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The contributions of biomass burning to primary and secondary organics: A case study in Pearl River Delta (PRD), China

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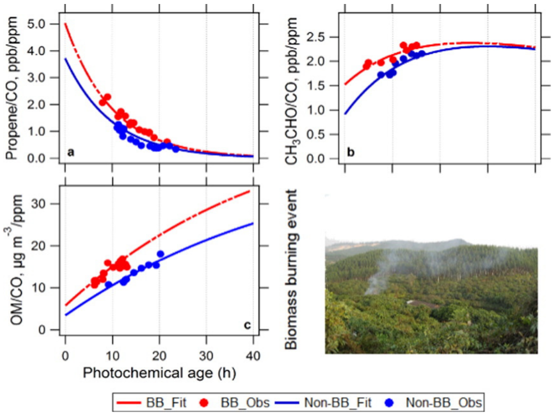
HIGHLIGHTS

- Simultaneous online measurements of VOCs and organic matters (OM) were conducted.
- Behaviors of VOCs and OM were described for biomass burning (BB) and non-BB plumes.
- Secondary organic aerosol formation rates were compared for BB and non-BB plumes.
- Emissions of VOCs and OM from BB in PRD were estimated based on field observations.

GRAPHICAL ABSTRACT



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ABSTRACT

Synchronized online measurements of gas- and particle- phase organics including non-methane hydrocarbons (NMHCs), oxygenated volatile organic compounds (OVOCs) and submicron organic matters (OM) were conducted in November 2010 at Heshan, Guangdong provincial supersite, China. Several biomass burning events were identified by using acetonitrile as a tracer, and enhancement ratios (EnRs) of organics to carbon monoxide (CO) obtained from this work generally agree with those from rice straw burning in previous studies. The influences of biomass burning on NMHCs, OVOCs and OM were explored by comparing biomass burning impacted plumes (BB plumes) and non-biomass burning plumes (non-BB plumes). A photochemical age-based parameterization method was used to characterize primary emission and chemical behavior of those three organic groups. The emission ratios (EmRs) of NMHCs, OVOCs and OM to CO increased by 27–71%, 34–55% and 67% in BB plumes, respectively, in comparison with non-BB plumes. The estimated formation rate of secondary organic aerosol (SOA) in BB plumes was found to be 24% faster than non-BB plumes. By applying the above emission ratios to the whole PRD, the annual emissions of VOCs and OM from open burning of crop residues would be 56.4 and 3.8 Gg in 2010 in PRD, respectively.

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1. Introduction

Biomass burning (BB) is known to be a significant source of volatile organic compounds (VOCs) and particulate organic matters (OM) (Akagi et al., 2011; Andreae and Merlet, 2001; Warneke et al., 2009; Yokelson et al., 2013). Photochemical oxidation of some reactive VOCs influences the formation of ground-level ozone and secondary organic aerosol (SOA). Both the resulting oxidants and OM play important roles in air quality and climate change (Langmann et al., 2009; Morris et al., 2006).

As a large agricultural country, China produces a substantial amount of crop residues, which were evaluated to be about 600 Tg/year, and the total amount of the crop straws burned were about 140 Tg/year (Cao et al., 2008). From emission inventories, annual VOCs and OM from biomass burning (including open fires and biofuel combustions) occupied 23% (Bo et al., 2008) and 15% (Cao et al., 2011) of the total VOCs and OM emissions in China, respectively. Large-scale open burnings of crop residues after harvesting frequently occur in central, east and southeast China, as reported in both ground-level measurements (He et al., 2011a; Huang et al., 2011; Kudo et al., 2014; Li et al., 2014; Yuan et al., 2010) and satellite-based observations (Xue et al., 2014). As shown in previous field measurements, noticeable increase in concentrations of NMHCs, OVOCs and OM were observed in agricultural biomass burning plumes. Yuan et al. (2010) estimated that biomass burning contributed 10–18% to reactive NMHCs and OVOCs at a site in Pearl River Delta (PRD) region, in China in 2008. The organic aerosol directly emitted from open fires (so-called BBOA) accounted for 25% of sub-μm OM at the same site (Huang et al., 2011).

Besides the direct effect of BB plumes on organic species, some studies have focused on SOA formation from oxidation of gaseous precursors released from BB plumes. Laboratory experiments by Hennigan et al. (2011) indicate that OM in saw grass burning smoke was enhanced by a factor of 2.6 after 3.5 h of exposure to typical atmospheric hydroxyl radicles (OH) level. Similar results in OM were found from wood (Grieshop et al., 2009; Heringa et al., 2011) and wheat straw combustions (Ortega et al., 2013). Aircraft measurements by Yokelson et al. (2009) validate a rapid SOA formation from BB plumes under high initial OH and nitrous acid (HONO) conditions. However, the impact of ambient BB plumes on SOA formation is still under discussion. Some conflicting results have occurred in field campaigns. For example, no net OM produced from BB emissions in the central Amazon (Brito et al., 2014) and a 30% depletion of OM over 5 h of aging in smoke from prescribed burning have been observed (May et al., 2015). The explicit reason for this discrepancy is unclear, but probably due to varied biomass types, combustion and photo-oxidation conditions (DeCarlo et al., 2010). Thus, more field studies are needed to better understand the contribution of BB emissions to SOA formation.

Combining with simultaneous measurements of NMHCs, OVOCs and sub-μm OM at a semi-rural site in PRD, this paper will focus on quantifying the impact of BB plumes on primary organics and SOA formation in a heavily polluted region. The chemical behaviors of gaseous and particulate organics with aging are also investigated.

2. Methods

2.1. Descriptions of the sampling site, measurements and instruments

Field measurements of trace gases and aerosols were performed in November–December in 2010 at Guangdong provincial supersite named "Heshan" (22.727°N, 112.929°E), which is located about 50 km and 80 km southwest from Foshan and Guangzhou City, respectively. The Heshan site is mainly surrounded by mountain areas with evergreen broad-leaf forest and farmlands, and about 10 km northwest of the site are small towns. Several open burning activities of crop residues were observed occasionally in the mountain areas. The dominant wind during this campaign came from the northwest where big cities (i.e. Guangzhou and Foshan) are located. This indicates that the sampled air masses were under the influence of local biogenic and biomass burning emissions, and also upwind urban plumes. In this study, two online instruments were deployed to measure NMHCs and OVOCs, i.e. a gas chromatography with mass spectrometer and flame ionization detectors (GC–MS/FID) and a proton transfer reaction mass spectrometer (PTR-MS). Submicron OM was measured by an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS).

The automated GC–MS/FID developed by Peking University has two parallel sampling and analyzing channels (Wang et al., 2014b). The FID channel is used to analyze acetylene and C_2–C_4 alkanes and alkenes, and the MS channel for heavier alkanes and alkenes (C_5–C_{10}) and C_6–C_{10} aromatics. Samples were collected and analyzed every 1 h. Daily calibrations were measured at midnight of each day and signal variations for most species were lower than 20%. The system was calibrated weekly by TO-15 (Air Environmental Inc., USA) and PAMS gas standards (Spectra Gases Inc., USA). The detection limits varied from 5 to 70 pptv. Technical details of this instrument were described elsewhere (Wang et al., 2014b; Yuan et al., 2012).

A commercial quadruple PTR-MS (IONICON, Austria) was used to measure C_1–C_4 OVOCs, isoprene, reactive aromatics and acetonitrile, with time resolution of 30 s. Instrument background signals were measured by passing through a platinum-coated catalyst converter for 15 min every 3 h. Aromatics, isoprene, oxygenates and acetonitrile were calibrated using a TO-15 standard mixture, and formaldehyde (HCHO) was calibrated by using a permeation tube (Kin-Tek, USA). The detection limits ranged from 40 to 200 pptv. The measurement uncertainty is estimated to be lower than 15%. The detailed information can be found in Yuan et al. (2010).

During this campaign, benzene, toluene and several other species were measured by both the GC–MS/FID and PTR-MS systems. Good agreements for most species were found between those two instruments, with correlation coefficients larger than 0.88 and slopes ranging from 0.87 to 1.02 (Shown in Fig. S1). NMHCs measured by GC–MS/FID and OVOCs and acetonitrile determined by PTR-MS are used in the following sections.

An aerodyne HR-TOF-AMS (Aerodyne Research, Inc., USA) was deployed to measure chemical composition of submicron aerosols (PM_1), including sulfate, nitrate, chloride and OM. Time resolution for this instrument was 4 min. The system was calibrated at the beginning and end of the campaign according to the standard protocols (Drewnick et al., 2005). Detailed setup and data processing for this system were described by Gong et al. (2012).

Ambient levels of CO were quantified by a commercial non-dispersive infrared sensor (Thermo Inco., USA) which is based on a gas filter correlation method. Additionally, temperature, wind speed, wind direction and relative humidity were measured by an automatic meteorological station at this site with a time resolution of 5 min.

2.2. The photochemical age based parameterization method

In this study, a photochemical age-based parameterization method developed by de Gouw et al. (2005, 2008) is used to characterize the photochemistry of gaseous and particulate organics in different plumes. Basically, this approach describes the concentrations of organics as a function of photochemical age exposure to OH radicals. The ratios of organics relative to an inert species (e.g. CO) are introduced to minimize the effect of atmospheric mixing.

2.2.1. Calculation of photochemical age

The removal of NMHCs is dominated by the reaction with OH in the atmosphere. After photochemical degradation of a plume, the ratio of two hydrocarbons which are emitted from the same sources and with different OH reaction rates will be changed, this can be used to indicate the photochemical age of the air mass (Roberts et al., 1984).