Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia

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[1] Throughout South Asia biomass is commonly used as a fuel source for cooking and heating homes. The smoke from domestic use of these fuels is expected to be a major source of atmospheric particulate matter in the region and needs to be characterized for input in regional source apportionment models and global climate models. Biomass fuel samples including coconut leaves, rice straw, jackfruit branches, dried cowdung patties, and biomass briquettes manufactured from compressed biomass material were obtained from Bangladesh. The fuel samples were burned in a wood stove to collect and characterize the particulate matter emissions. The bulk chemical composition including total organic and elemental carbon, sulfate, nitrate, ammonium and chloride ions, and bulk elements such as potassium and sodium did not show conclusive differences among the biomass samples tested. Unique features, however, exist in the detailed organic characterization of the combustion smoke from the different sources. The organic compound fingerprints of the particulate matter are shown to be distinct from one another and distinct from North American wood fuels. Fecal stanols including 5β-stigmastanol, coprostanol, and cholestanol are found to be good molecular markers for the combustion of cowdung. Additionally, the patterns of methoxyphenols and plant sterols provide a unique signature for each biomass sample and are conducive as source apportionment tracers. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0399 Atmospheric Composition and Structure: General or miscellaneous; 1699 Global Change: General or miscellaneous; *KEYWORDS:* biomass aerosol, molecular marker, organic

1. Introduction

[2] Biomass burning continues to be a major source of atmospheric particulate matter throughout the globe due in part to its widespread use as fuel for heating homes and cooking [*Simoneit*, 2002]. Numerous studies have been devoted to characterizing emissions from common particulate matter sources including combustion of biomass fuel and fossil fuel commonly utilized in North America [*Elias et al.*, 1999; *Fine et al.*, 2001; *Fine et al.*, 2002; *Fraser et al.*, 1999; *Hawthorne et al.*, 1989; *Hawthorne et al.*, 1988; *Nolte et al.*, 1999; *Oros and Simoneit*, 2000; *Oros and Simoneit*, 2001a; *Oros and Simoneit*, 2001b; *Rogge et al.*, 1991; *Rogge et al.*, 1993d; *Rogge et al.*, 1998; *Schauer et*

al., 1999a; *Schauer et al.*, 1999b; *Simoneit et al.*, 1993]. Previous work has been reported that measured emissions of particulate matter mass, CO, and select PAH using a variety of biomass fuels and cook stoves from developing countries [*Ezzati et al.*, 2000; *Gupta et al.*, 1998; *Oanh et al.*, 2002; *Oanh et al.*, 1999; *Saksena et al.*, 1992; *Venkataraman et al.*, 2002; *Venkataraman and Rao*, 2001; *Zhang et al.*, 1999]. The primary purpose of those studies was to provide a basis for estimating exposure to persons using these devices and fuels daily and/or to compare stove efficiencies. This research is focused on fulfilling the need for detailed chemical characterization of biomass fuel emissions in South Asia to better understand the impact of these sources on regional air quality and climate change rather than individual health.

[3] As a result of the detailed characterization of source emissions, many molecular markers have been identified for various North American fuels and utilized in molecular

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[1]Deceased June 2001.

marker source apportionment models [*Hildemann et al.*, 1996; *Rogge et al.*, 1993e; *Schauer and Cass*, 2000; *Schauer et al.*, 1996, 2002a; *Zheng et al.*, 2002]. There are two distinct goals in evaluating the detailed chemical composition of biomass combustion emissions for molecular markers. The first is to identify unique molecular tracers for that particular plant species or biomass material. The second goal is to discover a generic tracer for biomass combustion emissions. Regarding the former objective, *Simoneit et al.* [1993] reported that hardwood smoke contains significant substituted syringyl and guaiacyl compounds, while softwood smoke contains significant resin acids and guaiacyl compounds. Similarly, *Fine et al.* [2001] recently recommended betulin as a species-specific molecular marker for Paper Birch, and juvabione and dehydrojuvabione as tracers for Balsam Fir. On the other end of the spectrum, several different suggestions have been offered for generic biomass smoke tracers. Levoglucosan was suggested as an organic tracer for biomass by *Simoneit et al.* [1999] and has been used in studies around the world as a tracer for wood smoke [*dos Santos et al.*, 2002; *Elias et al.*, 2001; *Fabbri et al.*, 2002; *Fraser and Lakshmanan*, 2000; *Schauer and Cass*, 2000; *Simoneit and Elias*, 2000; *Zdrahal et al.*, 2002]. In addition, nonmineral potassium has also been used as a molecular marker for wood smoke, but it has other sources in the atmosphere besides wood smoke [*Sheffield et al.*, 1994].

[4] The uniqueness of emission profiles has been exploited for source apportionment models, but that is not the sole purpose of such work. The chemical and physical properties of different emission aerosols are a critical input needed by global climate forcing models [*Seinfeld and Pandis*, 1998]. Characteristics such as aerodynamic diameter, refractive index, and hygroscopicity directly impact how the aerosol from a particular source will behave in the atmosphere [*Seinfeld and Pandis*, 1998]. Refractive index is controlled by the chemical composition of the aerosol. Currently, modelers use the organic to elemental carbon ratio to estimate the refractive index of an aerosol [*Seinfeld and Pandis*, 1998]. In biomass burning, it is the organic carbon that dominates the mass emission rate [*Schauer et al.*, 2001]. Therefore the detailed organic characterization of biomass aerosols is especially important for modeling atmospheric conditions in nonindustrialized regions where the major source of aerosols is biomass burning [*Seinfeld and Pandis*, 1998]. Characterization of the distribution of organic compounds of a particular source could also aid in better estimating hygroscopic properties for aerosols in different regions by providing more specific information. The polarity of the predominant organic components of biomass aerosols will affect the hygroscopic character of the ambient atmospheric aerosols, and therefore their potential as cloud condensation nuclei [*Saxena et al.*, 1995]. Because climate forcing by aerosols is more of a regional than global effect, characterization of primary aerosols indicative of a given region becomes valuable. Therefore any major polarity differences in the organic composition of aerosols from biomass combustion sources in South Asia as compared to North American wood smoke aerosols will be reflected in different hygroscopic properties of the regional aerosols.

[5] At this point in time, the hydroscopic properties of a mixed organic and inorganic aerosol cannot be predicted solely by considering the solubility of the organic constituents along with the inorganic salts [*Ansari and Pandis*, 2000; *Choi and Chan*, 2002; *Cruz and Pandis*, 2000]. However, delineating the major organic species in primary emission sources around the globe will provide direction for future research in modeling hygroscopic properties of atmospheric aerosols. For example, knowledge of the organic composition of secondary organic aerosol has enabled studies directed at modeling its hygroscopic properties [*Ansari and Pandis*, 2000].

[6] This paper focuses on biomass used as fuel in Bangladesh and South Asia. Biomass, rather than fossil fuel, is commonly used in households as fuel in cooking stoves because of economic considerations and availability in rural regions [*Sinha et al.*, 1998]. Additionally, biofuels are also used in rural industries and services and urban service establishments [*Levine*, 1991]. Dried cowdung is used throughout the region as a fuel source. However, such agricultural residues as coconut leaves, rice straw, and jackfruit branches vary within the region depending upon the local crop and the season [*Levine*, 1991]. The major biofuel used in India is still firewood, with annual consumption of cowdung 70% that of firewood, and crop residues consumption only 30% of firewood [*Levine*, 1991]. However, the usage of the three different classes of biofuel: firewood, cowdung, and agricultural residues, varies widely among different agroclimate regions [*Sinha et al.*, 1998]. Overall it is difficult from the surveys conducted in the region to accurately predict the fuel usage, and thus the potential source contributors. Compiling source information on the biofuels used in the region will enable the use of source apportionment models in order to provide a more accurate estimate of the different source contributions. This regional aerosol characterization could then be used to refine aerosol parameters in global climate models.

2. Experimental Methods

2.1. Fuel Acquisition

[7] Biomass fuel samples including coconut leaves, rice straw, jackfruit branches, dried cowdung patties, and biomass briquettes manufactured from compressed biomass material were obtained from several local markets near Dhaka, Bangladesh. Table 1 summarizes the specifics of the fuel acquisition. The samples are representative of the biomass fuel available in the area. The fuel was transported to the United States for testing during May of 1999.

[8] The purchased cowdung patties were compacted by hand and dried under the Sun. The diet of the cows consisted of mostly rice straw and grasses. Biomass briquettes are made of rice husk, a local crop residue. The rice husk is heated and compacted in locally manufactured briquetting machines. Biomass briquettes are used as a fuel for heating urban hotels and tea shops, and for melting bitumen used in road paving operations.

[9] Cowdung patties and rice straw are two of the most common fuels used in rural areas all over South Asia. Coconut leaves and branches are used mostly in the coastal areas where the trees grow well. Jackfruit branches are mostly used in Bangladesh and some parts of India including West Bengal. The biomass briquette burned in this study is used solely in Bangladesh; Indian biomass briquettes are

Table 1. Fuel Sample Acquisition Information

Biomass Sample	Market Location	Source
Coconut Leaves	N/A	Backyard of a household, Mirpur-2, Dhaka
Rice Straw	Amin Bazar, Gabtali, Dhaka	Savar, Dhaka
Cowdung Patties	Amin Bazar, Gabtali, Dhaka	Savar, Dhaka
Biomass Briquettes	Chiriakhana Road, Mirpur-2, Dhaka	N/A
Jackfruit Branches	Mirpur-1 Bus Terminal, Dhaka	Savar, Dhaka

composed with different raw materials and would be expected to have different emission profiles when burned.

2.2. Source Testing Procedure

[10] For the source testing, a Vermont Castings, Inc., Encore Model #2190 catalyst-equipped wood stove was used. The procedure has been described previously in the dissertation by Fine, but will be summarized briefly here [*Fine*, 2002]. A wood stove was used for burning the biomass in order to provide efficient collection of the smoke. Although *Venkataraman et al.* [2002] and *Venkataraman and Rao* [2001] have reported differences in emissions from typical cooking stoves used in India, the organic molecular markers emitted during combustion of a particular fuel would be expected not to vary too significantly relative to organic carbon emission rates averaged over the complete burn cycle. Fine discussed the differences in concentrations of wood smoke tracers normalized to organic carbon (mg/g organic carbon) for fireplace versus wood stove combustion [*Fine*, 2002]. The general pattern of tracer emission remained the same despite different burn conditions, but the normalized emission factors did vary in a systematic fashion [*Fine*, 2002]. The variation was not too large (i.e., less than a factor of two) as to disallow rough approximations within a source apportionment model; however, it was suggested that it would be best to incorporate a weighted composite of source profiles from different stove types [*Fine*, 2002]. The stove has a 0.076 m^3 firebox. The primary air control lever was used to maintain an oven temperature between 150 and 250°C during the main segment of the biomass burning tests. The maximum oven temperature for each biomass test and their burn rates are included in Table 2. The damper, which directs the emissions through the catalyst, was not used for this test. The biomass was placed in the firebox with approximately 5–10 stalks of rice straw for ignition. Approximately 0.5–2.0 kg of biomass was consumed with a burn time of around 2 hours, except for the coconut leaves and rice straw, which burned over a period of 30 min. Collection of emission samples began before ignition and continued until no particles were emitted. Calorific values were not measured for these biomass samples; however, *Sinha et al.* [1998] reported values of 3800 kcal/kg for agricultural residues and 3140 kcal/kg for dried cowdung (dung cake).

[11] The sample was taken from the flue, 3 m above the stove. The dilution source sampler used in this study has been described previously by *Hildemann et al.* [1989] with the specific configuration detailed by *Fine et al.* [2001]. The conditions in the dilution source sampler have been optimized for collection of particulate matter. The emissions are diluted 20 to 30 times with activated carbon- and HEPA-filtered air and travel in the residence chamber long enough to allow condensation of vapors onto particles. This is done at ambient temperature to simulate gas-particle partitioning as occurs in the atmosphere downstream of the emission source. The flow is then directed through 6 parallel AIHL-design cyclones with 2.5 μm aerodynamic diameter cutoff. The flow containing particles <2.5 μm passes from each cyclone to a separate sampling train. The sampling trains contain a combination of Teflon and quartz filters for particle collection followed by polyurethane foam (PUF) for organic vapor absorption. The Teflon filters were used for gravimetric mass determination, instrumental neutron activation analysis of trace metals, and ion chromatography. The quartz filters were used for elemental and organic carbon analysis and detailed organic analysis of extracts by gas chromatography-mass spectrometry (GC-MS).

2.3. Chemical Analysis

[12] Organic analysis of gas and particle phase compounds was done on the quartz fiber filters and PUFs collected in the dilution source sampler. The method used in this study to quantify semivolatile and particulate organic compounds from the filters and the gas phase organic compounds from the PUFs was described by *Schauer et al.* [1999a]. However, a few details of the technique have been improved. The internal standard used in this study is a mixture of 13 deuterated compounds including: n-dodecane-d_{26}, n-hexadecane-d_{34}, n-eicosane-d_{42}, n-octacosane-d_{58}, n-hexatriacontane-d_{74}, n-decanoic acid-d_{19}, n-heptadecanoic acid-d_{33}, phthalic 3,4,5,6-d_4 acid, benzaldehyde-d_6, 4,4′-dimethoxybenzophenone-d_8, acenaphthene-d_{10}, chrysene-d_{12}, and dibenz[ah]anthracene-d_{14}. The methylated and unmethylated fractions of the extract were analyzed by GC-MS on a Hewlett-Packard GC/MSD (MSD Model 5973) using a 30 m, 0.25 mm diameter 5MS capillary column (0.25 μm film thickness, Agilent Technologies).

[13] Although new solvents (i.e., methanol and methylene chloride) and new derivatization techniques (silylation) have been proposed for the analysis of organic aerosols, the well established methods used in the current paper have been employed to maintain consistency with past studies [*Rogge et al.*, 1991, 1993a, 1993b, 1993c, 1993d, 1994, 1997a, 1997b, 1998; *Schauer et al.*, 1999a, 1999b, 2001, 2002b, 2002c] to aid in source attribution. The multiple solvent extraction combining hexane and benzene-isopropyl alcohol extracts is excellent for both nonpolar and polar compounds. This is also used as the solvent mixture for standard preparation of compounds including organic acids and levoglucosan. Although silylation can be employed to analyze polar compounds such as levoglucosan, silylation is not needed unless even more polar compounds are sought, such as glucose and monoglycerides. The accurate analysis of levoglucosan as an underivatized polar compound has been demonstrated in the past by *Nolte et al.* [2001] and *Schauer et al.* [2001]. These two studies used the same wood smoke samples, but *Nolte et al.* [2001] silylated the extracts while *Schauer et al.* [2001] quantified levoglucosan in the underivitized fraction. The average ratio of the levoglucosan and other polyhydroxylated compounds quan-

Table 2. Bulk Chemical and Metal Emissions[a]

	Coconut Leaves	Rice Straw	Cowdung	Biomass Briquettes	Jackfruit Branches
Average Fine Particle Emission Rate (Expressed as g kg^{-1} of Biomass Burned)					
Average rate ± SD	**3.1 ± 0.5**	**6.2 ± 1.0**	**8.5 ± 1.4**	**2.5 ± 0.4**	**6.9 ± 1.1**
Combustion Parameters					
Burn rate, kg/hr	2.3	9.0	3.5	2.0	2.2
Maximum stove temperature, °C	220	150	220	200	180
Fine Particle Chemical Composition of Emissions (Expressed as wt % of Fine Particle Mass)					
Organic carbon[b]	**49.4 ± 3.0**	**56.3 ± 3.0**	**47.8 ± 2.4**	**55.1 ± 2.9**	**53.9 ± 2.8**
Elemental carbon	**11.4 ± 1.1**	**1.10 ± 0.22**	**0.60 ± 0.07**	**1.12 ± 0.18**	**1.98 ± 0.18**
Ionic Species					
Sulfate	**1.01 ± 0.13**	**0.35 ± 0.04**	**0.92 ± 0.02**	**0.41 ± 0.03**	**0.22 ± 0.02**
Nitrate	**0.32 ± 0.12**	**0.08 ± 0.04**	**0.08 ± 0.02**	**0.24 ± 0.03**	**0.20 ± 0.02**
Ammonium	**1.23 ± 0.04**	**0.30 ± 0.01**	**1.10 ± 0.03**	**0.67 ± 0.01**	**0.09 ± 0.01**
Chloride	**7.43 ± 0.68**	**3.18 ± 0.22**	**4.73 ± 0.09**	**3.15 ± 0.17**	**1.44 ± 0.12**
Metals by INAA					
Sodium	**1.610 ± 0.030**	**0.013 ± 0.003**	**0.186 ± 0.004**	**0.015 ± 0.003**	**0.008 ± 0.001**
Magnesium	0.020 ± 0.026	0.000 ± 0.013	0.000 ± 0.025	0.000 ± 0.013	0.000 ± 0.006
Aluminum	0.000 ± 0.023	0.000 ± 0.008	0.000 ± 0.031	0.000 ± 0.079	0.000 ± 0.040
Chlorine	**7.03 ± 0.42**	**3.05 ± 0.18**	**4.36 ± 0.25**	**2.96 ± 0.17**	**1.277 ± 0.074**
Potassium	**3.04 ± 0.38**	**2.50 ± 0.15**	**2.007 ± 0.079**	**1.34 ± 0.13**	**1.166 ± 0.070**
Titanium	0.000 ± 0.030	0.000 ± 0.011	0.000 ± 0.048	0.000 ± 0.011	0.000 ± 0.006
Vanadium	0.000 ± 0.025	0.000 ± 0.009	0.000 ± 0.043	0.000 ± 0.009	0.000 ± 0.005
Chromium	0.000 ± 0.19	0.000 ± 0.092	0.001 ± 0.001	0.000 ± 0.005	0.000 ± 0.025
Manganese	**0.001 ± 0.000**	**0.001 ± 0.000**	**0.001 ± 0.000**	**0.001 ± 0.000**	0.000 ± 0.000
Iron	0.000 ± 0.043	0.000 ± 0.013	0.000 ± 0.008	0.000 ± 0.011	0.000 ± 0.003
Cobalt	**0.001 ± 0.000**	0.000 ± 0.29	**0.000 ± 0.000**	**0.001 ± 0.000**	0.000 ± 0.000
Zinc	0.000 ± 0.008	0.000 ± 0.044	**0.043 ± 0.003**	0.003 ± 0.002	0.000 ± 0.001
Arsenic	0.000 ± 0.025	0.000 ± 0.005	0.001 ± 0.001	0.000 ± 0.003	0.000 ± 0.001
Selenium	0.000 ± 0.032	0.000 ± 0.018	0.000 ± 0.006	0.000 ± 0.014	0.000 ± 0.005
Bromine	**0.055 ± 0.008**	0.000 ± 0.007	**0.014 ± 0.002**	0.000 ± 0.000	0.000 ± 0.000
Strontium	0.000 ± 0.082	0.000 ± 0.029	0.000 ± 0.019	0.000 ± 0.030	0.000 ± 0.014
Molybdenum	0.000 ± 0.17	0.000 ± 0.057	0.000 ± 0.024	0.000 ± 0.044	0.000 ± 0.017
Cadmium	0.000 ± 0.016	0.000 ± 0.004	**0.001 ± 0.000**	0.000 ± 0.004	0.000 ± 0.002
Antimony	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
Cesium	0.000 ± 0.43	0.000 ± 0.16	0.000 ± 0.009	0.000 ± 0.13	0.000 ± 0.042
Barium	0.000 ± 0.28	0.000 ± 0.000	0.000 ± 0.069	0.004 ± 0.027	0.000 ± 0.000
Lanthanum	**0.003 ± 0.000**	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
Cerium	0.005 ± 0.017	0.000 ± 0.027	0.000 ± 0.009	0.002 ± 0.005	0.000 ± 0.007
Neodymium	0.000 ± 0.035	**0.008 ± 0.003**	0.000 ± 0.006	**0.007 ± 0.002**	**0.002 ± 0.001**
Gold	0.000 ± 0.006	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.001
Mercury	0.000 ± 0.000	0.000 ± 0.014	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
Thorium	0.000 ± 0.019	0.001 ± 0.002	0.000 ± 0.000	0.001 ± 0.001	0.000 ± 0.001

[a]Values in bold are at least 2 standard deviations greater than zero.
[b]The organic carbon value represents the mass of organic carbon only and does not include any estimation factor to compensate for the H, O, N, and S present in organic compounds.

tified by *Schauer et al.* [2001] to the amount measured by *Nolte et al.* [2001] was 0.99 ± 0.14 (average ± standard deviation, n = 6).

[14] The uncertainty expressed for the organic compounds analyzed by GC-MS is calculated using the standard deviation of the relative response factors (rrf) for the quantification standards injected multiple times throughout the GC-MS analysis period. The compounds that do not have an exact equivalent in the standards use the rrf and uncertainty from a compound in the same class with similar polarity and molecular weight. The footnotes in Table 3 and the second column in Table A1 (Table A1 is available as electronic supporting material[1]) state how

each compound was quantified/identified with symbols explained at the end of the table. This method of identification and quantification has been reported in the past for detailed organic analysis of atmospheric aerosol sources [*Fine et al.*, 1999, 2001, 2002; *Hannigan et al.*, 1998; *Hays et al.*, 2002; *Mazurek et al.*, 1987; *Rogge et al.*, 1991, 1994; *Schauer et al.*, 1999a; 1999b; *Schauer et al.*, 2001, 2002b, 2002c] and is expected to introduce relatively small additional uncertainties due to the fact that response factors vary minimally within a compound class. For example, the range of response factors for PAH (molecular weight 178–276) is only 1.39 to 2.25, and for alkanoic acids (octanoic acid to dodecanoic acid) is 3.1 to 4.2.

[15] Elemental and organic carbon fractions were determined using a segment of the quartz filters by the NIOSH 5040 method of thermal evolution and combustion [*Birch and Cary*, 1996]. Ionic species including sulfate, nitrate, and chloride were determined by ion chromatography (Dionex Corp. Model 2020i) [*Mulik et al.*, 1976]. Ammo-

Table 3. Emission Concentration of Select Particle-Phase Organic Compounds in Mass Per Total Aerosol Mass (μg mg^{-1})[a]

Compound Note	Coconut Leaves	Rice Straw	Cowdung	Biomass Briquettes	Jackfruit Branches
		Aromatic Hydrocarbons			
2-Phenylnaphthalene[d]	0.30 ± 0.06	0.07 ± 0.01	0.19 ± 0.04	0.13 ± 0.03	0.09 ± 0.02
Fluoranthene[b]	1.26 ± 0.27	0.26 ± 0.05	0.64 ± 0.14	0.87 ± 0.18	0.46 ± 0.10
Acephenanthrylene[c]	0.58 ± 0.12	0.10 ± 0.02	0.24 ± 0.05	0.42 ± 0.09	0.21 ± 0.04
Pyrene[b]	1.34 ± 0.27	0.25 ± 0.05	0.54 ± 0.11	0.96 ± 0.19	0.48 ± 0.10
C$_1$-202 MW PAH[c]	1.99 ± 0.11	0.38 ± 0.03	1.22 ± 0.07	1.73 ± 0.10	1.28 ± 0.07
Retene[b]	1.67 ± 0.22	0.12 ± 0.02	0.22 ± 0.03	0.24 ± 0.03	0.14 ± 0.02
Benzo[ghi]fluoranthene[b]	0.36 ± 0.06	0.04 ± 0.01	0.10 ± 0.02	0.22 ± 0.04	0.14 ± 0.02
Cylcopenta[cd]pyrene[b]	1.07 ± 0.11	0.11 ± 0.01	0.27 ± 0.03	0.75 ± 0.08	0.55 ± 0.06
Benz[a]anthracene[b]	0.49 ± 0.08	0.06 ± 0.01	0.20 ± 0.03	0.34 ± 0.05	0.25 ± 0.04
Chrysene/triphenylene[b]	0.50 ± 0.08	0.07 ± 0.01	0.26 ± 0.04	0.41 ± 0.06	0.28 ± 0.04
C$_2$-202 MW PAH[d]	1.07 ± 0.48		0.65 ± 0.28	0.67 ± 0.29	0.79 ± 0.34
Benzo[b]fluoranthene[b]	0.30 ± 0.05	0.03 ± 0.01	0.12 ± 0.02	0.35 ± 0.06	0.14 ± 0.02
Benzo[k]fluoranthene[b]	0.37 ± 0.07	0.03 ± 0.01	0.10 ± 0.02	0.40 ± 0.08	0.14 ± 0.03
Benzo[j]fluoranthene[c]	0.20 ± 0.03	0.02 ± 0.00	0.06 ± 0.01	0.28 ± 0.05	0.09 ± 0.02
Benzo[e]pyrene[c]	0.26 ± 0.04	0.02 ± 0.00	0.09 ± 0.01	0.30 ± 0.05	0.10 ± 0.02
Benzo[a]pyrene[c]	0.51 ± 0.09	0.04 ± 0.01	0.14 ± 0.02	0.63 ± 0.11	0.19 ± 0.03
Perylene[b]	0.08 ± 0.01	0.01 ± 0.00	0.02 ± 0.00	0.12 ± 0.02	0.03 ± 0.01
Indeno[cd]fluoranthene[c]	0.22 ± 0.02			0.23 ± 0.02	0.05 ± 0.00
Indeno[cd]pyrene[b]	0.39 ± 0.05	0.02 ± 0.00	0.12 ± 0.01	0.48 ± 0.06	0.13 ± 0.02
Benzo[ghi]perylene[b]	0.37 ± 0.07	0.02 ± 0.00	0.09 ± 0.02	0.45 ± 0.08	0.11 ± 0.02
Anthanthrene[c]	0.15 ± 0.02	0.01 ± 0.00	0.03 ± 0.00	0.22 ± 0.03	0.05 ± 0.01
Coronene[b]	2.31 ± 0.02		0.34 ± 0.11	2.43 ± 0.81	0.52 ± 0.17
		Sugar Anhydricles			
Levoglucosan[b]	27.9 ± 5.3	18.3 ± 3.5	19.1 ± 3.6	98.4 ± 18.7	44.5 ± 8.5
Galactosan[c,e]		0.73 ± 0.14		2.80 ± 0.53	1.23 ± 0.23
Mannosan[c,e]		0.44 ± 0.08	0.65 ± 0.12	1.02 ± 0.19	1.35 ± 0.26
Other Sugars[c]	0.66 ± 0.13	0.45 ± 0.08	1.11 ± 0.21	8.40 ± 1.15	2.97 ± 0.40
		Substituted Phenols			
Catechol[c]		2.67 ± 0.52	14.6 ± 2.8	1.28 ± 0.25	3.08 ± 0.60
Hydroquinone[c]		1.96 ± 0.38		4.40 ± 0.86	
Resorcinol[c]		0.54 ± 0.11			2.95 ± 0.58
Methylbenzenediols[c]		3.82 ± 0.73	5.9 ± 1.1	3.72 ± 0.71	8.5 ± 1.6
Hydroxybenzaldehydes[b]	1.60 ± 0.22	0.98 ± 0.13	5.00 ± 0.62	4.21 ± 0.70	1.66 ± 0.22
3,5-Dihydroxytoluene[c]		0.72 ± 0.14			
4-Ethylcatechol[c]		2.38 ± 0.26	8.29 ± 0.91	3.29 ± 0.36	6.66 ± 0.73
1-(3-Hydroxyphenyl)-ethanone[d]				3.71 ± 0.94	2.37 ± 0.60
1-(2-Hydroxyphenyl)-ethanone[d]	1.56 ± 0.39	1.01 ± 0.26			
4-Hydroxyacetophenone[d]					0.76 ± 0.18
Methyl 4-hydroxy-benzenepropanoate[d]				4.9 ± 1.2	0.90 ± 0.23
Methyl 3-(4-hydroxyphenyl)-2-propenoate[d]			3.73 ± 0.94	6.9 ± 1.8	
		Guaiacyl Compounds			
Guaiacol[b]	0.22 ± 0.04		0.04 ± 0.01		0.05 ± 0.01
4-Methylguaiacol[c]		0.06 ± 0.01		0.07 ± 0.01	0.08 ± 0.01
4-Ethylguaiacol[c]	0.20 ± 0.04	0.18 ± 0.03	0.07 ± 0.01		0.16 ± 0.03
4-Propylguaiacol[c]					0.11 ± 0.02
Eugenol[b]					
cis-Isoeugenol[c]					
trans-Isoeugenol[c]	0.54 ± 0.06	0.46 ± 0.05			0.84 ± 0.09
Vinylguaiacol[c]	0.23 ± 0.05	0.47 ± 0.09	0.43 ± 0.08	0.28 ± 0.06	0.24 ± 0.05
Vanillin[b]		2.77 ± 0.08	6.07 ± 0.17		2.73 ± 0.08
Acetovanillone[b]		0.83 ± 0.20	3.47 ± 0.83	2.41 ± 0.58	2.95 ± 0.71
Guaiacyl acetone[c]			27.1 ± 6.9	34.2 ± 8.6	27.4 ± 7.0
Propyl alcohol guaiacol[c]	6.07 ± 1.54	1.06 ± 0.27	4.7 ± 1.2	12.8 ± 3.2	8.5 ± 2.2
Coniferyl aldehyde[b]	15.6 ± 4.1	2.70 ± 0.70		27.7 ± 7.2	28.8 ± 7.5
		Syringyl Compounds			
Syringol[b]	14.8 ± 3.8	5.51 ± 1.40	2.16 ± 0.55		4.6 ± 1.2
Methylsyringol[c]	32.9 ± 8.2	2.91 ± 0.73	2.26 ± 0.56	1.33 ± 0.33	10.7 ± 2.7
Ethylsyringol[c]	35.4 ± 9.0	3.82 ± 0.97	4.2 ± 1.0		21.0 ± 5.3
Propylsyringol[c]	13.4 ± 3.4	1.18 ± 0.30	2.07 ± 0.52	1.88 ± 0.48	14.5 ± 3.7
Allylsyringol[c]	9.86 ± 2.47	0.99 ± 0.25	2.06 ± 0.52	0.77 ± 0.19	8.2 ± 2.0
4-Propenylsyringol[c]	1.33 ± 0.33	3.08 ± 0.77	3.28 ± 0.82	2.15 ± 0.54	32.7 ± 8.2
Syringaldehyde[b]	10.3 ± 2.6	1.76 ± 0.45	4.5 ± 1.1	12.4 ± 3.1	20.0 ± 5.1
Acetosyringone[b]	1.62 ± 0.26	1.46 ± 0.23	3.86 ± 0.61	5.95 ± 0.94	4.73 ± 0.75
Acetonyl syringol[c]	19.6 ± 5.0	4.41 ± 1.12	14.5 ± 3.7	37.5 ± 9.5	51 ± 13
Propionyl syringol[c]	4.34 ± 1.1	1.22 ± 0.31	3.88 ± 0.98	8.2 ± 2.1	10.6 ± 2.7
Sinapyl aldehyde[b]	2.04 ± 0.11			2.31 ± 0.13	11.4 ± 0.6
4-Propanalsyringol[c]					11.2 ± 2.8

Table 3. (continued)

Compound Note	Coconut Leaves	Rice Straw	Cowdung	Biomass Briquettes	Jackfruit Branches
		Sterols and Stanols			
β-Tocopherol[c]	0.74 ± 0.42	0.24 ± 0.13	1.8 ± 1.0	1.74 ± 0.98	
Coprostanol[c,e]			9.3 ± 3.0		
Stigmastan-3,5-diene[d]	0.00 ± 0.00	2.62 ± 0.85	5.9 ± 1.9	7.3 ± 2.4	5.4 ± 1.8
Vitamin E[b]	1.01 ± 0.57	0.55 ± 0.31	3.2 ± 1.8	2.2 ± 1.2	0.33 ± 0.18
Cholestanol[c,e]			1.62 ± 0.53		
Campesterol[c,e]		5.6 ± 1.8	7.8 ± 2.6	10.5 ± 3.4	2.12 ± 0.69
Stigmasterol[b]		7.9 ± 2.6	8.6 ± 2.8	9.5 ± 3.1	2.79 ± 0.91
5β-Stigmastanol[c]			19.3 ± 6.3		
β-Sitosterol[c,e]	5.39 ± 1.76	10.6 ± 3.4	17.0 ± 5.5	30.6 ± 10.0	12.4 ± 4.0
5α-Stigmastanol[c,e]			6.7 ± 2.2		
Stigmasta-3,5-dien-7-one[d]		1.75 ± 0.57	5.2 ± 1.7	18.8 ± 6.1	1.38 ± 0.45
		Other Compounds			
Hexadecanamide[e]			0.78 ± 0.14	0.26 ± 0.05	0.07 ± 0.01
Octadecanamide[e]			0.71 ± 0.11		
Squalene[b]	7.88 ± 0.23		1.28 ± 0.04	0.75 ± 0.02	2.05 ± 0.06

[a]Values not reported for compounds whose concentration in a sample is within 3 times the concentration in the blank.
[b]Quantified by authentic standard.
[c]Quantified using authentic standard with similar structure and volatility.
[d]Identified by mass spectra and quantified with a surrogate standard.
[e]Identified by qualitative standard.

nium was determined by indophenol colorimetric procedure using an Alpkem rapid flow analyzer (model RFA-300) [*Bolleter et al.*, 1961]. Trace metal concentrations were determined by instrumental neutron activation analysis (INAA) [*Olmez*, 1989].

3. Results and Discussion
3.1. Bulk Chemical and Metal Emissions

[16] This discussion will focus on the chemistry of the particulate phase, as it is more useful in molecular marker source apportionment models. The mass emission data in Table 2 are consistent with published emissions for North American wood smoke [*Fine et al.*, 2001, 2002; *Schauer et al.*, 2001]. The organic carbon emissions for all samples are very consistent, as shown in Table 1. The mean value of the organic carbon emission is 52.5 weight percent of the fine particle mass aerosol with a standard deviation of 3.7. It should be noted that organic carbon emission is given in the table and not organic matter emission. The estimated organic matter mass values can be seen in Figure 1. The elemental carbon emission values show little variability among the biomass samples except for the coconut leaves. At 11.4%, the coconut leaf emission of elemental carbon is almost ten times the emission of the other biomass samples. The emission of the ionic species is also quite similar for all samples. Again, the coconut leaves show the highest emission for all the ionic species. Chlorine is the third highest single element emitted from coconut leaves and jackfruit branches, after organic and elemental carbon, but the fraction emitted by coconut leaves is about twice that of any other sample in this study. Regarding the high chlorine emission of the coconut leaves, it has been shown that salt (NaCl and/or KCl) applied by growers to enhance production increases the chlorine and sodium content of coconut leaves and decreases the potassium content [*Remison et al.*, 1988]. Since chlorine content depends upon the amount of salt applied to a particular plant, it varies among coconut leaves combustion emission samples, and the value reported in Table 1 cannot be assumed to be representative of all

possibilities. There is good agreement between the INAA (instrumental neutron activation analysis) chlorine measurements and the ion chromatography chloride measurements. This agreement indicates that all of the chlorine is water soluble.

[17] The particulate phase metal concentrations were analyzed by INAA. Few of the metals analyzed were above detection after blank subtraction. Potassium emissions were measured in all five biomass samples at significant levels, ranging from 1.34% for biomass briquettes to 3.04% for coconut leaves. As mentioned in the introduction, potassium has been proposed as a potential molecular marker for biomass combustion emission. However, as for coconut leaves, growing conditions may have too much of an impact on the final concentration of potassium in any given plant for it to be successfully predicted in the combustion emissions of that species, let alone throughout biomass in general. It has also been reported that the emission of potassium from meat cooking is significant enough to be a confounding factor when apportioning ambient concentrations [*Hildemann et al.*, 1991; *Rogge et al.*, 1991; *Schauer et al.*, 1999a]. The sodium levels of coconut leaf emissions are also significant in comparison to the total mass, but lower than chlorine despite their both resulting in part from salting of the plants by the growers, as discussed previously. As for trace metals, cowdung smoke has measurable quantities of zinc and bromine. There is also a small amount of bromine present in the coconut leaves emission. Trace metals are not a significant contributor to the total particulate emissions from the combustion of these biomass sources. A few trace elements were not measured by the INAA technique including silicon, phosphorus, and sulfur. However, previous biomass combustion emission profiles indicate that these are present only in trace amounts, not exceeding 1.00 weight percent of the total particulate mass emissions [*Fine et al.*, 2001, 2002; *Schauer et al.*, 2001].

3.2. Bulk Chemistry Mass Balance

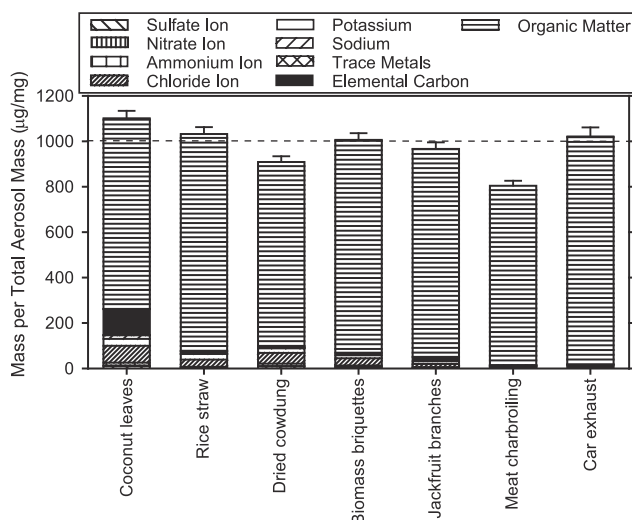[18] As expected, the organic matter mass dominates the emission profile in Figure 1. For almost all of the biomass

Figure 1. Mass balance of bulk composition for Bangladeshi biomass samples, meat charbroiling and noncatalyst, gasoline-powered motor vehicle exhaust. Meat charbroiling and car exhaust reported previously [*Schauer et al.*, 1999a, 2002b]. Organic matter values for Bangladeshi biomass smoke are estimated using a factor of 1.7 (see text for details).

samples, the organic mass is >90% of the total mass of identified species present in the particulate matter emissions. Jackfruit twigs had the highest percentage at 95%, while coconut leaves emission had the lowest at 76%. The emission profiles for charbroiling meat and noncatalyst, gasoline-powered motor vehicles show the same dominance of organic matter [*Schauer et al.*, 1999a, 2002c]. A ratio of 1.7 ± 0.3 was used to estimate organic matter mass from the organic carbon mass values by assuming that the balance mass is primarily composed of the hydrogen, oxygen, nitrogen, etc. that is associated with the organic carbon in organic matter. To determine an appropriate organic mass to carbon mass ratio, organic mass was initially estimated for each biomass sample by closing the mass balance using the species detailed in Figure 1. An organic mass to carbon mass ratio was calculated for each biomass sample and the average, 1.7, was then used to produce the final mass balances for all five biomass samples shown in Figure 1. This ratio parallels the ratio suggested by *Turpin and Lim* [2001] for urban aerosols (1.6 ± 0.2), and is lower than their suggested ratios for nonurban (2.1 ± 0.2), and heavily wood smoke-impacted aerosols (2.2–2.6). Traditionally, a value of 1.2 to 1.4 [*Countess et al.*, 1980; *Japar et al.*, 1984; *White and Roberts*, 1977] has been used to estimate organic matter, however, *Turpin and Lim* [2001] suggest that a higher ratio of 2.2 to 2.6 can be expected in aerosol impacted by wood smoke. One reason for the suggested higher ratio in wood smoke aerosols is the abundance of levoglucosan, which has an organic mass to carbon mass ratio of 2.25. These Bangladeshi biomass emissions, however, are not dominated by levoglucosan emissions, but emit a wide variety of compounds with lower organic mass to carbon mass ratio, such as syringyl and guaiacyl compounds, sterols, and alkanoic acids. The use of any standardized organic mass ratio can affect the accuracy of mass

balances, for the actual ratio of total mass to carbon mass will vary among different biomass emissions because of differences in organic composition. For example, the ratios calculated in this paper range from 1.5 for coconut leaves to 1.9 for dried cowdung. The profiles for meat charbroiling and noncatalyst, gasoline-powered motor vehicles used 1.4 and 1.2, respectively, for calculation of organic matter when originally published [*Schauer et al.*, 1999a, 2002c]. Since the organic component of noncatalyst, gasoline-powered motor vehicle exhaust is primarily composed of nonaromatic hydrocarbons, the ratio of 1.2 closes the mass balance quite well [*Schauer et al.*, 2002c].

[19] Figure 2 depicts bulk chemical composition excluding organic matter in order to allow better visualization of the smaller bulk chemical fractions. A similar trend for bulk chemicals in all samples can be seen, despite differences in actual values. If the large elemental carbon fraction is temporarily disregarded, the coconut leaves emission composition more closely parallels the other four biomass samples. Therefore bulk chemical composition could not easily be used to distinguish these biomass samples from one another nor from other sources. The high levels of elemental carbon in the coconut leaf smoke stands out among the sources shown in Figure 2. However, in the larger framework of combustion source profiles, elemental carbon concentrations are heavily influenced by diesel exhaust, which is comprised of a much higher elemental carbon fraction (30.8 ± 2.6 weight percent of fine particle mass) [*Schauer et al.*, 1999b]. For this reason, elemental carbon should not be used as a unique tracer for coconut leaf smoke. Only minor ionic species were emitted from the noncatalyst, gasoline-powered motor vehicle exhaust, but the elemental carbon emission is of the same magnitude as biomass, excluding coconut leaves. The bulk chemical emissions for the meat charbroiling reveal only low levels of ionic species and potassium. This illustrates the difficulty
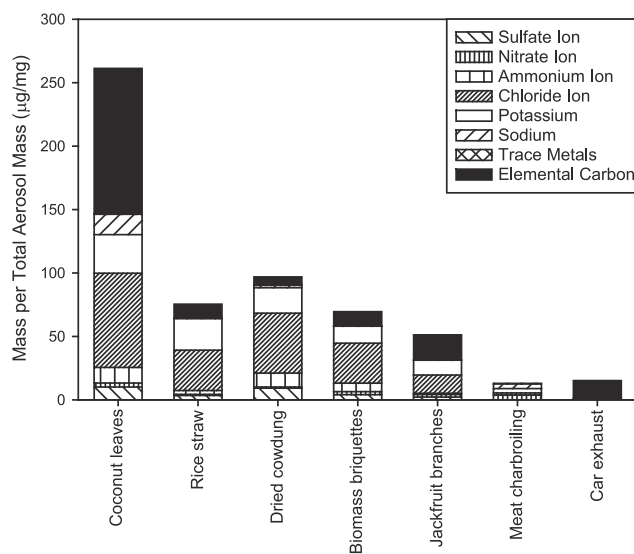

Figure 2. Mass balance of bulk composition excluding organic matter for Bangladeshi biomass, meat charbroiling, and noncatalyst, gasoline-powered motor vehicles. Meat charbroiling and car exhaust reported previously [*Schauer et al.*, 1999a, 2002b].
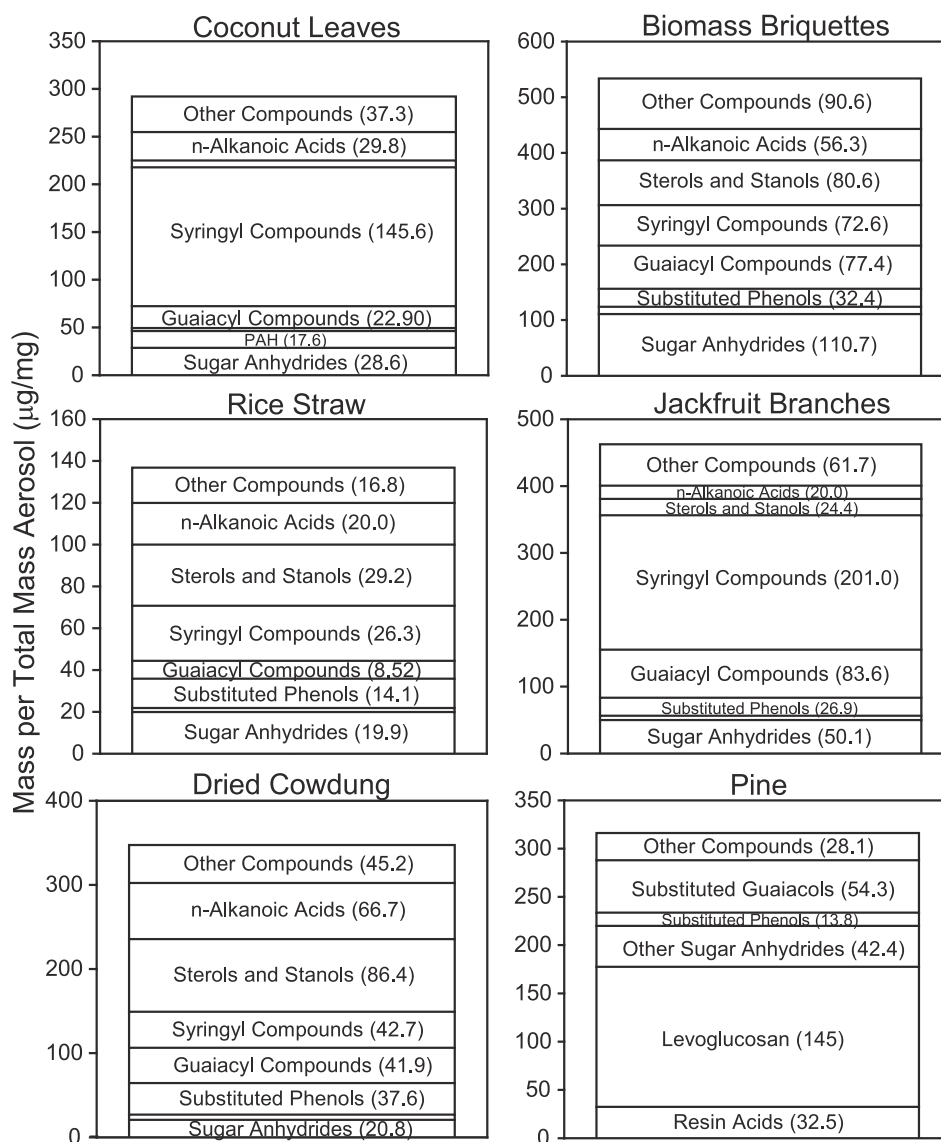
Figure 3. Emissions of organic compounds in Bangladeshi biomass samples and pine smoke. Pine combustion emission data from *Schauer et al.* [2001]. Categories representing <4% of total mass emission remain unlabeled.

in apportioning wood smoke in the atmosphere based upon ambient concentrations of nonmineral potassium. Although the emission fraction of potassium in smoke from meat charbroiling is significantly less than the fraction emitted in biomass smoke, smoke from both meat charbroiling and biomass combustion contribute appreciably to ambient particulate matter concentrations in some locations [*Schauer and Cass*, 2000].

3.3. Emissions of Resolved Organic Compounds

[20] Figure 3 compares the emissions of resolved organic compounds for the five biomass samples from Bangladesh and a North American soft wood pine, which was previously reported by *Schauer et al.* [2001]. The emission concentrations for the compounds discussed in this section are given in Table 3. At first glance the mass balances for the five Bangladesh samples look quite different from the pine mass balance. This illustrates the need for detailed

characterization of local biomass fuels in order to accurately predict biomass source contributions in a given area. For example, levoglucosan is considered a good tracer for biomass combustion emissions, but the fraction of levoglucosan varies in these samples from 2.0% in cowdung to over 10% of synthetic log emissions, and is almost 15% of total mass emissions for pine smoke. This variation in levoglucosan emission by species is consistent with the findings of Schauer et al., who reported in addition to the pine smoke, levoglucosan fractions of total aerosol as 13.8% and 22.8% for oak and eucalyptus smoke [*Schauer et al.*, 2001]. It is not surprising that cellulose pyrolysis product emissions vary in biomass burning emissions, for the cellulose content of these samples, which include leaves, grasses and cowdung, is expected to be lower than the cellulose content of wood. *Simoneit et al.* [1999] reported the thermal degradation pathway of cellulose leading to levoglucosan. The source of cellulose in cowdung would be residual undi-

gested organic matter from consumed plant material. Despite differences among species for biomass combustion emissions of levoglucosan, it is still a viable molecular marker when used in conjunction with other biomass burning tracers including methoxyphenols, resin acids, and plant sterols. By incorporating the summed source profiles of local biomass sources into a source apportionment model, the total contribution of all biomass smoke in a region could be determined [*Fine*, 2002].

[21] The resolved organic compound emissions in pine smoke are obviously dominated by levoglucosan, but only two of the Bangladeshi biomass samples show a dominance of one class of compounds. Smoke from both coconut leaves and jackfruit branches show a majority of resolved organics in the syringol compound class. This potentially indicates a higher percentage of lignin present in the unburned biomass sample, as syringyl-, guaiacyl-, and *p*-hydroxy phenyl-based compounds are degradation products of lignin [*Simoneit et al.*, 1993]. Jackfruit branches have the largest fraction from syringyl compounds at 201 μg/mg aerosol. This fraction is larger than the total resolved organics emission for rice straw. The other three samples, biomass briquettes, rice straw, and dried cowdung have resolved organic compound emissions more evenly distributed among a number of classes. The similarity in the distribution of resolved organic compound classes among these three samples is not surprising considering the cows' diet includes rice straw and biomass briquettes are composed primarily of rice husk.

[22] As has been mentioned previously in the literature, different taxa of plants contain different phenolics and the pattern of phenolics in a given biomass burning emission is characteristic of that biomass taxa [*Simoneit et al.*, 1993]. In Figure 3 it can be seen how the different lignins: *p*-coumaryl, coniferyl, and sinapyl impact the emission compound classes for the different biomass samples as *p*-hydroxy phenyl, guaiacyl, and syringyl compounds, respectively. The dried cowdung and synthetic log emissions have nearly 1:1 ratios of guaiacyl and syringyl compounds. While coconut leaves, rice straw and jackfruit branches emissions have a strong predominance of syringyl compounds. This predominance is indicative of angiosperms, while gymnosperms, like pine, emit only guaiacyl compounds [*Simoneit et al.*, 1993]. The structures for these lignins and their degradation products have been reported previously [*Schauer et al.*, 2001; *Simoneit et al.*, 1993].

[23] Coconut leaves, as mentioned above, have a higher emission of elemental carbon than the other four Bangladeshi smoke samples. This correlates with coconut leaves showing a considerable contribution from polycyclic aromatic hydrocarbons (PAH) (17.6 μg/mg aerosol). Again, like elemental carbon, PAH result from the combustion conditions and cannot be used to uniquely identify the emission source. The same PAH found in the emission of burning coconut leaves can be found in noncatalyst, gasoline-powered motor vehicle exhaust and meat charbroiling emissions, as shown in Figure 4 [*Schauer et al.*, 1999b, 2002c]. Certain patterns emerge in all the samples including high emissions for pyrene and fluoranthene versus acephenanthrylene, and higher emissions of chrysene/triphenylene than benz[a]anthracene or benzo[b]fluoranthene. However, the coconut leaf smoke consistently contains at least twice
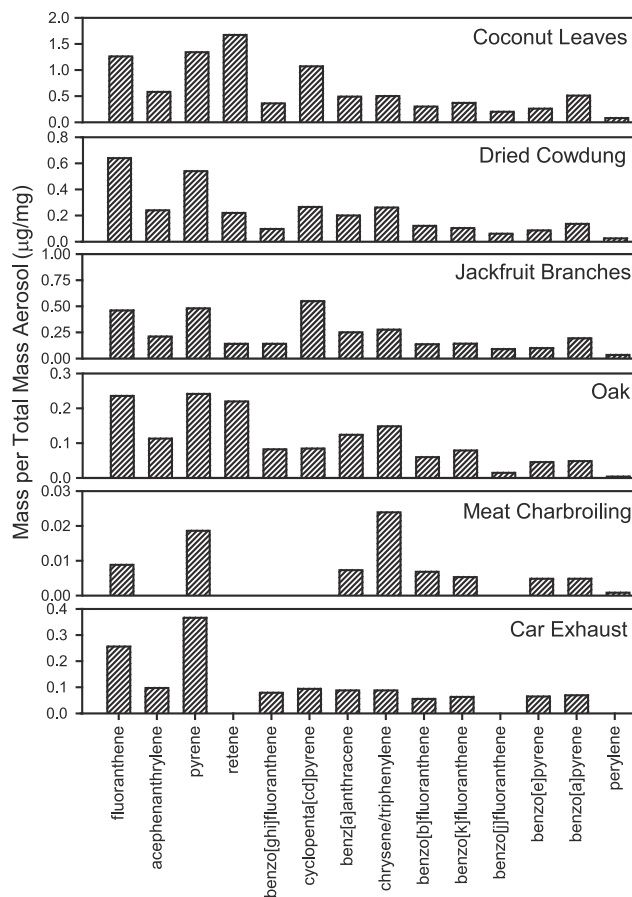

Figure 4. Emissions of select PAH from various sources. Meat charbroiling emissions reported previously [*Rogge et al.*, 1991]. Noncatalyst, gasoline-powered motor vehicle and oak combustion emission reported previously [*Schauer et al.*, 2001, 2002b].

the concentration of PAH as the other emission sources in Figure 4 when considering individual compound emissions.

[24] The *n*-alkanoic acids are a much more significant fraction of the resolved organic compounds for all the Bangladeshi biomass emissions than for the pine smoke (Figure 3). Dried cowdung has the largest emission at 66.7 μg/mg aerosol from *n*-alkanoic acids. Alkanoic acids, measured as their methyl ester, are not shown in a separate category in pine smoke because of low levels (Figure 3), but *Schauer et al.* [2001] reported a concentration for all alkanoic acids totaling 7.21 μg/mg aerosol.

[25] Compound classes that were not major fractions of most of the biomass smoke samples were combined into the "other compounds" class. The "other compounds" category includes a variety of compounds such as: hexadecanamide, octadecanamide, squalene, alkanes, oxygenated PAH, alkenoic acids, resin acids, dicarboxylic acids, and aromatic carbonyls. The emissions of all the quantified organic compounds are presented in Table A1.

3.4. Emission Fractions by Total Organic Mass

[26] Figure 5 illustrates the differences in the bulk characteristics of the organic mass for the samples, and shows the large degree of variability in the percentage of organic
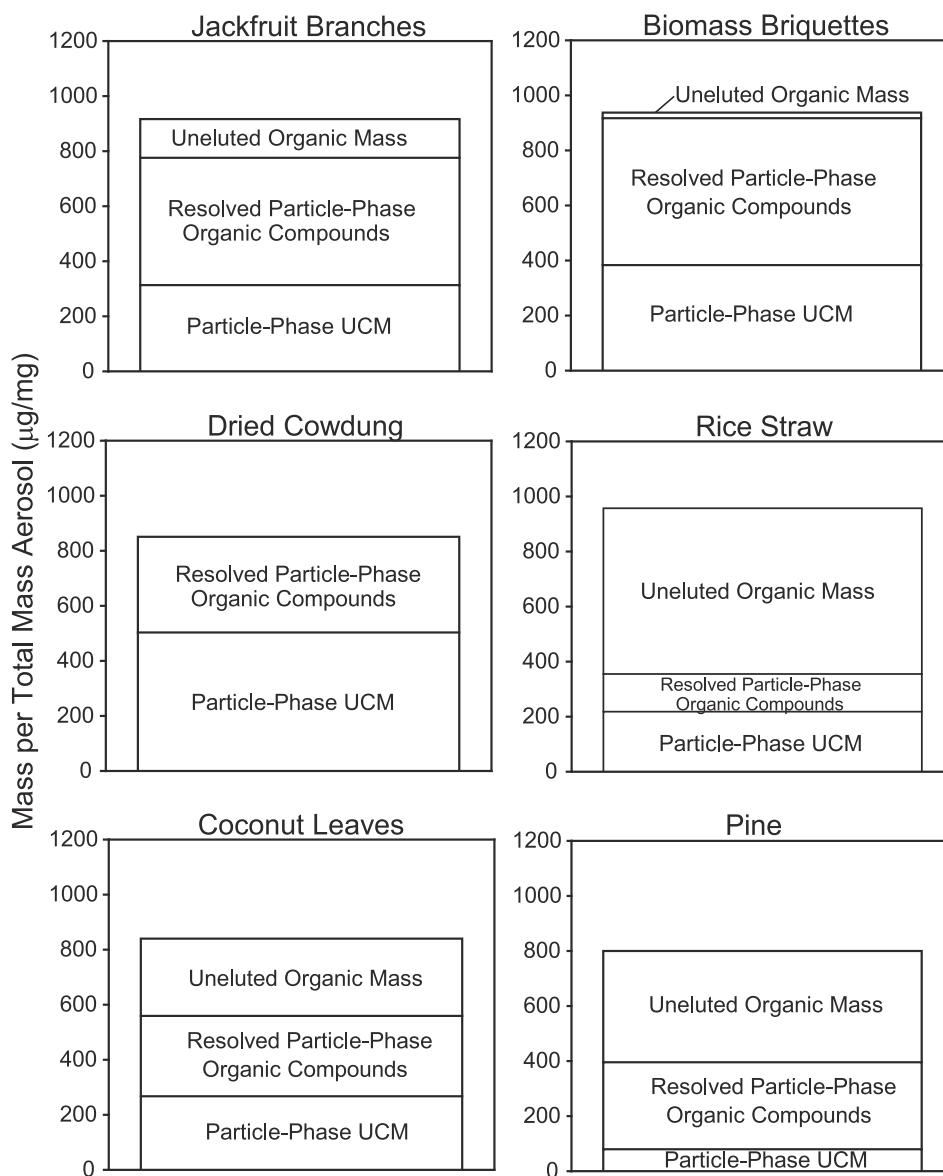
Figure 5. Mass balance of organic matter of Bangladeshi biomass samples and pine smoke. Pine combustion emission data from *Schauer et al.* [2001].

mass that can be resolved. The highest percentage can be resolved for emissions from biomass briquettes and jackfruit branches, 46.4% and 52.3%, respectively. The lowest percent of total organic mass that could be resolved was for rice straw with <13.1% resolved. To put this in perspective, the percent of the total organic mass that can be resolved for rice straw is less than the percent of total organic mass accounted for by levoglucosan in pine emissions. The majority of the organic matter in the rice straw combustion emissions is unelutable by this method because of polarity or molecular weight. Polarity or high molecular weight will inhibit the elution of a compound through the GC column used in this procedure. Additionally, high polarity could also prevent efficient extraction by the less polar solvents (isopropanol, hexane, and benzene), used in this method.

[27]   A comparison of the values of the unresolved complex mixture (UCM) reveals a consistency among most of the samples. UCM concentrations range from 220 to 380 μg/mg aerosol for all samples except cowdung, which is 500 μg/mg aerosol. Rice straw has the lowest fraction of UCM and resolved organic mass; therefore over 50% of its organic mass emission cannot be characterized by traditional extraction procedures and GC-MS analysis. For the other four Bangladeshi biomass emission samples, the majority of the organic mass can be characterized. Using the organic matter calculations outlined earlier, the resolved organic mass plus the particle-phase UCM for cowdung smoke exceed the total organic matter emission, but by <5.0%. Therefore closure of the organic mass balance is not statistically different than 100% when using a 95% confidence interval. When this is considered, the extraction/analysis technique is quite successful for the majority of these samples.

3.5. Molecular Markers

[28]   The structures of the organic compounds identified in this study for potential use as tracers for Bangladeshi
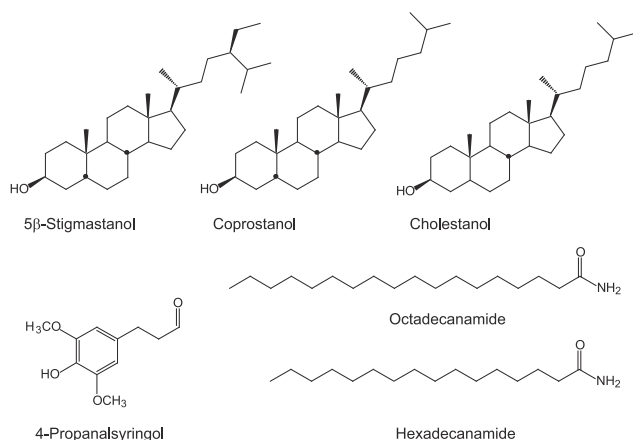
Figure 6. Structures of molecular markers for dried cowdung and jackfruit branch smoke.

biomass emission are shown in Figure 6. Of these five Bangladeshi biomass samples, only dried cowdung emits the three stanols 5β-stigmastanol, coprostanol, and cholestanol. The β configuration of the C-5 proton of 5β-stigmastanol and coprostanol is characteristic of anaerobic microbial reduction of sitosterol and cholesterol, which occurs during digestion in higher animals. In aquatic environments where aerobic microbes digest cholesterol and sitosterol, the C-5 proton has the α configuration. Cholestanol is the stereoisomer of coprostanol, with the C-5 proton in the α configuration and is the thermodynamically more stable product of the hydrogenation of cholesterol. However, it is formed by both microbial activity in the digestive tracts of higher animals and by marine organisms. This makes cholestanol a poor tracer for fecal matter in aquatic environments. However, in the atmosphere it would be expected that combustion of fecal material would be the major source of cholestanol, as sea spray would be expected to contain very low concentrations of this stanol. In fact, it is the ratio of coprostanol to the sum of coprostanol and cholestanol that has been applied to trace sewage impacts in aquatic environments [*Elhmmali et al.*, 2000]. Since cows are herbivores, the level of 5β-stigmastanol (or 24-ethyl-coprostanol) is much higher than in human feces because ofdifferences in diet [*Leeming et al.*, 1996]. This trend is replicated in the emissions from burning of dried cowdung, where the 5β-stigmastanol concentration is much higher than the coprostanol concentration, as seen in Figure 7. These three potential markers for combustion of dried cowdung (5β-stigmastanol, coprostanol, and cholestanol) might also be present in the combustion of sewage sludge, however, the relative amounts of the three species would be different.

[29] It is important to note that these stanols were detected at high levels in extracts that had not been silylated. With derivitization, it is expected that these compounds would be easier to detect in the lower levels present in ambient samples [*Choi et al.*, 1996]. However, no work has been done to determine the longevity of such compounds in the atmosphere. Ambient samples were not simultaneously collected in Bangladesh to determine if any potential tracers detected in the source emissions could be detected in ambient samples.

[30] The two amides also offer potential in molecular marker source apportionment models when used in conjunction with the stanols. Octadecanamide is only present in the smoke from dried cowdung, but hexadecanamide was detected at low levels in the biomass briquette and jackfruit branch emissions. Additionally, these two amides have been identified at similar concentrations in emissions from meat charbroiling [*Rogge et al.*, 1991; *Schauer et al.*, 1999a]. *Rogge et al.* [1991] detected them in an ambient aerosol particle composite from west Los Angeles, but at reduced concentrations when normalized to ambient cholesterol concentrations, a tracer for meat charbroiling. This would suggest degradation in the atmosphere over extended periods of time or different sources.

[31] Only one compound in the syringyl class is unique to one of the sampled sources discussed in this paper; that compound is 4-propanalsyringol present in jackfruit branches. It is still preferable to rely on the distinctive patterns of phenolic and syringyl emissions, rather than one particular marker for source apportionment models.

3.6. Emission Rates of Individual Organic Compounds

[32] Molecular markers unique to a particular source are difficult to find, so unique patterns of common compounds are often employed in conjunction with source-specific tracers. Both are employed in molecular marker source apportionment techniques to tease out source contributions. Figure 7 displays select organic compounds and their emission concentrations normalized to aerosol mass in order to illustrate differences in distribution of compounds among the emission samples.

[33] As mentioned before, the pattern of lignan breakdown products can be used in a molecular marker source apportionment model to distinguish among different biomass sources. In Figure 7, the concentrations of select phenolic and syringyl compounds that are present only in the particle phase are presented for the five different biomass samples. The highest emitted syringyl compound for all five samples is acetonyl syringol. However, the fraction of emission varies from 4.41 μg/mg aerosol for rice straw to 51 μg/mg aerosol for jackfruit branch smoke. This correlates with the high value for the syringol class of compounds in jackfruit branch emissions shown in Figure 3.

[34] Three of the syringyl compounds show the same pattern for all five samples: syringaldehyde, acetonyl syringol and propionyl syringol. However, if the focus is expanded to include the compounds surrounding these three, the pattern varies significantly. For example, jackfruit branch combustion, as mentioned previously, emits 4-propanalsyringol, while coconut leaf combustion emission contains allylsyringol at concentrations equivalent to syringaldehyde.

[35] The molecular markers illustrated in Figure 6 are shown in black in Figure 7. The amides are emitted at low concentrations in the dried cowdung smoke, especially in comparison with the stanols. The stanols are better suited for use as tracers because of their high concentrations. 5α-Stigmastanol, although not detected in any other Bangladeshi biomass smoke sample besides cowdung, has been reported to be emitted in wood smoke [*Fine et al.*, 2001]. It is not suggested for use as a unique tracer. Again, for each biomass smoke sample there is a characteristic pattern of
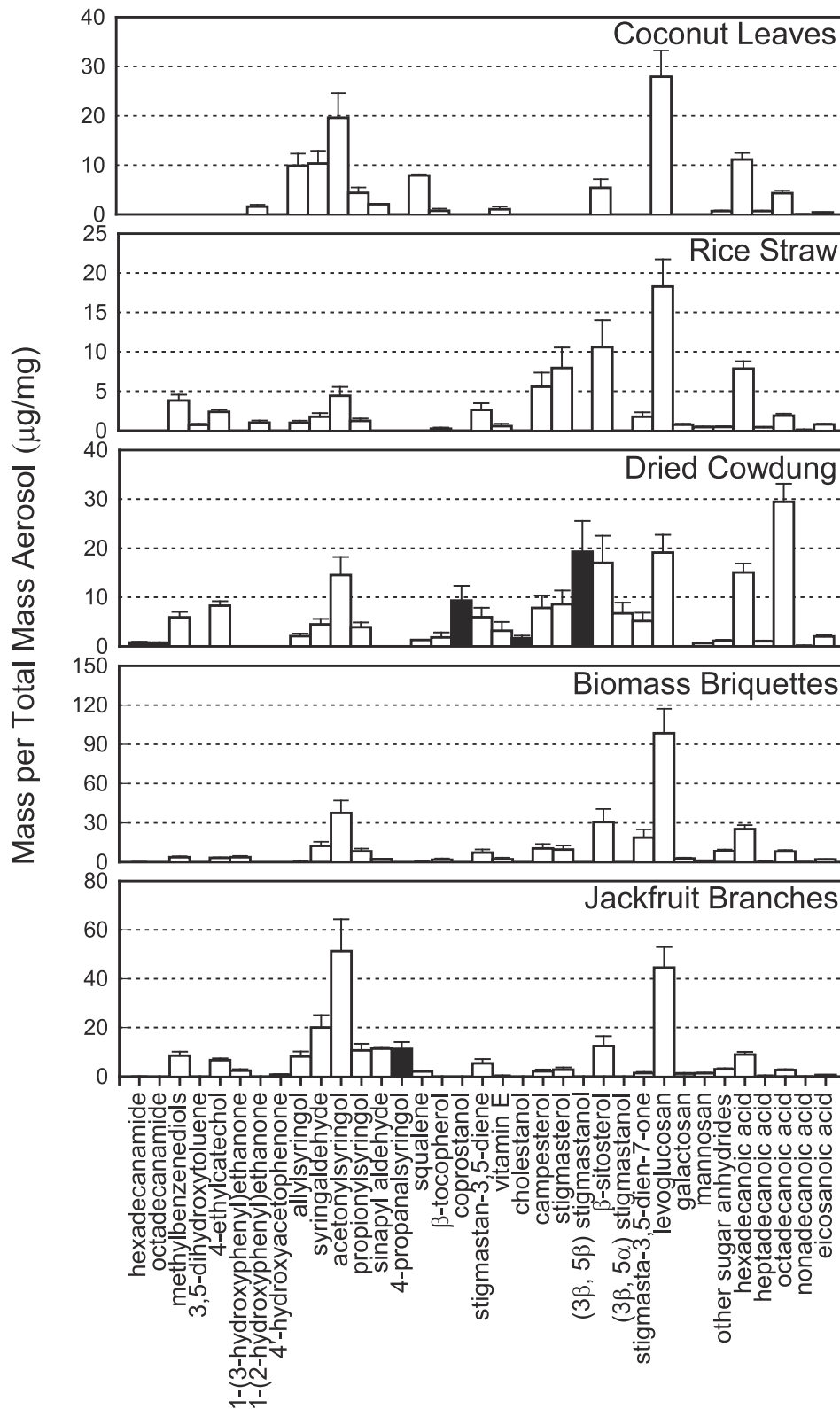
Figure 7. Emissions of individual organic compounds for biomass burning.

steroid emissions that could be exploited in source apportionment models. In a more general sense, β-sitosterol is emitted by each of the 5 different Bangladeshi biomass sources and has been found in emissions from combustion of various woods and other biomass from North America [*Fine et al.*, 2001, 2002; *Simoneit et al.*, 1993]. However, the fraction of the total emission contributed by β-sitosterol varies by sample ranging from 5.39 µg/mg aerosol for

coconut leaves to 30.6 µg/mg aerosol in biomass briquette emissions.

[36] Another compound common to all wood smoke [*Simoneit et al.*, 1999] and the emissions from these five biomass combustion samples is levoglucosan. Comparison of the concentration of levoglucosan emitted versus the concentration of the emissions of galactosan, mannosan and the total other sugars, reveals that its pattern varies significantly among the samples. For coconut leaves, 98% of the total pyrolyzed polysaccharide products is in the form of levoglucosan, while it is only 89% for biomass briquettes and jackfruit branches. Levoglucosan and the other sugar derivatives are generated from different sources in the plants. Levoglucosan is a thermal breakdown product of the glucose units of cellulose, while the other sugars presumably are derived from the hemi-cellulose and pectin components of plants [*Croteau et al.*, 2000; *Simoneit et al.*, 1999]. The biochemical composition of a plant predetermines the emission ratio of levoglucosan to other sugar pyrolysis products. Although the other sugar pyrolysis products besides levoglucosan are emitted only in small quantities, in regions where biomass smoke is one of the top sources of atmospheric particulate matter the pattern of sugar degradation products could be useful in distiguishing among biomass sources.

[37] Finally, there is a distinctly different pattern for cowdung smoke as opposed to the other biomass emissions for the n-alkanoic acid distribution. The other four samples have hexadecanoic acid as their most prevalent n-alkanoic acid, while cowdung smoke contains octadecanoic acid in the highest quantities (Figure 7). It is also the only biomass combustion sample with an alkanoic acid emitted in higher quantities than levoglucosan.

[38] In general, these emission patterns will facilitate apportionment of biomass combustion sources separately in South Asia. The steroids will be most useful in definitively apportioning the contribution of dried cowdung smoke. The phenolics combined with the steroid compounds will allow apportionment of the remainder of the Bangladeshi biomass samples in the ambient air in that region.

4. Conclusion

[39] Each Bangladeshi biomass combustion emission sample tested in this study had a characteristic pattern of organic compounds. The bulk chemical compounds including elemental carbon, ionic species, and metals, were not as distinctive as the organic compounds for the particle-phase of the combustion emissions. It is suggested that the steroids as well as the lignin breakdown products (syringyl, guaiacyl, and phenolic compounds) are best suited for use in molecular marker source apportionment models on a regional scale. The dried cowdung smoke revealed the most unique composition of steroids, including 5β-stigmastanol, coprostanol and cholestanol. These three are unique to feces of higher animals, and the specific pattern of concentration determined in this paper is unique to cowdung smoke.

[40] It is known that biomass smoke aerosols are efficient cloud condensation nuclei (CCN), despite the predominance of organic material over inorganic salts [*Eagan et al.*, 1974; *Halley et al.*, 1989; *Hobbs and Radke*, 1969; *Warner and Twomey*, 1967]. Additionally, it has been shown that levoglucosan, a major compound emitted by combustion of biomass, is CCN active because of its water solubility [*Novakov and Corrigan*, 1996]. Since an important property effecting an organic compound's hygroscopicity is its solubility in water and whether it is multifunctional [*Corrigan and Novakov*, 1999; *Saxena and Hildemann*, 1996], the high percentage of polar and multifunctional compounds present in these biomass smoke samples would make them efficient cloud condensation nuclei. For example, methoxyphenols and pyrolized sugars comprise from 41% for dried cowdung smoke to 76% for jackfruit branch smoke of the total resolved organic mass. Since a large percentage of the organic mass for rice straw smoke is uneluted and unresolved by the methods used in this paper, an analysis of the water soluble organic components by methanol extraction and silylation might reveal this sample to have an even higher potential for CCN activity. Therefore the high polarity and multi-functional nature of the organic component of biomass smoke aerosol should not be discounted in global climate models.

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