

Elemental characterization of particulate matter emitted from biomass burning: Wind tunnel derived source profiles for herbaceous and wood fuels

S.Q. Turn,^{1,2} B.M. Jenkins,¹ J.C. Chow,³ L.C. Pritchett,³

D. Campbell,⁴ T. Cahill,⁴ and S. A. Whalen⁵

Abstract. Particulate matter emitted from wind tunnel simulations of biomass burning for five herbaceous crop residues (rice, wheat and barley straws, corn stover, and sugar cane trash) and four wood fuels (walnut and almond prunings and ponderosa pine and Douglas fir slash) was collected and analyzed for major elements and water soluble species. Primary constituents of the particulate matter were C, K, Cl, and S. Carbon accounted for roughly 50% of the herbaceous fuel PM and about 70% for the wood fuels. For the herbaceous fuels, particulate matter from rice straw in the size range below 10 μm aerodynamic diameter (PM₁₀) had the highest concentrations of both K (24%) and Cl (17%) and barley straw PM₁₀ contained the highest sulfur content (4%). K, Cl, and S were present in the PM of the wood fuels at reduced levels with maximum concentrations of 6.5% (almond prunings), 3% (walnut prunings), and 2% (almond prunings), respectively. Analysis of water soluble species indicated that ionic forms of K, Cl, and S made up the majority of these elements from all fuels. Element balances showed K, Cl, S, and N to have the highest recovery factors (fraction of fuel element found in the particulate matter) in the PM of the elements analyzed. In general, chlorine was the most efficiently recovered element for the herbaceous fuels (10 to 35%), whereas sulfur recovery was greatest for the wood fuels (25 to 45%). Unique potassium to elemental carbon ratios of 0.20 and 0.95 were computed for particulate matter (PM₁₀ K/C(e)) from herbaceous and wood fuels, respectively. Similarly, in the size class below 2.5 μm , high-temperature elemental carbon to bromine (PM_{2.5} C(HT)/Br) ratios of ~7.5, 43, and 150 were found for the herbaceous fuels, orchard prunings, and forest slash, respectively. The molar ratios of particulate phase bromine to gas phase CO₂ (PM₁₀ Br/CO₂) are of the same order of magnitude as gas phase CH₃Br/CO₂ reported by others.

Introduction

Biomass burning has been identified as a significant source of atmospheric emissions in many regions of the world. This includes activities such as land clearing and disposal practices for agricultural and silvicultural wastes. Although easily recognized as the cause of local air quality degradation, long range transport of pollutants may result in impacts far from the source. Source receptor models, such as the chemical mass balance (CMB) model [Friedlander, 1973; Watson *et al.*, 1984; Hopke, 1991], have been developed to identify the origin of particulate matter (PM) collected at a given locale (receptor) by utilizing the known chemical composition of PM associated with a given source. Characterizing PM sources may also aid in illuminating pathways by which trace elements cycle through the biosphere.

The limited number of measurements of water soluble components of biomass burning PM was noted by Allen and Miguel [1995]. This paucity of information is more pronounced when searching for studies reporting elemental characterization of PM generated from biomass burning. Allen and Miguel [1995] reported ionic components of PM sampled in close proximity to fires at two locations in the Amazon encompassing three types of cerrado vegetation, primary and secondary rainforest and rough grassland resulting from previously converted rainforest. Emissions of organic and graphitic carbon and major inorganic components of PM generated from cerrado and tropical deforestation fires in Amazonas have been reported in numerous studies [Andreae *et al.*, 1988; Kaufman *et al.*, 1992; Ward *et al.*, 1992] which utilized both airborne and ground-based sampling systems. Similar ground-based work was reported by Cachier *et al.* [1991] for fires in the wooded savannah of western Africa. Field and laboratory studies by Hudson *et al.* [1991] quantified water soluble components of PM from forest fires. Similar characterization was reported by Rogers *et al.* [1991] for forest, chaparral, and agricultural grain stubble fires. Cofer *et al.* [1991] detailed the soluble inorganic ion components of PM from fires in wetland, chaparral, and boreal forest settings. Leslie [1981] determined the elemental composition of size segregated PM from cerrado, virgin jungle, and secondary land clearing fires in the southern Amazon basin. Many elemental studies have been directed toward PM samples at a given locale [Asubiojo *et al.*, 1993; Chow *et al.*, 1993b; Rojas *et al.*, 1990] rather than focusing on a specific source.

¹Department of Biological and Agricultural Engineering, University of California, Davis.

²Currently at Hawaii Natural Energy Institute, University of Hawaii, Honolulu.

³Desert Research Institute, University and Community College System of Nevada, Reno.

⁴Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis.

⁵Hawaiian Sugar Planters' Association, Aiea.

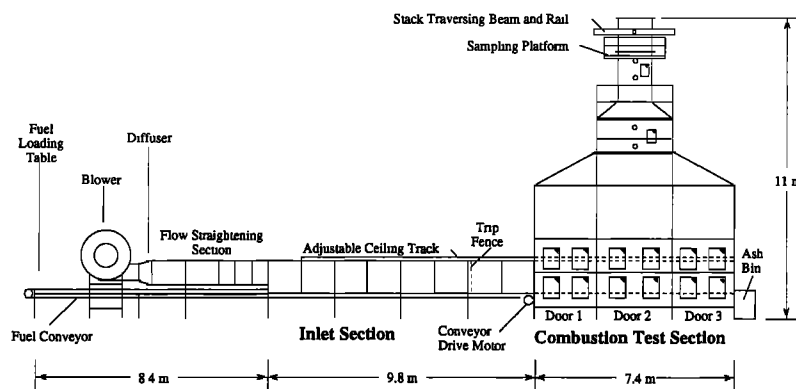


Figure 1. Combustion wind tunnel.

As part of a larger study evaluating the emissions from crop and forest biomass burning conducted for the state of California [Jenkins *et al.*, 1993], compositions of particulate matter were analyzed for the purpose of developing source profiles for important fuel types. Previous work identified the biomass materials most commonly open burned in the state of California [Jenkins *et al.*, 1992]: corn stover, rice, wheat and barley straw, and four wood fuels: almond and walnut tree prunings and ponderosa pine and Douglas fir slash. Among these, rice straw is open burned in most regions of the world where the crop is cultivated. A companion study was performed on sugar cane, a crop also commonly open burned in parts of the United States as well as other sugar producing countries. This paper reports elemental and water soluble species concentrations and emission factors obtained from PM collected during test burns of these fuels. The tests generating these source profiles were conducted in a combustion wind tunnel at the University of California, Davis.

Experimental Procedure

Test Facility

The wind tunnel used in the experiments was an open-circuit, forced-draft type, 1.2 m in width comprised of three main sections: an inlet section, a combustion test section, and a stack sampling section arranged as shown in Figure 1. A brief description is included below. For additional detail, see Jenkins *et al.* [1993].

The wind tunnel employed a system of conveyors to move the fuel bed downstream when operating with spreading fires (Figure 2). The inlet section housed the primary fuel conveyor, a flexible belt exposed at the upstream end which permitted the continuous loading and transport of fuel to the combustion test section. The fuel was transferred to a stainless steel rod chain conveyor at the junction of the inlet and combustion test sections. This second conveyor supported the fuel as it burned. A single variable-speed dc motor was used to operate both conveyors at the same linear velocity. Wind speeds in the range of 2 to 4 m s⁻¹ were generated by a 35 kW centrifugal blower. A series of 40 mesh (two each) and 60 mesh (three each) screens installed across the duct directly downstream of the blower outlet served as flow straighteners. The fuel surface provided roughness to develop a thick boundary layer similar to that in the atmosphere near the ground surface [Williams, 1992]. Turbulence was further enhanced by a trip fence located 2 m upstream of the combustion test section. Postcombustion residual material (ash) remaining on the conveyor in the combustion test section was recovered in a bin at the downstream end of the tunnel. The walls of the combustion test section extended vertically upward while narrowing into the sampling section of the stack.

Fuels

Barley, wheat, and rice straws were all cut near ground level in the course of normal harvest operations. Corn stover was machine shredded after grain harvest, a common preparation for field burning. All field crop residues were air dried prior to

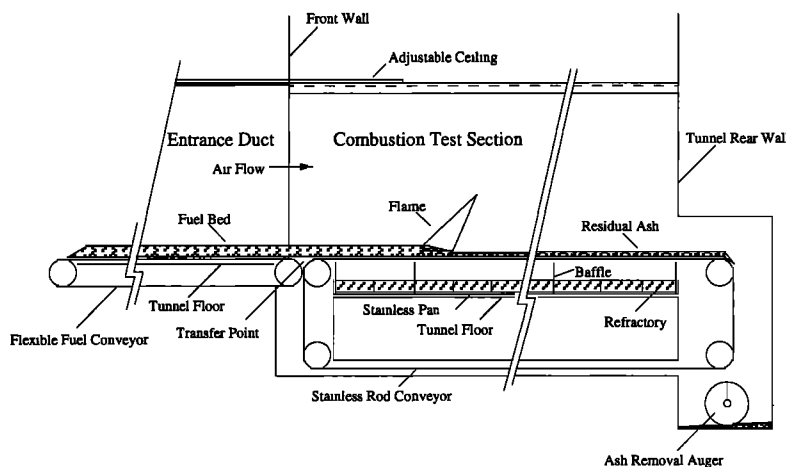


Figure 2. Conveyor system used with spreading fires.

Table 1. Summary of Analytical Measurements for Chemical Composition Determination of Particulate Matter

Species	Analytical Method ^e	Minimum Detectable Limit, ^f µg/filter	Lower Quantifiable Limit, ^g µg/filter
Mass	gravimetric	12	33
Cl ⁻	IC	0.12	1.4
NO ₃ ⁻	IC	0.12	1.1
SO ₄ ⁼	IC	0.12	0.56
NH ₄ ⁺	AA	0.12	0.69
Na ⁺	AA	0.072	0.87
K ⁺	AC	0.072	0.78
C(org) ^a	TOR	0.49	26
C(oh) ^b	TOR	0.49	19
C(e) ^c	TOR	0.49	3.9
C(eht) ^d	TOR	0.49	3.4
Al	XRF	0.037	0.26
Si	XRF	0.021	1.5
P	XRF	0.011	0.11
S	XRF	0.0084	0.16
Cl	XRF	0.024	0.20
K	XRF	0.011	0.27
Ca	XRF	0.011	0.23
Ti	XRF	0.0073	0.14
V	XRF	0.0049	0.083
Cr	XRF	0.0049	0.044
Mn	XRF	0.0043	0.035
Fe	XRF	0.0024	0.35
Co	XRF	0.0024	0.014
Ni	XRF	0.0024	0.021
Cu	XRF	0.0024	0.020
Zn	XRF	0.0049	0.027
Ga	XRF	0.0073	0.042
As	XRF	0.0049	0.034
Se	XRF	0.0049	0.015
Br	XRF	0.0024	0.015
Rb	XRF	0.0024	0.009
Sr	XRF	0.0049	0.019
Y	XRF	0.0049	0.020
Zr	XRF	0.0073	0.031
Mo	XRF	0.011	0.041
Pd	XRF	0.024	0.25
Ag	XRF	0.026	0.27
Cd	XRF	0.026	0.27
In	XRF	0.034	0.36
Sn	XRF	0.044	0.30
Sb	XRF	0.053	0.58
Ba	XRF	0.19	1.5
La	XRF	0.21	2.1
Au	XRF	0.020	0.054
Hg	XRF	0.013	0.036
Tl	XRF	0.016	0.048
Pb	XRF	0.011	0.070
U	XRF	0.019	0.042

^a Organic carbon evolved between 25°C and 550°C including pyrolyzed carbon.

^b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

^c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

^d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

^e Analysis methods are ion chromatography (IC), atomic absorption (AA), automated colorimetry (AC), thermal/optical reflectance (TOR), and energy dispersive X ray fluorescence (XRF).

^f Minimum detectable limit is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero.

^g Lower quantifiable limit equals 3 times the standard deviation of dynamic field blanks as determined from the sampling program.

collection and moisture contents were representative of conditions under which open burning normally occurs. All materials were collected from commercial fields in Yolo County, northern California.

The term wood fuels has been applied to the orchard prunings and forest slash materials used in these tests to indicate their origin. Whole logs, trees, or stumps were not included in the material burned. The pruning materials, originating from orchards in northern California's Yolo County, consisted of branches ranging in size up to 100 mm diameter which were devoid of leaf material. Forest slash was collected from contract harvest plots in the Sierra Nevada mountains of California. Material consisted of branches with butt diameters of up to 150 mm. Dried needles remained attached to the branches for both fuels with ponderosa pine exhibiting greater numbers of needles than the Douglas fir. No duff or litter was included in any of the forest slash burns.

Sugar cane test samples, consisting of cane trash (dead plant material which accumulates in the field during the growth period of the plant) and green tops from a seed cane harvest, were collected from fields of the Hawaiian Commercial & Sugar Company on the island of Maui and air freighted to Davis. In accordance with normal commercial sugar cultural practices throughout the world, this material is disposed of during preharvest field burning operations in standing cane. In the case of fields utilized for seed cane production, tops and leaf material are burned postharvest.

Integrated fuel samples were collected just prior to each test as material was loaded into the wind tunnel. Samples were reduced to a particle size of <6 mm before subsamples for analytical tests were obtained.

Methodology

A total of 24 tests were conducted: 7 rice straw, 3 sugar cane, and 2 for each of the remaining fuels. The wood fuel tests and one of the sugar cane tests were conducted as pile burns. Tests for the remaining fuels were conducted as fires spreading in opposition to the wind. Air supplied to the pile burns was a function of the natural draft admitted through the opened doors on the sides of the wind tunnel and induced by the buoyant plume. The spreading fires were subjected to a boundary layer flow with mean velocity of 2 to 4 m s⁻¹ generated by the centrifugal blower and developed over a 10 m length of fuel bed. These wind speeds are consistent with conditions under which

Table 2. Fuel combustion efficiencies and moisture contents

Fuel Type	Combustion Efficiency	Moisture Content, percent wet basis
Rice straw	0.89	9
Wheat straw	0.86	7
Barley straw	0.82	7
Corn stover	0.92	9
Walnut prunings	0.91	33
Almond prunings	0.91	18
Ponderosa pine	0.92	24
Douglas fir	0.93	30
Sugar cane	0.68	38

Table 3a. Average Mass Concentrations for Particulate Matter in 2.5 and 10 µm Size Classes, Herbaceous Fuels, Group 1 Analysis

	Average Percent Mass and Measurement Uncertainty, %											
	Rice Straw (n=7)			Wheat Straw (n=2)			Barley Straw (n=2)			Corn Stover (n=2)		
	PM2.5 ± Unc	f	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc
Cl-	27 ± 0.94		23 ± 0.82	22 ± 1.4	21 ± 1.3	5.3 ± 0.38	5.3 ± 0.38	5.4 ± 0.38	26 ± 1.5	27 ± 1.6	18 ± 1.4	18 ± 0.98
NO3-	0.25 ± 0.032		0.22 ± 0.023	0.34 ± 0.054	0.36 ± 0.053	0.35 ± 0.036	0.35 ± 0.036	0.36 ± 0.036	0.26 ± 0.024	0.28 ± 0.024	0.14 ± 0.025	0.14 ± 0.019
SO4=	4.2 ± 0.15		3.4 ± 0.12	4.8 ± 0.27	4.7 ± 0.37	7.5 ± 0.40	7.5 ± 0.40	7.8 ± 0.42	2.0 ± 0.10	2.0 ± 0.11	2.2 ± 0.15	2.3 ± 0.12
NH4+	5.4 ± 0.20		4.6 ± 0.18	3.6 ± 0.21	3.4 ± 0.20	0.34 ± 0.038	0.34 ± 0.038	0.37 ± 0.039	5.8 ± 0.33	6.0 ± 0.33	3.0 ± 0.19	3.0 ± 0.14
Na+	0.99 ± 0.045		0.81 ± 0.036	0.30 ± 0.029	0.32 ± 0.029	0.75 ± 0.048	0.75 ± 0.048	0.78 ± 0.050	0.061 ± 0.0091	0.051 ± 0.0085	0.49 ± 0.039	0.49 ± 0.027
K+	15 ± 0.49		12 ± 0.40	16 ± 0.94	16 ± 0.93	15 ± 0.87	15 ± 0.87	16 ± 0.92	14 ± 0.73	14 ± 0.76	12 ± 0.89	12 ± 0.63
C(org)a	22 ± 1.1		20 ± 0.96	37 ± 2.8	38 ± 2.8	38 ± 2.7	38 ± 2.7	40 ± 2.8	33 ± 2.3	35 ± 2.4	37 ± 2.9	37 ± 2.1
C(oh)b	18 ± 1.3		17 ± 1.2	35 ± 4.1	37 ± 4.2	35 ± 3.9	35 ± 3.9	37 ± 4.1	29 ± 3.1	32 ± 3.5	32 ± 2.8	32 ± 2.4
C(e)c	23 ± 1.1		18 ± 0.80	14 ± 0.96	14 ± 0.97	16 ± 1.1	16 ± 1.1	16 ± 1.1	14 ± 0.98	15 ± 1.0	15 ± 1.2	15 ± 0.98
C(eht)d	1.2 ± 0.33		1.5 ± 0.40	0.68 ± 0.31	1.3 ± 0.61	0.84 ± 0.43	0.84 ± 0.43	0.77 ± 0.46	0.52 ± 0.25	0.14 ± 0.073	0.79 ± 0.38	0.60 ± 0.28
C	45 ± 2.2		38 ± 1.8	51 ± 3.8	52 ± 3.8	54 ± 3.8	54 ± 3.8	56 ± 3.9	47 ± 3.3	50 ± 3.4	52 ± 4.1	52 ± 3.1
Al	0.0097 ± 0.047	e	0.0033 ± 0.047	0.16 ± 0.027	0.19 ± 0.028	0.11 ± 0.020	0.11 ± 0.020	0.12 ± 0.021	0.051 ± 0.066	0.087 ± 0.047	0.070 ± 0.016	0.084 ± 0.015
Si	0.53 ± 0.062		3.4 ± 0.13	0.13 ± 0.046	0.37 ± 0.050	0.093 ± 0.077	0.093 ± 0.077	0.18 ± 0.035	0.057 ± 0.087	0.20 ± 0.033	0.065 ± 0.055	0.27 ± 0.023
P	0.0000 ± 0.12	e	0.0000 ± 0.11	0.047 ± 0.14	0.063 ± 0.15	0.030 ± 0.093	0.030 ± 0.093	0.044 ± 0.093	0.0090 ± 0.16	0.013 ± 0.16	0.012 ± 0.11	0.024 ± 0.11
S	1.3 ± 0.066		1.0 ± 0.056	1.8 ± 0.11	1.9 ± 0.12	4.3 ± 0.22	4.3 ± 0.22	4.3 ± 0.22	0.63 ± 0.080	0.62 ± 0.0776	0.80 ± 0.068	0.90 ± 0.064
Cl	27 ± 0.82		24 ± 0.72	17 ± 0.91	18 ± 0.97	4.9 ± 0.31	4.9 ± 0.31	4.9 ± 0.30	21 ± 1.1	21 ± 1.0	14 ± 0.79	16 ± 0.74
K	20 ± 0.65		17 ± 0.52	15 ± 0.81	16 ± 0.87	17 ± 0.88	17 ± 0.88	17 ± 0.89	12 ± 0.62	13 ± 0.61	11 ± 0.64	12 ± 0.57
Ca	0.12 ± 0.11		0.63 ± 0.051	0.035 ± 0.16	0.069 ± 0.17	0.033 ± 0.18	0.033 ± 0.18	0.10 ± 0.18	0.039 ± 0.13	0.13 ± 0.12	0.079 ± 0.12	0.44 ± 0.12
Ti	0.0017 ± 0.021	e	0.011 ± 0.015	0.0009 ± 0.048	0.0069 ± 0.045	0.0013 ± 0.030	0.0013 ± 0.030	0.0027 ± 0.029	0.0013 ± 0.0194	0.0041 ± 0.019	0.0007 ± 0.024	0.0028 ± 0.018
V	0.0019 ± 0.0092	e	0.0008 ± 0.0068	0.0014 ± 0.021	0.0026 ± 0.020	0.0000 ± 0.013	0.0000 ± 0.013	0.0001 ± 0.013	0.0006 ± 0.0098	0.0009 ± 0.0081	0.0000 ± 0.014	0.0003 ± 0.010
Cr	0.0014 ± 0.0024	e	0.0029 ± 0.0018	0.0006 ± 0.0046	0.0015 ± 0.0044	0.0002 ± 0.0028	0.0002 ± 0.0028	0.0018 ± 0.0028	0.0007 ± 0.0025	0.0020 ± 0.0016	0.0006 ± 0.0039	0.0010 ± 0.0029
Mn	0.032 ± 0.0019		0.18 ± 0.0067	0.0017 ± 0.0032	0.0043 ± 0.0022	0.0009 ± 0.0020	0.0009 ± 0.0020	0.0040 ± 0.0014	0.0034 ± 0.0009	0.0078 ± 0.0010	0.0062 ± 0.0018	0.022 ± 0.0019
Fe	0.029 ± 0.0051		0.21 ± 0.0081	0.012 ± 0.0085	0.092 ± 0.0096	0.0038 ± 0.0052	0.0038 ± 0.0052	0.032 ± 0.0054	0.0074 ± 0.0033	0.063 ± 0.0045	0.010 ± 0.0019	0.082 ± 0.0044
Co	0.0004 ± 0.0011	e	0.0004 ± 0.0017	0.0004 ± 0.0019	0.0004 ± 0.0022	0.0004 ± 0.0012	0.0004 ± 0.0012	0.0003 ± 0.0013	0.0004 ± 0.0008	0.0002 ± 0.0011	0.0004 ± 0.0009	0.0003 ± 0.0011
Ni	0.0004 ± 0.0012	e	0.0016 ± 0.0009	0.0003 ± 0.0021	0.0010 ± 0.0020	0.0000 ± 0.0013	0.0000 ± 0.0013	0.0002 ± 0.0013	0.0001 ± 0.0008	0.0007 ± 0.0007	0.0003 ± 0.0010	0.0009 ± 0.0007
Cu	0.0032 ± 0.0012		0.0028 ± 0.0008	0.0011 ± 0.0022	0.0013 ± 0.0021	0.0001 ± 0.0013	0.0001 ± 0.0013	0.0000 ± 0.0013	0.0007 ± 0.0009	0.0011 ± 0.0006	0.0018 ± 0.0008	0.0020 ± 0.0006
Zn	0.046 ± 0.0021		0.038 ± 0.0016	0.0091 ± 0.0017	0.010 ± 0.0016	0.0051 ± 0.0010	0.0051 ± 0.0010	0.0063 ± 0.0010	0.016 ± 0.0010	0.016 ± 0.0011	0.0095 ± 0.0009	0.011 ± 0.0007
Ga	0.0002 ± 0.0022	e	0.0005 ± 0.0016	0.0000 ± 0.0039	0.0005 ± 0.0036	0.0000 ± 0.0024	0.0000 ± 0.0024	0.0000 ± 0.0024	0.0003 ± 0.0015	0.0000 ± 0.0015	0.0000 ± 0.0018	0.0000 ± 0.0014
As	0.0022 ± 0.0027	e	0.0025 ± 0.0019	0.0000 ± 0.0045	0.0001 ± 0.0042	0.0000 ± 0.0028	0.0000 ± 0.0028	0.0000 ± 0.0028	0.0002 ± 0.0018	0.0003 ± 0.0018	0.0001 ± 0.0021	0.0000 ± 0.0016
Se	0.0019 ± 0.0015		0.0014 ± 0.0011	0.0000 ± 0.0024	0.0004 ± 0.0023	0.0006 ± 0.0016	0.0006 ± 0.0016	0.0000 ± 0.0015	0.0001 ± 0.0010	0.0006 ± 0.0010	0.0008 ± 0.0011	0.0010 ± 0.0009
Br	0.13 ± 0.0043		0.12 ± 0.0037	0.070 ± 0.0042	0.074 ± 0.0044	0.11 ± 0.0064	0.11 ± 0.0064	0.11 ± 0.0064	0.067 ± 0.0035	0.066 ± 0.0034	0.19 ± 0.0096	0.21 ± 0.0093
Rb	0.023 ± 0.0014		0.020 ± 0.0011	0.0064 ± 0.0016	0.0058 ± 0.0016	0.0057 ± 0.0014	0.0057 ± 0.0014	0.0054 ± 0.0014	0.0043 ± 0.0008	0.0047 ± 0.0008	0.0075 ± 0.0028	0.0083 ± 0.0029
Sr	0.0007 ± 0.0013		0.0046 ± 0.0008	0.0000 ± 0.0023	0.0013 ± 0.0021	0.0008 ± 0.0014	0.0008 ± 0.0014	0.0016 ± 0.0011	0.0007 ± 0.0009	0.0019 ± 0.0006	0.0007 ± 0.0010	0.0032 ± 0.0007
Y	0.0006 ± 0.0017	e	0.0011 ± 0.0013	0.0004 ± 0.0028	0.0009 ± 0.0026	0.0003 ± 0.0018	0.0003 ± 0.0018	0.0003 ± 0.0018	0.0011 ± 0.0011	0.0004 ± 0.0011	0.0004 ± 0.0014	0.0005 ± 0.0012
Zr	0.0036 ± 0.0018		0.0016 ± 0.0014	0.0000 ± 0.0034	0.0003 ± 0.0032	0.0000 ± 0.0021	0.0000 ± 0.0021	0.0000 ± 0.0021	0.0006 ± 0.0013	0.0002 ± 0.0013	0.0004 ± 0.0015	0.0004 ± 0.0012
Mo	0.0011 ± 0.0033	e	0.0013 ± 0.0024	0.0005 ± 0.0058	0.0018 ± 0.0054	0.0000 ± 0.0037	0.0000 ± 0.0037	0.0007 ± 0.0036	0.0019 ± 0.0023	0.0002 ± 0.0023	0.0004 ± 0.0013	0.0004 ± 0.0012
Pd	0.0000 ± 0.015	e	0.0013 ± 0.011	0.0000 ± 0.0021	0.0006 ± 0.0020	0.0044 ± 0.013	0.0044 ± 0.013	0.0000 ± 0.013	0.0019 ± 0.0089	0.0019 ± 0.0087	0.0004 ± 0.0026	0.0001 ± 0.0020
Ag	0.0025 ± 0.017	e	0.0048 ± 0.013	0.014 ± 0.024	0.010 ± 0.023	0.0555 ± 0.015	0.0555 ± 0.015	0.0037 ± 0.015	0.0004 ± 0.010	0.0044 ± 0.0098	0.0013 ± 0.011	0.0017 ± 0.0084
Cd	0.0093 ± 0.018	e	0.0019 ± 0.013	0.0008 ± 0.026	0.016 ± 0.025	0.0020 ± 0.016	0.0020 ± 0.016	0.0030 ± 0.016	0.0007 ± 0.011	0.0000 ± 0.011	0.0049 ± 0.012	0.0052 ± 0.0090
In	0.0023 ± 0.020	e	0.0014 ± 0.015	0.0008 ± 0.029	0.0022 ± 0.028	0.0000 ± 0.018	0.0000 ± 0.018	0.0045 ± 0.018	0.0000 ± 0.012	0.0000 ± 0.012	0.0000 ± 0.013	0.0000 ± 0.010

Table 3a. (continued)

	Average Percent Mass and Measurement Uncertainty, %														
	Rice Straw (n=7)			Wheat Straw (n=2)			Barley Straw (n=2)			Corn Stover (n=2)			Sugar Cane (n=3)		
	PM2.5 ± Unc f	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	
Sn	0.0084 ± 0.025 e	0.0059 ± 0.019 e	0.0003 ± 0.037 e	0.0042 ± 0.035 e	0.0041 ± 0.023 e	0.0007 ± 0.023 e	0.0000 ± 0.023 e	0.0000 ± 0.015 e	0.0003 ± 0.015 e	0.0007 ± 0.016 e	0.0011 ± 0.013 e				
Sb	0.0064 ± 0.029 e	0.0032 ± 0.021 e	0.0000 ± 0.042 e	0.0056 ± 0.040 e	0.0065 ± 0.026 e	0.0087 ± 0.026 e	0.0024 ± 0.017 e	0.0024 ± 0.017 e	0.0013 ± 0.016 e	0.0000 ± 0.018 e	0.0000 ± 0.014 e				
Ba	0.042 ± 0.099 e	0.033 ± 0.071 e	0.0000 ± 0.15 e	0.019 ± 0.14 e	0.021 ± 0.091 e	0.0035 ± 0.089 e	0.0018 ± 0.057 e	0.011 ± 0.056 e	0.011 ± 0.056 e	0.011 ± 0.063 e	0.015 ± 0.048 e				
La	0.0008 ± 0.13 e	0.018 ± 0.096 e	0.0000 ± 0.19 e	0.011 ± 0.19 e	0.0000 ± 0.12 e	0.0000 ± 0.12 e	0.025 ± 0.076 e	0.0054 ± 0.074 e	0.017 ± 0.084 e	0.028 ± 0.065 e					
Au	0.0011 ± 0.0038 e	0.0009 ± 0.0028 e	0.0000 ± 0.0064 e	0.0024 ± 0.0061 e	0.0000 ± 0.0040 e	0.0002 ± 0.0040 e	0.0000 ± 0.0025 e	0.0000 ± 0.0025 e	0.0001 ± 0.0030 e	0.0000 ± 0.0023 e					
Hg	0.0015 ± 0.0031 e	0.0009 ± 0.0022 e	0.0026 ± 0.0054 e	0.0024 ± 0.0050 e	0.0002 ± 0.0033 e	0.0013 ± 0.0033 e	0.0011 ± 0.0021 e	0.0006 ± 0.0021 e	0.0000 ± 0.0024 e	0.0000 ± 0.0019 e					
Tl	0.0013 ± 0.0029 e	0.0013 ± 0.0021 e	0.0000 ± 0.0051 e	0.0000 ± 0.0047 e	0.0000 ± 0.0032 e	0.0000 ± 0.0031 e	0.0006 ± 0.0020 e	0.0000 ± 0.0020 e	0.0008 ± 0.0023 e	0.0003 ± 0.0018 e					
Pb	0.0045 ± 0.0037 e	0.0028 ± 0.0027 e	0.0000 ± 0.0067 e	0.0020 ± 0.0062 e	0.0001 ± 0.0042 e	0.0000 ± 0.0041 e	0.0002 ± 0.0026 e	0.0000 ± 0.0026 e	0.0008 ± 0.0029 e	0.0008 ± 0.0024 e					
U	0.0011 ± 0.0034 e	0.0007 ± 0.0026 e	0.0001 ± 0.0052 e	0.0002 ± 0.0049 e	0.0000 ± 0.0035 e	0.0001 ± 0.0035 e	0.0009 ± 0.0022 e	0.0002 ± 0.0022 e	0.0004 ± 0.0032 e	0.0006 ± 0.0028 e					

a Organic carbon evolved between 25°C and 550 °C including pyrolyzed carbon.

b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

e Average less than associated measurement uncertainty.

f Unc is abbreviation for Uncertainty.

open burning is permitted by the local air quality districts. Large-scale wind-aided fires (e.g., wild fires) were not simulated.

For each fuel, particulate matter was collected from the wind tunnel stack using four different sampling probes. Large amounts of dilution air in the wind tunnel resulted in gas temperatures at the sampling location being only 10° to 50°C above ambient. The first probe was connected to a sampling system which collected four simultaneous samples onto two different 47 mm substrates in two different size fractions: <2.5 mm (PM2.5) and <10 mm (PM10). Filter media used were poly methyl pentane ringed, 2.0 mm pore size PTFE Teflon membrane filters (#R2PJ047, Gelman, Ann Arbor, Michigan) and pre-fired quartz fiber filters (#2500QAT-UP, Pallflex Products Corp., Putnam, Connecticut). Controlled flow rates of 10 L min⁻¹ through each filter were individually monitored using critical orifices. The sampling system incorporated a filter bypass line which enabled the total flow through the probe to be maintained at isokinetic conditions. A total of 128 filter samples were collected, 36 of which were field blanks. Teflon membrane filters were analyzed gravimetrically to determine PM mass concentrations and by X ray fluorescence (XRF) using an energy dispersive X ray fluorescence analyzer (Model 700/8000, Kevex Corporation) for 38 elements, Al through U. The water soluble fraction from half of each quartz fiber filter was extracted and analyzed for Cl⁻, NO₃⁻ and SO₄⁼ using ion chromatography (IC) (Model 4000i, Dionex, Sunnyvale, California), K⁺ and Na⁺ using atomic absorption spectrophotometry (AA) (Model 2380 Double Beam Atomic Absorption Spectrometer, Perkin Elmer, Norwalk, Connecticut), and NH₄⁺ using automated colorimetry (AC) (TRAACS 800 Automated Colorimetric System, Technicon, Tarrytown, New York). A 0.5 cm² punch from each quartz fiber filter was analyzed for organic carbon (C(org)) and elemental carbon (C(e)) by the thermal/optical reflectance (TOR) method [Chow *et al.*, 1993a]. Organic high temperature carbon (C(oh)) and elemental high temperature carbon (C(eht)) fractions for the two carbon components were also quantified. For these analyses, the operational definition of C(oh) is that portion of organic carbon evolving at temperatures in excess of 120°C in a pure helium environment. C(eht) is defined as elemental carbon evolving at analysis temperatures of 700 and 800°C in a 2% oxygen in helium environment, with any pyrolyzed organic carbon subtracted from the 700°C step. Analytical methods are described by Chow [1987]. Table 1 provides a summary of the measured species, analytical techniques and minimum detectable and lower quantifiable limits. Samples and analyses associated with this sampling system are referred to as group 1.

A second probe was used to collect total PM samples on 47 mm Teflon filters which were analyzed gravimetrically to determine PM mass concentrations and by particle-induced X ray emission (PIXE) for elements Na through U. No attempt was made to maintain isokinetic conditions for this probe. Size fractionated samples were also collected through this probe using an eight-stage Davis Rotating-Drum Unit for Monitoring (DRUM) type impactor [Cahill *et al.*, 1987]. Size ranges of the impactor stages were 10-15 mm, 5-10 mm, 2.5-5 mm, 1.15-2.5 mm, 0.56-1.15 mm, 0.34-0.56 mm, 0.24-0.34 mm and <0.24 mm. PM on each stage was analyzed by PIXE. The samples and analyses associated with this system are referred to as group 2.

The two remaining probes collected an in-stack total PM sample and an in-stack size fractionated sample using a 7-stage cascade impactor (Sierra Instruments model 228, Carmel Valley, California) on 47 mm Teflon-coated glass fiber filters (Pallflex type TX40HI20, Pallflex Products Corp., Putnam, Connecticut).

Table 3b. (continued)

	Average Percent Mass and Measurement U ₁ certainty, %										
	Walnut Prunings (n=2)			Almond Prunings (n=2)			Pont erosa Pine Slash (n=2)			Douglas Fir Slash (n=2)	
	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	PM2.5 ± Unc	PM10 ± Unc	
Sn	0.0000 ± 0.013 e	0.0002 ± 0.014 e	0.0035 ± 0.019 e	0.0046 ± 0.018 e	0.0057 ± 0.016 e	0.0023 ± 0.015 e	0.0039 ± 0.012 e	0.0000 ± 0.012 e	0.0000 ± 0.012 e	0.0000 ± 0.012 e	
Sb	0.0000 ± 0.015 e	0.0038 ± 0.016 e	0.0002 ± 0.021 e	0.0029 ± 0.021 e	0.0026 ± 0.018 e	0.0000 ± 0.017 e	0.0000 ± 0.013 e	0.0000 ± 0.014 e	0.0000 ± 0.014 e	0.0000 ± 0.014 e	
Ba	0.011 ± 0.053 e	0.0066 ± 0.055 e	0.018 ± 0.075 e	0.0000 ± 0.072 e	0.0000 ± 0.062 e	0.0000 ± 0.061 e	0.0000 ± 0.048 e	0.0000 ± 0.049 e	0.0000 ± 0.049 e	0.0000 ± 0.049 e	
La	0.0000 ± 0.071 e	0.0059 ± 0.074 e	0.014 ± 0.10 e	0.0093 ± 0.097 e	0.0008 ± 0.084 e	0.036 ± 0.082 e	0.0000 ± 0.065 e	0.0000 ± 0.065 e	0.0000 ± 0.065 e	0.0000 ± 0.065 e	
Au	0.0001 ± 0.035 e	0.0000 ± 0.037 e	0.0000 ± 0.016 e	0.0000 ± 0.016 e	0.0000 ± 0.011 e	0.0000 ± 0.010 e	0.0000 ± 0.0041 e	0.0000 ± 0.0041 e	0.0000 ± 0.0041 e	0.0000 ± 0.0041 e	
Hg	0.0000 ± 0.0020 e	0.0000 ± 0.0020 e	0.0000 ± 0.0028 e	0.0000 ± 0.0027 e	0.0000 ± 0.0024 e	0.0000 ± 0.0022 e	0.0000 ± 0.0018 e	0.0000 ± 0.0019 e	0.0000 ± 0.0019 e	0.0000 ± 0.0019 e	
Tl	0.0001 ± 0.0020 e	0.0000 ± 0.0021 e	0.0000 ± 0.0027 e	0.0000 ± 0.0026 e	0.0001 ± 0.0023 e	0.0004 ± 0.0022 e	0.0000 ± 0.0018 e	0.0000 ± 0.0018 e	0.0000 ± 0.0018 e	0.0000 ± 0.0018 e	
Pb	0.025 ± 0.0022	0.026 ± 0.0023	0.0087 ± 0.0025	0.010 ± 0.0024	0.0046 ± 0.0020	0.0068 ± 0.0021	0.0024 ± 0.0015	0.0019 ± 0.0024 e	0.0019 ± 0.0024 e	0.0019 ± 0.0024 e	
U	0.0002 ± 0.0020 e	0.0001 ± 0.0021 e	0.0001 ± 0.0028 e	0.0001 ± 0.0026 e	0.0000 ± 0.0037 e	0.0000 ± 0.0033 e	0.0000 ± 0.0018 e	0.0000 ± 0.0018 e	0.0000 ± 0.0018 e	0.0000 ± 0.0018 e	

a Organic carbon evolved between 25°C and 550 °C including pyrolyzed carbon.

b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

e Average less than associated measurement uncertainty.

The information obtained from these samples was used to compute emission factors for total PM and for the size ranges $\leq 10 \mu\text{m}$ and $\leq 2.5 \mu\text{m}$. In all cases, the PM10 mass concentration represented at least 90% of the total PM concentration and usually was greater than 95%.

Results and Discussion

Combustion Efficiencies

Simultaneous measurements of permanent gases were made during each test. From these, combustion efficiency averaged over the test period was computed. Combustion efficiency is defined as the mass of carbon released as CO_2 divided by the total mass of carbon released [Ward *et al.*, 1992]. Combustion efficiency and moisture content for each fuel are presented in Table 2. Because of the relatively small fuel elements and low moisture contents, combustion efficiencies are high for all of the fuels with the exception of sugar cane. Cane tops were on average 68% moisture content on a wet basis, whereas leaves were much drier averaging 17%.

Group 1

Average percentage mass of each analyte in the PM2.5 and PM10 size fractions are presented in Tables 3a and 3b by fuel type. Average concentrations were computed for two categories of fuels with straws, stover, and cane composing an herbaceous category, and the remaining fuels grouped into a wood category. The results are presented in Table 4. In all cases, carbon is the dominant element, accounting for roughly 40 to 50% of the particulate mass for the herbaceous fuels and 65 to 75% for the wood fuels. The remainder is comprised principally of K, Cl, and S.

For the herbaceous fuels, carbon fractions were roughly 70% organic and 30% elemental. Rice straw is an exception, with the abundance of the two forms nearly equal. In general, C(oh) accounts for more than 80% of the organic fraction, whereas C(eht) is found at levels of less than 10% in the elemental fraction.

Elemental carbon accounts for 35% of the PM carbon fraction from the wood fuels, except for Douglas fir, where the fraction is ~20%. C(oh) and C(eht) as fractions of total organic and elemental carbon are present at levels similar to those found in the herbaceous fuels, except that C(oh) is roughly 60% of total organic carbon in the case of Douglas fir PM10.

Potassium in the PM of the wood fuels is in the range of 5 to 6%, again with the exception of Douglas fir which has a concentration of 1%. The herbaceous fuels have higher PM potassium levels ranging from 10 to 20%.

Chlorine is present at concentrations of 1 to 3% for almond and walnut fuels, whereas PM from the forest species has Cl concentrations of less than 1%. The range of Cl concentrations in PM of the herbaceous fuels is 15 to 25% excepting barley which yielded a much lower concentration of 5%.

Sulfur is present in the wood fuel PM in a range of 1 to 2%, again with the exception of Douglas fir at 0.25%. Douglas fir has the lowest fuel S concentration of any of the tested materials (see Table 7) and the low PM sulfur concentration was substantiated by the analyses of group 2 filter samples. Sulfur is found in the PM of herbaceous fuels at concentrations of 0.5 to 2% with the exception of barley with levels slightly higher than 4%. The high S emission in the PM for barley straw is consistent with the very

Table 4. Composite Average Mass Concentrations for Herbaceous and Wood Fuels in 2.5 and 10 μm Size Classes, Group 1 Analysis

Average Percent Mass and Measurement Uncertainty, %				
	Herbaceous Fuels (n=16)		Woody Fuels (n=8)	
	PM2.5 \pm Unc	PM10 \pm Unc	PM2.5 \pm Unc	PM10 \pm Unc
Cl-	21 \pm 0.54	20 \pm 0.47	1.5 \pm 0.062	1.7 \pm 0.071
NO ₃ -	0.26 \pm 0.016	0.25 \pm 0.013	0.63 \pm 0.024	0.68 \pm 0.026
SO ₄ =	4.0 \pm 0.096	3.8 \pm 0.093	2.8 \pm 0.092	3.1 \pm 0.10
NH ₄ +	4.1 \pm 0.10	3.7 \pm 0.094	0.53 \pm 0.022	0.59 \pm 0.024
Na+	0.64 \pm 0.021	0.58 \pm 0.017	0.12 \pm 0.0066	0.14 \pm 0.0071
K+	14 \pm 0.33	14 \pm 0.29	4.2 \pm 0.14	4.4 \pm 0.15
C(org)a	31 \pm 0.94	31 \pm 0.85	46 \pm 1.8	49 \pm 1.9
C(oh)b	27 \pm 1.2	27 \pm 1.1	39 \pm 2.5	38 \pm 2.4
C(e)c	18 \pm 0.54	16 \pm 0.44	22 \pm 0.87	25 \pm 0.99
C(eht)d	0.91 \pm 0.17	1.0 \pm 0.20	0.83 \pm 0.25	1.7 \pm 0.47
C	49 \pm 1.5	47 \pm 1.3	68 \pm 2.7	74 \pm 2.9
Al	0.061 \pm 0.021 e	0.070 \pm 0.020 e	0.025 \pm 0.010 e	0.042 \pm 0.0096 e
Si	0.26 \pm 0.032 e	1.5 \pm 0.054	0.048 \pm 0.014 e	0.090 \pm 0.013
P	0.014 \pm 0.062 ef	0.021 \pm 0.057 ef	0.016 \pm 0.020 ef	0.026 \pm 0.020 e
S	1.6 \pm 0.046	1.5 \pm 0.044	1.5 \pm 0.048	1.6 \pm 0.049
Cl	19 \pm 0.41	18 \pm 0.38	1.6 \pm 0.056	1.6 \pm 0.058
K	16 \pm 0.34	15 \pm 0.30	5.2 \pm 0.16	5.2 \pm 0.16
Ca	0.078 \pm 0.061 e	0.38 \pm 0.048 e	0.087 \pm 0.027 e	0.27 \pm 0.014
Ti	0.0013 \pm 0.013 ef	0.0067 \pm 0.010 ef	0.0000 \pm 0.011 ef	0.0008 \pm 0.011 ef
V	0.0010 \pm 0.0058 ef	0.0009 \pm 0.0048 ef	0.0000 \pm 0.0048 ef	0.0002 \pm 0.0050 ef
Cr	0.0009 \pm 0.0015 ef	0.0021 \pm 0.0012 e	0.0000 \pm 0.0011 ef	0.0001 \pm 0.0012 ef
Mn	0.015 \pm 0.0010 e	0.078 \pm 0.0027	0.0012 \pm 0.0007 e	0.0036 \pm 0.0007 e
Fe	0.017 \pm 0.0025 e	0.13 \pm 0.0037	0.0058 \pm 0.0019 e	0.026 \pm 0.0021
Co	0.0004 \pm 0.0006 ef	0.0003 \pm 0.0008 ef	0.0000 \pm 0.0005 ef	0.0000 \pm 0.0005 ef
Ni	0.0003 \pm 0.0006 ef	0.0010 \pm 0.0005 e	0.0000 \pm 0.0005 ef	0.0000 \pm 0.0005 ef
Cu	0.0019 \pm 0.0006 e	0.0018 \pm 0.0005 e	0.0028 \pm 0.0004 ef	0.0023 \pm 0.0004 ef
Zn	0.024 \pm 0.0009	0.022 \pm 0.0007	0.31 \pm 0.012	0.31 \pm 0.012
Ga	0.0001 \pm 0.0011 ef	0.0003 \pm 0.0009 ef	0.0000 \pm 0.0010 ef	0.0000 \pm 0.0010 ef
As	0.0009 \pm 0.0014 ef	0.0011 \pm 0.0011 e	0.0013 \pm 0.0015 ef	0.0008 \pm 0.0016 ef
Se	0.0010 \pm 0.0007 e	0.0009 \pm 0.0006 e	0.0005 \pm 0.0006 ef	0.0003 \pm 0.0006 ef
Br	0.12 \pm 0.0028	0.12 \pm 0.0026	0.016 \pm 0.0007	0.016 \pm 0.0007
Rb	0.013 \pm 0.0008	0.012 \pm 0.0008	0.0084 \pm 0.0005	0.0079 \pm 0.0005
Sr	0.0006 \pm 0.0007 ef	0.0031 \pm 0.0005 e	0.0010 \pm 0.0005 e	0.0026 \pm 0.0004
Y	0.0006 \pm 0.0009 ef	0.0007 \pm 0.0007 ef	0.0001 \pm 0.0007 ef	0.0001 \pm 0.0007 ef
Zr	0.0016 \pm 0.0010 e	0.0008 \pm 0.0008 ef	0.0000 \pm 0.0008 ef	0.0001 \pm 0.0008 ef
Mo	0.0010 \pm 0.0017 ef	0.0009 \pm 0.0014 ef	0.0000 \pm 0.0014 ef	0.0000 \pm 0.0013 ef
Pd	0.0009 \pm 0.0072 ef	0.0016 \pm 0.0058 ef	0.0000 \pm 0.0047 ef	0.0004 \pm 0.0047 ef
Ag	0.0039 \pm 0.0082 ef	0.0047 \pm 0.0067 ef	0.0027 \pm 0.0054 ef	0.0015 \pm 0.0054 ef
Cd	0.0052 \pm 0.0087 ef	0.0043 \pm 0.0070 ef	0.0003 \pm 0.0058 ef	0.0004 \pm 0.0058 ef
In	0.0010 \pm 0.0096 ef	0.0015 \pm 0.0078 ef	0.0006 \pm 0.0065 ef	0.0011 \pm 0.0065 ef
Sn	0.0041 \pm 0.012 ef	0.0033 \pm 0.0098 ef	0.0028 \pm 0.0083 ef	0.0020 \pm 0.0082 ef
Sb	0.0037 \pm 0.014 ef	0.0034 \pm 0.011 ef	0.0005 \pm 0.0095 ef	0.0022 \pm 0.0094 ef
Ba	0.022 \pm 0.048 ef	0.021 \pm 0.038 ef	0.0097 \pm 0.033 ef	0.0022 \pm 0.033 ef
La	0.0070 \pm 0.063 ef	0.015 \pm 0.051 ef	0.0048 \pm 0.044 ef	0.011 \pm 0.044 ef
Au	0.0005 \pm 0.0020 ef	0.0007 \pm 0.0016 ef	0.0000 \pm 0.0059 ef	0.0000 \pm 0.0059 ef
Hg	0.0011 \pm 0.0016 ef	0.0009 \pm 0.0013 ef	0.0000 \pm 0.0012 ef	0.0000 \pm 0.0012 ef
Tl	0.0008 \pm 0.0015 ef	0.0006 \pm 0.0012 ef	0.0001 \pm 0.0012 ef	0.0001 \pm 0.0012 ef
Pb	0.0020 \pm 0.0019 e	0.0015 \pm 0.0016 ef	0.012 \pm 0.0012	0.014 \pm 0.0012 ef
U	0.0006 \pm 0.0018 ef	0.0004 \pm 0.0015 ef	0.0001 \pm 0.0013 ef	0.0001 \pm 0.0013 ef

a Organic carbon evolved between 25°C and 550 °C including pyrolyzed carbon.

b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

e Value calculated with one or more measurements which were less than or equal to the measurement uncertainty.

f Composite average less than associated measurement uncertainty.

Table 5a. Average Emission Factor for Particulate Matter in 2.5 and 10 μm Size Classes, Herbaceous Fuels, Group 1 Analysis

	Average Emission Factor, mg/kg									
	Rice Straw (n=7)		Wheat Straw (n=2)		Barley Straw (n=2)		Corn Stover (n=2)		Sugar Cane (n=3)	
	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10
Cl-	890.	940.	1200.	1200.	390.	410.	1300.	1400.	690.	740.
NO3-	7.3	7.9	19.	21.	27.	28.	13.	14.	5.6	6.0
SO4=	120.	120.	260.	260.	580.	610.	96.	100.	87.	96.
NH4+	210.	210.	190.	190.	25.	28.	290.	310.	120.	120.
Na+	19.	21.	16.	18.	58.	61.	3.0	2.6	19.	20.
K+	450.	480.	890.	900.	1200.	1300.	670.	730.	480.	500.
C(org)	900.	940.	2100.	2200.	3000.	3200.	1700.	1800.	1500.	1500.
C(oh)	730.	780.	2000.	2200.	2800.	3000.	1400.	1600.	1300.	1300.
C(e)	460. e	500. e	790.	800.	1200.	1200.	670. e	750.	590.	610.
C(eht)	42.	52.	39.	79.	69.	64.	26. e	7.3	32.	25.
C	1400. e	1400. e	2900. e	3000. e	4300. e	4400. e	2300. e	2600. e	2100. e	2100. e
Al	0.61	0.23	8.6	10.	8.4	9.3	2.6	4.5	2.8	3.5
Si	10.	88.	7.0	21.	7.1	14.	2.9	10.	2.7	12.
P	0.00	0.00	2.6	3.6	2.4	3.4	0.45	0.67	0.53	1.0
S	34.	36.	96. e	100. e	330. e	340. e	31. e	32.	32. e	37.
Cl	780. e	840. e	920. e	970. e	360. e	370. e	1000. e	1100. e	560. e	650. e
K	500. e	530. e	840. e	890. e	1300. e	1300. e	610. e	620. e	420. e	480. e
Ca	2.5 e	16.	1.9 e	3.9 e	2.5 e	8.0 e	1.9 e	6.8	3.4 e	19. e
Ti	0.060	0.49	0.046 e	0.40	0.089 e	0.20	0.067	0.21	0.032	0.12
V	0.055	0.044	0.071	0.14	0.00 e	0.0037	0.031	0.046	0.00	0.011
Cr	0.049 e	0.10 e	0.028 e	0.080 e	0.011 e	0.14 e	0.034 e	0.10 e	0.026 e	0.044 e
Mn	0.70 e	4.6	0.089 e	0.24 e	0.065 e	0.30 e	0.17 e	0.40	0.27 e	0.95
Fe	0.66	5.8	0.69 e	5.3 e	0.29 e	2.5 e	0.37 e	3.2	0.42	3.6
Co	0.014	0.015	0.020	0.018	0.025	0.018	0.017	0.0076	0.016	0.012
Ni	0.0093 e	0.045 e	0.013 e	0.052 e	0.00 e	0.011 e	0.0026 e	0.036 e	0.012 e	0.036 e
Cu	0.081 e	0.088	0.056 e	0.073 e	0.0036 e	0.00 e	0.034 e	0.054 e	0.071 e	0.084 e
Zn	0.80	0.92	0.49 e	0.56 e	0.38 e	0.49 e	0.76 e	0.84 e	0.39 e	0.46
Ga	0.0026	0.011	0.0000	0.029	0.00	0.00	0.013	0.00	0.00	0.00
As	0.069	0.091	0.0000	0.0064	0.00	0.00	0.010	0.013	0.0034	0.00
Se	0.046 e	0.048	0.0000 e	0.020 e	0.039 e	0.00	0.0052 e	0.028	0.032 e	0.043
Br	4.6 e	5.0 e	3.8 e	4.0 e	8.1 e	8.4 e	3.3	3.4 e	7.6 e	8.7 e
Rb	0.51	0.56	0.35 e	0.31 e	0.44 e	0.42 e	0.21 e	0.24 e	0.30 e	0.34 e
Sr	0.019 e	0.11 e	0.0000 e	0.069 e	0.057 e	0.12 e	0.032 e	0.097 e	0.029 e	0.14 e
Y	0.016 e	0.032 e	0.020 e	0.051 e	0.025 e	0.025 e	0.054 e	0.018 e	0.018 e	0.022 e
Zr	0.13 e	0.042 e	0.0000 e	0.015 e	0.00 e	0.00 e	0.028 e	0.0078 e	0.017 e	0.015 e
Mo	0.017 e	0.040 e	0.025 e	0.097 e	0.00 e	0.048 e	0.094 e	0.010 e	0.042 e	0.0050 e
Pd	0.00 e	0.027 e	0.0000 e	0.40 e	0.32 e	0.00 e	0.088 e	0.099 e	0.015 e	0.00 e
Ag	0.054 e	0.14 e	0.77 e	0.52 e	0.44 e	0.28 e	0.021 e	0.22 e	0.054 e	0.068 e
Cd	0.16 e	0.074 e	0.049 e	0.88 e	0.17 e	0.24 e	0.036 e	0.00 e	0.18 e	0.20 e
In	0.041 e	0.034 e	0.049 e	0.14 e	0.00 e	0.33 e	0.00 e	0.00 e	0.00 e	0.00 e
Sn	0.17 e	0.14 e	0.015 e	0.27 e	0.33 e	0.059 e	0.00 e	0.013 e	0.029 e	0.049 e
Sb	0.11 e	0.099 e	0.00 e	0.28	0.55 e	0.66 e	0.12 e	0.068 e	0.00 e	0.00 e
Ba	0.77 e	0.77 e	0.00 e	0.93 e	1.7 e	0.29 e	0.090 e	0.57 e	0.43 e	0.59 e
La	0.046 e	0.41 e	0.00 e	0.70 e	0.00 e	0.00 e	1.2 e	0.27 e	0.62 e	1.1 e
Au	0.017	0.021	0.00 e	0.13 e	0.00 e	0.011 e	0.00 e	0.00 e	0.0051 e	0.00 e
Hg	0.024 e	0.033 e	0.13 e	0.14 e	0.014 e	0.096 e	0.053 e	0.028 e	0.0014 e	0.00 e
Tl	0.023	0.031	0.00	0.00	0.00	0.00	0.031	0.00	0.031	0.010
Pb	0.072	0.059	0.00	0.11	0.0036	0.00	0.0070	0.00	0.033	0.032
U	0.028	0.025	0.0051	0.0076	0.00	0.0037	0.043	0.0076	0.015	0.026

a Organic carbon evolved between 25°C and 550 °C including pyrolyzed carbon.

b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

e Value calculated with one or more measurements which were less than or equal to the measurement uncertainty.

low SO₂ emission for this fuel compared with the other straw fuels. SO₂ emission was determined simultaneously by an on-line continuous SO₂ analyzer. Barley appears to be distinctly different in this regard.

Silicon, calcium, and iron appeared in the PM of all the fuels at concentrations of less than 1%, except for the PM10 sample

from rice straw where Si accounted for almost 3.5%. Rice straw has the highest concentration of silicon (Table 7). Bromine was a consistent component of the PM of the herbaceous fuels in the range of 0.05 to 0.1%, whereas zinc was present in the PM of the wood fuels in the 0.1 to 0.65% range.

For the water soluble species, NO₃⁻ was present in the PM of

Table 5b. Average Emission Factor for Particulate Matter in 2.5 and 10 μm Size Classes, Wood Fuels, Group 1 Analysis

	Average Emission Factor, mg/kg							
	Walnut Prunings (n=2)		Almond Prunings (n=2)		Ponderosa Pine Slash (n=2)		Douglas Fir Slash (n=2)	
	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10
Cl-	150.	160.	65.	69.	31.	30.	20.	20.
NO ₃ -	43.	47.	39.	41.	16.	16.	31.	32.
SO ₄ =	180.	210.	160.	160.	140.	140.	120.	130.
NH ₄ ⁺	57.	56.	21.	23.	4.9	5.5	25.	24.
Na ⁺	4.5	4.1	6.8	9.4	7.9	9.1	16.	15.
K ⁺	230.	250.	250.	260.	250.	260.	140.	150.
C(org)	2200.	2300.	2100.	2100.	2500.	3100.	10000.	9900.
C(oh)	1900.	2000.	1800.	1700.	2200.	2400.	7800.	5900.
C(e)	1200.	1400.	1000. e	1200. e	1500. e	1600.	2000.	2600.
C(eht)	65.	120.	24. e	32.	21.	110.	130.	330.
C	3400. e	3700. e	3100. e	3300. e	4000. e	4600. e	12000.	13000.
Al	2.6	2.9	0.51	1.3	1.2	2.5	1.8	7.1
Si	4.0	6.0	0.84	2.4	5.0	6.7	3.0	13.
P	1.4	1.6	0.74	1.1	0.53	1.2	1.6	3.2
S	100.	90.	89. e	96.	75. e	74.	44.	47.
Cl	170. e	140. e	69. e	73. e	33. e	34. e	23. e	26. e
K	350. e	290. e	290. e	310. e	300. e	300. e	160. e	170. e
Ca	9.7 e	21. e	3.0 e	6.9 e	1.7 e	14. e	5.6 e	40. e
Ti	0.00	0.066	0.00 e	0.00 e	0.00	0.00	0.00	0.29
V	0.00	0.00	0.00	0.036	0.00 e	0.00	0.00	0.00
Cr	0.00 e	0.011 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e
Mn	0.057 e	0.16 e	0.00 e	0.033 e	0.14 e	0.36 e	0.39 e	1.3 e
Fe	0.40	1.4	0.30	0.87	0.17	2.0	0.65 e	4.8 e
Co	0.00	0.0029	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e
Cu	0.061 e	0.065 e	0.22 e	0.17 e	0.25 e	0.22 e	0.00	0.00
Zn	6.1 e	4.9 e	29. e	30. e	16. e	17. e	16. e	17. e
Ga	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	0.052	0.0057	0.023	0.00	0.00	0.00	0.79	0.78
Se	0.049	0.027	0.015 e	0.0055	0.00 e	0.00	0.067 e	0.1023
Br	1.8 e	1.5 e	0.53 e	0.58 e	0.18 e	0.19 e	0.67 e	0.65 e
Rb	0.34 e	0.29 e	0.29 e	0.30 e	1.2 e	1.2 e	0.55 e	0.58 e
Sr	0.11 e	0.24 e	0.046 e	0.10 e	0.010 e	0.064 e	0.017 e	0.1875 e
Y	0.00 e	0.00 e	0.012 e	0.0089 e	0.00 e	0.012 e	0.00 e	0.00 e
Zr	0.00 e	0.00 e	0.00 e	0.015 e	0.00 e	0.00 e	0.00 e	0.00 e
Mo	0.00 e	0.00 e	0.00 e	0.0000 e	0.00 e	0.00 e	0.00 e	0.00 e
Pd	0.00 e	0.034 e	0.00 e	0.0000 e	0.00 e	0.00 e	0.00 e	0.15 e
Ag	0.11 e	0.073 e	0.31 e	0.085 e	0.0052 e	0.00 e	0.28 e	0.34 e
Cd	0.00 e	0.00 e	0.023 e	0.071 e	0.00 e	0.00 e	0.13 e	0.00 e
In	0.00 e	0.00 e	0.00 e	0.13 e	0.10 e	0.070 e	0.28 e	0.10 e
Sn	0.00 e	0.0086 e	0.14 e	0.19 e	0.30 e	0.13 e	0.65 e	0.00 e
Sb	0.00 e	0.22 e	0.0060 e	0.12 e	0.14 e	0.00 e	0.00 e	0.00 e
Ba	0.38 e	0.25 e	0.95 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e
La	0.00 e	0.22 e	0.73 e	0.38 e	0.042 e	2.1 e	0.00 e	0.00 e
Au	0.0082	0.00	0.00	0.00	0.00	0.00	0.00	0.00 e
Hg	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e	0.00 e
Tl	0.0082	0.00	0.00	0.00	0.0052	0.023	0.00	0.00
Pb	1.5	1.3	0.38	0.47	0.24	0.40	0.40	0.32
U	0.0070	0.0038	0.0052	0.0055	0.00	0.00	0.00	0.00

a Organic carbon evolved between 25°C and 550 °C including pyrolyzed carbon.

b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

e Value calculated with one or more measurements which were less than or equal to the measurement uncertainty.

herbaceous and wood fuels in the range of 0.1 to 1%. NH₄⁺ levels in wood fuel particulate varied from 0.1 to 1% and 3 to 6% for the herbaceous fuels. Barley straw is again an exception with about 0.35% NH₄⁺. Na⁺ concentrations in the PM of the herbaceous fuels are 0.3 to 1% except for corn stover at 0.06%. Na⁺ levels in PM from wood fuels are in the range of 0.05 to

0.2%. Na is not normally present in high concentration because of its toxicity to plants. The other major alkali metal species, K, is a macronutrient typically at 1 to 2% in biomass. Cl⁻ and SO₄⁼ concentrations determined by IC and K⁺ concentrations determined by AA exhibit the same general trends as Cl, K, and S as determined by XRF, but individual determinations for Cl⁻ gave

higher concentrations than for Cl by XRF in some cases. This also occurred, but with less frequency, for K^+ and SO_4^{2-} . These inconsistencies are apparent in the tables of averages (Tables 3–6). Generally, this should be interpreted as the element being present almost exclusively in its ionic form and is associated with the additional sample preparation required for the wet analyses. XRF is performed directly on the filtered sample and is inherently less prone to analytical error.

The emission factors (mg of analyte per kg dry fuel) for each of the fuels are presented in Tables 5a and 5b, with herbaceous and wood fuel averages shown in Table 6. The data indicate that SO_4^{2-} , NH_4^+ , Na^+ , Cl, K, Cl^- , K^+ , S, and Br are emitted almost exclusively in the size fraction less than 2.5 μm , whereas Ca and Fe and to a lesser extent Si are emitted in the larger particles. The latter three species are associated with particulate emission of crustal origin. The fine particulate mode would be expected to persist in the atmosphere with the possibility of transport outside of the source region, whereas the coarse fraction would more likely be removed by dry deposition near the point of emission.

Barley straw has the highest emission factors of SO_4^{2-} , S, Na^+ , K, and K^+ . Corn stover has the largest emission factors for NH_4^+ and Cl. Walnut prunings emit the highest fraction of NO_3^- and Ca. Rice straw has the largest emission factors for Si and Fe. The large silicon emission rate is due to the high silicon content of rice straw (see Table 7). Barley straw and sugar cane both have high emission factors for Br, 8.4 and 8.7 $mg\ kg^{-1}$, respectively.

Elemental and proximate analyses for the fuels are presented in Table 7. The ratio of mass in the particulate matter to that in the fuel for selected elements (indicating, in the absence of other sources, element recovery) is presented in Tables 8a and 8b. With the exception of barley straw, Cl has the highest recovery for the herbaceous fuels with values ranging from 10 to 35%, followed by S, K, N as NO_3^- and NH_4^+ , Zn, and Na as Na^+ , all with recovery in the 2 to 5% range. Sodium recovery for sugar cane is higher at roughly 8%. For barley straw, S has the greatest recovery at 25%. Fuel nitrogen recovery as NO_3^- and NH_4^+ for barley is lower than for the other herbaceous fuels. Bromine was present at levels of <0.005% (the minimum detection limit for the method employed) in rice straw and sugar cane fuels. PM10 recovery factors computed using this as an upper concentration limit were ~10% and 17% respectively. The remaining elements generally exhibit recoveries of less than 2%. In four instances, the recovery of an element is greater in the PM2.5 fraction than it is in the PM10 fraction, Cu for barley straw, Na for corn stover, and N for rice and wheat straw. This follows directly from the particulate composition data (see Table 3a) for these elements. NH_4^+ , NO_3^- , and Na^+ were determined using wet chemistry analytical methods as discussed earlier which may be responsible for these discrepancies. Similarly, XRF analysis of barley straw particulate revealed copper levels which were always smaller than the uncertainty of the measurement. Another possible source of error lies in the fuel analyses and sample preparation. Subsamples from the same fuel sample were sent to different independent laboratories for analysis, and the results were found to vary by as much as 2.5% (absolute) for sugar cane Si analysis, 920 $mg\ kg^{-1}$ for Zn in Douglas fir slash, and 60 $mg\ kg^{-1}$ for Na in walnut prunings.

High sulfur recovery is characteristic of the wood fuels, whereas Cl recovery levels are in the same range as the herbaceous fuels. K is recovered in the 10 to 20% range, at least

Table 6. Average Emission Factor of Each Analyte in Two PM Size Ranges for Herbaceous and Wood Fuels

	Average Emission Factor, mg/kg			
	Herbaceous Fuels (n=16)		Wood Fuels (n=8)	
	PM2.5	PM10	PM2.5	PM10
Cl-	880	920	66	69
NO ₃ -	14	15	32	34
SO ₄ =	230	240	150	160
NH ₄ +	170	170	27	27
Na+	23	24	8.7	9.5
K+	730	770	220	230
C(org)a	1800	1900	4200	4300
C(oh)b	1600	1800	3400	3000
C(e)c	750	780	1400	1700
C(eht)d	42	45	60	150
C	2600	2700	5600	6000
Al	4.6 e	5.6 e	1.5 e	3.5 e
Si	6.0 e	29	3.2 e	6.9
P	1.2 e	1.8 e	1.1 e	1.8 e
S	100	110	78	77
Cl	730	780	75	69
K	720	760	280	270
Ca	2.4 e	11 e	5.0 e	20
Ti	0.059 e	0.29 e	0.0000 e	0.089 e
V	0.031 e	0.049 e	0.0000 e	0.0089 e
Cr	0.030 e	0.093 e	0.0000 e	0.0026 e
Mn	0.26 e	1.3	0.14 e	0.46 e
Fe	0.49 e	4.1	0.38 e	2.3
Co	0.019 e	0.014 e	0.0000 e	0.0007 e
Ni	0.0073 e	0.036 e	0.0000 e	0.0000 e
Cu	0.049 e	0.060 e	0.13 e	0.12 e
Zn	0.56	0.65	17	17
Ga	0.0031 e	0.0079 e	0.0000 e	0.0000 e
As	0.016 e	0.022 e	0.22 e	0.20 e
Se	0.025 e	0.028 e	0.033 e	0.034 e
Br	5.5	5.9	0.80	0.73
Rb	0.36	0.37	0.60	0.58
Sr	0.027 e	0.11 e	0.047 e	0.15
Y	0.027 e	0.030 e	0.0030 e	0.0052 e
Zr	0.035 e	0.016 e	0.0000 e	0.0038 e
Mo	0.036 e	0.040 e	0.0000 e	0.0000 e
Pd	0.084 e	0.11 e	0.0000 e	0.047 e
Ag	0.27 e	0.25 e	0.18 e	0.12 e
Cd	0.12 e	0.28 e	0.039 e	0.018 e
In	0.018 e	0.10 e	0.097 e	0.075 e
Sn	0.11 e	0.11 e	0.27 e	0.083 e
Sb	0.16 e	0.22 e	0.036 e	0.084 e
Ba	0.59 e	0.63 e	0.33 e	0.063 e
La	0.37 e	0.49 e	0.19 e	0.68 e
Au	0.0045 e	0.032 e	0.0021 e	0.0000 e
Hg	0.044 e	0.059 e	0.0000 e	0.0000 e
Tl	0.017 e	0.0083 e	0.0034 e	0.0059 e
Pb	0.023 e	0.040 e	0.64	0.62 e
U	0.018 e	0.014 e	0.0031 e	0.0023 e

a Organic carbon evolved between 25°C and 550 °C including pyrolyzed carbon.

b Organic carbon evolved between 120°C and 550 °C including pyrolyzed carbon.

c Elemental carbon evolved between 550°C and 800 °C excluding pyrolyzed carbon.

d Elemental carbon evolved between 700°C and 800 °C excluding pyrolyzed carbon.

e Emission factor calculated with one or more measurements which were less than or equal to the measurement uncertainty.

Table 7. Average Fuel Compositions

Fuel Type	Rice Straw	Wheat Straw	Barley Straw	Corn Stover	Walnut Pruning	Almond Pruning	Ponderosa Pine Slash	Douglas Fir Slash	Sugar Cane
Number of sample analyses	6	2	2	2	2	2	2	2	2
Ultimate analysis, % dry weight									
C	38.06	44.28	44.85	44.78	48.23	49.16	52.41	51.65	42.35
H	5.28	5.77	5.85	5.88	6.00	6.24	6.20	6.24	5.83
Elemental analysis, % dry weight									
N	0.72	0.62	0.77	0.58	0.60	0.49	0.30	0.27	0.40
P	0.07	0.05	0.12	0.08	0.04	0.03	0.02	0.02	0.06
K	1.71	1.89	2.50	1.76	0.30	0.29	0.16	0.17	0.79
Ca	0.27	0.11	0.26	0.17	1.33	0.28	0.35	0.35	0.30
Mg	0.20	0.11	0.11	0.38	0.28	0.12	0.06	0.03	0.20
Cl	0.48	0.29	0.20	0.36	0.13	0.03	0.00	0.01	0.62
Si	7.03	2.32	1.24	1.22	0.23	0.27	0.28	0.14	1.35
Elemental analysis, mg/kg dry weight									
S	894	1835	1300	596	372	208	202	166	1611
B	14	6	7	12	30	15	4	5	10
Zn	24	14	12	18	40	10	10	940	13
Mn	693	22	66	53	33	12	66	118	143
Fe	265	251	128	285	225	1329	175	245	392
Na	983	550	1700	100	40	20	10	10	244
Cu	9	3	4	4	3	4	3	2	10
Br ^a	50	-	-	-	-	-	50	-	50
Total, % dry weight	47.06	53.37	54.96	54.08	56.99	56.84	59.63	58.85	54.60
Proximate analysis, % dry weight									
Ash	18.59	9.38	7.61	6.12	3.67	1.33	1.22	0.55	8.57
Volatiles	68.77	76.24	78.06	77.33	82.96	82.28	81.51	82.95	76.45
Fixed Carbon	12.64	14.38	14.33	16.55	13.37	16.39	17.27	16.50	14.97

a Dash indicates analysis not available.

Table 8a. Average Fuel Element Recovery in PM by Size Fraction for Herbaceous Fuels

	Fuel Analyte Recovered in PM, ^a %									
	Rice Straw		Wheat Straw		Barley Straw		Corn Stover		Sugar Cane	
	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10
Si	0.01	0.12	0.03	0.09	0.06	0.11	0.02	0.09	0.02	0.09
S	3.8	4.0	5.2	5.6	25	26	5.2	5.4	2.0	2.3
Cl	16	18	32	34	19	19	29	29	9	11
K	2.9	3.1	4.5	4.7	5.0	5.2	3.5	3.5	5.3	6.1
Ca	0.09	0.61	0.18	0.35	0.10	0.31	0.11	0.40	0.11	0.63
Fe	0.25	2.2	0.28	2.1	0.22	1.9	0.13	1.1	0.11	0.91
N from NO ₃ ⁻ and NH ₄ ⁺	2.3	2.3	2.5	2.4	0.33	0.37	3.9	4.2	2.4	2.4
Zn	3.3	3.8	3.6	4.2	3.3	4.3	4.2	4.6	3.0	3.6
C	0.36	0.38	0.66	0.69	0.95	0.99	0.52	0.57	0.49	0.50
Mn	0.10	0.67	0.41	1.1	0.10	0.46	0.31	0.75	0.19	0.67
Na	1.9	2.1	3.0	3.2	3.4	3.6	3.0	2.6	7.7	8.1
Cu	0.92	1.0	2.2	2.9	0.09	0.00	0.84	1.3	0.75	0.88
P	0.00	0.00	0.59	0.81	0.21	0.30	0.06	0.09	0.09	0.17
Br ^b	9.3	9.9	-	-	-	-	-	-	15	17

a On the basis of data and number of measurements shown in Tables 5 and 7.

b Dash indicates analysis not available.

2 times greater than for the herbaceous fuels. Less than 2% of the Si, Ca, Fe, N, C, Mn, and P present in the wood fuels is recovered in the particulate. Cu recoveries are slightly higher but still less than 10%. Br was detected at levels of <0.005% in ponderosa pine fuel samples, the only wood fuel analyzed for this element. Br recovery calculated using this upper limit was 0.4%. Zinc recovery in excess of 100% was computed for almond prunings and ponderosa pine slash. Excess PM sodium was found in the case of Douglas fir. Possible sources of error are discussed above. For the wood fuels, numerous PM2.5 element recoveries were found to be greater than those computed for PM10. Differences were less than 4% (absolute) for all those where element recovery was less than 100%.

Group 2

PIXE results for the DRUM samples are presented in Figures 3 through 7. The results are given as relative abundances of the major elements in each of the size fractions with respect to the 10–15 μm size fraction. The graphs indicate that for the herbaceous fuels, Cl and K are enriched and Si, Ca, and Fe are depleted in the smaller size fractions. This confirms the trends exhibited by the analyses of the group 1 samples.

The total PM samples of group 2 were also analyzed by PIXE. A comparison of the PM elemental mass concentrations of group 2 against the PM10 size fraction of group 1 for Cl, Fe, K, and Si is presented in Figure 8. Individual points appear for all fuel

Table 8b. Average Fuel Element Recovery in PM by Size Fraction for Wood Fuels

	Fuel Analyte Recovered in PM, ^a %							
	Walnut Prunings		Almond Prunings		Ponderosa Pine Slash		Douglas Fir Slash	
	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10
Si	0.17	0.26	0.03	0.09	0.18	0.24	0.22	0.90
S	27	24	43	46	37	37	27	28
Cl ^b	13	11	20	22	-	-	23	26
K	11	10	10	11	19	19	9.5	10
Ca	0.07	0.16	0.11	0.25	0.05	0.39	0.16	1.1
Fe	0.18	0.64	0.02	0.07	0.10	1.1	0.27	1.9
N from NO ₃ ⁻ and NH ₄ ⁺	0.90	0.89	0.52	0.55	0.24	0.26	0.98	0.96
Zn	15	12	290	300	160	160	1.7	1.8
C	0.70	0.77	0.63	0.67	0.76	0.88	2.3	2.4
Mn	0.17	0.49	0.00	0.27	0.21	0.55	0.33	1.09
Na	11	10	34	47	79	91	160	160
Cu	2.3	2.4	5.7	4.4	8.8	8.0	0.00	0.00
P	0.39	0.45	0.23	0.35	0.29	0.67	0.63	1.3
Br ^c	-	-	-	-	0.37	0.39	-	-

a Based on data and number of measurements shown in Tables 5 and 7.

b Dash indicates Cl was not found in fuel.

c Dash indicates analysis not available.

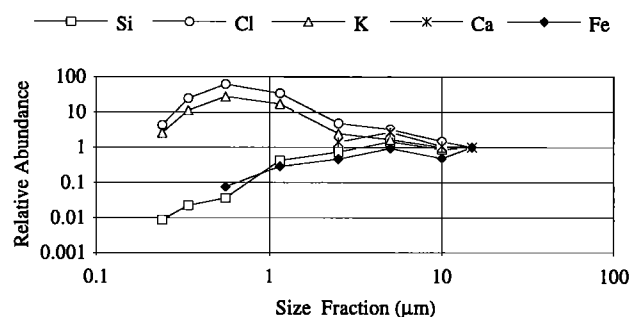


Figure 3. Relative abundance by size fraction of major elements in Davis Rotating-Drum Unit for Monitoring (DRUM) sampled particulate matter (PM) generated from rice straw fuel.

types. Agreement is good for the elements K and Cl, but the PIXE values for Fe and Si are larger than the XRF values. Because K and Cl are concentrated in the smaller size particles, whereas Fe and Si are present in the larger size fractions, the exclusion of particles larger than 10 μm in the group 1 samples may possibly contribute to the differences observed between the two analytical techniques. Other factors pertaining to the sensitivity of the techniques may also play a role.

Comparison to Other Studies

The results for the wood fuels generally agree with the data of Hudson *et al.* [1991] for concentrations of water soluble compounds in the smoke from forest fires and laboratory experiments with chaparral brush. The average of wheat and barley data from the current study compares well with that of Rogers [1991] for California wheat and barley stubble.

Andreae *et al.* [1988] reported K to soot carbon ratios of 0.1 to be a signature for biomass particulate, where soot carbon was measured using a reflectance method. In the present study, average values of potassium to elemental carbon in PM₁₀ for wood and herbaceous fuels calculated from Table 4 were 0.20 and 0.95, respectively. From PM composition data reported by Cachier *et al.* [1991] for aerosols collected during the savanna burning season in the Ivory Coast, a K^+ to "black" carbon ratio of 1.1 can be calculated which compares well with the value reported here for herbaceous fuels. Although some portion of the differences among the potassium to elemental carbon ratios reported by these investigations may be due to the methodologies and analytical techniques employed, as well as the age and upper size limit of the PM samples collected, there exists strong evidence to suggest that lower ratios [e.g., Andreae *et al.*, 1988] are more representative of wood burning, with higher ratios [e.g.,

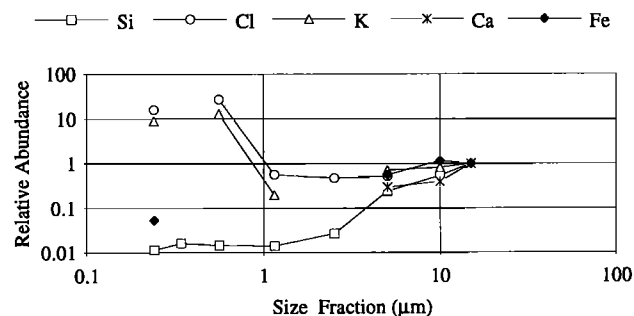


Figure 4. Relative abundance by size fraction of major elements in DRUM sampled PM generated from wheat straw fuel.

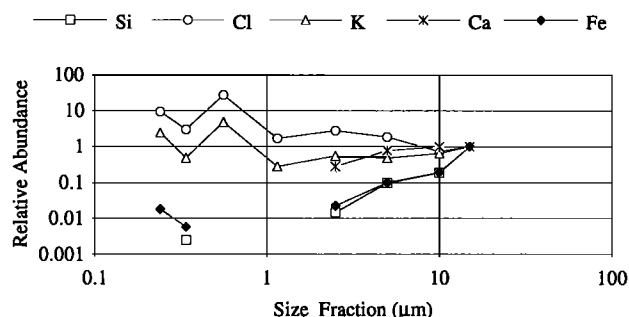


Figure 5. Relative abundance by size fraction of major elements in DRUM sampled PM generated from barley straw fuel.

Cachier *et al.*, 1991] representative of herbaceous (grass) fuels, and that the $\text{K}/\text{C}(\text{e})$ ratio may be used to distinguish between the two fuel types. This assertion is further supported by the work of Allen and Miguel [1995] which reported lower K^+ concentrations in PM collected from fires in primary and secondary rainforests compared to four grassland dominated ecosystems; campo limpo, campo sujo, campo cerrado, and rough grasslands resulting from previously converted forest.

Sulfate and nitrate concentrations reported by Cachier *et al.* [1991] were used to calculate ratios of black carbon to SO_4^{2-} , $\text{K}^+/\text{SO}_4^{2-}$, $\text{NO}_3^-/\text{SO}_4^{2-}$, black carbon to NO_3^- , and K^+/NO_3^- . Agreement between the computed ratios and those derived from the current study was found to be poor. This may be due in part to differences in sulfur and nitrogen availability in the soils at the two locales. Similar regional differences were observed for correlations for K^+ versus NO_3^- and K^+ versus SO_4^{2-} from two locations in Brazil [Allen and Miguel, 1995].

Potassium and chlorine are the two dominant inorganic elements present in the results from the current study. Figure 9 compares the average concentrations for the herbaceous and wood fuel types with values from other studies. Potassium levels measured in the present work are bounded by literature values. However, the chlorine concentration of the PM_{2.5} from herbaceous fuels is roughly two times greater than any other reported. In the herbaceous fuel PM, K and Cl are present in roughly equal amounts on a molecular basis and were found to occur as KCl salts on filters examined with a scanning electron microscope and electron beam microprobe. This ratio is evident in the data from Allen and Miguel [1995] for grassland fires. Differences among the studies may be due in part to plant type and nutritional status, fire type and dynamics, plume ages, analytical techniques, and sample masses collected on the filter media.

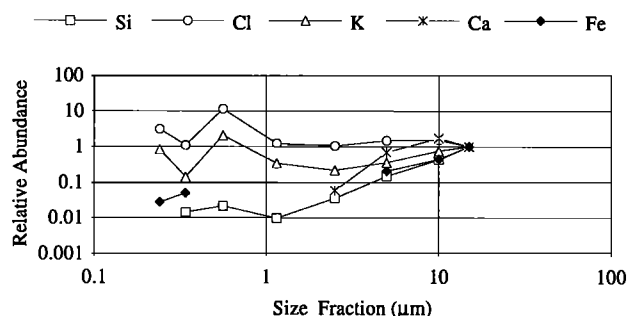


Figure 6. Relative abundance by size fraction of major elements in DRUM sampled PM generated from sugar cane fuel.

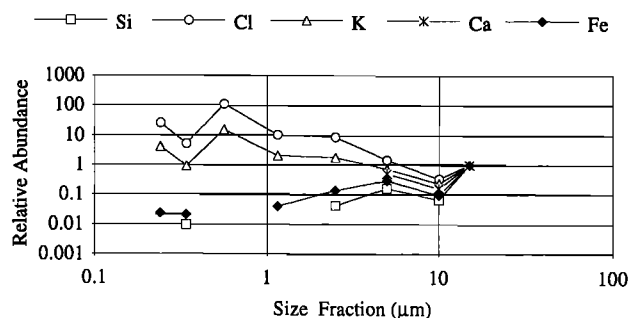


Figure 7. Relative abundance by size fraction of major elements in DRUM sampled PM generated from corn stover fuel.

Leslie's [1981] determination of the elemental content of size segregated PM emitted from fires in three types of vegetative ecosystems found the fine mode PM ($< 2 \mu\text{m}$) to be enriched in S and Cl, whereas the coarse mode ($> 2 \mu\text{m}$) was dominated by K, Ca, and Fe. Results from the current work are in general agreement with the exception of potassium, which was found to be present in the smaller size fraction in greater abundance.

A recent estimate in the literature [Manö and Andreae, 1994] has identified biomass burning to be a substantial source of methyl bromide emission, with implications for the destruction of stratospheric ozone. Additional issues were raised [Cicerone, 1994] pertaining to the manner in which bromine is released by the combustion process and the need for constructing more complete bromine inventories. Manö and Andreae [1994] found molar emission ratios of methyl bromide to carbon dioxide (molar emission rate of CH_3Br divided by the molar emission rate of CO_2 , $(\text{CH}_3\text{Br}/\text{CO}_2)$) for boreal forest fires to be 2 to 3 times higher than the emission ratios from savanna and chapparal fires. Using CO_2 emission factors (mg CO_2 per kg dry fuel) derived from the same tests as the current data set, PM₁₀ Br to gaseous CO_2 emission ratios were computed on a molar basis. The values are presented in Table 9, along with the gas phase $\text{CH}_3\text{Br}/\text{CO}_2$ ratios reported by Manö and Andreae [1994]. The trend of higher gas phase $\text{CH}_3\text{Br}/\text{CO}_2$ emission ratios for wood

fuels compared to savanna/chapparal fuels [Manö and Andreae, 1994] is reversed in the case of PM₁₀ Br/ CO_2 emission ratios for wood and herbaceous fuels (current work), suggesting that low gas phase CH_3Br emission is accompanied by elevated Br emission in particulate matter and vice versa. Unfortunately, both studies lack the simultaneous gas and PM bromine measurements and fuel bromine analyses necessary to draw stronger conclusions.

Bromine is also useful as a signature element in identifying particulate matter emitted from biomass burning by determining its mass ratio with elemental high-temperature carbon, $\text{C(elt)}/\text{Br}$ as shown in Table 9. Within the scope of the current study, $\text{C(elt)}/\text{Br}$ in the PM_{2.5} fraction permits differentiation not only between herbaceous ($\text{C(elt)}/\text{Br} \sim 7$) and wood fuels, but between PM originating from orchard ($\text{C(elt)}/\text{Br} \sim 43$) and forest ($\text{C(elt)}/\text{Br} \sim 150$) sources.

Summary and Conclusions

Particulate matter emitted from wind tunnel simulations of biomass burning for five herbaceous crop residues and four wood fuel was collected and analyzed. The herbaceous crop group included rice, wheat and barley straws, corn stover, and sugar cane trash. Walnut and almond prunings and ponderosa pine and Douglas fir slash comprised the wood fuels. Herbaceous fuels were burned as spreading fires in opposition to the wind, whereas wood fuels were burned in stationary piles.

XRF analysis revealed the particulate matter composition to be dominated by the elements C, K, Cl, and S. Carbon accounted for roughly 50% of the herbaceous fuel PM and about 70% for the wood fuel PM, with more than 50% of the carbon component consisting of organic forms. High-temperature organic carbon accounted for about 80% of the organic carbon fraction. K, Cl, and S concentrations in the PM of the herbaceous fuels were in the range of 10 to 20%, 5 to 30% and 0.5 to 4% respectively. For the herbaceous fuels, rice straw PM₁₀ had the highest concentrations of both K (24%) and Cl (17%) and barley straw PM₁₀ contained the highest sulfur content (4%). K, Cl, and S were present in the PM of the wood fuels at reduced levels with

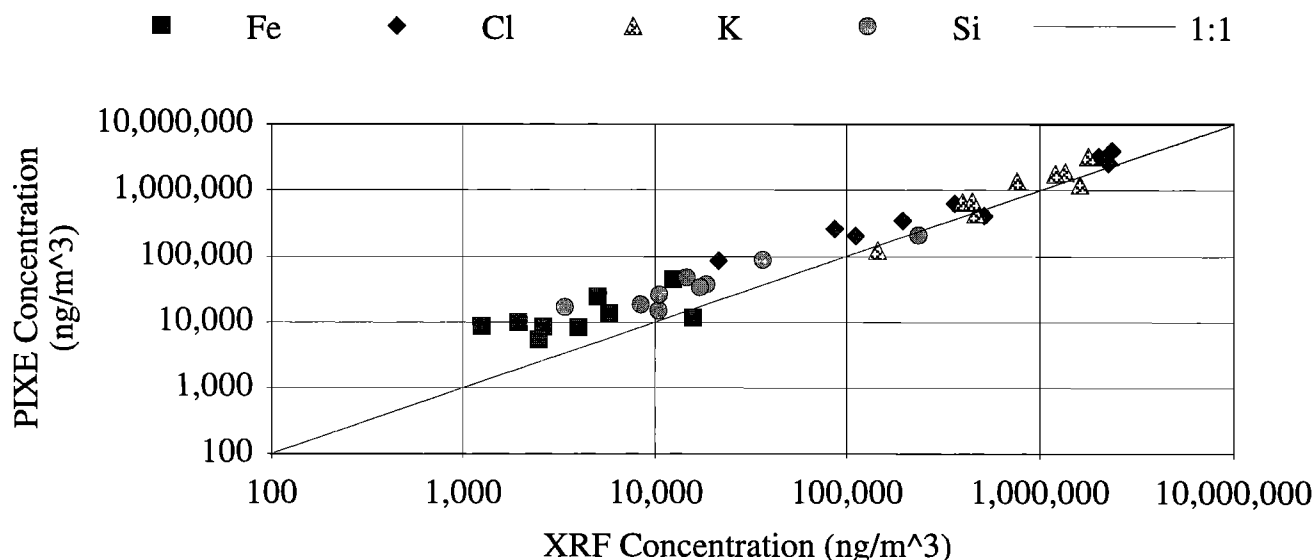


Figure 8. Comparison of PM analyses by particle induced X ray emission and X ray fluorescence for four elements from nine fuels.

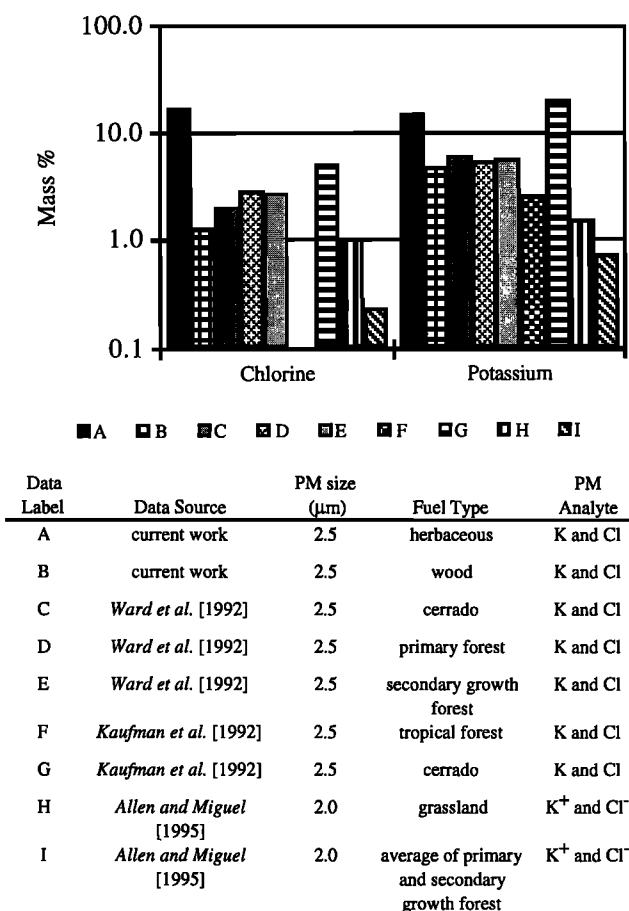


Figure 9. Average potassium and chlorine mass concentrations in PM_{2.5} from herbaceous and woody fuels compared to similar measurements reported in the literature.

maximum concentrations of 6.5% (almond prunings), 3% (walnut prunings), and 2% (almond prunings), respectively.

Of the herbaceous fuels, rice straw PM₁₀ had the highest concentrations of Si, Ca, and Fe. PM₁₀ from walnut prunings produced the highest Si and Ca concentrations and ponderosa pine slash PM₁₀ exhibited the greatest Fe levels for the wood fuels. Bromine was a consistent component of the PM from herbaceous fuels in the 0.05 to 0.2% range, whereas wood fuel PM levels were in the range of 0.003 to 0.03%.

Analysis of water soluble species indicated that ionic forms of K, Cl, and S predominate in the particulate matter from all fuels. NO₃⁻, NH₄⁺, and Na⁺ are found in the particulate from wood fuels at levels of less than 1%. Similar concentrations were found for NO₃⁻ and Na⁺ in particulate matter from herbaceous fuels. Corn stover PM₁₀ had the highest NH₄⁺ concentration at 6%.

Fuel elemental and proximate analyses were performed and element balances testing extent of analytical closure were determined. K, Cl, S, and N were found to have the highest recovery in particulate matter for the fuel elements analyzed. In general, chlorine was the most efficiently recovered element for the herbaceous fuels (10 to 35%), whereas sulfur recovery was greatest for the wood fuels (25 to 45%).

Ca, Fe, and Si were emitted primarily in the coarse particle fraction. Water soluble species were more abundant in the fine fraction. Agreement of XRF and PIXE for elemental composition was found to be good for K and Cl.

Table 9. Molar Emission Ratios of Gas Phase CH₃Br/CO₂ and PM₁₀ Br/CO₂ From Total Fires (Smoldering and Flaming Phases) and Mass Ratios of Elemental High Temperature Carbon (C(elt)) to Bromine in PM_{2.5}

	CH ₃ Br/CO ₂ ^a (x10 ⁶)	PM ₁₀ Br/CO ₂ (x10 ⁶)	C(elt)/Br PM _{2.5}
Laboratory fires	0.29	-	-
Chaparral fires	0.65	-	-
African savanna fires	0.46	-	-
Boreal forest fires	1.30	-	-
Rice straw	-	2.36	8.9
Wheat straw	-	1.87	9.8
Barley straw	-	4.00	7.7
Corn stover	-	1.42	7.8
Walnut prunings	-	0.50	42.8
Almond prunings	-	0.18	44.3
Ponderosa pine slash	-	0.05	114.7
Douglas fir slash	-	0.16	195.6
Sugar cane	-	4.48	4.2

^a Data from Manö and Andreae [1994]

Comparison of the PM₁₀ K/C(e) ratios with literature values indicate values of 0.20 and 0.95 to be signatures of particulate from wood and herbaceous fueled fires respectively. The ratios for elemental high-temperature carbon to bromine (C(elt)/Br) in PM_{2.5} produced by biomass burning demonstrated substantial differences among herbaceous, orchard prunings, and forest slash materials (7.5, 43, and 150 respectively). The mass of Br found in the particulate phase is roughly equivalent to that in gas phase methyl bromide emission (reported by others) per unit mass of CO₂ emitted by the fire. The form of bromine in PM from biomass burning and its environmental implications are largely undetermined and perhaps warrant further investigation.

Acknowledgments. This work was funded in part by the California Air Resources Board, Sacramento, California, the Hawaiian Sugar Planters' Association, Aiea, Hawaii; the Sugar Research and Development Corporation, Brisbane, Australia; Centro de Tecnologia Copersucar, Sao Paulo State, Brazil; Cenicaña, Cali, Colombia; the South African Sugar Experiment Station, Natal, South Africa; the Florida Sugar Cane League Inc., Clewiston, Florida; and the American Sugar Cane League, Thibodaux, Louisiana.

References

- Allen, A.G., and A.H. Miguel, Biomass burning in the Amazon: Characterization of the ionic component of aerosols generated from flaming and smoldering rainforest and savannah, *Environ. Sci. Technol.*, 29(2), 486-493, 1995.
- Andreae, M.O., et al., Biomass-burning emissions and associated haze layers over Amazonia, *J. of Geophys. Res.*, 93(D2), 1509-1527, 1988.
- Asubiojo, O.I., I.B. Obich, E.A. Oluwemi, A.G. Oluwale, N.M. Spyrou, A.S. Farooqi, W. Arshed and O.A. Akanle, Elemental characterization of airborne particulates at two Nigerian locations during the harmattan season, *J. Radioanal. Nucl. Chem.*, 167(2) 283-293, 1993.
- Cachier, H., J. Ducret, M.P. Brémond, V. Yoboué, J.P. Lacaux, A. Gaudichet, and J Baudet, Biomass burning in a savanna region of the Ivory Coast, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implication*, edited by J. Levine, pp. 174-180, MIT Press, Cambridge, Mass., 1991.
- Cahill, T.A., P.J. Feeney, and T.A. Eldred, Size-time composition profile of aerosols using the DRUM sampler, *Nucl. Instrum. Methods Phys. Res.*, B22, 344-348, 1987.
- Chow, J.C., Quality assurance project plan for the determination of particle size distributions and chemical composition of particulate matter from selected sources in California, II, Laboratory operations,

- DRI Doc. 8096.1F1, prepared for the Calif Air Resources Board, Sacramento, by the Desert Res. Inst., Reno, Nev., 1987.
- Chow, J.C., J.G. Watson, L.C. Pritchett, W.R. Pierson, C.A. Frazier, and R.G. Purcell, The DRI thermal/optical carbon analysis system: Description, evaluation and applications in U.S. air quality studies, *Atmos. Environ.*, 27A(8), 1185-1201, 1993a.
- Chow, J.C., J.G. Watson, D.H. Lowenthal, P.A. Solomon, K.L. Magiano, S.D. Ziman, and L.W. Richards, PM₁₀ and PM_{2.5} compositions in California's San Joaquin Valley, *Aerosol Sci. Technol.*, 18, 105-128, 1993b.
- Cicerone, R.J., Fires, atmospheric chemistry, and the ozone layer, *Science*, 263, 1243-1244, 1994.
- Cofer, W.R., J.S. Levine, E.L. Winstead, and B.J. Stocks, Trace gas and particulate emissions from biomass burning in temperate ecosystems, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implication*, edited by J. Levine, pp. 203-208, MIT Press, Cambridge, Mass., 1991.
- Friedlander, S.K., Chemical element balances and the identification of air pollution sources, *Environ. Sci. Technol.*, 7, 235-240, 1973.
- Hopke, P.K. Receptor modeling for air quality management, in *Data Handling in Science and Technology*, Vol. 7, edited by P.K. Hopke, pp. 303-329, Elsevier, New York, 1991.
- Hudson, J.G., C.F. Rogers, and J. Hallett, Field and laboratory measurements for cloud-forming properties of combustion aerosols, *J. Geophys. Res.*, 96(D6), 10847-10859, 1991.
- Jenkins, B.M., S.Q. Turn, and R.B. Williams, Atmospheric emissions from agricultural burning in California: Determination of burn fractions, distribution factors, and crop-specific contributions, *Agric. Ecosys. Environ.*, 38, 313-330, 1992.
- Jenkins, B.M., I.M. Kennedy, S.Q. Turn, R.B. Williams, S.G. Hall, S.V. Teague, D.P.Y. Chang, and O.G. Raabe, Wind tunnel modeling of atmospheric emissions from agricultural burning: Influence of operating configuration on flame structure and particle emission factor for a spreading-type fire, *Environ. Sci. Technol.*, 27(9), 1763-1775, 1993.
- Kaufman, Y.J., A. Setzer, D. Ward, D. Tanre, B.N. Holben, P. Menzel, M.C. Pereira, and R. Rasmussen, Biomass burning airborne and spaceborne experiment in the Amazonas (BASE-A), *J. Geophys. Res.*, 97(D13) 14581-14599, 1992.
- Leslie, A.C.D., Aerosol emissions from forest and grassland burnings in the southern Amazon basin and central Brazil, *Nucl. Instrum. Methods*, 181, 345-351, 1981.
- Manö, S., and M.O. Andreae, Emission of methyl bromide from biomass burning, *Science*, 263, 1255-1257, 1994.
- Rogers, C.F., J.G. Hudson, B. Zielinska, R.L. Tanner, J. Hallett, and J.G. Watson, Cloud condensation nuclei from biomass burning, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implication*, edited by J. Levine, pp. 431-438, MIT Press, Cambridge, Mass., 1991.
- Rojas, C.M., L. Figueroa, K.H. Janssens, P.E. Van Espen, F.C. Adams, and R.E. Van Grieken, The elemental composition of airborne particulate matter in the Atacama Desert, Chile, *Sci. Total Environ.*, 91, 251-267, 1990.
- Ward, D.E., R.A. Susott, J.B. Dauffman, R.E. Babbitt, D.L. Cummings, B. Dias, B.N. Holben, Y.J. Kaufman, R.A. Rasmussen, and A.W. Setzer, Smoke and fire characteristics for cerrado and deforestation burns in Brazil: BASE-B experiment., *J. Geophys. Res.*, 97(D13), 14601-14619, 1992.
- Watson, J.G., J.A. Cooper, and J.J. Huntzicker, The effective variance weighting for least squares calculations applied to the mass balance receptor model, *Atmos. Environ.*, 18, 1347-1355, 1984.
- Williams, R.B., A wind tunnel investigation of the turbulent flow upstream of a freely spreading fire, M.S. thesis, Univ of Calif., Davis, 1992.

S.Q. Turn, Hawaii Natural Energy Institute, University of Hawaii, 2540 Dole St., Holmes Hall 246, Honolulu, HI 96822. (e-mail: sturn@hawaii.edu)

B.M. Jenkins, Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616. (e-mail: bmjenkins@ucdavis.edu)

J.C. Chow and L.C. Pritchett, Desert Research Institute, P.O. Box 60220, Reno, NV 89506. (email: judyc@jarbridge.sage.dri.edu; lylep@jarbridge.sage.dri.edu)

D. Campbell and T. Cahill, Crocker Nuclear Laboratory, University of California, Davis, CA 95616. (email: campbell@crocker.ucdavis.edu; cahill@crocker.ucdavis.edu)

S. Whalen, Hawaiian Sugar Planters' Association, 99-193 Aiea Heights Drive, P.O. Box 1057, Aiea, HI 96701. (email: swhalen@harc-hspa.com)

(Received October 27, 1995; revised March 28, 1996; accepted September 1, 1996.)