High secondary aerosol contribution to particulate pollution during haze events in China

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Rapid industrialization and urbanization in developing countries has led to an increase in air pollution, along a similar trajectory to that previously experienced by the developed nations[1]. In China, particulate pollution is a serious environmental problem that is influencing air quality, regional and global climates, and human health[2,3]. In response to the extremely severe and persistent haze pollution experienced by about 800 million people during the first quarter of 2013 (refs 4, 5), the Chinese State Council announced its aim to reduce concentrations of $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 micrometres) by up to 25 per cent relative to 2012 levels by 2017 (ref. 6). Such efforts however require elucidation of the factors governing the abundance and composition of $PM_{2.5}$, which to date remain poorly constrained in China[3,7,8]. Here we combine a comprehensive set of novel and state-of-the-art offline analytical approaches and statistical techniques to investigate the chemical nature and sources of particulate matter at urban locations in Beijing, Shanghai, Guangzhou and Xi'an during January 2013. We find that the severe haze pollution event was driven to a large extent by secondary aerosol formation, which contributed 30–77 per cent and 44–71 per cent (average for all four cities) of $PM_{2.5}$ and of organic aerosol, respectively. On average, the contribution of secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA) are found to be of similar importance (SOA/SIA ratios range from 0.6 to 1.4). Our results suggest that, in addition to mitigating primary particulate emissions, reducing the emissions of secondary aerosol precursors from, for example, fossil fuel combustion and biomass burning, is likely to be important for controlling China's $PM_{2.5}$ levels and for reducing the environmental, economic and health impacts resulting from particulate pollution.

In the first quarter of 2013, China experienced extremely severe and persistent haze pollution, affecting ~1.3 million km^2 and ~800 million people. Measurements at 74 major cities showed that the daily average concentrations of $PM_{2.5}$ exceeded the Chinese pollution standard of 75 μg m^{-3} (about twice that of the US EPA standard of 35 μg m^{-3}) for 69% of days in January, with a record-breaking daily concentration of 772 μg m^{-3} (ref. 4). This acute pollution was accompanied by extremely poor visibility and air quality, as reflected in the aerosol optical depth (AOD; Fig. 1), and a sharp increase in respiratory diseases[5]. On a longer timescale, long-range transport of pollutants from China may affect North America, the Pacific and the Arctic, making Chinese air pollution a truly global problem[2,9]. In response to the severe haze events of 2013, the Chinese State Council quickly released the 'Atmospheric Pollution Prevention and Control Action Plan' on 10 September 2013, which aims to reduce $PM_{2.5}$ by up to 25% by 2017 relative to 2012 levels, and is backed by US $277 billion in investments from the central government[6]. Achieving this highly ambitious goal requires targeted, optimized emission control strategies. However, the factors governing $PM_{2.5}$ concentrations in China are poorly constrained[3,7,8], significantly hindering such

efforts. Here we combine a comprehensive set of novel and state-of-the-art offline (filter-based) analytical approaches and statistical techniques to elucidate the chemical nature and predominant sources of aerosol particles during the January 2013 severe haze pollution events in China. Our results may aid the initiation of practical measures for $PM_{2.5}$ emission reductions. Furthermore, owing to the widespread availability of ambient filters, the measurement strategies and analysis techniques developed herein are applicable to other emerging economies or developing countries, potentially facilitating their efforts to design effective mitigation strategies.

We investigated the 2013 haze pollution events with measurements at urban locations in Beijing, Shanghai, Guangzhou and Xi'an, located respectively in the northern, eastern, southern and western regions of China (see Supplementary Information section S1 for details). Average $PM_{2.5}$ concentrations were approximately 1–2 orders of magnitude higher than those observed in urban areas in the US and European countries[3,10]. As shown in Fig. 1, daily average $PM_{2.5}$ concentrations at Xi'an (345 μg m^{-3}) were more than twice those of the other sites, followed by Beijing (159 μg m^{-3}), Shanghai (91 μg m^{-3}) and Guangzhou (69 μg m^{-3}). Chemical analyses (see Supplementary Information section S2, and Supplementary Table 1) shows that organic matter (OM) constitutes a major fraction (30–50%) of the total $PM_{2.5}$ in all cities studied here, followed by sulphate (8–18%), nitrate (7–14%), ammonium (5–10%), elemental carbon (EC, 2–5%) and chloride (2–4%) (Fig. 1). Only about 10–15% was unidentified for Beijing, Shanghai and Guangzhou, though this increases to ~35% in Xi'an owing to elevated dust concentrations (see below), most probably consisting of crustal material such as aluminium and silicon oxides[8].

The sources of $PM_{2.5}$ and OM are apportioned by applying two complementary bilinear receptor models—that is, chemical mass balance (CMB)[11] and positive matrix factorization (PMF) using the multilinear engine ME-2 (ref. 12), see Supplementary Information section S3, Supplementary Table 2, and Supplementary Figs 1–21—and a sampling algorithm (that is, pseudo Monte Carlo calculation, see Supplementary Information section S4) to an unprecedented data set. This data set includes (1) high resolution (HR) mass spectra (by analysing nebulized water-extracts of the filter samples with a high resolution time-of-flight aerosol mass spectrometer, HR-ToF-AMS[13]), (2) organic marker compounds[14], (3) radiocarbon (^{14}C) content of EC and OC (organic carbon)[15], (4) EC and OC, and (5) ions (see Supplementary Information section S2). The performance of the models was extensively evaluated. Model uncertainty and the sensitivity of the results to model inputs were assessed via pseudo Monte Carlo simulations (see Supplementary Information section S4, Supplementary Table 3, and Supplementary Figs 22–25). The representativeness of the measurement sites is justified in Supplementary Information section S6 and in Supplementary Fig. 28.

Critical questions for the development of pollution control strategies include both the identification of predominant sources and whether these sources are primary (that is, particles that are directly emitted to the atmosphere) or secondary (aerosol mass formed in the atmosphere from reaction products of gaseous precursors). Seven sources/factors were identified; their mean contributions are shown in Fig. 1 and factor profiles in Supplementary Fig. 17. A large fraction (51–77%) of PM$_{2.5}$ mass in Beijing, Shanghai and Guangzhou consists of secondary species, that is, SOA and SIA (the latter being sulphate, nitrate and ammonium), though this drops to ~30% in Xi'an due to higher dust levels (46% of PM$_{2.5}$ mass) in western China[16]. The SOA/SIA ratios were significantly higher in north China (for example, 1.4 at Xi'an and 1.3 at Beijing) than in south China (for example, 0.6 at Shanghai and 0.7 at Guangzhou). The total secondary fraction is separated into two subtypes, secondary organic-rich and secondary inorganic-rich, reflecting differences in precursor emission patterns. The secondary organic-rich fraction correlates with the aggregate primary emissions from traffic, coal burning, biomass burning and cooking ($R^2 = 0.77$, see Supplementary Fig. 14), suggesting that this fraction is probably from oxidation products of co-emitted volatile organic compounds (VOCs), including semivolatile and intermediate volatility species[17]. The secondary inorganic-rich fraction correlates with the SIA species ($R^2 = 0.72$–0.82, see Supplementary Fig. 13), indicating a more regional nature[8]. Because Beijing, Shanghai, Guangzhou and Xi'an are part of larger city clusters (Beijing-Tianjin-Hebei, Yangtze River Delta, Pearl River Delta and Guanzhong city clusters, respectively), our results suggest that the transport of pollutants from the heavily populated, urbanized and industrialized surrounding areas to the city core, and probably emissions over broader geographical scales, may also contribute significantly to the formation of secondary aerosol. The differences in the contribution of secondary organic-rich/inorganic-rich fraction in each city (see Fig. 2 and more discussion below) suggest that targeted measures for SOA and SIA need to consider the effects of regional transport and local differences in emissions patterns.

Compared to the secondary fraction, the relative contribution of primary particulate emissions to PM$_{2.5}$ from individual sources is smaller: ~6–9% from traffic, 5–7% from biomass burning, 1–2% from cooking, 3–26% from coal burning and 3–10% from dust-related emission (with the exception of 46% in Xi'an) (Fig. 1). The relatively high contribution from coal burning in Beijing and Xi'an (interquartile range: 9–21% of PM$_{2.5}$ mass (or 17–47 μg m^{-3}) compared to 3–5% of PM$_{2.5}$ mass (or 2–5 μg m^{-3}) in Shanghai and Guangzhou) can be attributed to its extensive use in residential heating in northern and western China[18]. Our study shows that on average ~37% of sulphate is directly emitted from coal burning in Xi'an and Beijing. Coal burning emissions also dominate the levels of species associated with adverse respiratory and cardiovascular health outcomes, including polycyclic aromatic hydrocarbons and heavy metals (for example, lead and

arsenic). The contribution from biomass burning is notably higher in Guangzhou and Xi'an (interquartile range: 5–9% of PM2.5 mass; 13–18% of OM) compared to that in Beijing and Shanghai (4–7% of PM2.5 mass; 8–15% of OM), consistent with previous studies[19]. Note that the absolute contribution from traffic in Xi'an is 2.7–4.0 times the levels at the other cities studied here, although the total vehicle fleet in Xi'an is 30–70% lower. This can be attributed to the lag in implementation of more stringent vehicle emission standards in Xi'an (see Supplementary Information section S1). The high dust levels found in Xi'an most probably originate from deserts in northwest China, consistent with back trajectory analyses (Supplementary Fig. 22), although fugitive dust from construction sites and unpaved roads could also be an important emission source, given the numerous construction activities in this region[16]. Measurements of crustal and anthropogenic elements by energy-dispersive X-ray fluorescence spectrometry (ED-XRF, including Fe, Ti, Ca, Zn, As, Pb, Cu, V and Ni) show that the primary sources identified above explain the levels and the variability of these elements rather well (see Supplementary Information section S5, and Supplementary Figs 26 and 27).

Figure 2a and b shows the factors driving the high pollution events by binning the fractional contribution of each factor to total PM2.5 and OM mass, respectively. The figures clearly show that high pollution events are characterized by an increasing secondary fraction, which accounts for up to 81% of PM2.5 mass and up to 73% of OM mass. On average, compared to that in the lowest PM2.5 bins, the secondary fraction in the highest PM2.5 bins increases by a factor of 1.4 for PM2.5 and 1.3 for OM, demonstrating the importance of secondary aerosol formation in driving particulate pollution during high pollution events.

The significant SOA formation under wintertime conditions, though not yet widely recognized, is well supported by our low-temperature smog chamber studies on the ageing of biomass burning emissions (see Supplementary Information section S7 and Supplementary Fig. 29). We show that low temperature does not significantly reduce SOA formation rates of biomass burning emissions ($k_{OH} = (2.5–6.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at −10 °C, comparable to the oxidation rates of many SOA precursors at room temperature[20]) and significant amounts of SOA are rapidly produced, exceeding primary organic aerosol (POA) at an OH exposure (that is, OH concentration × time) of only $(1.6–5.5) \times 10^6$ molecules cm^{-3} h. At OH radical concentrations typical of wintertime China ($>0.4 \times 10^6$ molecules cm^{-3}, 24 h average, for the cities of this study), these exposures are reachable in 4–14 h, which is fast with respect to atmospheric transport especially during stagnant conditions. The OH concentrations given above are simulated from the Geos-Chem model, which are consistent with wintertime observations at polluted urban locations such as Birmingham (UK), Tokyo (Japan) and New York City (see Supplementary Information

section S7, Supplementary Fig. 30 for more details). Note that processes other than OH-initiated oxidation may contribute to or even dominate SOA formation during winter, including aqueous-phase oxidation and NO_3-initiated nocturnal chemistry, as is certainly the case for SIA species sulphate and nitrate[21,22].

Sources of SIA are relatively well constrained: in urban areas, sulphate forms primarily through atmospheric oxidation of SO_2 emitted mainly from coal burning, while nitrate derives from NO_x emitted mainly from vehicle exhaust and power plants[23]. By contrast, SOA sources are highly uncertain[24]. We previously discussed the secondary organic-rich and secondary inorganic-rich factors in terms of likely geographic origin; here we combine the factor analysis with ^{14}C analysis to quantify the fossil and non-fossil carbon contributions to SOA (see Supplementary Information section S4 for details). This helps to constrain the relative importance of specific sources to SOA production—for example, SOA precursors emitted by traffic/coal burning would increase the fossil content. As shown in Fig. 3, the calculated contributions of fossil SOA to total OA mass are 1.1–2.4 times larger for high pollution events than for low pollution events, highlighting the importance of fossil SOA to particulate pollution. Fossil SOA accounts for ~25–40% of OA mass (or ~45–65% of SOA mass) in Shanghai and Beijing, consistent with the large emissions of SOA precursors from high traffic flow and/or large coal usage for domestic heating/cooking at these locations[18,25]. The fossil SOA fraction, however, decreases to ~10–20% of OA mass in Guangzhou and Xi'an, with the non-fossil SOA fraction increasing to ~30–60% of the OA mass (or ~65–85% of the SOA mass), mostly due to the enhanced biomass burning activities as discussed above. Note that biogenic emissions may produce a small fraction of non-fossil SOA in Guangzhou owing to the relatively high temperature (5–18 °C), while this source is probably negligible in other cities of this study due to lower temperatures (that is, −12 to 2 °C at Beijing, −7 to 7 °C at Xi'an and −1 to 9 °C at Shanghai).

Our analysis suggests that emission control strategies to mitigate $PM_{2.5}$ pollution in China should, in addition to primary particulate emissions, also address the emission reduction of secondary aerosol precursors including SO_2, NO_x, and, in particular, VOCs. The Chinese government is already making efforts to mitigate SIA precursor gases. SO_2 emissions have decreased since 2006 due to the strict nationwide implementation of flue gas desulfurization in coal-fired power plants[26], but NO_x continues to increase because of the lag in emission control legislations and the increase in fuel consumption by power plants and vehicles[26]. By 2020, VOC emissions are predicted to increase by 49% relative to 2005 levels[27], and are not fully considered in the current Chinese air pollutant control strategy although they account for on average ~25–30% (with the exception of 16% in Xi'an) of the $PM_{2.5}$ mass (via SOA production) and 44–71% of OM

mass observed here. The importance of VOCs to controlling PM has only been recognized very recently for a few sectors, but measures are not yet well defined, being limited to the traffic and petrochemical industries[6]. However, our findings suggest that stringent controls on VOC emissions from vehicles and coal burning (introducing clean-burning stoves) could be efficient measures in regions like Beijing and Shanghai where fossil SOA formation is dominant. Control of biomass burning activities (including heating and open fires of agricultural and other waste) could be an efficient strategy in all regions, especially near Guangzhou and Xi'an where non-fossil VOC emissions are significant. Further, strategies to improve air quality within the cities need also to consider advection from extra-urban emission sources.

In general, our results suggest that reduction in SIA and SOA precursors (NO_x, SO_2, NH_3, and, particularly, the currently much less constrained VOCs) can help achieving $PM_{2.5}$ reduction targets and diminishing the environmental, economic and health costs of particulate pollution. Such measures should be considered by policy makers given the disastrous effects of particle pollution in China. It should be investigated if similar considerations apply to other emerging economies, for example India or some African nations[28,29], which are also experiencing severe particle pollution. Effective air pollution control measures are imperative for cleaning the air we breathe, as highlighted by the recent World Health Organization (WHO) report attributing approximately 7 million premature deaths in 2012 to air pollution and demonstrating that particle pollution risks are far greater than previously thought[30].

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Figure 1 | Chemical composition and source apportionment of PM$_{2.5}$ collected during the high pollution events of 5–25 January 2013 at the urban sites of Beijing, Shanghai, Guangzhou and Xi'an. Centre, map showing locations of the four sites, indicated by arrows. Pie charts around the map show PM$_{2.5}$ composition and sources for each site. The measured PM$_{2.5}$ concentrations (shown next to the site name) are approximately 1–2 orders of magnitude higher than those observed in the urban areas of US and European countries[3,10]. OM is the main PM$_{2.5}$ component, and secondary organic-rich and inorganic-rich aerosols are the major contributor to the PM$_{2.5}$ mass in all cities studied here except Xi'an where dust aerosol is the dominant contributor. The uncertainties (relative standard deviation, RSD) on the source contribution estimates depend on the site considered, but are on average 24% for traffic, 39% for coal burning, 8% for biomass burning, 35% for dust related emissions, and 7% for secondary aerosols, respectively (see Supplementary Information section S4 for details). The measured trace elements include K, Na, Ca, Mg, Fe, Ti, Pb, As, Cu, Zn and Ni, while the major crustal elements, Si and Al, could not be measured due to interference from the quartz fibre substrate of the sample. The central map presents aerosol optical depth (AOD, colour-coded, see key at right), retrieved from satellite (Terra/Modis) observations over the whole month of January 2013 (www.nasa.gov), and shows the large coverage of severe particle pollution in China.
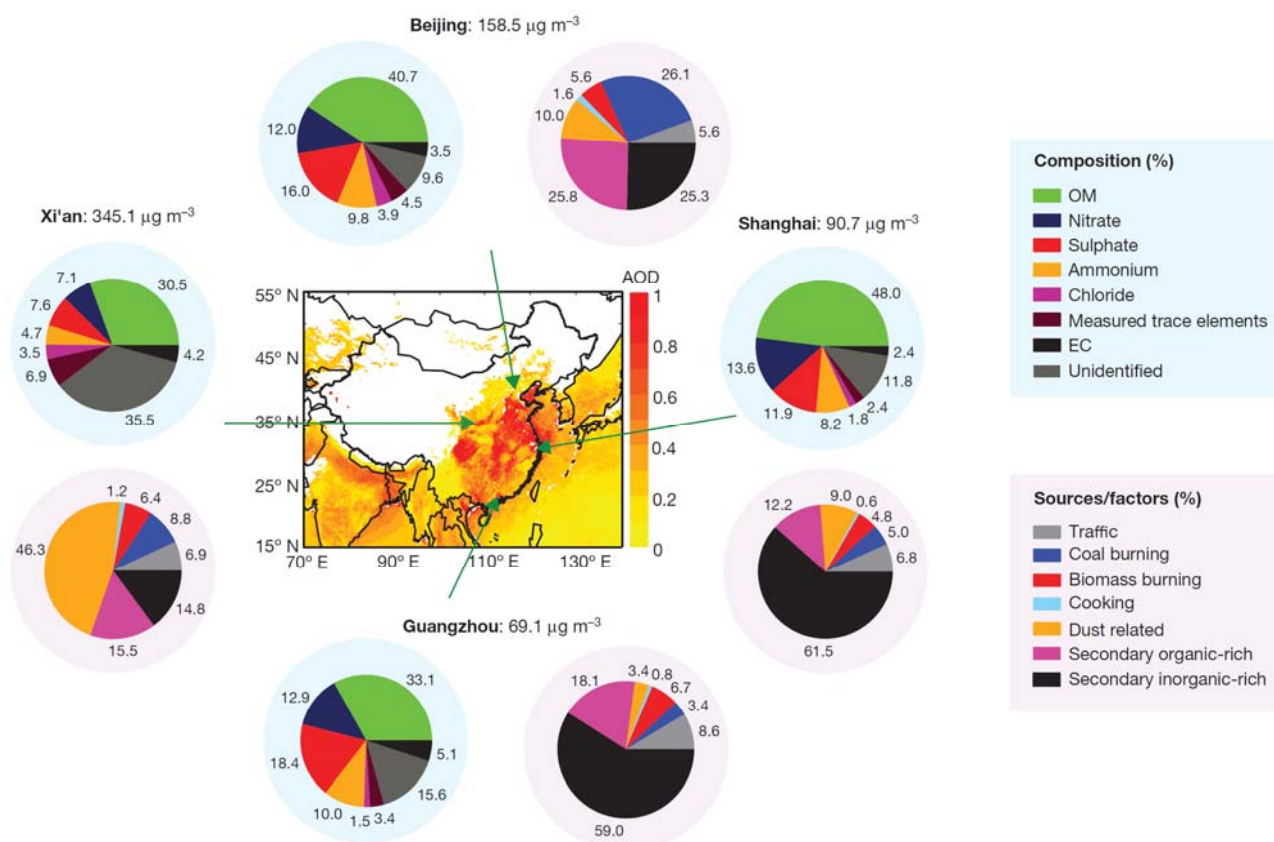
Figure 2 | Source contribution to total particulate and organic matter. a, **b**, The fractional contribution to PM (**a**) and OM (**b**) as a function of the PM₂.₅ bins is shown. The uncertainties of these estimates for PM₂.₅ are given in Fig. 1 legend. The uncertainties (RSD) for OM are on average 33% for traffic, 47% for coal burning, 8% for biomass burning, 45% for dust related emissions, and 13% for secondary aerosol (see Supplementary Information section S4 for details). The high pollution events are characterized by an increasing secondary fraction, accounting for up to 81% of PM₂.₅ mass and 73% of OM mass. The differences in secondary organic-rich/inorganic-rich ratios of PM and OM in each city indicate the regional transport and local differences in emissions patterns. Note the high contribution from coal burning at Beijing and Xi'an due to its large usage for residential heating in wintertime, and the notably high contribution from biomass burning at Guangzhou and Xi'an. The numbers above the bars (in **b**) represent the average OM concentration in $\mu g\ m^{-3}$.
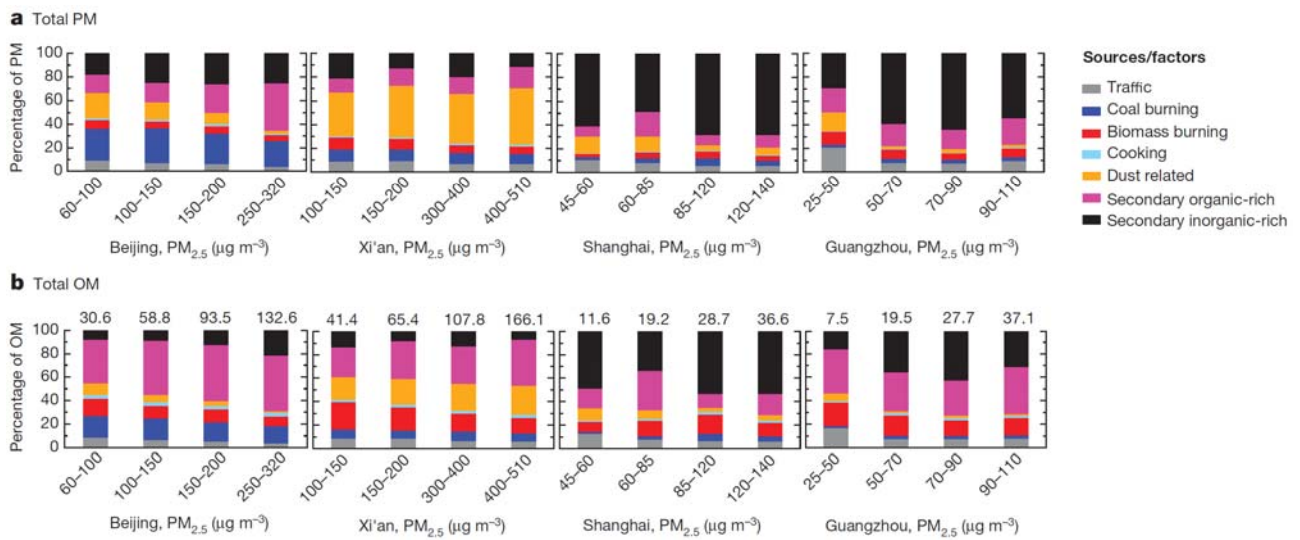
Figure 3 | Fossil and non-fossil fractional contributions of each source during low and high PM$_{2.5}$ levels observed in different cities. For each city we measured the ^{14}C content of carbonaceous aerosols in three samples with the lowest PM mass and three samples with the highest PM mass to represent the low and high pollution events, respectively. The numbers above the bars represent the average OM concentration and those in parentheses the percentage of the fossil fraction in SOA. The uncertainties (RSD) on the fossil and non-fossil SOA contribution to OA are on average 11% and 17%, respectively. Note that the contributions of fossil SOA to total OA mass are 1.1–2.4 times larger for high pollution events than for low pollution events, highlighting the importance of fossil SOA in particulate pollution. The fossil SOA is a dominant fraction (~25–40% of OA mass, or ~45–65% of SOA mass) in Shanghai and Beijing, consistent with the large emissions of SOA precursors from high traffic flow and large coal usage. However, non-fossil SOA is abundant in Xi'an and Guangzhou (~30–60% of OA mass, or ~65–85% of SOA mass) owing to the enhanced biomass burning activities.