Chemical Composition of Post-Harvest Biomass Burning Aerosols in Gwangju, Korea

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The main objective of this study was to investigate the chemical characteristics of post-harvest biomass burning aerosols from field burning of barley straw in late spring and rice straw in late fall in rural area in Korea. 12-hr integrated intensive sampling of PM_{10} and $PM_{2.5}$ biomass burning aerosols had been conducted continuously at Gwangju, Korea 4-15 June 2001 and 8 October-14 November 2002. The fine and coarse particles of biomass burning aerosols were collected for mass, ionic, elemental, and carbonaceous species analysis. Average fine and coarse mass concentrations of biomass burning aerosols were measured to be 129.6, 24.2 μgm^{-3} in June 2001 and 47.1, 33.2 μgm^{-3} in October to November 2002, respectively. Exceptionally high level of $PM_{2.5}$ concentration up to 157.8 μgm^{-3} well above 24-hour standard was observed during the biomass burning event days under stagnant atmosphere condition. During biomass burning periods dominant ionic species were Cl^-, NO_3^-, SO_4^{2-}, and NH_4^+ in fine and coarse mode. In the fine mode Cl^- and K^+ were unusually rich due to the high content of the semiarid vegetation. High OC values and OC/EC ratios were also measured during the biomass burning periods. Increased amount of fine aerosols with high enrichment, which were originated from biomass burning of post-harvest agricultural waste, resulted in extremely severe particulate air pollution and visibility degradation in the region. Particulate matters from open field burning of agricultural wastes cause great adverse impact on local air quality and regional climate.

Key words : Biomass burning aerosol, Chemical composition, Fine particles, Dust aerosol

1. Introduction

Biomass burning is a widespread annually occurring phenomenon to clear land for cultivation, to convert forests to agricultural lands, and to remove the vegetation in order to promote agricultural productivity and growth of high yield grasses. Biomass burning aerosols have been recognized as a globally important source of trace gases and atmospheric particulate matter[1)]. Trace gases and particulate matters from biomass burning over many parts of the world have been studied to date by many reserchers[2-9)]. Especially, the African continent and tropical forest regions such as Savanna, Amazon basin, and Southeast Asia have been recognized as the sources of the biomass burning of the earth, thus producing significant man-made contributions of radiatively active, carbon containing aerosols in the atmosphere. Biomass burning aerosol consist of two major chemical components: black carbon, which primarily absorbs solar radiation, and organic carbon, which primarily scatters solar radiation. The strongest negative forcing is associated with regions of intense biomass burning activity and differ from the regions where the sulphate radiative forcing is strongest. The global, annual mean radiative forcing due to biomass burning aerosols is estimated as -0.2 Wm^{-2} [10)].

The haze problem in Asia region is particularly acute because of the large increase in emissions and the extended dry season, which prevents washout of the pollution from the atmosphere. Due to long-range transport, the mostly urban (fossil fuel related) and rural (biomass burning related) aerosols are transformed into a regional haze or cloud that can span an entire continent or even the entire North Pacific[11)].

In Korea, open field burning of agricultural waste is common practice by many farmers after

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harvest. Atmospheric particulate matters from both long-range transported Asian dust and anthropogenic sources directly affect the particulate pollution in Gwangju, Korea. There are two typical biomass burning phenomena in Korea, one is the burning of agricultural waste after harvesting barley in late spring and the other is the burning after harvesting rice in fall. The high levels of fine particulate matter concentration during these event periods result in adverse effects on not only local air quality but also human health and visibility degradation.

In this paper, the particulate matters directly influenced by agricultural biomass open burning have been collected and analyzed to characterize their chemical composition and assess their impact on air quality. Chemical composition characteristics of aerosol from burning of barley straw in late spring and rice straw in lat fall has been investigated. An unusual Asian dust event was also observed during the fall intensive sampling period. Differences in chemical composition between biomass burning aerosol and other types of aerosols including Asian dust and urban pollution in Gwangju, Korea have also been investigated.

2. Experimental Methods

Post-harvest biomass burning aerosols were collected at Gwangju, Korea (35.10N, 126.53E), during two intensive periods; 4 to 15 June, 2001 and 8 October to 14 November, 2002, respectively. The sampling site is located in the city of Gwangju, which is the fifth largest city in Korea and located 200 miles south of Seoul. It has population of about 1.4 million people in 501.4 km^2 area with 0.3 million motor vehicles. Aerosol sampling was made in a mobile laboratory trailer on the rooftop of one of the buildings of Kwangju Institute of Science and Technology (KJIST) located in the northern suburb of Gwangju. General climatological weather condition in Gwangju is characterized by cool and dry fall from September to November and hot and humid summer from June to August. The prevailing wind at Gwangju, Korea is southwesterly in June and northwesterly in October and November.

A total of fifty one 12-hr integrated $PM_{2.5}$ and PM_{10} samples were collected using an URG Versatile Air Pollutant Sampler (VAPS, URG-3000K) with a PM_{10} cyclone inlet, an URG PM_{10} cyclone sampler (URG-2000-30ENB), and a Dichotomous PM_{10} sampler (ASI/GMW series 241) on pre-baked quartz fiber filters for carbonaceous species, on teflon filters for mass, ionic and elemental species analysis. The PM_{10} URG sampler is equipped with an aluminum cyclone with a cut size of 10 μm operated at a 16.7 lpm flow-rate. URG-VAPS and Dichotomous samplers were operated at a 32 lpm and 16.7 lpm flow-rate, respectively. The 47mm quartz fiber filters for carbon analysis were preheated under 550□ furnace for 8 hours to minimize their carbon blanks, put in petri dishes, then wrapped with Teflon tape and aluminum foil, and stored in a refrigerator before sampling. After sampling, all samples were refrigerated between collection and analysis to minimize losses due to volatilization and evaporation during the transportation. Fine and coarse fraction of aerosol mass concentrations were obtained by a gravimetric method using an electronic microbalance with 1 μg sensitivity. The collected samples from each intensive sampling were analyzed by ion chromatography (Dionex, DX-120) for ionic species (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) concentrations. PM_{10} and $PM_{2.5}$ samples collected on the quartz filters were analyzed at AtmAA, Calabasas, CA, USA for analysis of carbonaceous species; elemental carbon (EC) and organic carbon (OC) by the selective thermal oxidation method with MnO_2 catalyst[12]. The fine and coarse samples collected on the filters of the URG-VAPS sampler were used to analyze twenty two species of the trace elements using Inductively Coupled Plasma (ICP)-Atomic Emission Spectrometry (AES) and ICP-MS (Mass Spectrometry) at the Korea Basic Science Institute, Daejon, Korea. Meteorological data were collected by an automatic weather station (AWS) collocated at the sampling site.

3. Results and Discussion

3.1 Aerosol mass concentration in fine and coarse modes

Each sampling period has been categorized into five distinct groups according to aerosol event characteristics and meteorological and air mass history conditions: (1) biomass burning of barley straw in late spring (BBB); (2) background condition of non event (BG); (3) urban pollution under stagnation condition (UP); (4) biomass burning of rice straw in late fall (BBR); and (5) biomass burning of rice straw plus Asian dust (BBR+AD). Table 1 summarizes the results of average concentrations of biomass burning aerosols obtained in this study along with seasonal average values measured previously in Gwangju by Kim et al., 2001[13].

Significant increases in fine mass concentration were observed during both biomass burning events. Average fine and coarse average mass concentrations of biomass burning aerosol in June 2001 were 129.6 and 24.2 μgm^{-3}, respectively, while they were 47.1 and 33.2 μgm^{-3}, respectively in fall of 2002. Exceptionally high level of $PM_{2.5}$ concentration exceeding in the 24-hour average National Ambient Air Quality Standards (NAAQS)[14], 60μgm^{-3}, was observed during the intensive sampling period of June 2001. Figure 1 shows the variations of aerosol mass concentration in the fine and coarse modes measured during the intensive sampling periods.

Major wind direction was southwesterly and southeasterly in June 2001 and northwesterly and southwesterly in October to November, 2002. During the entire sampling period in June 2001 extremely high level of fine mass concentration exceeding the US 24-hr standard for $PM_{2.5}$ was observed with an average $PM_{2.5}/PM_{10}$ ratios of 0.84. Aerosol from biomass burning of barley straw was accumulated in the atmosphere under stagnant meteorological conditions prevailed 4-14 June 2001 at Gwnagju. Thus exceptionally high fine aerosol mass concentration was observed during that period, impacting heavily on local air quality. From 12 to 14 October 2002 stagnation phenomena were also appeared and prevailing wind direction was southwesterly and northwesterly. Emission from an industrial complex located southwest of the sampling site caused high mass concentration during that period.

During two sampling days, 11-12 November 2002 in addition to local biomass burning event unusual Asian dust storm had passed over Gwangju. Although wind speed was high, which is typical for Asian dust storm period, very high levels of mass concentration was measured in the fine and coarse mode. Air quality at the sampling site was greatly affected by biomass burning events, resulting in high mass concentration in the fine mode.

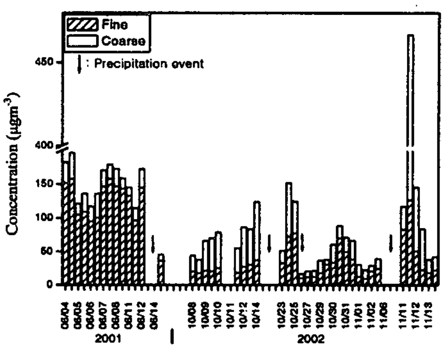


Fig. 1. Variations of aerosol mass concentration in the fine and coarse modes measured at Gwangju, Korea in 2001 and 2002.

3.2 Soluble ionic species

Concentration of the soluble eight ionic species in the fine and coarse mode: chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium, and calcium were determined by Ion Chromatography (IC) analysis. The major soluble species from biomass burning were chloride, nitrate, sulfate, ammonium, and potassium. Table 2 summarizes the average concentration of ionic species during the intensive sampling periods. During the biomass burning period (BBB and BBR), increase of Cl^-, NO_3^-, NH_4^+ and K^+ in fine mode were remarkable, while SO_4^{2-} in fine mode, NO_3^- and Ca^{2+} in coarse mode increased during the Asian dust period (BB+AD) compared to those during background period (BG). Potassium is a highly useful tracer for pyrogenic aerosols, because the combustion of plant matter, which contains K^+ as a major electrolyte within its cytoplasm, release large amounts of K-rich particles in the submicron size fraction[8,15-16].

Variation of concentration of major ionic species were shown same pattern while a tracer of biomass burning, potassium ion increased unproportionally in the fine fraction during the biomass burning events. Andreae et. al[8] reported the major ionic species from savanna fires were Cl^-, SO_4^{2-}, K^+ and NH_4^+, and Yamasoe et. al[9] found that the dominant ionic species from fires of Amazon basin were K^+, Cl^-, and SO_4^{2-}, while Cl^-, NO_3^-, SO_4^{2-}, and NH_4^+ were dominant in this study. The dominant anion was NO_3^- in this study, while Cl^- was dominant in savanna fires and Amazon basin fires[8-9].

Table 1. Average mass concentrations of atmospheric particulate matters at Gwangju, Korea.

Intensive period	Fine mass (μgm^{-3})	Coarse mass (μgm^{-3})	Remarks
06/04-06/15/01	129.6 ± 24.6	24.2 ± 7.7	This study, BBB*
10/08-11/14/02	18.5 ± 6.4	20.9 ± 14.9	This study, BG
	29.8 ± 7.5	57.0 ± 20.1	This study, UP*
	47.1 ± 19.4	33.2 ± 19.9	This study, BBR
	70.4 ± 44.2	132.6 ± 141.2	This study, BBR+AD
1999 Summer	45.4	13.3	Kim et al. 2001[13]
1999 Fall	41.1	11.9	Kim et al. 2001[13]
1999 Winter	15.3	25.8	Kim et al. 2001[13]
2000 Spring	15.3	44.5	Kim et al. 2001[13]
2000 Asian dust	20.9	138.3	Kim et al. 2001[13]

Note: Mean ± standard deviation, *: stagnation phenomena
BG : Background (10/08-11, 26-29, 11/01-02, 13, 2002), UP : Urban pollution (10/12-14, 2002), BBB : Biomass burning of barley straw (6/04-14, 2001), BBR : Biomass burning of rice straw (10/23, 25, 30-31, 11/05-06, 14, 2002), BBR+AD : Biomass burning of rice straw plus Asian dust (11/11-12, 2002)

Table 2. Average concentration of ionic species during the intensive periods.

Species	BG (μgm^{-3})		BBB (μgm^{-3})		BBR (μgm^{-3})		BBR+AD (μgm^{-3})	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Cl^-	0.64	0.85	2.90	0.83	1.40	0.61	1.03	2.17
NO_3^-	1.08	0.59	17.48	6.70	3.64	1.68	3.27	3.58
SO_4^{2-}	2.59	0.29	23.31	5.73	4.43	0.63	6.80	1.99
Na^+	0.11	0.42	0.67	0.88	0.15	0.32	0.39	1.38
NH_4^+	1.29	0.10	10.62	1.31	2.82	0.24	2.83	0.64
K^+	0.15	0.05	4.19	1.09	0.49	0.08	0.96	0.25
Ca^{2+}	0.06	0.22	0.23	0.88	0.10	0.60	0.37	3.25

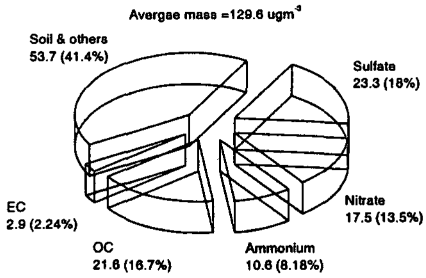
Note: BG : Background (10/08-11, 26-29, 11/01-02, 13, 2002), UP : Urban pollution (10/12-14, 2002), BBB : Biomass burning of barley straw (6/04-14, 2001), BBR : Biomass burning of rice straw (10/23, 25, 30-31, 11/05-06, 14, 2002), BBR+AD : Biomass burning of rice straw plus Asian dust (11/11-12, 2002)

The observed differences may also be explained by the variability in biomass density, amount of water present in the vegetation before burning and distinct vegetation elemental composition. Agricultural waste burning in Korea is much denser and wetter than cerrado and tropical forest vegetation and consequently, it burns less efficiently.

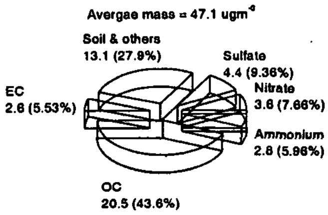
3.3 Chemical composition

Figure 2 shows the composition of biomass burning aerosols from two different vegetation types; barley straw and rice straw. In case of post-harvest biomass burning of rice straw, major component was organic carbon consisting of 44% of total fine mass. Mass fractions of major ionic species; sulfate, nitrate and ammonium were higher for the post-harvest biomass burning of barley straw than those measured during the fall intensive sampling period of 2002 for the rice straw burning, while organic carbon fraction decreased.

Composition of $PM_{2.5}$ for four different categories; background (BG), urban pollution (UP), biomass burning (BBR), and biomass burning plus Asian dust (BBR+AD) are summarized in Figure 3. Dominant component of fine aerosol was OC during biomass burning events, soil and others during the Asian dust event, OC during urban pollution days, respectively. Soil and others fraction was highly increased as expected during the Asian dust events compared to other events.

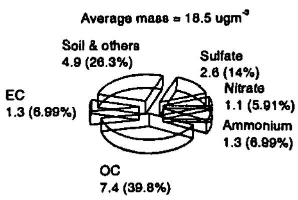


(a)



(b)

Fig. 2. Comparison of $PM_{2.5}$ composition for two different types of biomass burning; (a) barley straw burning in 2001, and (b) rice straw burning in 2002.



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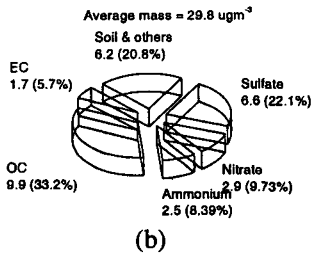

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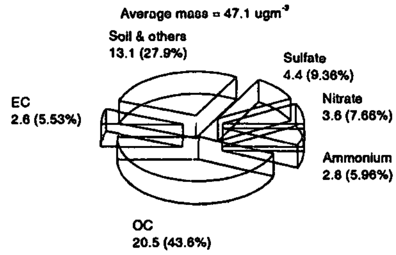
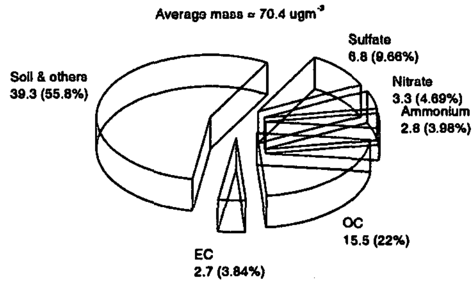


(c)



(d)

Fig. 3. Comparison of $PM_{2.5}$ composition measured at Gwangju in the fall of 2002 for four different categories; (a) non event days (BG), (b) urban pollution days (UP), (c) biomass burning of rice straw (BBR), and (d) biomass burning plus Asian dust (BBR+AD).

4. Conclusions

In order to investigate the chemical characteristics of biomass burning aerosols from the burning of post-harvest agricultural waste, ambient aerosol samples were collected in Gwangju, Korea 4-14 June 2001 and 9 October-14 November 2002. Significant increases in fine aerosol mass were observed during the biomass burning event especially organic carbon component. Average mass concentration in the fine and coarse mode was 129.6 μgm^{-3} and 24.2 μgm^{-3} in June 2001, and 47.1 μgm^{-3} and 33.2 μgm^{-3} in October to November 2002, respectively. In case of post-harvest biomass burning of rice, major component was organic carbon and the percentage was 44% of total fine mass fraction. Comparing with the results of rice, post-harvest biomass burning of barley fractions of sulfate, nitrate and ammonium which are major ionic species of biomass burning aerosols were more increased, while carbon fraction was decreased. Enrichment in the fine particles was remarkable and these increased aerosols which were originated from biomass burning after harvest brought about visibility reduction and increase of fine particles also may affect the human health.

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