Chemical Compositions of Primary PM$_{2.5}$ Derived from Biomass Burning Emissions

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ABSTRACT

A number of field studies have provided evidence that biomass burning is one of the major global sources of atmospheric particles. In this study, we have collected PM$_{2.5}$ emitted from biomass burning combusted at open burning and laboratory chamber situations. The open burning experiment was conducted with the cooperation of 9 farmers in Chiba Prefecture, Japan, while the chamber experiment was designed to evaluate the characteristics of chemical components among 14 different plant species. The analyzed categories were PM$_{2.5}$ mass concentration, organic carbon (OC), elemental carbon (EC), ionic components (Na$^+$, NH$_4^+$, Ca^{2+}, Mg^{2+}, K$^+$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$), water-soluble organic carbon (WSOC), water-insoluble inorganic carbon (WIOC), char-EC and soot-EC. OC was the dominant chemical component, accounting for the major fraction of primary PM$_{2.5}$ derived from biomass burning, followed by EC. Ionic components contributed a small portion of PM$_{2.5}$, as well as that of K$^+$. In some cases, K$^+$ is used as biomass burning tracer; however, the observations obtained in this study suggest that K$^+$ may not always be suitable as a tracer for biomass burning emissions. Also, the results of all the samples tested indicate relatively low values of char-EC compared to soot-EC. From our results, careful consideration should be given to the usage of K$^+$ and char-EC as indicators of biomass burning. The calculated ratios of WSOC/OC and WIOC/OC were 55.7% and 44.3% on average for all samples, which showed no large difference between them. The organic materials to OC ratio, which is often used for chemical mass closure model, was roughly estimated by two independent methods, resulting in a factor of 1.7 for biomass burning emissions.

Key words: PM$_{2.5}$, Biomass burning, Organic carbon, Elemental carbon, Ionic composition, Japan

1. INTRODUCTION

According to the announcement of the Ministry of the Environment of Japan (MOEJ), the attainment ratio of Environmental Quality Standards for atmospheric particulate matter with diameter less than 2.5 μm (PM$_{2.5}$) was quite low during the period 2010-2014 (http://www.env.go.jp/air/osen/, in Japanese, Accessed on October 10, 2016). Effectively reducing levels of PM$_{2.5}$ will require understanding not only their complex physical and chemical characteristics in ambient atmosphere, but also their sources.

During and after the harvest period (generally fall to winter), farmers often burn crop residues in their fields to dispose of agricultural waste and to advance crop rotation. Previous studies have discussed biomass burning emissions as one of the main factors causing the elevation of PM$_{2.5}$ levels during the same period in Japan (Ichikawa et al. 2015a; Hasegawa et al., 2014; Kumagai et al., 2010; Hagino et al., 2006). On November 4th, 2013, a high PM$_{2.5}$ level was observed in Ichihara, Chiba Prefecture, Japan. Ichikawa et al. (2015a) reported that levoglucosan, commonly used as the tracer of biomass burning (Simoneit et al., 1999), exhibited relatively high concentrations on the same date and concluded, therefore, that biomass burning was likely an important influence on PM$_{2.5}$. Furthermore, numerous field studies conducted in other parts of the world have provided evidence of the effect of biomass burning smoke emitted from crop residue burning, and forest or grassland fires are responsible for the input of organic aerosol components to the atmosphere (Li et al., 2016; Yang et al., 2016; Alves et al., 2015; Wang et al., 2015a, b; Huang et al., 2014; Jung et al., 2014; Urban et al., 2014; Piletic et al., 2013; Sang et al., 2013; Jia et al., 2010; Gelencsér et al., 2007; Abas et al., 2004; Simoneit et al., 2004). Due to the accumulation of atmospheric measurement data, attention to the impact of biomass burning emissions to the PM$_{2.5}$ has been increasing. However, measurement studies of PM$_{2.5}$ in biomass burning emissions are still insufficient.

The use of receptor models is a powerful technique for apportioning and quantifying the contributions of individual species of air pollutants at receptor sites. EPA CMB (https://www3.epa.gov/scram001/receptor_cmb.htm, Accessed on October 10, 2016) is one of the most widely used receptor modeling methods, but this model requires the emission characteristics of individual sources for calculation and that of biomass burning emission is needed to analyze precisely.

In Japan, experimental data on the emission characteristics of sources are insufficient, especially from biomass burning studies. To the best of our knowledge, there are only two domestic papers (Takahashi *et al.*, 2011; Tokyo Metropolitan Government, 2011) reporting the emission characteristics of biomass burning. Thus, it is essential to identify the chemical profiles and contributions made from biomass burning in order to better understand the impact of biomass burning emissions to $PM_{2.5}$.

In this study, $PM_{2.5}$ samples emitted from biomass burning were collected at both open burning and chamber experiments to analyze their chemical compositions and characteristics. Collected samples were analyzed for $PM_{2.5}$ mass concentration, organic carbon (OC), elemental carbon (EC), ionic species (Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, NO_3^- and SO_4^{2-}), water-soluble organic carbon (WSOC), water-insoluble organic carbon (WIOC), char-EC and soot-EC. Our results aim to provide further information and understanding of the influence of biomass burning emissions on $PM_{2.5}$ and thereby contribute to better air quality management strategies.

2. MATERIALS AND METHODS

2.1 $PM_{2.5}$ Sampling

2.1.1 Sampling Conditions

$PM_{2.5}$ samples for both open burning and chamber experiments were collected on 47 mm diameter quartz filter paper (Pall Corp., 2500QAT-UP, Q-filter) by a portable air sampler (Airmetrics, MiniVol) equipped with two size selective impactors of PM_{10} in front stage and $PM_{2.5}$ in back stage (Fig. 1). Samples were taken at a flow rate of 5 L/min. From the preparatory examination conducted before the study began, a sampling time of 10 minutes per sample was selected because it provided enough sample amounts to be used in chemical analyses. All samples were stored in a freezer at ca. −30°C until usage to prevent evaporation and degradation of components.

As reported previously, the amounts of chemical substances emitted from biomass burning are to some
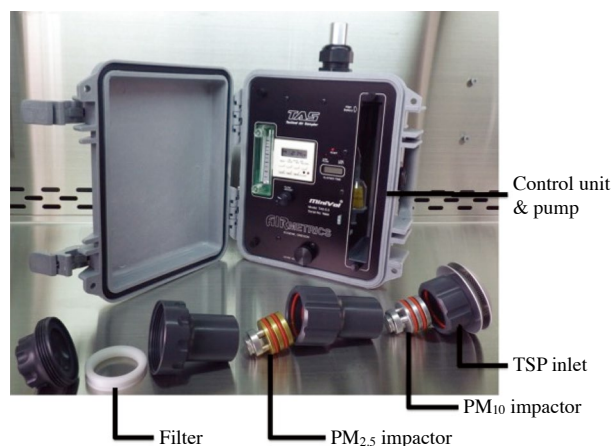
Fig. 1. Photograph of the Minivol $PM_{2.5}$ portable sampler used in this study.

extent determined by the ratio of flaming and smoldering phases (Andreae and Merlet, 2001). It may be desirable to analyze flaming phases and smoldering phases separately. However, this cannot be achieved by means of filter sampling because both processes occur simultaneously under the usual conditions of agricultural waste burning. There are few publications reporting on-line monitoring of chemical substances emitted from biomass burning in separate combustion phases by employing the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) instrument under laboratory conditions (Lee *et al.*, 2010), but this developed instrument is still expensive and not widely used in research facilities. For the above reason, samples were collected for the mixture of combustion phases at both open burning and chamber experiments. As uncertainties may exist due to the fluctuation of combustion conditions during the individual experiments, sampling was repeated 2-4 times for the individual open burning experiment in continuous combustion situations, and each plant species was burned and sampled independently 3 times for the chamber experiment. All of the data reported in this study were averaged by individual samples and the variability of the averaged value was estimated as one standard deviation (σ).

Typically, Q-filters are combusted in a furnace with high temperatures to remove the existing OC prior to sampling. However, combustion could activate the Q-filter, resulting in positive artifacts due to the absorption of gas phase organic materials onto the filter. As described in Section 2.2, instead of being combusted, $PM_{2.5}$ collected in Q-filters was measured gravimetrically to avoid potentially creating positive artifacts during transport, sampling, storage and chemical analysis.
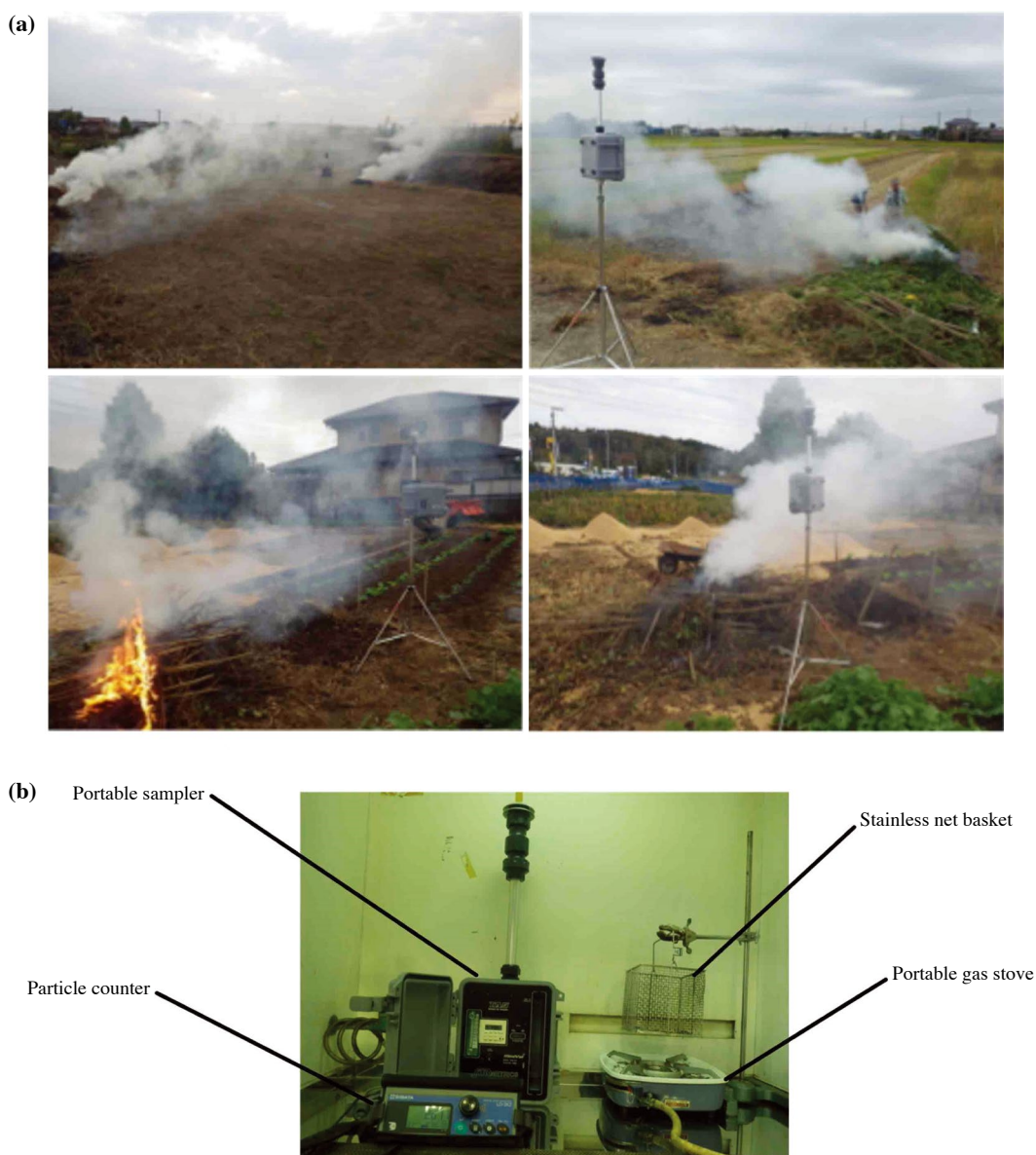
Fig. 2. Photographs showing the sampling locations. (a) Open burning experiment, (b) Chamber experiment.

Travel blank filters were prepared and placed in the same container as the samples and were transported and treated in the same way (e.g., making contact with the sampling devices, and being exposed to the conditions of the sampling site, storage, and all analytical procedures). Sample results reported in this paper are corrected for the travel blank filters.

2. 1. 2 Open Burning Experiment

In order to collect the primary PM$_{2.5}$ emitted from biomass burning smoke, the portable sampler was located in farmlands. The portable sampler was placed in an enclosure near the fire zone, as shown in Fig.

2(a). The sampler was set on a tripod and the inlet was fixed at a height of ca. 2 m above ground level.

Details of the open burning experiment are summarized in Table 1. The sampling period was scheduled from October 2015 to January 2016, and 9 farmers burning plants residues on farmlands in Chiba Prefecture cooperated in this study. Most of the plants residues were a mixture of various types of agricultural plants.

2. 1. 3 Chamber Experiment

In contrast to the open burning experiment, in which most of the samples were a mixture of agricultural

Table 1. Description of sampling conditions for the open burning experiment.

Sample	Location	Sampling date	Sampling time (min)	n	Species of biomass burned
Farmland A	Ichihara city, Chiba, Japan	Oct. 15, 2015	10	3	Weeds
Farmland B	Ichihara city, Chiba, Japan	Oct. 29, 2015	10	3	Mixture of podocarp (leaves and branches) and weeds
Farmland C	Ichihara city, Chiba, Japan	Oct. 29, 2015	10	3	Japanese black pine (leaves and branches)
Farmland D	Ichihara city, Chiba, Japan	Oct. 29, 2015	10	3	Mixture of sweet potato (leaves and stems) and bamboo
Farmland E	Ichihara city, Chiba, Japan	Oct. 29, 2015	10	3	Mixture of green soybeans (leaves and stems), bamboo, fig tree (leaves and branches), peach tree (leaves and branches) and weeds
Farmland F	Ichihara city, Chiba, Japan	Nov. 4, 2015	10	3	Mixture of rice straw and weeds
Farmland G	Ichihara city, Chiba, Japan	Nov. 4, 2015	10	2	Weeds
Farmland H	Ichihara city, Chiba, Japan	Nov. 6, 2015	10	3	Mixture of Japanese black pine (leaves and branches), Japanese plum tree (branches), bambboo, rice straw, okura (leaves and stems), chrysanthemum (flowers, leaves and stems)
Farmland I	Nagara town, Chiba, Japan	Jan. 7, 2016	10	4	Peanut (leaves and stems)

plants, the chamber experiment at the laboratory was designed to evaluate the chemical compositions of primary $PM_{2.5}$ derived from individual biomass species (14 different types of plants commonly seen in Japan), thus allowing a comparison of variations in chemical compositions among samples. Details of biomass species selected for the chamber experiment are shown in Table 2. Samples used for this experiment were dried prior to application. The experiment was conducted under the draft chamber condition (volume of $0.65\,m^3$), whose experimental image is shown in Fig. 2(b). Samples were cut into small pieces and placed in the stainless net basket individually, and then burned from the bottom of the basket with a portable propane gas stove. The size of fire ignition was manually adjusted to prevent burning the sample too quickly with a flame, according to the situation of individual samples. From our observations, farmers burn dried agricultural wastes in the order of a brief flaming phase followed by an extended period of smoldering. The burning processes and conditions were simulated as close as possible to those practiced on real farms (i.e., a brief ignition stage with a visible flame followed by a longer period of smoldering with smoke). Also, a particle counter (Shibata Scientific Technology Ltd., LD-3K2) was installed to monitor the occurrence of particles inside the chamber, and the amounts of samples were adjusted. Sampling began immediately after sample ignition. An exhaust port on the chamber was closed during the experiments, and then opened once the experiments were finished to ventilate and clean the inside of the chamber.

Table 2. Description of sampling conditions for the chamber experiment.

Sample	Amount used (g)	Sampling time (min)	n
Rice straw	15	10	3
Rice husk	15	10	3
Japanese cedar	15	10	3
Red pine	15	10	3
Hinoki	15	10	3
Peanut (stem)	15	10	3
Wheat straw	15	10	3
Bamboo	15	10	3
Cherry tree (leaves)	5-6	10	3
Pine bark	10-15	10	3
Lawn grass	7-9	10	3
Rubus microphyllus (leaves)	6	10	3
Cherry tree (branch)	15	10	3
Rubus microphyllus (branch)	8-11	10	3

2. 2 PM$_{2.5}$ Mass Concentration

$PM_{2.5}$ mass (μg) was determined gravimetrically using an electronic microbalance (A&D Company Ltd., BM-20) with a reading precision of 1 μg. Prior to weighing, all Q-filters were left to equilibrate to conditions of constant temperature ($21.5 \pm 1.5°C$) and relative humidity ($35 \pm 5\%$) for at least 24 hours. An ionizing blower was used to eliminate the effects of static electricity on the weighing process. The collected $PM_{2.5}$ mass was calculated by subtracting pre-weight from post-weight of the Q-filters. $PM_{2.5}$ mass concentrations (μg/m^3) were calculated by $PM_{2.5}$ mass per total volume of suction.

2.3 Chemical Analysis

Sampled Q-filters (deposition area of 11.95 cm^2) were cut into 4 pieces, size to be quartered. Each of them was prepared for sequential chemical analysis to determine the following categories: organic carbon (OC), elemental carbon (EC), ionic components (Na$^+$, NH$_4^+$, Ca^{2+}, Mg^{2+}, K$^+$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$), water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC, OC-WSOC).

OC and EC were determined by the thermal/optical reflectance carbon analysis system (Sunset Laboratory Inc., Lab OC-EC Aerosol Analyzer). The analytical conditions of the IMPROVE method (Chow *et al.*, 1993) were used with the thermal optical reflection protocol (Han *et al.*, 2010; Han *et al.*, 2007; Chow, *et al.*, 2001). A total of seven fractions (OC1, OC2, OC3, OC4, EC1, EC2 and EC3) and the optical pyrolysis correction of OC (PyC) were determined. OC was defined as OC1 + OC2 + OC3 + OC4 + PyC and EC was defined as EC1 + EC2 + EC3 − PyC.

Ionic components were extracted using a sonicator in ultrapure water. After sonication, the extract was filtered through a hydrophilic polymer syringe filter (ADVANTEC Co. Ltd., DISMIC, pore size of 0.22 μm) before the quantification using ion chromatography.

An aliquot of the extract used to analyze ionic components was used to measure WSOC. The quantification of WSOC was performed by total organic carbon analyzer (Shimadzu Corp., TOC-5000).

Respective analytical procedures were based on the PM$_{2.5}$ analytical procedure manual officially announced by MOEJ. The limits of detection and quantification were calculated using the standard deviation of 5 standard solution values multiplied by 3 and 10, respectively. Details of these measurement methods are described in a previous paper (Ichikawa *et al.*, 2015a, b).

3. RESULTS AND DISCUSSION

3.1 Emitting Amounts and Ratios of Chemical Components

Measured PM$_{2.5}$ mass concentrations (μg/m^3) and individual chemical component concentrations (μg/m^3) for all the samples analyzed are displayed in Table 3. To make the comparisons easier, the contributions of OC, EC and ionic components to PM$_{2.5}$ mass concentrations observed from open burning and chamber experiments, respectively, were calculated in wt/wt% and are shown in Table 4 and Fig. 3. OC to PM$_{2.5}$ mass concentration exhibited the highest ratio for both experiments, which ranged from 46.1-58.9% (average ± σ: 52.7 ± 4.2%, median: 52.8%) for the open burning experiment and 47.9-76.5% (59.4 ± 7.6%,

58.6%) for the chamber experiment, respectively. The overall sample tested was 46.1-76.5% (56.8 ± 7.2%, 56.7%). These results indicate that OC is the main chemical component contributing to the primary PM$_{2.5}$ emitted from biomass burning. Zhang *et al.* (2007) have combusted three types of Chinese cereal straws in the laboratory under both smoldering and flaming conditions, and reported that the percentage of OC to PM$_{2.5}$ mass concentration ranged from 43.8-61.9%, averaging 54.6 ± 6.0%, which is similar to those obtained in present study.

Regarding the chamber experiment, more than 10% of the emitting ratios of OC vary among the plant species. Both *Rubus microphyllus* (branches and leaves) and cherry tree (branches and leaves) exhibited high OC ratios exceeding 60% on average. Previous publications (Vicente *et al.*, 2015; Simoneit *et al.*, 1993) have documented that organic materials (OM) emitted from biomass burning smoke vary among plant classes, which could be due to the different types of plant tissues (Sullivan *et al.*, 2008) and combustion conditions (Lee *et al.*, 2010). For further understanding into the differences of the emitting ratios of OC among plant species, identification and quantification of the OM of samples collected in this study will be conducted in future research. On the other hand, all of the results obtained from the open burning experiment showed OC ratios around 50%. This result could be attributed to the mixture of plant species in the open burning experiment, which includes plant species of high and low emitting OC ratios that equalizes to around 50%, reflecting the actual status of biomass burning practiced on farmlands. It should be noted that samples were collected directly from biomass burning emissions without a dilution process in this study. Thus, the OC concentrations may be biased higher due to the presence of semi-volatile compounds on the primary particles emitted (Lin *et al.*, 2010).

The second largest components contributing to PM$_{2.5}$ mass concentration for both experiments was EC, which ranged from 2.9-16.4% (average ± σ: 8.1 ± 4.1%, median: 7.9%) for the open burning experiment and 1.2-7.6% (4.1 ± 1.9%, 4.3) for the chamber experiment, respectively. And that of overall sample tested was 1.2-16.4% (5.7 ± 3.5%, 4.9%). Since all of the sampling locations of the open burning experiment were fully exposed to the atmosphere without the interference of any obstacles, hoisting cinders and ash by means of winds derived from biomass burning emissions might have contributed to the elevation of EC ratio.

Ionic components accounted for a small portion of the emission ratio of primary PM$_{2.5}$ for both experiments. The observations of the sum of ionic compo-

Table 3. Concentrations of PM$_{2.5}$, chemical components and others obtained from the open burning and chamber experiments (μg/m³).

Sample	PM$_{2.5}$	OC	EC	Na$^+$	NH$_4^+$	Mg^{2+}	Ca^{2+}	K$^+$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	Others
Open burning experiment												
Farmland A	8430±5850	4560±3000	282±183	2.51±2.88	4.48±2.35	0.192±0.241	9.06±12.0	18.5±14.8	33.4±21.0	10.2±5.73	31.5±8.29	3480±2650
Farmland B	8180±4330	4270±2490	756±256	7.24±6.96	10.2±2.30	0.394±0.542	5.92±4.66	92.2±46.6	146±51.9	4.26±2.85	66.7±27.8	2820±1480
Farmland C	4710±2480	2240±1210	837±659	0.511±0.447	4.24±3.08	0.631±0.453	6.18±3.00	21.9±14.3	15.9±10.7	3.05±3.14	19.8±14.9	1550±576
Farmland D	11300±386	6690±730	661±251	11.8±20.5	3.96±2.15	0.172±0.297	7.61±12.2	72.8±69.7	44.5±37.9	3.06±1.15	22.5±17.5	3830±139
Farmland E	20800±12500	11800±7540	1840±1080	1.30±0.879	9.08±4.68	0.012±0.016	7.09±7.98	194±175	105±74.9	8.58±5.20	104±71.4	6800±3640
Farmland F	5220±3290	2750±1760	146±94.3	0.224±0.389	8.67±2.72	0.028±0.048	1.02±0.749	6.44±2.72	27.8±9.19	1.03±1.06	21.1±14.9	2260±1440
Farmland G	5350±2970	2710±1460	449±326	0.175±0.248	10.2±8.54	0.002±0.002	0.329±0.420	67.6±58.7	96.3±74.2	7.21±2.28	68.2±44.7	1940±1000
Farmland H	1610±742	667±216	104±61.4	0.717±0.888	2.24±2.15	0.012±0.021	0.875±0.407	11.6±8.10	22.4±13.8	6.41±0.992	15.2±6.56	776±534
Farmland I	13600±3270	7600±1450	1460±383	0.461±0.082	7.27±1.47	0.051±0.008	2.55±0.622	12.0±4.76	22.1±2.96	7.02±0.365	14.6±1.93	4440±1690
Average±σ	8810±5790	4810±3400	727±592	2.78±4.07	6.70±3.02	0.166±0.217	4.51±3.33	55.2±60.9	57.1±46.8	5.65±2.99	40.3±31.5	3100±1810
Median	8180	4270	661	0.717	7.27	0.051	5.92	21.9	33.4	6.41	22.5	2820
Range	1610-20800	667-11800	104-1840	0.175-11.8	2.24-10.2	0.002-0.631	0.329-9.06	6.44-194	15.9-146	1.03-10.2	14.6-104	776-6800
Chamber experiment												
Rice straw	8910±1550	5230±906	146±40.0	0.126±0.216	9.83±0.575	0.041±0.041	2.72±0.799	4.74±1.65	41.8±1.32	11.4±2.66	19.4±4.74	3440±621
Rice husk	7700±1240	4120±604	90.9±32.0	0.255±0.194	5.79±1.70	0.025±0.028	3.80±1.38	0.503±0.304	9.83±1.89	9.56±4.50	8.62±1.91	3450±619
Japanese cedar	17600±2090	10100±1970	737±867	7.42±10.7	5.02±2.38	0.845±1.27	13.1±16.5	6.51±2.87	8.45±2.12	10.4±4.93	15.5±9.82	6670±927
Red pine	12400±2560	6070±1360	895±329	0.404±0.069	10.7±0.980	N.D.	3.81±0.559	3.56±1.57	6.34±1.02	6.66±2.74	6.61±0.672	5440±1400
Hinoki	8840±4880	4300±2460	137±189	0.718±0.504	13.4±3.46	0.211±0.263	5.84±3.43	0.647±0.422	4.23±3.66	12.6±1.29	5.71±0.724	4360±2370
Peanut (stem)	12600±1790	7140±865	666±357	8.52±13.2	13.5±6.25	0.335±0.140	1.47±0.939	92.9±42.8	23.9±3.31	7.45±2.86	33.5±24.5	4570±993
Wheat straw	12900±4310	7870±2830	510±166	0.292±0.372	18.8±7.62	1.14±0.398	3.21±1.47	23.5±9.09	69.7±29.3	9.45±2.77	61.6±20.8	4350±1540
Bamboo	6270±2250	3380±1280	459±407	0.864±0.481	9.38±6.12	0.177±0.168	2.31±1.66	8.03±1.68	29.6±20.0	6.05±1.79	6.84±1.14	2370±780
Cherry tree (leaves)	5770±1140	3640±597	282±72.5	1.61±1.26	0.553±0.699	N.D.	1.18±0.457	64.8±6.92	18.9±3.30	9.50±4.17	9.93±2.18	1740±458
Pine bark	13400±2590	7840±1640	370±325	2.54±2.93	13.2±3.14	0.346±0.493	7.27±1.25	1.39±1.48	44.9±63.8	98.8±160	23.8±24.7	4970±1240
Lawn grass	10100±2840	6280±1920	413±82.5	0.629±0.728	5.61±2.54	0.034±0.026	2.54±0.672	42.2±9.38	41.3±12.5	4.08±1.64	27.5±9.42	3250±812
Rubus microphyllus (leaves)	7720±977	5920±1020	226±60.9	1.15±1.18	4.81±1.86	0.037±0.027	1.59±1.26	37.9±5.72	28.0±7.04	13.2±6.66	18.1±4.28	1470±211
Cherry tree (branch)	12200±4260	8280±3660	528±428	0.164±0.190	5.01±4.53	0.054±0.047	2.39±1.19	9.00±5.36	15.1±6.02	11.0±0.785	11.7±7.92	3300±475
Rubus microphyllus (branch)	8000±1410	5480±1550	436±185	1.19±0.740	4.85±0.549	0.583±0.253	2.22±1.11	10.7±3.64	8.19±0.680	8.06±2.90	5.03±0.648	2040±373
Average±σ	10300±3310	6120±1960	421±237	1.85±2.68	8.60±4.91	0.274±0.354	3.82±3.15	21.9±28.1	25.0±19.0	15.6±24.1	18.1±15.3	3670±1490
Median	9490	5990	424	0.791	7.58	0.115	2.63	8.51	21.4	9.53	13.6	3440
Range	5770-17600	3380-10100	90.9-895	0.126-8.52	0.553-18.8	N.D.-1.140	1.18-13.1	0.503-92.9	4.23-69.7	4.08-98.8	5.03-61.6	1470-6670

N.D.: Below detection limit.
All results have been rounded to no more than three significant figures.

Table 4. Ratios of chemical components, sum of ionic components, and others accounting for PM$_{2.5}$ calculated from the open burning and chamber experimental results, respectively (%).

Sample	OC	EC	Na	NH	Mg	Ca	K	Cl	NO	SO	Σionic components	Others
Open burning experiment												
Farmland A	55.4±2.9	3.8±1.3	0.1±0.1	0.1±0.0	0.0±0.0	0.3±0.5	0.3±0.1	0.5±0.2	0.3±0.4	0.5±0.4	2.1±0.8	38.8±5.4
Farmland B	51.4±3.0	9.9±1.8	0.1±0.1	0.2±0.1	0.0±0.0	0.1±0.1	1.1±0.1	1.9±0.4	0.1±0.0	0.9±0.2	4.4±0.5	34.4±1.6
Farmland C	47.5±0.9	16.4±4.4	0.0±0.0	0.1±0.0	0.0±0.0	0.2±0.1	0.5±0.2	0.3±0.1	0.1±0.0	0.4±0.1	1.6±0.3	34.7±4.9
Farmland D	58.9±4.4	5.9±2.4	0.1±0.2	0.0±0.0	0.0±0.0	0.1±0.1	0.6±0.6	0.4±0.3	0.0±0.0	0.2±0.2	1.4±0.7	33.8±2.3
Farmland E	54.9±3.9	9.1±0.8	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.8±0.4	0.5±0.1	0.0±0.0	0.5±0.1	1.8±0.4	34.2±3.8
Farmland F	52.8±4.6	2.9±1.0	0.0±0.0	0.2±0.2	0.0±0.0	0.0±0.0	0.1±0.1	0.7±0.4	0.0±0.0	0.4±0.1	1.4±0.5	42.9±6.2
Farmland G	51.0±1.1	7.9±1.7	0.0±0.0	0.2±0.1	0.0±0.0	0.0±0.0	1.1±0.5	1.7±0.5	0.1±0.0	1.2±0.2	4.3±0.7	36.7±1.7
Farmland H	46.1±16.4	6.4±1.4	0.0±0.0	0.1±0.1	0.0±0.0	0.1±0.0	0.7±0.3	1.4±0.4	0.5±0.4	1.0±0.3	3.8±0.7	43.6±16.0
Farmland I	56.7±5.7	10.8±1.1	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.3±0.0	0.4±0.0	0.1±0.0	0.2±0.0	1.1±0.0	31.4±5.1
Average±σ	52.7±4.2	8.1±4.1	0.0±0.1	0.1±0.1	0.0±0.0	0.1±0.1	0.6±0.4	0.9±0.6	0.1±0.2	0.6±0.4	2.4±1.3	36.7±4.2
Median	52.8	7.9	0.0	0.1	0.0	0.1	0.6	0.5	0.1	0.5	1.8	34.7
Range	46.1-58.9	2.9-16.4	0.0-0.1	0.0-0.2	0.0-0.0	0.0-0.3	0.1-1.1	0.3-1.9	0.0-0.5	0.2-1.2	1.1-4.4	31.4-43.6
Chamber experiment												
Rice straw	58.7±0.4	1.6±0.3	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.5±0.1	0.1±0.0	0.2±0.1	1.0±0.1	38.6±0.3
Rice husk	53.6±0.9	1.2±0.4	0.0±0.0	0.1±0.0	0.0±0.0	0.1±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.4±0.0	44.7±0.9
Japanese cedar	57.2±5.4	4.6±5.8	0.0±0.1	0.0±0.0	0.0±0.0	0.1±0.1	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.3±0.2	37.8±1.0
Red pine	48.7±3.6	7.6±3.9	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.4±0.0	43.4±2.2
Hinoki	47.9±2.2	1.5±1.7	0.0±0.0	0.2±0.1	0.0±0.0	0.1±0.0	0.0±0.0	0.1±0.1	0.2±0.1	0.1±0.1	0.7±0.2	50.0±3.1
Peanut (stem)	57.1±5.7	5.3±2.7	0.1±0.1	0.1±0.0	0.0±0.0	0.0±0.0	0.7±0.2	0.2±0.0	0.1±0.0	0.3±0.2	1.5±0.3	36.2±3.0
Wheat straw	60.5±2.1	4.3±1.8	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.2±0.1	0.6±0.3	0.1±0.0	0.5±0.2	1.5±0.4	33.6±2.2
Bamboo	53.9±5.1	6.9±4.7	0.0±0.0	0.2±0.1	0.0±0.0	0.0±0.0	0.1±0.0	0.5±0.2	0.1±0.0	0.1±0.0	1.0±0.2	38.1±1.6
Cherry tree (leaves)	63.3±2.0	4.9±0.3	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	1.1±0.2	0.3±0.0	0.2±0.1	0.2±0.0	1.8±0.2	29.9±1.9
Pine bark	58.5±1.6	3.2±3.3	0.0±0.0	0.1±0.0	0.0±0.0	0.1±0.0	0.0±0.0	0.3±0.5	0.7±1.2	0.2±0.2	1.4±1.3	36.9±2.4
Lawn grass	62.2±1.4	4.2±0.3	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.4±0.0	0.4±0.0	0.0±0.0	0.3±0.1	1.2±0.1	32.4±1.0
Rubus microphyllus (leaves)	76.5±4.0	2.9±0.5	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.5±0.0	0.4±0.1	0.2±0.1	0.2±0.0	1.4±0.1	19.3±4.1
Cherry tree (branch)	66.3±7.6	4.3±3.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.4±0.0	28.9±8.0
Rubus microphyllus (branch)	67.8±7.0	5.3±1.5	0.0±0.0	0.1±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.5±0.0	26.4±8.3
Average±σ	59.4±7.6	4.1±1.9	0.0±0.0	0.1±0.1	0.0±0.0	0.0±0.0	0.2±0.3	0.3±0.2	0.2±0.2	0.2±0.1	1.0±0.5	35.4±7.9
Median	58.6	4.3	0.0	0.1	0.0	0.0	0.1	0.3	0.1	0.2	1.0	36.6
Range	47.9-76.5	1.2-7.6	0.0-0.1	0.0-0.2	0.0-0.0	0.0-0.1	0.0-1.1	0.0-0.6	0.0-0.7	0.1-0.5	0.3-1.8	19.3-50.0

(a)

(b)
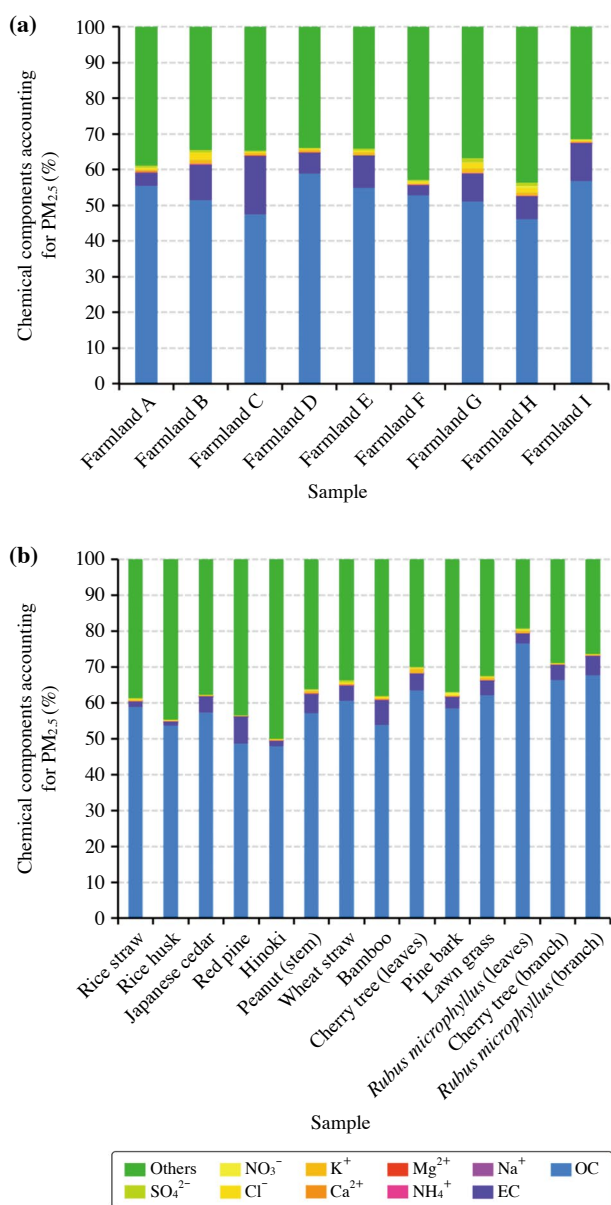
Fig. 3. Average ratios of the chemical components to $PM_{2.5}$ mass concentrations obtained from the open burning and chamber experiments (%). (a) Result of open burning experiment, (b) Result of chamber experiment.

nents contributing to primary $PM_{2.5}$ were 1.1-4.4% (average $\pm \sigma$: 2.4 $\pm$ 1.3%, median: 1.8%) for the open burning experiment and 0.3-1.8% (1.0 $\pm$ 0.5%, 1.0%) for the chamber experiment, respectively. And that of overall sample tested was 0.3-4.4% (1.5 $\pm$ 1.2%, 1.4%). Among the ionic components, K^+, Cl^- and SO_4^{2-} observed during the open burning experiment showed slightly higher ratios compared to other ionic components; however, they were an order of magnitude lower than the corresponding OC ratios. Opinion is divided on

the usage of K^+ as a tracer of biomass burning emissions (Scaramboni *et al*., 2015; Jung *et al*., 2014; Rastogi *et al*., 2014; Chuang *et al*., 2013; Theodosi *et al*., 2011; Kaneyasu *et al*., 2007). From the results obtained in this study, as mentioned above, the emission ratios of K^+ were quite low, and some samples, such as rice husk, Japanese cedar, red pine, hinoki, park barks, most of which are wood burning emissions, were close to zero. Few previous publications concerning biomass burning source studies have reported skepticism about the use of K^+ as a tracer for biomass burning, due to its relatively low abundance (Fujii *et al*., 2015; Hays *et al*., 2005), nor have they promoted better alternatives (e.g., organic compounds) to K^+ for biomass burning identification (Fine *et al*., 2002, 2001). Interestingly, Echalar and Gaudichet (1995) observed that K^+ emission abundance from biomass burning is higher in the flaming phase and lower in the smoldering phase. In this study, $PM_{2.5}$ emitted from both phases were collected together, and the low existence of K^+ might be explained by the relative lack of exposure to the flame phase. However, considering our results and previous publications mentioned, the variability of K^+ among biomass burning emissions is quite high, and thus it may not always be suitable as a tracer for biomass burning emissions. The use of K^+, therefore, should always be carefully considered.

Shahid *et al*. (2015) collected total particulate matter (TSP) emitted during the ignition of three types of Pakistani woods in a traditional brick stove and quantified the chemical components. They obtained emitting ratios of 64.8-70.2% for OC, 11.9-29.5% for EC and only a few percent for total ionic components, respectively. Except for the EC emitting ratios, their observations correspond to our results. In addition, among the ionic components, K^+ and Cl^- were the most abundant species, accounting for 2-4% of TSP mass concentration, which also resembled our observations.

An undetermined fraction (defined as "Others" in Tables 2, 3 and Fig. 3) of the average values of $PM_{2.5}$ mass concentration represented 36.7% for the open burning experiment and 35.4% for the chamber experiment. This fraction is assumed to contain metallic elements, atoms other than carbon constituting OM, moisture content and analytical uncertainties of the measurement. Previous publications (Tokyo Metropolitan Government, 2011; Schmidl *et al*., 2008) indicate that small amounts of metallic elements can be found in biomass burning emissions. Considering the large amount of OC in the emitting ratios, most of the "Others" could be attributed to atoms other than carbon, such as oxygen, hydrogen, nitrogen, sulfur, chlorine, and other elements associated with OM. Simoneit

(2002) showed that biopolymers such as cellulose, hemicellulose and lignin constitute a major fraction of the OM in biomass. From that point of view, it is possible to envisage biomass burning emissions as being composed of a large amount of OM generated from the chemical transformations and thermal decomposition of these polymeric compounds during the complex combustion process (Mayol-Bracero *et al.*, 2002), which supports our assumption that most of the "Others" fraction could be attributed to atoms associated with OM.

3.2 Correlation Analysis

The correlation analysis between PM$_{2.5}$ mass concentration and chemical species was performed by using the Pearson correlation coefficient (R) in order to establish the preliminary relationships among the research results. The correlation coefficients obtained are shown in Table 5, and correlation coefficients above 0.80 are marked in bold symbol to indicate strong correlation.

Correlation between PM$_{2.5}$ mass concentration and OC showed remarkably strong positive correlations of R=0.99 and R=0.94 for the open burning and chamber experiments, respectively. It is noteworthy that OM is most likely dominating the primary PM$_{2.5}$ emitted

from biomass burning smoke, which supports the assumption that most of the "Others" is attributed to atoms other than carbon constituting organic materials mentioned above in Section 3.1. There were few relationships among species that showed R>0.80 for the open burning experiment. On the other hand, the correlation between PM$_{2.5}$ mass concentration and OC was the only one that showed R>0.80 for the chamber experiment.

Good correlation was observed (R=0.87) between EC and PM$_{2.5}$ mass concentration for the open burning experiment. Hoisting cinders and ash carried by winds might have caused the elevation of EC for the open burning experiment, due to the lack of any obstacles around the sampling location. Zhang *et al.* (2015) measured gaseous, black carbon (BC, generally used interchangeably with EC) and PM$_{2.5}$ mass concentration directly from biomass burning smoke emitted from wheat, rice and rapeseed residues on Chinese farmland. Differences were observed between the correlation coefficients of BC and PM$_{2.5}$ mass concentration due to the condition of the burning phase (flaming phase, R=0.97; smoldering phase, R=0.92). Their observations were in good agreement with our results obtained from the open burning experiment.

Furthermore, K$^+$, Cl$^-$ and SO$_4^{2-}$ also showed good

Table 5. Correlation coefficient (R) matrix between PM$_{2.5}$ and the measured chemical components from the open burning and chamber experiments.

| Open burning experiment (n=27) | | | | | | | | | | |
	PM$_{2.5}$	OC	EC	Na$^+$	NH$_4^+$	Mg^{2+}	Ca^{2+}	K$^+$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$
PM$_{2.5}$	1										
OC	**0.99**	1									
EC	**0.87**	**0.85**	1								
Na$^+$	0.06	0.07	−0.05	1							
NH$_4^+$	0.45	0.43	0.44	0.07	1						
Mg^{2+}	−0.15	−0.16	−0.07	0.45	−0.13	1					
Ca^{2+}	0.09	0.10	0.04	0.67	−0.07	0.53	1				
K$^+$	0.74	0.75	0.64	0.32	0.53	0.04	0.24	1			
Cl$^-$	0.49	0.48	0.40	0.31	0.69	0.07	0.18	**0.80**	1		
NO$_3^-$	0.39	0.39	0.40	−0.03	0.12	−0.13	0.39	0.36	0.27	1	
SO$_4^{2-}$	0.67	0.66	0.58	0.17	0.66	0.03	0.20	**0.91**	**0.87**	0.45	1

Chamber experiment (n=42)										
PM$_{2.5}$	1										
OC	**0.94**	1									
EC	0.33	0.21	1								
Na$^+$	0.29	0.26	0.06	1							
NH$_4^+$	0.47	0.36	0.14	−0.02	1						
Mg^{2+}	0.48	0.50	−0.03	0.45	0.42	1					
Ca^{2+}	0.50	0.44	−0.08	0.56	0.15	0.65	1				
K$^+$	−0.03	0.02	0.16	0.18	0.01	−0.00	−0.25	1			
Cl$^-$	0.07	0.13	−0.03	0.03	0.37	0.31	−0.08	0.14	1		
NO$_3^-$	0.14	0.15	−0.14	0.15	0.17	0.23	0.14	−0.11	0.59	1	
SO$_4^{2-}$	0.35	0.38	0.09	0.08	0.55	0.47	−0.00	0.40	0.77	0.30	1

mutual correlation for the open burning experiment (R > 0.80). K^+ is commonly known as a plant nutrient, and in some agricultural environments, KCl is widely used as fertilizer, because of potassium's importance in transpiration control (stomatal functioning), osmoregulation, nutrition, and growth, whereas chlorine may inhibit disease and is also important in osmotic control (Hays *et al.*, 2005). Therefore, the good correlation between K^+ and Cl^- observed in the open burning experiment is most likely due to hoisting farm dust by means of winds and adsorbed portions of plant nutrients contained in the plants. In addition, KCl, K_2SO_4 and KNO_3 are also used as fertilizers (Lin *et al.*, 2010). Accordingly, SO_4^{2-} showing relatively high correlation with $PM_{2.5}$, K^+ and Cl^- could be attributed to hoisting farm dust and the adsorbed portion of plant nutrients. This inference also supports the assumption that hoisting cinders and wind-blown ash from biomass burning might have contributed to the elevation

of the EC ratio, as mentioned in Section 3.1. In terms of the weak correlation of NO_3^- with $PM_{2.5}$ and K^+, KNO_3 were probably not used as fertilizer in the farmland we have examined.

3. 3 Fractions of OC

The abundance ratios of individual fractions of OC to total OC are presented in Table 6. The average abundances of OC1, OC2, OC3, OC4, and PyC were 6.1%, 36.7%, 27.5%, 12.8%, and 16.4% for the open burning experiment and 10.7%, 35.8%, 24.4%, 9.3% and 19.9% for the chamber experiment, respectively. Many, but not all, of the samples tested exhibited similar characteristics. Among the OC fractions, OC2 was the highest contributor, followed by OC3, on average. Conversely, the abundances of OC1, OC4 and PyC were relatively low, with little variability for both the open burning and chamber experiments. The sum of the OC2 and OC3 fractions contributed 60% or more

Table 6. Ratios of individual fractions of OC to total OC (%) and OC2/OC3 calculated from the open burning and chamber experimental results, respectively.

Sample	Open burning experiment					
	OC1	OC2	OC3	OC4	PyC	OC2/OC3
Farmland A	7.8±4.9	33.9±3.6	28.3±1.3	11.6±5.3	18.4±2.4	1.2±0.2
Farmland B	5.7±0.7	34.1±5.0	30.0±2.4	12.6±4.3	17.6±1.9	1.1±0.2
Farmland C	5.4±3.7	39.4±6.7	26.9±0.6	15.7±2.6	12.5±7.4	1.5±0.3
Farmland D	8.2±1.7	41.9±1.0	28.6±1.3	7.8±0.6	13.5±0.8	1.5±0.1
Farmland E	15.2±7.3	39.1±1.8	24.6±1.4	7.7±3.5	13.3±4.1	1.6±0.2
Farmland F	2.8±2.1	29.1±2.1	24.0±2.5	14.7±4.0	29.4±2.7	1.2±0.1
Farmland G	3.7±2.2	32.8±5.6	26.4±0.8	17.8±3.2	19.2±3.8	1.2±0.3
Farmland H	0.2±0.3	38.8±6.6	28.7±0.3	19.6±1.5	13.3±4.5	1.4±0.2
Farmland I	10.9±2.5	41.5±1.0	29.9±1.8	7.7±1.2	10.0±1.8	1.4±0.1
Average ± σ	6.1±4.5	36.7±4.4	27.5±2.2	12.8±4.5	16.4±5.8	1.3±0.2
Median	5.6	38.8	28.3	12.6	13.5	1.4
Range	0.2-15.2	29.1-41.9	24.0-30.0	7.7-19.6	10.0-29.4	1.1-1.6
	Chamber experiment					
Rice straw	6.1±1.0	31.6±0.6	26.1±0.3	10.5±2.0	25.7±0.6	1.2±0.0
Rice husk	12.7±1.7	35.5±2.8	17.5±0.5	10.7±1.7	23.6±3.8	2.0±0.2
Japanese cedar	32.7±5.0	38.1±3.4	11.8±1.6	6.1±0.9	11.2±7.9	3.3±0.4
Red pine	11.5±2.2	42.3±4.8	20.7±2.2	8.2±1.7	17.3±7.4	2.1±0.4
Hinoki	9.6±3.5	45.7±2.0	15.7±1.7	9.3±2.6	19.8±2.3	2.9±0.5
Peanut (stems)	8.5±1.4	36.9±2.3	28.7±1.3	7.9±0.5	17.9±3.1	1.3±0.1
Wheat straw	12.3±3.9	35.3±1.2	23.7±1.3	7.1±2.2	21.6±1.6	1.5±0.1
Bamboo	10.9±5.2	31.3±2.2	21.6±1.9	11.4±3.8	24.8±5.6	1.4±0.0
Cherry tree (leaves)	3.4±1.1	27.1±2.3	36.9±1.0	14.0±1.4	18.7±2.1	0.7±0.1
Pine bark	7.3±2.5	48.0±2.3	20.2±1.5	7.9±1.2	16.6±1.2	2.4±0.2
Lawn grass	5.8±1.9	32.1±2.5	32.3±0.5	10.6±3.1	19.3±2.6	1.0±0.1
Rubus microphyllus (leaves)	2.5±0.2	36.8±1.2	34.8±0.9	9.1±1.0	16.8±1.1	1.1±0.0
Cherry tree (branches)	14.8±7.8	31.5±0.6	25.4±2.0	7.8±3.1	20.5±5.4	1.2±0.1
Rubus microphyllus (branches)	11.0±1.7	29.2±3.8	25.6±4.8	9.0±1.8	25.2±1.6	1.2±0.3
Average ± σ	10.7±7.3	35.8±6.1	24.4±7.2	9.3±2.0	19.9±4.0	1.7±0.8
Median	10.3	35.4	24.6	9.1	19.6	1.4
Range	2.5-32.7	27.1-48.0	11.8-36.9	6.1-14.0	11.2-25.7	0.7-3.3

of the total OC.

However, there were few samples displaying different categories. Chow *et al.*(2004) suggested that those individual carbon fractions could be apportioned to specific pollution sources. OC1 of Japanese cedar accounted for more than 30% of total OC, which could possibly mean that volatilized OM are abundantly included, indicating the differences of the characteristics of OM emitted from biomass burning smoke in species. The abundance of PyC to total OC was relatively high (29.4%) for Farmland F. PyC is the fraction indicating pyrolyzed or charred OC generated during thermal treatment under the He atmosphere of carbon analysis. Yu *et al.*(2002) pointed out that WSOC usually accounts for the majority of charring during heating under inert atmospheres. The abundance of WSOC to OC was relatively high in the Farmland F sample. From the data obtained in the present study, correlation analysis was carried out between WSOC and PyC, resulting in a value of R=0.83, in good agreement with the statement of Yu *et al.*(2002). Further results of WSOC will be discussed in Section 3.5.

The concentrations of constituting compounds and their ratios can give some indication as to the impact of different sources of airborne compounds. The ratios of OC2/OC3 were 1.3±0.2 and 1.7±0.8 on average for the open burning and chamber experiments, respectively, both close to a value of 1.5. The anhydrosaccharide compound levoglucosan is used as a molecular marker of biomass burning, as it is known as the main thermal breakdown product of cellulose present in plants (Schmidl *et al.*, 2008; Zhang *et al.*, 2007; Simoneit *et al.*, 1999). For reference, we spiked a standard solution of levoglucosan to 1 cm^2 of the blank Q-filter that was subjected to the carbon analyzer to confirm the abundance of OC fractions. The percentages of OC2 and OC3 to total OC for the levoglucosan standard solution were 47.4±3.5% (n=9) and 34.7±2.9% (n=9), respectively, and the OC2/OC3 ratio was calculated as 1.4±0.3, which is similar to our experimental results (nearly 1.5). Our observations suggest that the OC2/OC3 ratio of ambient PM$_{2.5}$ influenced by biomass burning emission might be close to a value of 1.5. However, the OC2/OC3 ratios of wood species such as Japanese cedar, red pine, hinoki, and pine bark ranged from 2.1-3.3, higher than 1.5, indicating the different characteristics of OC fractions of wood species compared to other plant species. Future research seeking to identify and quantify the OM of biomass burning smoke emitted from individual plant species might help to clarify such points.

3.4　Char-EC and Soot-EC

Han *et al.*(2007) suggested an analytical methodology of dividing EC into two classes: char-EC and soot-EC. According to their explanation, char-EC is calculated as EC1−PyC and is defined as tar-like carbon produced by the incomplete combustion of organic substances. Char-EC is mainly emitted from biomass and coal combustion. Soot-EC is calculated as EC2＋EC3 and is defined as carbonaceous particles that formed through the high temperature condensation of hot gases emanating from solid and liquid fuels during combustion. Soot-EC is considered to be emitted largely from vehicle emissions (Han *et al.*, 2010, 2009). In our previous publication, this methodology was applied to atmospheric measurement data collected daily from February 2013 to March 2014 in Chiba Prefecture, Japan to analyze the sources that are contributing to PM$_{2.5}$ over time (Ichikawa *et al.*, 2015b). However, the analytical data that Han *et al.*(2007) used to verify and define char-EC and soot-EC were based on char and soot reference materials. To our knowledge, verifications of char-EC and soot-EC using basic measurement data obtained from biomass burning smoke have not been conducted. Therefore, char-EC and soot-EC were calculated from the data obtained in this study and comparisons between the samples were tested.

Using the char-EC/soot-EC ratio is a simple way to identify sources of PM$_{2.5}$ (Chuang *et al.*, 2013; Han *et al.*, 2010, 2009). Fig. 4 presents the average±σ of char-EC/soot-EC obtained from all samples tested in this work. Char-EC/soot-EC ranged from 0.22-0.83 (average±σ: 0.50±0.19, median: 0.45) for the open burning experiment and 0.52-0.91 (0.74±0.11, 0.75) for the chamber experiment, respectively. That of the overall sample tested was 0.22-0.91 (0.65±0.19, 0.69). Although there were few similar sample types between the open burning and chamber experiments, the chamber experiment exhibited relatively higher values than the open burning experiment. For instance, the char-EC/soot-EC ratio of Farmland I for the open burning experiment was 0.33 in average and that of peanut (stems) for the chamber experiment was 0.65. We were not able to determine the main cause of these differences, but considering how char-EC and soot-EC are thermally produced, it might be attributed to differences in the combustion conditions (e.g., temperature, concentrations of emission gases, etc.) between the experiments.

According to the interpretation of previous studies (Chuang *et al.*, 2013; Han *et al.*, 2010), motor vehicle emissions have a char-EC/soot-EC ratio of less than 1.0-2.0, while burning biomass by smoldering at low temperatures results in high char-EC/soot-EC ratios. However, the char-EC/soot-EC ratios obtained from all of the samples in this study were less than 1.0,
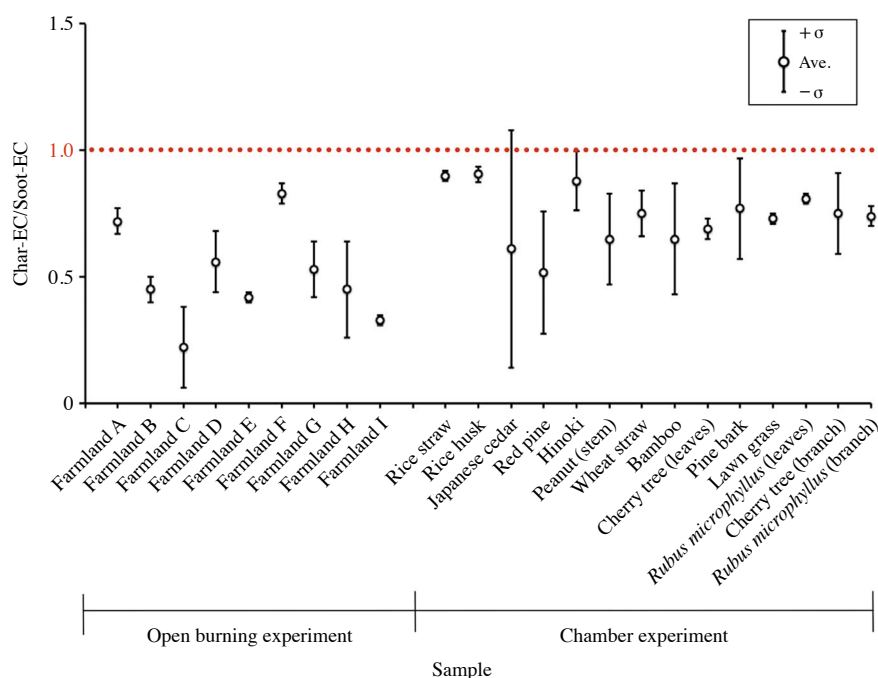
Fig. 4. Average ratios of char-EC/soot-EC obtained from the open burning and chamber experiments. Dotted line indicates the value of char-EC/soot-EC = 1.

which were different to previous studies (Chuang *et al.*, 2013; Han *et al.*, 2010). These differences might be attributed to differences in the sample types; i.e., samples collected from ambient atmospheric conditions that are influenced by many emission sources and samples that are collected directly from biomass burning emissions. Novakov and Corrigan (1995) pointed out that concentrations of inorganic matter in the biomass samples would affect the separation of carbonaceous fragments, leading to uncertainty in the char-EC and soot-EC determinations. Also, as mentioned above, it could be caused by the differing combustion conditions of the samples. However, it should be noted that our samples, especially those collected from the open burning experiment, reflect real biomass burning emissions affecting the atmospheric environment.

A recent report from the Tokyo Metropolitan Government (2011) supports our result, as they also collected/measured $PM_{2.5}$ of biomass burning smoke samples emitted from rice straw and a mixture of lawn grass and pruned branches in the chamber facility and found char-EC/soot-EC ratios that were less than 1.0 (close to zero) for both samples. From our and the Tokyo Metropolitan Government (2011) results, careful consideration should be given to the use of char-EC as an indicator of biomass burning.

3.5 WSOC and WIOC

OC is often categorized into WSOC and WIOC fractions. A significant fraction of OC derived from biomass burning is thought to be an important source of WSOC, which could potentially act as cloud condensation nuclei (CCN) and affect the global climate (Park *et al.*, 2016; Urban *et al.*, 2014; Hennigan *et al.*, 2012; Mayol-Bracero *et al.*, 2002; Novakov and Corrigan, 1996).

Table 7 shows the absolute concentrations of WSOC and WIOC and the ratios of WSOC/OC and WIOC/OC determined in the open burning and chamber experiments. Also, the ratios of WSOC/OC and WIOC/OC obtained by both experiments are shown in Fig. 5. The observed WSOC/OC ratios were 34.2-54.8% (average ± σ: 45.9 ± 7.3%, median: 44.9%) and 29.7-87.6% (62.1 ± 16.4%, 59.7%), and the WIOC/OC ratios were 45.2-65.8% (54.1 ± 7.3%, 55.1%) and 12.4-70.3% (37.9 ± 16.4%, 40.3%) for the open burning and chamber experiments, respectively. And those of overall sample tested were 29.7-87.6% (55.7 ± 15.6%, 53.6%) and 12.4-70.3% (44.3 ± 15.6%, 46.4%). Focusing on the average values of the WSOC/OC and WIOC/OC ratios, there was no large difference between them. From laboratory experiments on smoke particles produced by the combustion of eucalyptus and redwood, Novakov and Corrigan (1996) report WSOC ratios of 29-64%, implying similarity to

Table 7. Concentrations of WSOC and WIOC (μg/m^3), and ratios of WSOC/OC and WIOC/OC (%) obtained from the open burning and chamber experiments.

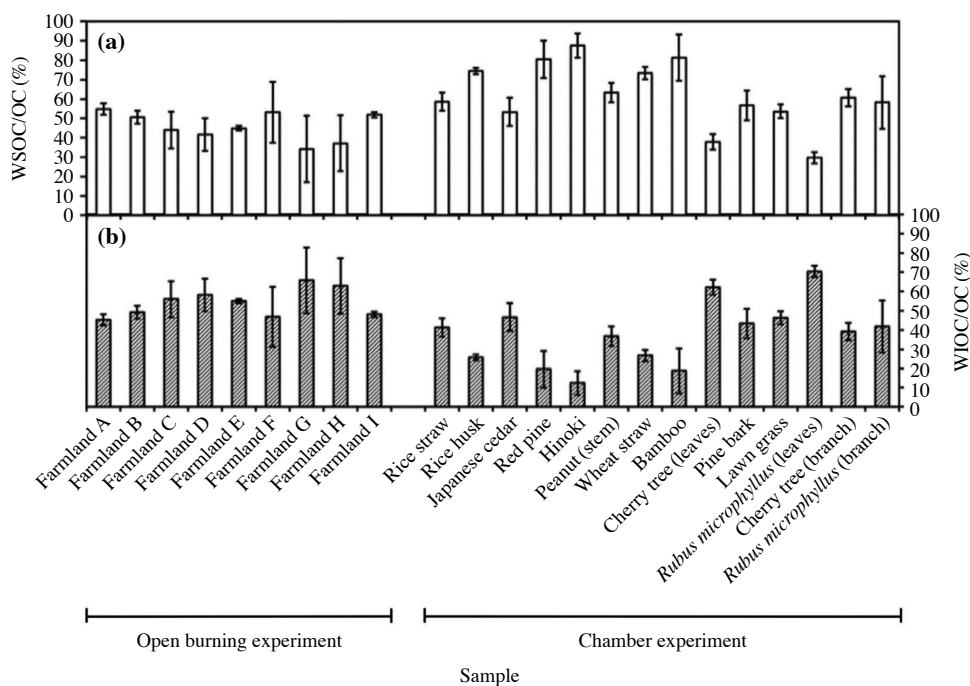| Sample	Open burning experiment			
	WSOC*	WIOC*	WSOC/OC	WIOC/OC
Farmland A	2560 ± 1770	2000 ± 1240	54.8 ± 2.9	45.2 ± 2.9
Farmland B	2200 ± 1390	2080 ± 1110	50.7 ± 3.4	49.3 ± 3.4
Farmland C	1020 ± 672	1230 ± 574	44.0 ± 9.4	56.0 ± 9.4
Farmland D	2750 ± 276	3940 ± 1000	41.7 ± 8.5	58.3 ± 8.5
Farmland E	5340 ± 3480	6430 ± 4050	44.9 ± 1.1	55.1 ± 1.1
Farmland F	1420 ± 804	1340 ± 1040	53.2 ± 15.7	46.8 ± 15.7
Farmland G	1050 ± 963	1660 ± 492	34.2 ± 17.1	65.8 ± 17.1
Farmland H	255 ± 129	411 ± 135	37.1 ± 14.4	62.9 ± 14.4
Farmland I	3940 ± 715	3670 ± 751	51.9 ± 1.4	48.1 ± 1.4
Average ± σ	2280 ± 1600	2530 ± 1850	45.9 ± 7.3	54.1 ± 7.3
Median	2200	2000	44.9	55.1
Range	255-5340	411-6430	34.2-54.8	45.2-65.8
	Chamber experiment			
Rice straw	3040 ± 306	2190 ± 613	58.7 ± 4.7	41.3 ± 4.7
Rice husk	3060 ± 434	1060 ± 187	74.4 ± 1.6	25.6 ± 1.6
Japanese cedar	5310 ± 406	4830 ± 1570	53.3 ± 7.3	46.7 ± 7.3
Red pine	4790 ± 518	1270 ± 859	80.5 ± 9.6	19.5 ± 9.6
Hinoki	3680 ± 2030	619 ± 465	87.6 ± 6.3	12.4 ± 6.3
Peanut (stems)	4510 ± 568	2630 ± 561	63.3 ± 5.0	36.7 ± 5.0
Wheat straw	5810 ± 2190	2060 ± 669	73.4 ± 3.1	26.6 ± 3.1
Bamboo	2650 ± 706	731 ± 626	81.3 ± 11.8	18.7 ± 11.8
Cherry tree (leaves)	1370 ± 143	2270 ± 486	37.9 ± 4.0	62.1 ± 4.0
Pine bark	4380 ± 681	3460 ± 1150	56.7 ± 7.6	43.3 ± 7.6
Lawn grass	3360 ± 1010	2920 ± 949	53.6 ± 3.5	46.4 ± 3.5
Rubus microphyllus (leaves)	1760 ± 406	4160 ± 668	29.7 ± 3.0	70.3 ± 3.0
Cherry tree (branches)	4920 ± 1930	3360 ± 1730	60.7 ± 4.5	39.3 ± 4.5
Rubus microphyllus (branches)	3050 ± 164	2430 ± 1510	58.2 ± 13.6	41.8 ± 13.6
Average ± σ	3690 ± 1320	2430 ± 1260	62.1 ± 16.4	37.9 ± 16.4
Median	3520	2350	59.7	40.3
Range	1370-5810	619-4830	29.7-87.6	12.4-70.3

*All valuess have been rounded to no more than three significant figures.

our chamber experiment observations.

Respective coefficient of variations (CV) calculated were 15.9% and 13.5% for the ratios of WSOC/OC and WIOC/OC in the open burning experiment, indicating little variance among samples under these conditions. This tendency corresponds to the OC/PM$_{2.5}$ results mentioned in Section 3.1 that could be attributed to the characteristics of open biomass burning emissions, which is a combination of various types of plant species including high and low emitting ratios of WSOC and WIOC. On the other hand, in the chamber experiment, the ratios showed considerable variability among plant species. For example, the difference between the WSOC/OC ratios of *Rubus microphyllus* (leaves) and hinoki was 57.9%. We expect that the reason for such differences among plant samples will be revealed by the identification and quantification of organic materials of individual plant samples.

3. 6 Assumption of OM/OC

To achieve chemical mass closure model in the source apportionment and ambient particle measurements, a calculated factor of OM to OC ratio is often multiplied by measured OC to estimate total OM. From the statement of Section 3.1, we roughly assumed that "OM = OC + Others" and estimated the OM/OC ratio from our measurements. The respective OM/OC factors calculated were 1.57-2.16 (average ± σ: 1.73 ± 0.18, median: 1.69) and 1.25-2.01 (1.61 ± 0.21, 1.64) for the open burning and chamber experiments, respectively. And that of overall sample tested was 1.25-2.16 (1.66 ± 0.20, 1.66). Aiken *et al.* (2008) employed AMS equipment to quantify the elemental composition of the biomass burning emissions of lodgepole pine and a combination of sage and rabbitbrush combusted inside a laboratory chamber, respectively, and reported that the OM/OC ratios were in the range of 1.56-1.70, which

Fig. 5. Average ratios of WSOC/OC and WIOC/OC obtained from the open burning and chamber experiments (%). (a) WSOC/OC, (b) WIOC/OC.

was similar to the factor obtained in the present study. Furthermore, a factor of 1.7 based on wood combustion sources was reported in the supporting information of Reff *et al.* (2009).

As an alternative methodology to estimate the OM/OC ratio, water-soluble and water-insoluble organic materials (WSOM and WIOM, respectively) could be obtained by applying specific conversion factors. Based on the works of Turpin and Lim (2001) and Zhang *et al.* (2005), Favez *et al.* (2009) suggested conversion factors of 2.1 and 1.4, respectively; i.e., $WSOM = 2.1 \times WSOC$, $WIOM = 1.4 \times WIOC$. OM is the sum of WSOM and WIOM. The OM/OC ratios were 1.64-1.78 (average $\pm \sigma$: 1.72 ± 0.05, median: 1.71) and 1.61-2.01 (1.83 ± 0.11, 1.82) for the open burning and chamber experiments. And that of overall sample tested was 1.61-2.01 (1.79 ± 0.11, 1.78), which is similar to the estimated value calculated above. Our results imply that a OM/OC ratio of approximately 1.7 (median of overall value of OM/OC obtained by the two independent methods) will likely be adopted for biomass burning emissions.

4. SUMMARY AND CONCLUSION

In this study, mass concentrations of $PM_{2.5}$ and its

chemical components in biomass burning emissions were analyzed. The samples were collected under both open burning and laboratory chamber conditions. The open burning experiment was conducted with the cooperation of 9 farmers in Chiba Prefecture, Japan, while the chamber experiment was designed to evaluate the characteristics of chemical components among 14 different plant species. The measurements included $PM_{2.5}$ mass concentration, organic carbon (OC), elemental carbon (EC), ionic species (Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, NO_3^- and SO_4^{2-}), water-soluble organic carbon (WSOC), water-insoluble organic carbon (WIOC), char-EC and soot-EC. The main findings are as follows:

(1) OC was the dominant chemical component and made the largest contribution to $PM_{2.5}$ mass concentration for all the samples tested. The results were in the range of 46.1-76.5% (average $\pm \sigma$: $56.8 \pm 7.2\%$, median: 56.7%).
(2) EC was the second largest component contributing to $PM_{2.5}$ mass concentration for all the samples tested, and ranged from 1.2-16.4% (average $\pm \sigma$: $5.7 \pm 3.5\%$, median: 4.9%).
(3) Ionic components contributed to a small portion of the emission ratio of primary $PM_{2.5}$, accounting for 0.3-4.4% (average $\pm \sigma$: $1.5 \pm 1.2\%$, median: 1.4%).
(4) The emission ratios of K^+ were quite low for some

samples; therefore, K$^+$ may not always be suitable as a tracer for biomass burning emissions.

(5) Among the OC fractions, the sum of OC2 and OC3 fractions contributed 60% or more of total OC. The averaged ratio of OC2/OC3 was nearly 1.5.

(6) Char-EC/soot-EC ratios obtained from all of the samples in this study showed values below 1.0, which was different to the results of previous publications. From our results, careful consideration should be given to the use of char-EC as an indicator of biomass burning.

(7) The calculated ratios of WSOC/OC and WIOC/OC from overall samples were 55.7% and 44.3% in average.

(8) The two independent methods for estimating the OM/OC ratios were roughly estimated, resulting in a factor of 1.7 for biomass burning emissions.

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