al., 2004). However, other sources, such as sea salt, mineral dust and meat cooking, contribute additional potassium to atmospheric PM (Lawson and Winchester, 1979; Morales et al., 1996; Schauer et al., 2002). This may cause a certain bias in the quantitative estimation of contributions from biomass burning emissions when using potassium as source tracer, although a correction for sea-salt contributions is possible. Potassium/levoglucosan ratios which could be utilized for the identification of open/stove
Fires are below 0.2 for wood combustion in fireplaces and ovens, while they approach 0.5 for open fires (Fine et al., 2001; Fine et al., 2002; Fine et al., 2004a; Puxbaum et al., 2007).

![Typical chemical composition of smoke particles derived from rice straw burning](image)

**Fig. 4.**

Table 2 gives a summary of ambient concentrations of levoglucosan, mannose and galactose in rural, suburban and urban regions around the world. Anhydrosugar concentrations at rural sites have been observed with the highest levels, reaching thousands of ng/m$^3$, while they were in the hundreds ng/m$^3$ levels in suburban and urban locations. The variability in these data is mainly influenced by the biofuel usage patterns and potential smoke transport.

<table>
<thead>
<tr>
<th>Location</th>
<th>Season</th>
<th>Particle Size</th>
<th>Levoglucosan (ng m$^3$) (Range (ave)/Ave±S.D.)</th>
<th>Mannose (ng m$^3$) (Range (ave)/Ave±S.D.)</th>
<th>Galactose (ng m$^3$) (Range (ave)/Ave±S.D.)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>Dry</td>
<td>PM$_{2.5}$</td>
<td>1182 - 6900 (2460)</td>
<td>6.0 - 371 (126)</td>
<td>2.3 - 148 (55.4)</td>
<td>Graham et al., 2002</td>
</tr>
<tr>
<td>Rural</td>
<td>Dry</td>
<td>PM$_{2.5}$</td>
<td>40 - 2660 (1180)</td>
<td>1.7 - 127 (49.5)</td>
<td>1.6 - 44.6 (22.7)</td>
<td>Graham et al., 2002</td>
</tr>
<tr>
<td>Rural</td>
<td>Dry</td>
<td>PM$_{2.5}$</td>
<td>446 - 4106 (2006)</td>
<td>21 - 259 (116)</td>
<td>7.6 - 61.5 (31)</td>
<td>Zdral et al., 2002</td>
</tr>
<tr>
<td>Rural</td>
<td>Dry</td>
<td>PM$_{2.5}$</td>
<td>1182 - 6900 (2460)</td>
<td>6 - 371 (126)</td>
<td>2 - 148 (55)</td>
<td>Simoneit et al., 2004</td>
</tr>
<tr>
<td>Rural</td>
<td>Dry</td>
<td>PM$_{2.5}$</td>
<td>284 - 7485 (2222)</td>
<td>23.7 - 543 (152)</td>
<td>7.7 - 261 (58.7)</td>
<td>Decesari et al., 2006</td>
</tr>
<tr>
<td>Rural</td>
<td>Dry</td>
<td>PM$_{2.5}$</td>
<td>763 - 7903 (3698)</td>
<td>34.0 - 345 (151)</td>
<td>16.4 - 193 (80.3)</td>
<td>Decesari et al., 2006</td>
</tr>
<tr>
<td>Suburban</td>
<td>Winter</td>
<td>PM$_{10}$</td>
<td>134 - 971 (407)</td>
<td>34 - 286 (116)</td>
<td>1.7 (2)</td>
<td>Yttri et al., 2007</td>
</tr>
<tr>
<td>Suburban</td>
<td>Winter</td>
<td>PM$_{10}$</td>
<td>232 - 971 (605)</td>
<td>56 - 286 (167)</td>
<td>1.1 - 6.8 (4.0)</td>
<td>Yttri et al., 2007</td>
</tr>
<tr>
<td>Suburban</td>
<td>Summer</td>
<td>PM$_{10}$</td>
<td>n.d. - 151 (47)</td>
<td>n.d. - 42 (10)</td>
<td>n.d. - 7.5 (3)</td>
<td>Yttri et al., 2007</td>
</tr>
<tr>
<td>Location</td>
<td>Season</td>
<td>Particle Size</td>
<td>Levoglucosan (ng m$^{-3}$) (Range (ave)/Ave±S.D.)</td>
<td>Mannosan (ng m$^{-3}$) (Range (ave)/Ave±S.D.)</td>
<td>Galactosan (ng m$^{-3}$) (Range (ave)/Ave±S.D.)</td>
<td>Reference</td>
</tr>
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<td>---------------</td>
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<td>-------------------------------------------------</td>
<td>----------------------------------------------</td>
<td>-----------------------------------------------</td>
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</tr>
<tr>
<td>Urban Winter</td>
<td>PM$_{10}$</td>
<td>121 - 1133 (477)</td>
<td>17.3 - 153 (66)</td>
<td>4.4 - 44.2 (19.6)</td>
<td>Zdrahal et al., 2002</td>
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<tr>
<td>Urban Winter</td>
<td>PM$_{10}$</td>
<td>420</td>
<td>61</td>
<td>25</td>
<td>Pashynska et al., 2002</td>
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<tr>
<td>Urban Summer</td>
<td>PM$_{10}$</td>
<td>19.1</td>
<td>3</td>
<td>1</td>
<td>Pashynska et al., 2002</td>
<td></td>
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<tr>
<td>Urban Winter</td>
<td>PM$_{10}$</td>
<td>121 - 1133 (477)</td>
<td>17 - 153 (66)</td>
<td>4 - 44 (20)</td>
<td>Simoneit et al., 2004</td>
<td></td>
</tr>
<tr>
<td>Urban Winter</td>
<td>TSP</td>
<td>6 - 56</td>
<td>0.2 - 15</td>
<td>0.6 - 2.4</td>
<td>Simoneit et al., 2004</td>
<td></td>
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<tr>
<td>Urban Winter</td>
<td>TSP</td>
<td>1162 - 33400 (14460)</td>
<td>154 - 4430 (1422)</td>
<td>84 - 2410 (1014)</td>
<td>Simoneit et al., 2004</td>
<td></td>
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<tr>
<td>Urban Winter</td>
<td>TSP</td>
<td>1350</td>
<td>108</td>
<td>106</td>
<td>Simoneit et al., 2004</td>
<td></td>
</tr>
<tr>
<td>Urban Winter</td>
<td>PM$_{10}$</td>
<td>n.d. - 475 (166)</td>
<td>n.d. - 155 (41)</td>
<td>n.d. - 17 (3)</td>
<td>Yttri et al., 2007</td>
<td></td>
</tr>
<tr>
<td>Urban Summer</td>
<td>PM$_{2.5}$</td>
<td>860 - 6090</td>
<td>330 - 1090</td>
<td>130 - 490</td>
<td>Ward et al., 2006</td>
<td></td>
</tr>
<tr>
<td>Urban Fall</td>
<td>PM$_{10}$</td>
<td>n.d. - 475 (193)</td>
<td>n.d. - 155 (52)</td>
<td>n.d. - 6.9 (1.7)</td>
<td>Yttri et al., 2007</td>
<td></td>
</tr>
<tr>
<td>Urban Yearly</td>
<td>PM$_{10}$</td>
<td>120 - 160(140)</td>
<td>18 - 44 (31)</td>
<td>5 - 12 (8.5)</td>
<td>Caseiro et al., 2009</td>
<td></td>
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<tr>
<td>Urban Yearly</td>
<td>PM$_{10}$</td>
<td>250 - 480 (380)</td>
<td>37 - 114 (84)</td>
<td>14 - 37 (28)</td>
<td>Caseiro et al., 2009</td>
<td></td>
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<tr>
<td>Urban Yearly</td>
<td>PM$_{10}$</td>
<td>150 - 220 (193)</td>
<td>27 - 40 (35)</td>
<td>7 - 12 (10)</td>
<td>Caseiro et al., 2009</td>
<td></td>
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<tr>
<td>Urban Winter</td>
<td>PM$_{10}$</td>
<td>430 - 1894 (901)</td>
<td>22 - 134 (54)</td>
<td>30 - 186 (96)</td>
<td>Xie et al., 2011</td>
<td></td>
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<tr>
<td>Urban Spring</td>
<td>PM$_{10}$</td>
<td>87 - 644 (261)</td>
<td>3.8 - 37 (15)</td>
<td>7.2 - 85 (30)</td>
<td>Xie et al., 2010</td>
<td></td>
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<tr>
<td>Urban Winter</td>
<td>PM$_{10}$</td>
<td>422 ± 165</td>
<td>71.2 ± 25.8</td>
<td>19.5 ± 7.67</td>
<td>Krumal et al., 2010</td>
<td></td>
</tr>
<tr>
<td>Urban Winter</td>
<td>PM$_{2.5}$</td>
<td>572 ± 71.3</td>
<td>105 ± 14.1</td>
<td>48.7 ± 2.92</td>
<td>Krumal et al., 2010</td>
<td></td>
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<tr>
<td>Urban Summer</td>
<td>PM$_{10}$</td>
<td>15.6 - 472.9</td>
<td></td>
<td></td>
<td>Zhang et al., 2010</td>
<td></td>
</tr>
<tr>
<td>Urban Spring</td>
<td>PM$_{2.5}$</td>
<td>26.2 – 133.7 (36.0)</td>
<td></td>
<td></td>
<td>Sang et al., 2011</td>
<td></td>
</tr>
<tr>
<td>Suburban Spring</td>
<td>PM$_{2.5}$</td>
<td>21.1 – 91.5 (30.0)</td>
<td></td>
<td></td>
<td>Sang et al., 2011</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Ambient concentrations of anhydrosugars reported in the literature
Table 3. The ratios of Lev/Man, Lev/Gal and Lev/(Gal+Man) for various types of biomass

The ratios of levoglucosan to other anhydrosugars in biomass burning smoke particles can be used to identify the specific biomass burning types. For example, levoglucosan to

<table>
<thead>
<tr>
<th>Biomass type</th>
<th>Combustion type</th>
<th>Location</th>
<th>Particle size</th>
<th>Lev/Man</th>
<th>Lev/Gal</th>
<th>Lev/(Gal+Man)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cereal straw</td>
<td>Chamber burn</td>
<td>China</td>
<td>PM$_{2.5}$</td>
<td>55.7</td>
<td>52.4</td>
<td></td>
<td>Zhang et al., 2007</td>
</tr>
<tr>
<td>Rice straw</td>
<td>Chamber burn</td>
<td>Taiwan</td>
<td>PM$_{2.5}$</td>
<td>40</td>
<td>14.0</td>
<td>10.3</td>
<td>Engling et al., 2009</td>
</tr>
<tr>
<td>Rice straw</td>
<td>Chamber burn</td>
<td>Bangladesh</td>
<td>PM$_{2.5}$</td>
<td>41.6</td>
<td>25.1</td>
<td>15.6</td>
<td>Sheesley et al., 2003</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>Chamber burn</td>
<td>Malaysia</td>
<td>TSP</td>
<td>12.7</td>
<td>12.7</td>
<td>6.4</td>
<td>Oros et al., 2006</td>
</tr>
<tr>
<td>Peat</td>
<td>Chamber burn</td>
<td>Sumatra, Indonesia</td>
<td>PM$_{10}$</td>
<td>11.4</td>
<td>28.1</td>
<td>8.1</td>
<td>Iinuma et al., 2007</td>
</tr>
<tr>
<td>Leaves</td>
<td>Open air burning</td>
<td>Lower-Austria</td>
<td>PM$_{10}$</td>
<td>5.5</td>
<td>1.3</td>
<td>1.0</td>
<td>Schmidl et al., 2008</td>
</tr>
<tr>
<td>Pine</td>
<td>Chamber burn</td>
<td>Germany</td>
<td>PM$_{10}$</td>
<td>3.8</td>
<td>5.0</td>
<td>2.1</td>
<td>Iinuma et al., 2007</td>
</tr>
<tr>
<td>Pine</td>
<td>Wildfire</td>
<td>Canada</td>
<td></td>
<td>2.5</td>
<td>10.0</td>
<td>2.0</td>
<td>Otto et al., 2006</td>
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<tr>
<td>Pine</td>
<td>Chamber burn</td>
<td>US</td>
<td>PM$_{2.5}$</td>
<td>3.0</td>
<td>12.6</td>
<td>2.4</td>
<td>Engling et al., 2006a</td>
</tr>
<tr>
<td>Spruce</td>
<td>Residential stove</td>
<td>Austria</td>
<td>PM$_{10}$</td>
<td>3.6</td>
<td>12.6</td>
<td>2.8</td>
<td>Schmidl et al., 2008</td>
</tr>
<tr>
<td>White spruce</td>
<td>Residential fireplace</td>
<td>Western US</td>
<td>PM$_{2.5}$</td>
<td>3.9</td>
<td>14.2</td>
<td>3.1</td>
<td>Fine et al., 2004</td>
</tr>
<tr>
<td>Douglas fir</td>
<td>Residential fireplace</td>
<td>Western US</td>
<td>PM$_{2.5}$</td>
<td>4.4</td>
<td>22.6</td>
<td>3.7</td>
<td>Fine et al., 2004</td>
</tr>
<tr>
<td>Hemlock</td>
<td>Residential fireplace</td>
<td>Northern-Eastern US</td>
<td>PM$_{2.5}$</td>
<td>3.7</td>
<td>38.7</td>
<td>3.4</td>
<td>Fine et al., 2001</td>
</tr>
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<td>Cottonwood</td>
<td>Chamber burn</td>
<td>US</td>
<td>PM$_{2.5}$</td>
<td>14</td>
<td>23.4</td>
<td>8.7</td>
<td>Engling et al., 2006a</td>
</tr>
<tr>
<td>Beech</td>
<td>Residential stove</td>
<td>Austria</td>
<td>PM$_{10}$</td>
<td>14.6</td>
<td>20.5</td>
<td>8.5</td>
<td>Schmidl et al., 2008</td>
</tr>
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<td>Musasa</td>
<td>Chamber burn</td>
<td>Africa</td>
<td>PM$_{10}$</td>
<td>22.7</td>
<td>25.0</td>
<td>11.9</td>
<td>Iinuma et al., 2007</td>
</tr>
<tr>
<td>White oak</td>
<td>Residential fireplace</td>
<td>Western US</td>
<td>PM$_{2.5}$</td>
<td>12.9</td>
<td>20.4</td>
<td>7.9</td>
<td>Fine et al., 2004</td>
</tr>
<tr>
<td>Sugar maple</td>
<td>Residential fireplace</td>
<td>Western US</td>
<td>PM$_{2.5}$</td>
<td>19.8</td>
<td>84.0</td>
<td>16.0</td>
<td>Fine et al., 2004</td>
</tr>
<tr>
<td>Red maple</td>
<td>Residential fireplace</td>
<td>Northern-Eastern US</td>
<td>PM$_{2.5}$</td>
<td>33.2</td>
<td>33.2</td>
<td></td>
<td>Fine et al., 2001</td>
</tr>
<tr>
<td>Red oak</td>
<td>Residential fireplace</td>
<td>Northern-Eastern US</td>
<td>PM$_{2.5}$</td>
<td>35.4</td>
<td>47.7</td>
<td>20.3</td>
<td>Fine et al., 2001</td>
</tr>
</tbody>
</table>
mannosan (Lev/Man) could be used to distinguish the biomass/biofuel types, such as softwood versus hardwood or coniferous versus deciduous wood (Ward et al., 2006; Oliveira et al., 2007; Pio et al., 2008; Schmidl et al., 2008a; 2008b; Engling et al., 2009). Galactosan is usually 10-50 times less abundant in smoke PM than levoglucosan and 1-3 times lower than mannosan levels (Schmidl et al., 2008a). The levoglucosan/galactosan (Lev/Gal) ratio, for example, has been used to distinguish smoke aerosol from leaf and wood burning (Schmidl et al., 2008a). Moreover, levoglucosan to mannosan (Lev/Man) and levoglucosan to mannosan plus galactosan (Lev/(Man+Gal)) ratios were proposed as discriminators of smoke aerosol from lignite and extant biomass due to the lower galactosan content in lignite (Fabbri et al., 2009).

Table 3 summarizes the typical Lev/Man ratios for various biomass/biofuels reported in the literature. Sheesley et al. (2003) reported a Lev/Man ratio in PM$_{2.5}$ for rice straw burning in Bangladesh of 41.6, similar to the ratio of 40 found for rice straw in Taiwan (Engling et al., 2009), while that of mixed cereal straw (wheat, rice and corn) in China was 55.7 (Zhang et al., 2007). Compared with rice straw burning, the ratios of sugarcane and bamboo smoke in the same grass family are relatively low with a range of 5-13, while that of peanuts in the bean family was in the range of sugarcane and bamboo (Oros et al., 2006; Iinuma et al., 2007) (Table 3). The Lev/Man ratio for soft wood (spruce, fir and pine) ranged from 3-6 in the US (Fine et al., 2001; Fine et al., 2004b) and 2.5-4 in Germany, Austria and Canada (Otto et al., 2006; Iinuma et al., 2007; Schmidl et al., 2008b) (Table 3). Fine et al. (2001; 2004b) and Engling et al. (2006a) showed that the Lev/Man ratios for hard wood (oak, maple, beech, cherry and aspen) varied from 13-35, while that of peanuts in the bean family was in the range of sugarcane and bamboo (Iinuma et al., 2007; Schmidl et al., 2008b) in Austria and Africa (Table 3). Thus, we could conclude that the Lev/Man ratios could be used to at least differentiate soft wood (2-6), hard wood (13-35), and crop residue (40-55.7).

5. Size-resolved composition of biomass burning smoke

The investigation of the size-resolved composition of biofuel burning smoke has recently gained attention in source/near source and ambient studies. Typically, biofuel smoke emissions are characterized by predominantly fine (<2.5 µm aerodynamic diameter) particles (Engling et al., 2006b), which has also been observed in ambient aerosol particles influenced by biomass/biofuel smoke (Wang et al., 2009). For instance, carbonaceous aerosol and biomass smoke markers in particular were found predominantly in submicron particles during a long-range transport episode of wood smoke affecting Yosemite National Park in California, US (Herckes et al., 2006). A temporal variation in PM size distributions suggested a certain dependence on the burning process or atmospheric processing of the smoke particles. In contrast, a substantial mass fraction of the anhydrosugar tracers, including levoglucosan, was recently found in aerosol particles with diameters larger than 10 µm in ambient aerosols (Lee et al., 2008), indicating possible influence by the ambient atmospheric conditions, such as high relative humidity, in addition to unique properties of the biofuel and the specific burning practices.

Likewise, a distinct bimodal distribution was observed with a large fraction of levoglucosan present in a super-coarse mode (>10 µm aerodynamic particle diameter) as well as a fine mode (<0.49 µm aerodynamic particle diameter) in a rice straw field burning study conducted by Engling et al. (2009) (Figure 5). In a more precise size distribution study, Wang et al. (2009) reported that concentrations of particulate matter (PM) mass, n-alkanes,
and low molecular weight (LMW) PAHs and levoglucosan showed a unimodal size distribution, peaking at 0.7-1.1 μm during the hazy days impacted by wheat straw burning, and a bimodal distribution, peaking at 0.7-1.1 μm and 4.7-5.8 μm in normal days.

![Graph showing size distribution of smoke particles](image)

Fig. 5. Levoglucosan size distributions based on 7 particle size ranges (<0.49 μm; 0.49–0.95 μm; 0.95–1.5 μm; 1.5–3 μm; 3–7.2 μm; 7.2–10 μm; and 10–50 μm) in smoke particles generated during field burning of rice straw

### 6. Chemical analysis methods

Much effort has been put into developing methods for the quantification of biomass burning products and particularly the smoke tracers, such as the anhydrosugars. Both gas chromatographic (GC) and aqueous-phase methods have been reported (Schkolnik and Rudich, 2006). The former methods are the most common ones with good separation and high sensitivity by utilizing mass spectrometric (MS) detectors (Zdrahal et al., 2002), but require complex sample preparation, large amounts of solvents, and expensive equipment. The latter ones, including Electrospray Ionization–Mass Spectrometry (ESI-MS) (Wan and Yu, 2006), Microchip Capillary Electrophoresis (microchip-CE) with Pulsed Amperometric Detection (PAD) (Garcia et al., 2005), Ion-exclusion Chromatography (IEC) (Schkolnik et al., 2005), High Performance Liquid Chromatography (HPLC) (Dye and Yttri, 2005; Dixon and Baltzell, 2006), and High Performance Anion Exchange Chromatography (HPAEC) coupled with PAD or MS (Engling et al., 2006a), have been developed more recently and are, therefore, at present applied less frequently for the quantification of levoglucosan and other biomass/biofuel combustion products. However, these methods are rapidly gaining attention due to their speed and no need for chemical derivatizations (Ma et al., 2010). The IEC-HPLC-PDA method, for instance, is suitable for measuring levoglucosan, inorganic ions and carboxylic acids in a large set of water-extracted aerosols or aqueous samples. HPLC-ESI-MS has been shown to completely separate levoglucosan from its isomers in concentrations ranging from background to polluted levels with short sample preparation, good separation and high sensitivity. However, for detailed organic speciation of smaller sets of samples, GC-MS analysis remains the method of choice to date.
Recently, stable carbon isotope analysis is emerging as a powerful tool to provide additional constraints on the atmospheric budgets, and to increase our understanding of source emissions and ambient aerosols influenced by biomass burning (Goldstein and Shaw, 2003; Huang et al., 2006) and secondary formation processes (Fisseha et al., 2009a). Stable carbon isotopic composition can be determined for both bulk material (e.g., total carbon) and for individual compounds (Hoefs, 1987; Flanagan et al., 2005). However, until recently few studies have applied stable isotope measurements to atmospheric chemistry and particularly for biomass burning aerosols (Rudolph, 2007). The measurement of isotopic ratios for the biomass burning tracer levoglucosan is still not explored because of the high polarity of the sugars and the resulting difficult separation. Martinelli et al. (2002) determined the bulk stable carbon isotopic composition of organic matter in aerosols in order to assess sugar cane sources. Rudolph et al. (1997) and Iannone et al. (2007) presented a new method named gas chromatography coupled to isotope ratio mass spectrometry (GC-C-IRMS) to determine the isotopic ratio of volatile organic carbons (VOCs). Fisseha et al. (2009a) determined the $\delta^{13}C$ values of formic, acetic and oxalic acid in ambient gas and aerosol phases using a wet oxidation method followed by isotope ratio mass spectrometry. The first chamber study of investigating the stable carbon isotopic composition of secondary organic aerosol (SOA) formed from ozonolysis of $\beta$-pinene was conducted by Fisseha et al. (2009b). As for biomass burning aerosols, O'Malley et al. (1997) and Czapiewski et al. (2002) determined the isotopic composition of the non-methane hydrocarbons in emissions from biomass burning by using a GC-MS/C/IRMS system.

7. Impact of biomass burning smoke

The influence of smoke emissions from biomass/biofuel burning on the immediate surroundings and on areas downwind of the fire activity can be manifold. In this section, findings from several case studies are used to demonstrate the significant impacts that can be exerted by biomass smoke particles. The importance of the impact of biomass burning in the tropics on atmospheric chemistry and biogeochemical cycles was pointed out in the early 1990s by Curtzen and Andreae (1990). South and Southeast Asia are the two major biomass burning source regions in the world with natural forest fires and human initiated burning activities (Haberle et al., 2001; Pochanart et al., 2003; Radojevic, 2003; Sheesley et al., 2003; Venkataraman et al., 2005; Hasan et al., 2009; Chang and Song, 2010; Ram and Sarin, 2010). Chan et al. (2000) first showed with in-situ sounding measurements, satellite data and trajectory analyses that the frequently observed springtime ozone enhancements in the lower troposphere over Hong Kong were due to photochemical reactions during the transport of ozone precursors originating from the upwind Southeast Asian subcontinent, where intensive biomass burning activities occur during each spring. The enhanced ozone accompanied with a layer of increased biomass burning tracers, such as methyl chloride and carbonaceous aerosol, was shown to further extend to other parts of subtropical south China, the east Asian coast and western Pacific (Chan et al., 2003a,b).

In addition, aircraft and mountain-top measurements have shown that smoke aerosol derived from biomass burning activities in Southeast and East Asia can be transported eastward towards (and across) the Pacific Ocean (Bey et al., 2001; Jacob et al., 2003; Ma et al., 2003b). Ma et al. (2003a) observed biomass burning plumes with enhanced fine particle potassium and CO concentrations originating from Southeast Asia during the experimental period of the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign in
March, 2001. Lin et al. (2010) observed elevated carbon monoxide (CO) mixing ratios in central Taiwan due to biomass burning activities in the Asian continent, including India, the Indochina Peninsula and south Coastal China from January to April 2008. Stohl et al. (2007) predicted that an air pollution plume in the upper troposphere over Europe on 24-25 March 2006 originated from Southern and Eastern Asia with the FLEXPART particle dispersion model. Most recently, it was shown that biomass (rice straw) smoke generated in the Philippines could be transported to southeast coastal China and can contribute to 16-28% of the ambient OC burden in the background atmosphere during spring (Zhang et al., 2011).

Fig. 6. Smoke pixels estimated from AVHRR on (left) October 7 and 12, and (right) November 28 and 30, 1997 during the Indonesian forest fire period in 1997. The borders indicate the coverage area of the satellite images.

During the extreme El Nino period in 1997, when agricultural burning went out of control and resulted in widespread forest fires in Indonesia, Chan et al. (2003b) showed that the smoke aerosol can span over large geographical regions to high latitudes of south China (Figure 6), while Thompson et al. (2001) reported that it can reach longitudinally as far as to the Indian Ocean. Chan et al. (2003b) further showed with evidence form in-situ ozonesonde measurements and empirical formulation results that such large-scale biomass burning can result in significant changes in atmospheric composition and radiative forcing in tropical...
and subtropical Asia and the western Pacific. Furthermore, Wang et al. (2007b) reported that plumes of biomass burning aerosols in South Asia had been extended to the Indian Ocean and the western Pacific Ocean.

The Tibetan Plateau is the largest plateau in the world, which exerts profound effects on the regional and global radiative budget and climate (Lau et al., 2006; Wang et al., 2006). However, scarce data of trace gases and aerosols were observed in this region, let alone biomass burning smoke aerosol. Chan et al. (2006) showed that pollution from active fire regions of Southeast Asia and South Asia had relatively strong impact on the abundance of O₃, trace gases and aerosols in the background atmosphere of the Tibetan Plateau.

According to the characteristic levoglucosan/mannosan (Lev/Man) ratios, Sang et al. (2011) identified for the first time that a mountain site in the Tibetan Plateau was affected by long-range transported biomass burning smoke derived from soft wood and crop residue burning in South/Southeast Asia, while a suburban site was mainly affected by local (residential) soft-wood burning. At a remote mountain site in the southeastern part of the Tibetan Plateau during spring, Engling et al. (2011) showed a substantial regional build-up of BC and other aerosol components during the dry period, accompanied by fire activities and transport of pollution from the nearby regions of Southeast Asia and the northern part of the Indian Peninsula (Figure 7). Moreover, BC and aerosol mass concentrations during episodic events were found to be comparable to those reported for certain large Asian cities, mainly due to influence from biomass/biofuel smoke.

Fig. 7. Daily average concentrations of PM₂.₅, PM₁₀, black carbon and rainfall at a remote mountain site in the southeastern Tibetan Plateau at Tengchong during April-May 2004.

In the highly developed Pearl River Delta, biomass smoke contributes a sizeable portion of the ambient aerosol mass as well, as shown by high concentrations of the biomass burning gas-phase tracer CH₃Cl (Chan et al., 2003a). The biomass burning smoke contributions to
fine particles were 3-19% (Wang et al., 2007a) and to organic carbon in PM$_{10}$ were 7.0-14% (Zhang et al., 2010) in Guangzhou. Aerosols in Beijing were heavily influenced by different kinds of biofuel burning all year long. The wheat harvest season in summer is the most intensive period, while biomass smoke influence could be detected in spring (due to field preparation burning) and autumn as well (burning of maize residue and fallen dead leaves) (Duan et al., 2004). The contributions from biofuel burning were 18-38% and 14-32% to the PM$_{2.5}$ and PM$_{10}$ organic carbon in Beijing, respectively (Zhang et al., 2008).

8. Conclusions

The combustion of biomass/biofuels for agricultural residue removal and domestic use (for cooking and heating) is a major source of smoke emissions, in addition to large-scale savanna and forest fires, on a global scale. The Asian continent in particular is a major source region of smoke aerosol. As most of these burning processes occur with little/no control and at low combustion efficiency, the amount of smoke emitted and the resulting effects on air quality and global climate are substantial. While important advances have been made lately, by conducting detailed source emissions studies and using novel chemical analysis methods for smoke particle characterization, the uncertainty in the estimates of biofuel smoke emissions and their environmental effects remains rather large. It is, therefore, critical to assess the particle-size dependent chemical composition and physical as well as optical properties of biomass/biofuel smoke particles in future source and ambient studies.

9. Acknowledgement

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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