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Levoglucosan enhancement in ambient aerosol during springtime transport events of biomass burning smoke to Southeast China

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ABSTRACT

An intensive field experiment was conducted at an urban and a rural site in Hong Kong to identify the influence of biomass burning emissions transported from distinct regions on ambient aerosol in coastal southeast China. Water-soluble ionic and carbonaceous species, specifically the biomass burning tracer levoglucosan, were analysed. Elevated levoglucosan concentrations with maxima of 91.5 and 133.7 ng m^{-3} and overall average concentrations of 30 and 36 ng m^{-3} were observed at the rural and urban sites, respectively. By combining the analysed meteorological data, backward trajectories, fire counts and Aerosol Index from the Earth Probe satellite, southwest China and the northern Philippines, together with the southeast China coast, were identified for the first time as source regions of the transported biomass burning particles at the surface level in rural Hong Kong. Occasional levoglucosan enhancements observed at urban Hong Kong were attributed to local incense and joss paper burning during the Ching-Ming festival period. The contributions of transported biomass burning emissions, especially from the northern Philippines, were estimated to account for 7.5% and 2.9% of OC and $PM_{2.5}$, respectively.

1. Introduction

Atmospheric particles have attracted much scientific and public attention as they play vital roles in climate systems and atmospheric chemistry, and impose strong adverse impacts on human health. Fine particles (with aerodynamic diameters $\leq 2.5\,\mu$m, $PM_{2.5}$) can be inhaled into human lungs and cause deterioration of the human respiratory system (Holgate et al., 1999). In east China, there are diverse aerosol sources in various industrial and urban centres spreading across the territory. The Yangtze River Delta (YRD) and the Pearl River Delta (PRD) are typical regions in China with serious particulate pollution problems. Fugitive dust, industrial emissions from fossil fuel combustion and manufacturing processes, and vehicle exhaust are major sources of aerosols in these regions, while emissions from combustion of biomass/biofuels, such as crop residues and wood in rural areas, as well as the formation of secondary aerosol during transport of pollutants are important sources of ambient aerosol as well in many Asian countries, and specifically in China.

In tropical and subtropical regions of Southeast (SE) Asia and China, biomass burning activities reach their full strength in spring (Chan et al., 2003a; Streets et al., 2003). Open burning of agricultural residues and domestic usage of biofuels are important sources of carbonaceous particles (black carbon, BC, and organic carbon, OC) and gases (such as CO, NO_x,) during this period (Streets et al., 2003; Duan et al., 2004). Previous aircraft and mountain-top measurements have shown that smoke aerosol from biomass burning activities in Southeast and East Asia can be transported eastward towards (and across) the Pacific Ocean (Bey et al., 2001; Jacob et al., 2003; Ma et al., 2003). In fact, Chan et al. (2003a,b) showed that springtime ozone enhancement in the lower troposphere over Hong Kong and southeast China is related to photochemical reactions during the transport of ozone precursors originating from the upwind SE Asian subcontinent, where intensive biomass burning activities occur during each spring.

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Hong Kong is located on the southeast coast of China and is a commercial city with very limited biomass/biofuel burning activities. Geographically, it is a perfect location to capture the signals of biomass burning emissions from the upwind source regions, as it lies in the transport pathways of air masses from higher latitudes of East Asia to the South China Sea as well as from tropical and subtropical SE Asia (Chan et al., 2003b; Cheng et al., 2006). However, few studies have explored the impact of transported biomass smoke particles at the surface level in Hong Kong despite the fact that biomass burning emissions from the SE Asian subcontinent have been identified in the free troposphere (Chan et al., 2003a).

In this paper, we present the measurement results of $PM_{2.5}$ mass concentrations and associated chemical species, including water-soluble inorganic ions, carbonaceous species (OC and EC) and levoglucosan (LG) in samples collected at an urban and a relatively remote site in Hong Kong during spring 2004. Levoglucosan is a widely used molecular tracer for biomass burning processes, released as a major component of fine smoke particles during thermal decomposition of cellulose (Simoneit et al., 1999). Based on the ambient levels of levoglucosan, we illustrate that biomass burning activities in the source regions of the southeast China coast, southwest China and occasionally the Philippines have relatively strong impact on Hong Kong. Our findings highlight the importance of contributions from biomass/biofuel burning activities on the regional aerosol budget in south China.

2. Field experiment and laboratory analysis

2.1. Sampling sites and field experiment

Aerosol samples ($PM_{2.5}$) were collected at an urban site in the centre of Kowloon Peninsula (22.2°N, 114.1°E) and a rural site, approximately 40 km away from the urban site, in Hok Tsui (HT) (22.1°N, 114.1°E), which is located on the southeastern tip of Hong Kong Island facing the South China Sea (Fig. 1), from April 7 to May 12, 2004. The urban sampling site was located on the rooftop of a seven-story building on the campus of Hong Kong Polytechnic University (PolyU), near the road leading to the entrance of the Cross Harbor Tunnel, which has one of the highest traffic flows in the territory. The rural sampling site was on top of a cliff about 60 m high, influenced to a much smaller extent by anthropogenic emissions and was regarded as a background site of Hong Kong (Wang et al., 2003), as it is at some distance from major urban areas. In addition, it is sheltered from road traffic by surrounding hills, despite the fact that it is close to maritime traffic and thus ship emissions.

Particulate samples were collected by mini-volume (Minivol) samplers (Airmetrics Eugene, OR, USA) with $PM_{2.5}$ inlets, operating at a flow rate of 5 l min^{-1}. The typical sampling duration was 24 h, with one sample collected every second day at the urban site, and 48 h at the rural site. Field blanks, obtained by placing filters in the sampler for 5–10 min without air flow, were collected every 6 days. In total, 14 field blanks were collected at the two sites during the sampling period. The sampling dates reported here represent the dates when the sampling started. Aerosol samples were collected on 47 mm quartz microfibre filters (Whatman, Piscataway, NJ, USA), which were baked at 500°C for 8 h before sampling and were stored in a freezer at –20°C after sampling. All filters were weighed before and after sampling on an electronic balance after conditioning at constant temperature (23 ± 1°C) and humidity (40%) for 24 h.

2.2. Laboratory analysis of chemical species

The chemical analyses were conducted at the Research Center of Environmental Changes, Academia Sinica, Taipei. All

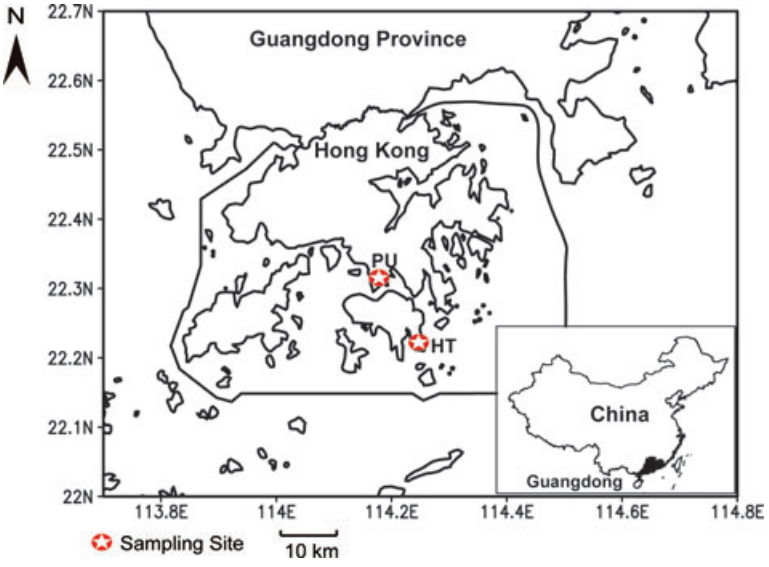

Fig. 1. Location of the two sampling sites in urban (PU) and rural (HT) areas of Hong Kong.

filter samples were analysed for OC, EC, levoglucosan and inorganic ions. Carbonaceous species were determined by a Sunset Laboratory carbon analyser (Model 4) using a thermal-optical transmittance (TOT) technique based on the NIOSH protocol (Birch and Cary, 1996). A detailed description of the analytical procedures as well as quality control and assurance procedures is available in the literature Engling et al. (2009).

Sample filters were extracted with deionized water ($>18.2\,M\Omega\ cm^{-1}$) under ultrasonic agitation for 60 min, followed by filtration of the extracts with a syringe filter, using pre-combusted quartz filters (Tissuquartz, 2500 QAT-UP; Pall Corporation, East Hills, NY, USA). Sample extracts were stored at 4°C until analysis. Levoglucosan in the aqueous sample extracts was separated and quantified by high performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) on a Dionex ICS-3000 ion chromatograph, using a Dionex CarboPak MA1 analytical column (4 × 250 mm) and sodium hydroxide solution (400 mM, 0.4 ml min^{-1}) as eluent (Engling et al., 2006; Iinuma et al., 2009). Ionic species were measured in the same extract solutions as levoglucosan. Eleven ionic species, including five cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and six anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), were measured by ion chromatography (Dionex, DX120). CS12A and AS4A columns were used to determine cations and anions, respectively. The eluents were 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3 for anions and 20 mM CH_4O_3S for cations with a flow rate of 1.5 and 1.0 ml min^{-1}, respectively. Field blanks were used to correct the concentrations of ionic species. The detection limits of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} were 0.016, 0.002, 0.003, 0.001, 0.002, 0.002, 0.032, 0.033, 0.003, 0.003 and 0.002 $\mu g\ m^{-3}$, respectively.

2.3. Backward air mass trajectory and MM5 analysis

To identify various source regions of pollutants reaching Hong Kong, 5-day backward trajectories at 00:00 UTC on every sampling day were calculated by the HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php) to demonstrate the synoptic patterns and associated long-range transport processes of air masses. The model adopts meteorological data from FNL (Final Operational Global Analysis) as the input.

To better show the flow of air masses on sub-regional scale, the meteorological field in the boundary layer of the concerned region was simulated by the Fifth-Generation PSU/NCAR Mesoscale Modeling System, MM5 (Grell et al., 1994). The initial and boundary conditions for MM5 simulation were obtained from the NCAR/NCEP reanalysis data set, which has horizontal resolution of 1°×1° and 26 vertical pressure levels, and time resolution of 6-h intervals. The simulations were run in three nested domains centred at 28.67°N and 110.65°E. The three nested domains contained 151 × 151, 130 × 130 and 100 × 100 grid boxes in the east–west and north–south directions with the horizontal grid spaces of 36, 12 and 4 km, respectively. The second nested domain was used to simulate the wind field at the altitude of 500 m at 3-h intervals.

Meteorological data collected from the Waglan Island Meteorological Station and King's Park Automatic Weather Station of the Hong Kong Observatory (available at http://www.hko.gov.hk/contentc.htm) were also used to show the local winds nearby our monitoring stations. Waglan Island is located next to the rural sampling site with limited anthropogenic activities other than emissions from occasional marine vessels. King's Park Automatic Weather Station was about 1 km northwest of the urban sampling site at PolyU. Therefore, the meteorological data of Waglan Island and King's Park Automatic Weather Station were believed to reflect in general the conditions at Hok Tsui and PolyU.

2.4. Fire count map and Aerosol Index from satellite observations

Fire counts detected by Moderate Resolution Imaging Spectroradiometer on NASA satellites (available at http://maps.geog.umd.edu/firms/maps.htm) were used to identify the geographical hot spots of biomass burning activities with a horizontal resolution of 1 × 1 km^2. The span of the fire counts was determined by the starting date and termination date of the 5-day backward air mass trajectories described earlier. The aerosol index determined from TOMS on board of NASA's Earth Probe satellite (available at http://toms.gsfc.nasa.gov/) was used to obtain the geographical distribution of aerosols in the region of interest during the major biomass burning events.

3. Results and discussion

3.1. Levoglucosan levels and chemical characteristics of $PM_{2.5}$

The mass concentrations of $PM_{2.5}$ and analysed chemical species, including inorganic ions, OC, EC and levoglucosan are statistically summarized in Table 1 and the time series are shown in Figs 2 and 3. The average mass concentration of $PM_{2.5}$ was 37.5 $\mu g\ m^{-3}$ at the urban site, slightly lower than the seasonal average range of 39–60 $\mu g\ m^{-3}$ reported previously (Ho et al., 2003; 2006; Lai et al., 2007), and 30.8 $\mu g\ m^{-3}$ at the rural site, in good agreement with the seasonal range of 15–41 $\mu g\ m^{-3}$ (Ho et al., 2003; Louie et al., 2005, 2006; Lai et al., 2007). The respective average concentrations of levoglucosan were 36.0 and 30.0 ng m^{-3} at the urban and rural sites, slightly higher than that reported in urban Hong Kong in summer (3.5–97.7, averaging at 27.5 ng m^{-3}) (Hu et al., 2008), but relatively low when compared to many Chinese cities. Zhang et al. (2008) reported higher levoglucosan concentrations (178 ng m^{-3} on average) in urban Beijing during April 2003. Similarly, Wang et al. (2007b) measured substantially higher concentrations of levoglucosan with a range of 120–950 ng m^{-3}

Table 1. Mass concentrations of ionic species, OC, EC and levoglucosan in $PM_{2.5}$ at the urban and rural sites (unit: $\mu g\ m^{-3}$)

	PolyU				Hok Tsui			
	Max	Median	Average	S.D.	Max	Median	Average	S.D.
$PM_{2.5}$	91.6	35.1	37.5	17.5	62.6	29.8	30.8	13.4
OC	14.3	6.5	7.2	2.7	8.5	4.1	4.8	2.0
EC	7.1	3.8	3.7	1.6	2.0	1.2	1.3	0.4
LG[a]	133.7	26.2	36.0	29.6	91.5	21.1	30.0	22.2
Na^+	1.8	0.7	0.8	0.5	15.9	6.0	5.5	4.5
NH_4^+	10.1	2.2	2.7	2.4	7.0	2.3	2.4	1.5
K^+	1.3	0.7	0.7	0.4	3.2	0.9	1.1	0.8
Mg^{2+}	0.2	0.1	0.1	b	0.1	0.1	0.1	b
Ca^{2+}	1.3	0.4	0.5	0.3	0.9	0.3	0.4	0.2
F^-	b	b	b	b	b	b	b	b
Cl^-	1.8	0.1	0.2	0.4	0.8	0.1	0.2	0.2
NO_2^-	0.2	b	b	0.1	0.7	0.1	0.1	0.2
NO_3^-	5.0	1.3	1.7	1.1	2.3	0.8	0.8	0.6
PO_4^{3-}	0.7	0.1	0.2	0.3	0.6	0.3	0.3	0.2
SO_4^{2-}	30.9	8.9	11.2	6.7	24.6	10.8	11.9	4.7

[a]The unit of levoglucosan is ng m^{-3}.
[b]Lower than 0.04.

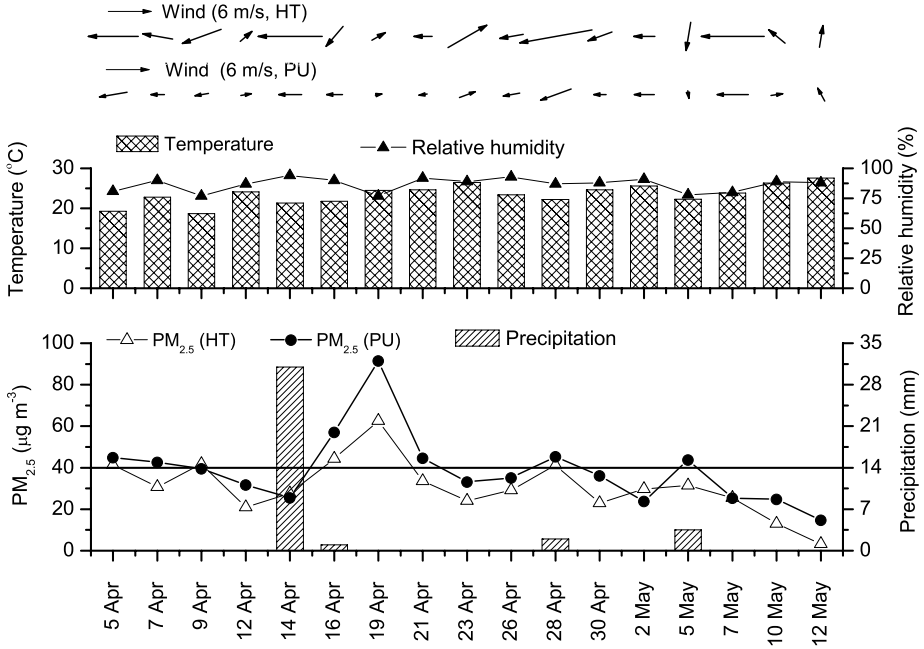

Fig. 2. Temporal variations of $PM_{2.5}$ mass concentrations and meteorological variables at the rural and urban sites.

and 200–660 ng m^{-3} in suburban and downtown locations of Guangzhou, respectively, during October 2004, and Zhang et al. (2010) reported values of 15–273 ng m^{-3} (averaging at 107 ng m^{-3}) in urban Guangzhou as well in summer 2006. The lower values in Hong Kong might be explained by lack of large-scale biomass burning and biofuel usage in the territory. In fact, large-scale agricultural burning activities are seldom observed in Hong Kong, in contrast to Guangzhou and Beijing, where extensive agricultural and domestic biomass/biofuel combustion takes place in their surrounding areas, although accidental hill fires do occur throughout the year in Hong Kong. Domestic usage of biomass/biofuels, such as crop residues, wood or coal, is very rare in the immediate upwind cities Shenzhen and Macau as well.

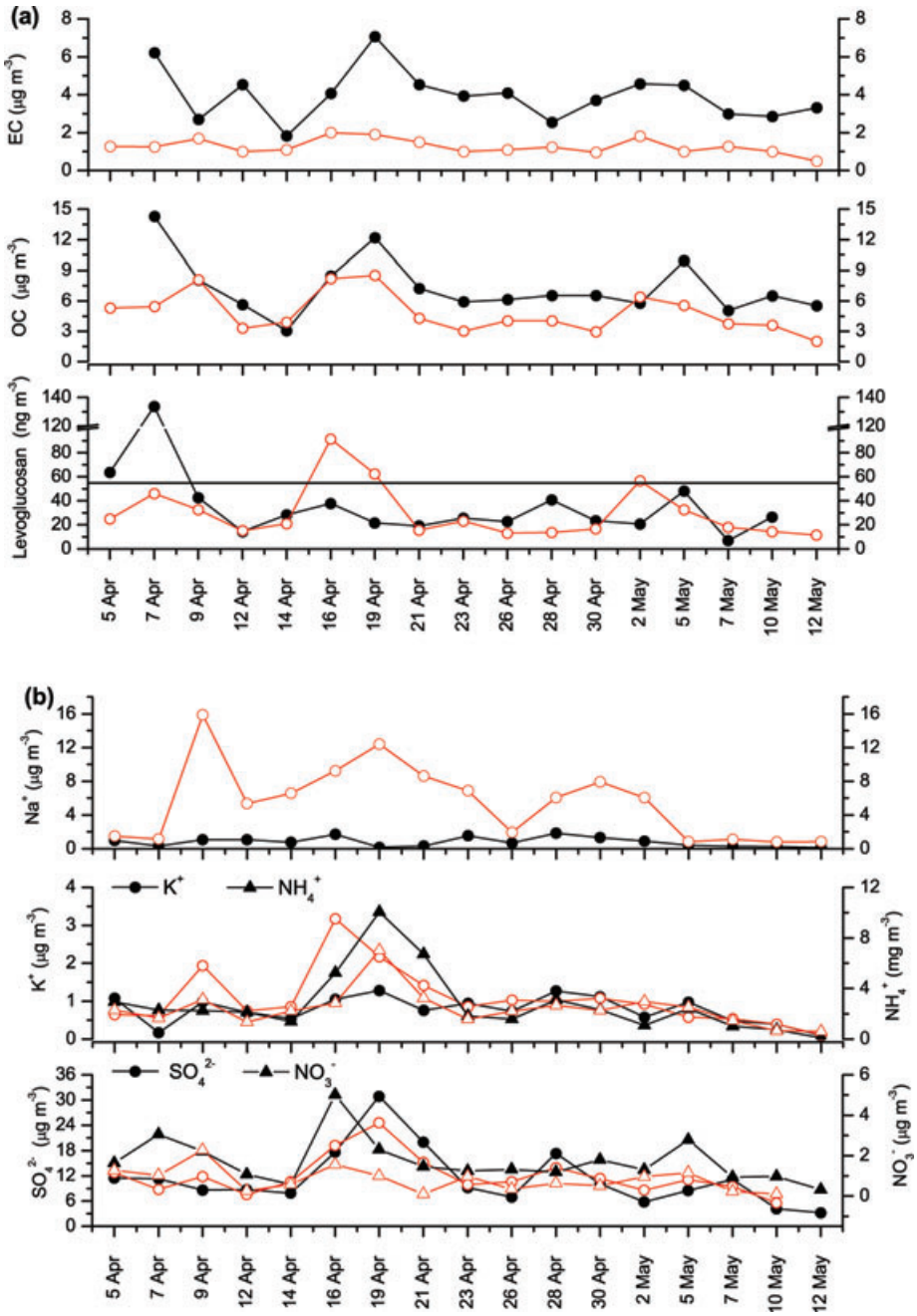

Fig. 3. Temporal variations of levoglucosan, OC and EC (a) and ionic species (b) at HT and PU (unit: μg m^{-3}, except for levoglucosan: ng m^{-3}; PU: solid symbols; HT: open symbols; Circles: Levoglucosan, OC, EC, SO_4^{2-}, K^+, Na^+; Triangles: NO_3^-, NH_4^+).

However, episodic events with significant enhancements in levoglucosan levels were observed at both sites, coinciding with increases in other biomass burning tracer concentrations, such as water-soluble potassium (K^+), for example on April 16 (Fig. 3). Potassium is present in high concentrations in biomass smoke plumes and has been widely used as tracer for biomass burning as well (Chow, 1995; Andreae and Merlet, 2001), although additional K^+ sources exist. Therefore, non-sea-salt-potassium (nss-K^+, $C_{\text{nss-K}^+} = C_{K^+} - 0.0355 \times C_{Na^+}$) concentrations (Lai et al., 2007) were calculated to exclude the influence of sea-salt potassium in this study. Relatively good Spearman's correlation between levoglucosan and nss-K^+ was observed at the rural site ($r^2 = 0.6$, $p < 0.05$), while the correlation at the urban site was poor, indicating other potassium sources, such as meat cooking. The maximum levoglucosan concentrations reached 133.7 and 91.5 ng m^{-3} at the urban and rural sites, respectively. The

presence of elevated levoglucosan in the ambient fine particles indicated that biomass burning activities from various upwind source regions do affect the aerosol in both urban and rural Hong Kong to some extent in springtime, despite the fact that the territory is dominated by vehicular and power plant emissions (Ho et al., 2006).

The analysed ionic species accounted for 46.2% and 69.0% of the fine particle mass concentration at the urban and rural sites, respectively, representing the largest chemical group in fine particles. The most abundant ionic species followed the order of $SO_4^{2-} > Na^+ > NH_4^+ > NO_3^-$ at the rural site, and $SO_4^{2-} > NH_4^+ > NO_3^- > Na^+$ at the urban site. The average mass concentrations of OC and EC were 7.2 and 3.7 μg m^{-3} at the urban site and 4.8 and 1.3 μg m^{-3} at the rural site, respectively. Duan et al. (2007) reported that the concentrations of OC and EC were 1.56–13.4 μg m^{-3} and 0.8–4.5 μg m^{-3} in Hong Kong during 2004 and 2005, showing good agreement with our observations.

3.2. *Biomass burning source regions during periods with elevated levoglucosan*

Typically, March and April are the months during which farmers in SE Asia and South China start field preparation and burn crop residues, such as straw, that are left over on fields from the previous growing season (Duan et al., 2004), resulting in extensive emissions of biomass burning smoke aerosol. Although the sampling period during this study did not cover the entire spring biomass burning season, we were able to capture several episodic cases of interest. Build-up of $PM_{2.5}$ (>40.0 μg m^{-3}) was observed on April 5, 9, 16, 19 and 28 at the rural site, averaging at 46.3 μg m^{-3} (Fig. 2). Eight days with elevated $PM_{2.5}$ (>40.0 μg m^{-3}) were observed at the urban site with a range of 40.0–91.6 μg m^{-3}, which include April 7 and 21, May 5 and the same 5 elevated days as the rural site. Build-up of levoglucosan (>55 ng m^{-3}) was observed on April 16 and 19, and May 2 at the rural site and on April 5 and 7 at the urban site (Fig. 3a). These enhancement events of levoglucosan and/or $PM_{2.5}$ were selected for further discussion in the following paragraphs.

3.2.1 Biomass burning source regions in southwest China and along the southeast China coast. Enhancements in both $PM_{2.5}$ and levoglucosan concentrations at the rural site were observed on April 16 and 19. The concentrations of levoglucosan (91.5 ng m^{-3}) and K^+ (3.2 μg m^{-3}) on April 16 were the highest during the entire study period, and the OC (8.2 μg m^{-3}) level was relatively high as well. The highest $PM_{2.5}$ value (62.7 μg m^{-3}) was observed on April 19, coinciding with the lowest daily average wind speed (2.1 m s^{-1}). Elevated concentrations of levoglucosan (62.6 ng m^{-3}), OC (8.5 μg m^{-3}) and K^+ (2.2 μg m^{-3}) were also observed on that day (Fig. 3).

Biomass burning activities were apparent in provinces of southwest China (Guangxi, Guizhou and western part of Guangdong) and the southeast China coastal provinces (Jiangsu, Fujian and east Guangdong) in the period of April 14–20, as shown by satellite-derived fire counts (Fig. 4a). Five-day backward trajectories showed that the air masses had passed through biomass burning regions of the southwestern provinces on April 19 (Fig. 5a) and the southeast China coastal region on April 16 (Fig. 5b) before reaching Hong Kong. It should be noted that the main energy source in rural China are biofuels, including crop residues and fuel wood (Yan et al., 2006). The total estimated amount of dry matter for burned biomass (open field burning of crop residues and domestic burning of biofuel) were 17.5–34.4 Tg for the three southwestern provinces and 13–24 Tg for the three southeastern provinces mentioned above in 2000 (Yan et al., 2006). The observations of active fires in the regions through which the air masses with enhanced levoglucosan and $PM_{2.5}$ levels had passed explain that surface-level fine particles in rural Hong Kong were likely influenced by biomass burning emissions from southwest China and the southeast China coast. Specifically, the western part of Guangdong Province, located to the west of Hong Kong, was identified as an important biomass

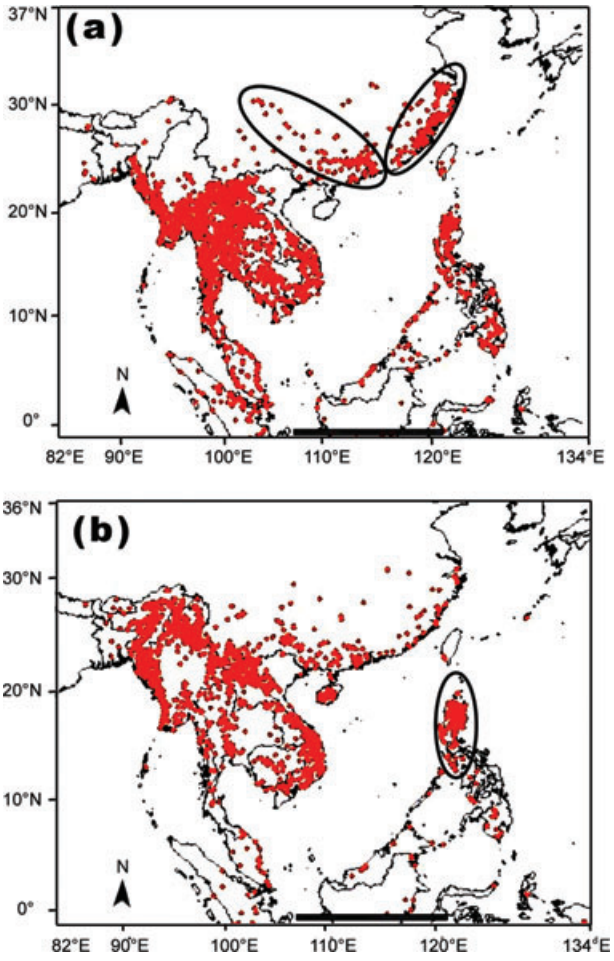

Fig. 4. Fire counts during the periods of April 14–20 (a) and April 28–May 3 (b) (the arrows denote the north direction).

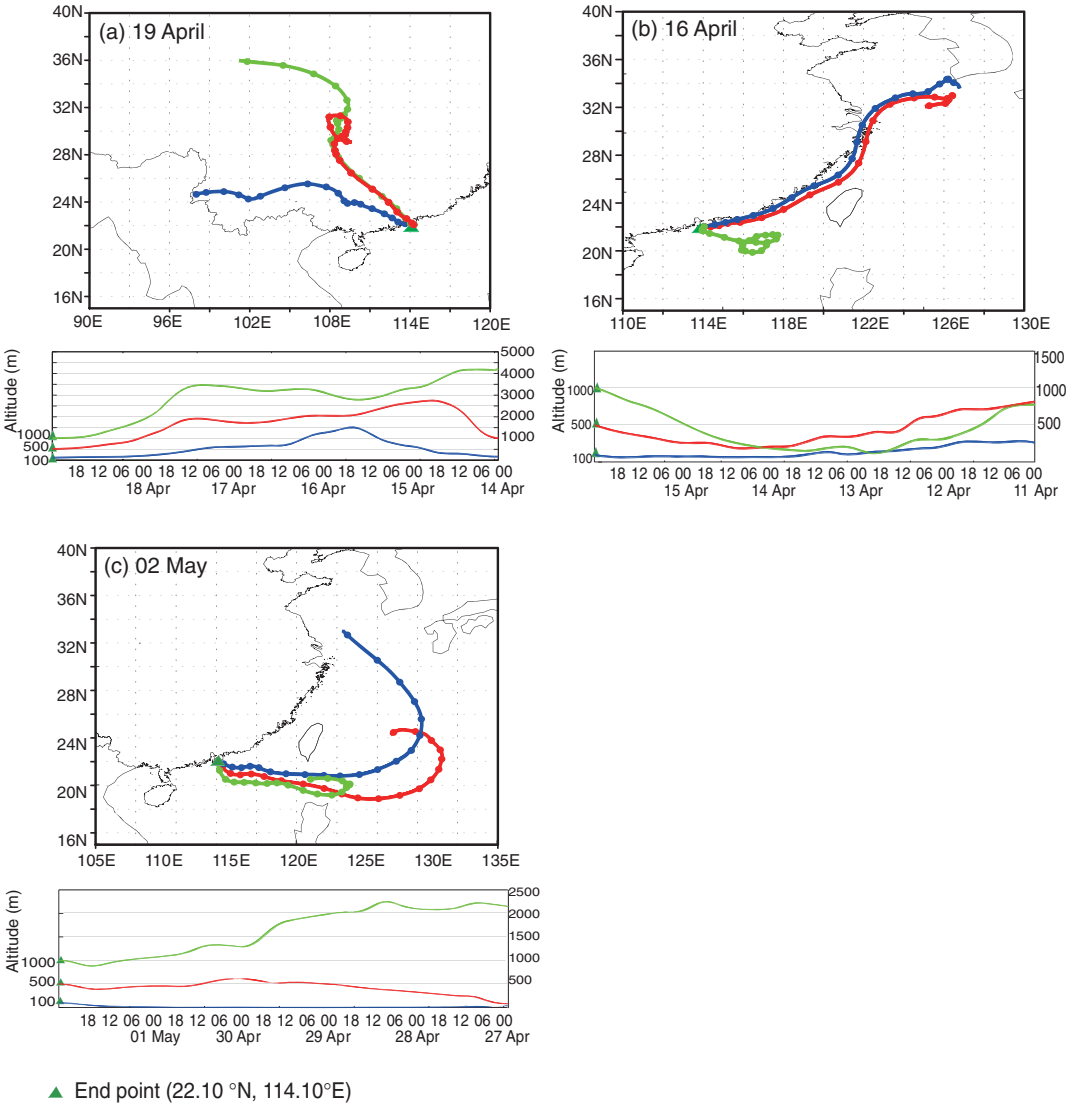

Fig. 5. Backward air mass trajectories at the rural site on April 19 (a); April 16 (b) and May 2 (c).

burning source region based on the satellite-observed fire hot spots.

Unfavourable meteorological conditions may intensify pollution levels through accumulation of air pollutants. Wind fields were simulated to identify the variation in the prevailing winds in the study region. Figure 6 shows the wind field on April 19. As similar patterns were found throughout the day, only a representative wind field at 02:00 (LST) was shown. Air flow starting from the western part of Guangdong Province was divided into two branches. The upper branch moved along the northern boundary of Guangdong Province, passed through Fujian Province and headed to the Taiwan Strait. The lower branch passed over the South China Sea and joined the upper air parcels in the north of Taiwan. Noticeably, the whole Guangdong Province experienced stagnant meteorological conditions, characterized by low wind speeds (Fig. 6), which caused regional accumulation of air pollutants, including $PM_{2.5}$ and levoglucosan, in the Pearl River Delta and Hong Kong. For instance, the wind speeds on April 19 at urban (0.91 m s^{-1}) and rural Hong Kong (2.1 m s^{-1}) were the lowest during the entire sampling duration. Consequently, the ambient levels of $PM_{2.5}$ mass (Fig. 2) and most chemical species (Figs 3a and b) were elevated on that day.

3.2.2 Biomass burning source region in the Northern Philippines. A total of five sampling days was influenced by marine air masses (April 14 and 23, May 10, 12 and 2) at the rural site during the study period. In case of the former 4 days, the air masses had passed over the South China Sea, ranging between 14–22°N and 110–120°E, resulting in low $PM_{2.5}$ and levoglucosan levels. This was in agreement with observations by Wang

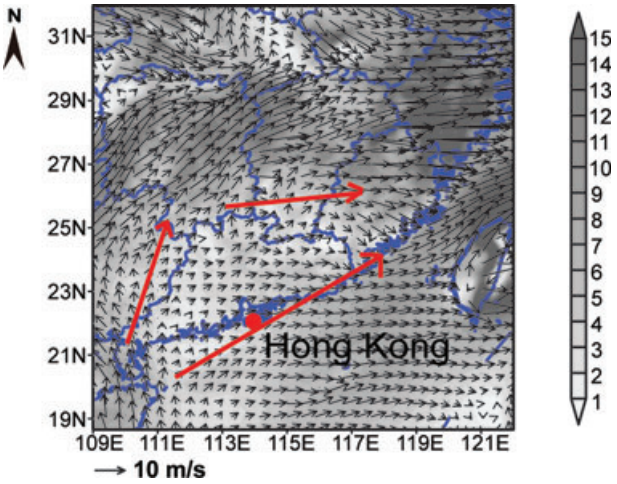

Fig. 6. Wind vector at 02:00 (LST) on April 19 based on MM5 modeling. The scale of the vertical bar indicates the wind speed, with the colours denoting regions with certain wind speeds. The red arrows represent the general directions of the prevailing winds.

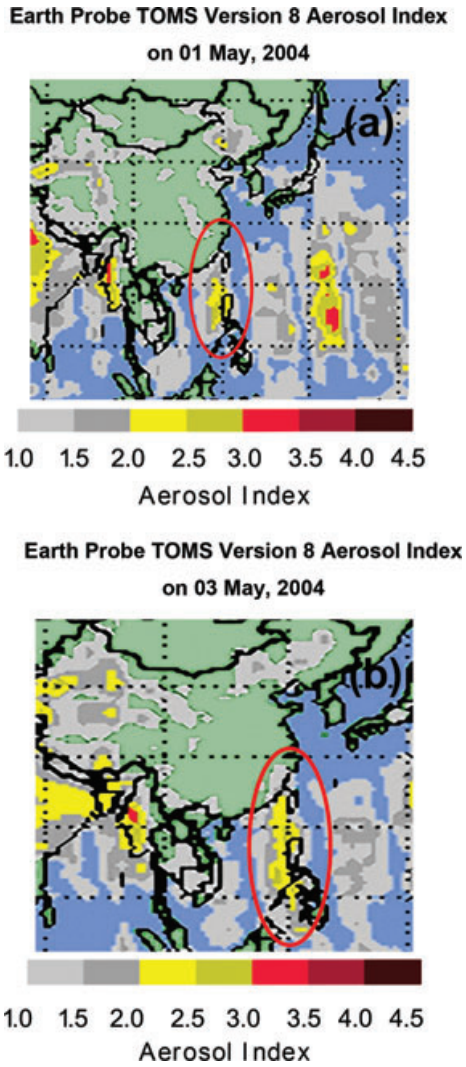

Fig. 7. Aerosol Index (AI) on May 1 (a) and May 3 (b). AI is positive for absorbing aerosols and negative for non-absorbing aerosols (pure scattering) (http://toms.gsfc.nasa.gov/aerosols/aerosols_v8.html). Dark brown indicates the largest amount of smoke in the atmosphere.

et al. (1997; 2003), who reported that marine air masses reaching Hong Kong are typically associated with low concentrations of trace gases and aerosols.

However, the case of May 2 at the rural site was abnormal. The sampling duration for this sample was 40 h. Although the mass concentration of $PM_{2.5}$ was only 29.8 μg m^{-3}, the levoglucosan concentration (56.7 ng m^{-3}) was elevated. The air masses on May 2 and 3 originated from the South China Sea and passed over the northern part of the Philippines before reaching the rural Hong Kong site (Fig. 5c shows the air mass trajectory for May 2 only). Extensive biomass burning activities were observed in the Philippines from April 28 to May 3 when the levoglucosan-rich air masses were travelling over the northern Philippines (Fig. 4b). The TOMS aerosol index revealed elevated absorbing aerosol (biomass burning smoke) over the South China Sea extending from the Philippines to Taiwan and Fujian Province on May 1 and 3 (Fig. 7). The prevailing wind in Hong Kong was easterly during the two sampling days (Fig. 2). Moreover, Gadde et al. (2009) estimated that the annual amount of rice straw subject to open field burning in the Philippines was 10.15 Tg from 2002 to 2006, only slightly lower than that in India (13.92 Tg). Therefore, the enhancement in levoglucosan levels on May 2 was most likely the result of biomass burning activities in the northern Philippines, which was observed here for the first time to the best of our knowledge.

3.2.3 Local biomass burning emissions. In addition to transported biomass burning smoke aerosol, influence of occasional local biomass burning activities was observed at the urban site. Enhancements in both levoglucosan and $PM_{2.5}$ mass concentrations at the urban site were observed on April 5 and 7 with levoglucosan concentrations of 63.6 and 133.7 ng m^{-3}, respectively. The highest OC concentration (14.3 μg m^{-3}) during the entire study period was observed on April 7 (Fig. 3a).

It is noteworthy that 4 April 2004 was the traditional Ching-Ming festival. Following Chinese traditions, incense and joss paper are commonly burned to worship deceased ancestors, especially during the weekend of the holiday period, aside from open burning of weeds, leaves and other plant material on graveyards. A recent study showed that the most abundant anhydrosugar emitted during burning of incense and joss paper was levoglucosan (Chen, 2009). Additional species, such as formaldehyde and other carbonyl compounds (Wang et al., 2007a), as well as PAHs, including chrysene, benzo[ghi]perylene, benzo[*a*]pyrene and fluoranthene, have been detected in incense smoke (Navasumrit et al., 2008; Estrellan and Iino, 2010). No unique

source tracers for incense or joss paper burning have been identified to date according to our knowledge. Nevertheless, the drastic enhancement in levoglucosan levels on April 5 and 7 can likely be attributed to local burning activities associated with traditional practices during the festival. Additional minor contributions of levoglucosan at the urban site may have been derived from cooking activities in the surrounding residential areas. Two studies revealed the presence of levoglucosan in smoke emissions from Chinese-style cooking (He et al., 2004; Zhao et al., 2007).

3.3 Contributions of transported biomass burning smoke

The five sampling days (April 14 and 23 and May 2, 10 and 12) mentioned in Section 3.2.2 at the rural site were characterized by low concentrations of $PM_{2.5}$ mass and associated chemical species, except for elevated levoglucosan and OC levels on May 2. The average mass concentrations and certain ratios of chemical species on the other 4 days with low values were taken as reference for comparison with the sampling dates of elevated levoglucosan (April 16, 19 and May 2; Table 2).

The $PM_{2.5}$ mass concentrations on the three levoglucosan-elevated days at the rural site were 1.8–3.7 times higher than the reference value, whereas levoglucosan levels were 3.2–5.2 times higher, with good Spearman's correlation between levoglucosan and OC ($r^2 = 0.61$, $p < 0.01$). In contrast, levoglucosan concentrations at the urban site were only 1.2–2.1 times higher, with low Spearman's correlation between levoglucosan and OC ($r^2 = 0.34$, $p < 0.05$). Hoffmann et al. (2010) reported that levoglucosan could be oxidized by free radicals in deliquescent particles, especially OH radicals. Similarly, Hennigan et al. (2010) observed degradation of levoglucosan in biomass burning particles exposed to OH radicals. Moreover, Theurer (1999) reported the type and arrangement of buildings and outer flow in a city could effect the air flow direction and velocity at urban sites. Therefore, the lower levoglucosan levels observed at the urban site during those 3 days might be associated with both the complex in situ chemical reactions of levoglucosan in the atmosphere and the shielding effect of high-rise buildings.

Levoglucosan to OC ratios have been used to estimate contributions from biomass burning to the aerosol OC mass (Zdrahal et al., 2002; Puxbaum et al., 2007; Zhang et al., 2010). In biomass burning source emission tests for three major types of cereal straw (corn, wheat and rice) in China, Zhang et al. (2007) reported a levoglucosan to OC ratio of 0.082 for $PM_{2.5}$. We can use this ratio in combination with the levoglucosan/OC ratios from our $PM_{2.5}$ samples to obtain a rough estimate of the contributions of transported biomass burning smoke to ambient OC, which ranged from 6.5% to 11% (Table 2). Our calculated biomass burning contributions were lower than those for Beijing (with a range of 18–38%) calculated by the same levoglucosan/OC ratio (Zhang et al., 2008), which was likely due to the more extensive burning activities in the surrounding rural areas of Beijing.

In addition, the impact of biomass burning could be assessed by using the ratio of levoglucosan to $PM_{2.5}$ (Wang et al., 2007b). Fine et al. (2001) and Schauer et al. (2001) reported that the levoglucosan content in $PM_{2.5}$ for wood burning in fire places was in a range of 7.1–22.8%. In contrast, Zhang et al. (2008) estimated that the average levoglucosan content in $PM_{2.5}$ for cereal

Table 2. Comparisons of mass concentrations and ratios of analysed species between reference values and those on levoglucosan-elevated days at the rural site (April 16, April 19 and May 2) under the influence of transported biomass burning emissions

	Reference[a]	Apr 16	Apr 19	May 2
$PM_{2.5}$	19.6	44.3	62.6	29.8
OC	3.8	8.2	8.5	6.4
EC	1.1	2.0	1.9	1.8
Levoglucosan	17.5	91.5	62.6	56.7
K^+	0.6	3.2	2.2	0.9
Nss-K^+	0.5	2.1	1.7	0.7
K^+ /OC	0.16	0.39	0.26	0.14
Nss-K^+ /OC	0.12	0.26	0.20	0.11
Levoglucosan/OC	0.006	0.011	0.007	0.008
Contribution of biomass burning to OC[b]		11	6.5	7.5
Contribution of biomass burning to $PM_{2.5}$[c]		3.7	1.6	2.9

[a]The reference levels of chemical species are the average concentrations of samples collected on 5 days at Hok Tsui affected by marine air masses passing through regions with little/no biomass burning emissions (April 14 and 23 and May 2, 10 and 12), except levoglucosan and OC on May 2.
[b]Contributions of biomass burning to OC $= \frac{(\text{Levoglucosan}-17.5)/(1000\times\text{OC})}{0.082} \times 100\%$.
[c]Contributions of biomass burning to $PM_{2.5} = \frac{(\text{Levoglucosan}-17.5)/(1000\times PM_{2.5})}{4.5\%} \times 100\%$ (Wang et al., 2007b).

straw burned in China was only 4.5%. Cereal straw burning is the major type of biomass burning in both China and the Philippines (Gadde et al., 2009). Thus, the factor of 4.5% could be used to estimate contributions of biomass burning smoke to fine particles at our selected sites in Hong Kong, which ranged from 1.6% to 3.7% in the three selected days (Table 2), somewhat lower than the biomass burning contributions in Guangzhou estimated during autumn (3–19%) (Wang et al., 2007b).

4. Conclusions

Concentrations of inorganic ions, carbonaceous species and levoglucosan were measured at an urban and a rural site in Hong Kong to investigate the influence of transported biomass burning emissions on fine particles ($PM_{2.5}$) at the surface-level. Three biomass burning source regions were identified. The April 16 case was influenced by air masses, which had passed over biomass burning regions in the southeast China coast region, characterized by the highest concentration of levoglucosan. The April 19 case had the highest $PM_{2.5}$ mass levels with air masses having passed over biomass burning regions of southwest China, especially the western part of Guangdong Province. The marine air masses on May 2 had passed over the South China Sea where they were mixed with smoke aerosol derived from active biomass burning regions in the northern Philippines. To the best of our knowledge, this is the first time that such long-range transport of biomass burning smoke over the open ocean to Hong Kong was reported. In addition, incense and joss paper burning activities during the traditional Ching-Ming festival were identified as possible causes for enhancement of levoglucosan at the urban site. In the three long-range transport events of biomass smoke particles, levoglucosan levels were 3.2–7.6 times higher than the reference level, resulting in biomass burning contributions of 6.5–11% to OC and 1.6–3.7% to $PM_{2.5}$.

In summary, we have shown that biomass burning contributions cannot be ignored even when $PM_{2.5}$ concentrations are low, as was the case during our study period (spring time) when long-range transported smoke particles from the southeast China coast, southwest China and northern Philippines affected the sampling sites, whereas in highly polluted seasons, such as autumn and winter, the percentage of biomass smoke in ambient aerosol particles is obviously higher.

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