

Author' Response to Referees' Comments

Anonymous Referee #1

Yang et al. present VOC observational results at a rural site in the Beijing metropolitan area before, during, and after a strict emission control implementation for the APEC summit event. They mainly discussed on changes in the VOC composition during three different periods. Then, they move ahead to discuss the potential sources from the PFM analysis and the impacts of VOCs in the context of ozone and aerosol formation rates. Overall the manuscript is very clearly written, and the goals seem to be well achieved.

[1] However, I have a couple of concerns regarding whether this manuscript is well fit in this particular journal. Although the significance in understanding of Chinese pollution problems cannot be overstated considering the large population in China, this manuscript is too narrowly focused on Chinese local air pollution problems without discussion on the bigger context such as regional or global impacts.

Reply: Thanks for the insightful comments. Maybe we have not interpreted our findings properly and fully in the manuscript. We think the findings from our study are implicative at least in two aspects:

1) While exposure to indoor air pollution from burning solid fuels (biomass and coal) affects nearly half of the world's population, and household air pollution has been considered as a major environmental cause of death (Martin et al., 2011; Lim et al., 2012; Subramanian, 2014), a previous study (Liu et al., 2016) revealed that in the Beijing-Tianjian-Hebei (BTH) region, residential use of solid fuels might be a major and underappreciated ambient pollution source for PM_{2.5} (particularly BC and OC) during winter heating period based on the Multiresolution Emission Inventory of China (MEIC; www.meicmodel.org) for January and February 2010. Here we demonstrated that, based on our field monitoring, burning solid fuels (mainly coal) to heat homes would also be a major source of volatile organic compounds (VOCs) during winter in the region. As VOCs are important precursors of secondary aerosols and ozone, our study also suggests that cleaner residential energy use for cooking and heating not only benefit lowering indoor air pollution with great health benefits for the residents, but also benefit lowering the exposure to ambient air pollution for a wider range of people.

2) Due to high secondary aerosol contribution to particulate pollution during haze events (Huang et al., 2014), reducing emissions of VOCs as precursors of secondary organic aerosols is important for combating fine particle air pollution and heavy hazes. Enhancing the controls over emissions from vehicles and industry sector would be effective for reducing ambient VOCs, as demonstrated in our study during the APEC before the start of winter heating period. During the winter heating period, since residential coal/biomass burning was found to be a major source for ambient VOCs even in the Beijing metropolitan area, solely enhancing the emission control in the traffic and industry sectors would be not so effective as did in the non-heating period. This is an important message for regions, particularly less developed regions, to control emissions of VOCs to combat air pollution due to ozone and PM_{2.5}.

Therefore, although we conducted our study at a rural site in Beijing, the findings are not just locally significant but also have important implications for other regions. We have incorporated these aspects into our revised manuscript. We have rewritten our introduction, and modified our conclusions and abstract as well.

[2] Moreover, the scientifically relevant analyses such as ozone forming potential and secondary aerosol forming potential are just adapted from previous publications without detailed discussion whether the method is relevant to this particular photochemical environment.

Reply: Thanks. This comment is scientifically very important. It reminds us of remembering that the potentials are related to particular photochemical environments. As for the ozone formation potentials, the Maximum Incremental Reactivity (MIR) scale, originally developed by Carter (1994), has been widely used as a simplified approach to evaluate the relative ground-level ozone impacts of volatile organic compounds. The MIR scale in its nature represents conditions where ambient ozone is most sensitive to changes in VOC emissions, therefore the potentials based on the MIR scale are maximums that can hardly be achieved under real atmospheric conditions, particularly depending on the relative availability of NO_x (Dondge, 1984; Carter and Atkinson, 1989). However, for the convenience of regulating VOCs based on calculations of their relative ground-level ozone impacts, the metrics used for calculating OFP in the present study have been used worldwide, and therefore we remain the calculation in its present state but indicate in the revised manuscript that it is only a simplified approach.

Organic aerosol formation potentials are comparatively much more complicated. They are largely affected by factors such as the reactivity of the parent compound and volatility of the product species (Odum et al., 1997). The reactivity of the parent species can be directly measured by their reaction rate constants with oxidants. The oxidation products, however, are both numerous and difficult to quantify analytically. Therefore, the SOA yield (Y), defined as mass of SOA formed divided by mass of VOCs reacted, has been used as an indirect measure for a specific VOC species to indicate its ability to form SOA (Odum et al., 1997). This way the secondary organic aerosol formation potentials (SOAFPs) by a mixture of VOCs can be estimated as $\sum_i X_i \times Y_i$, where X_i is the mass concentration ($\mu\text{g m}^{-3}$) and Y_i (%) is the SOA yield of precursor i. SOA yield data have been obtained in controlled smog chamber studies. In this study, the SOA yields are taken from studies by Ng et al (2007), Lim and Ziemann (2009) and Loza et al (2014). As SOA formation depends on nitrogen oxides (NO_x) (Ng et al., 2007), SOAFPs are typically calculated under low-NO_x and high-NO_x conditions, approximating the higher and lower limits, respectively. Although widely used in a lot of literatures, this kind of calculation is also a simplified approach to indicate SOA potentially formed if the observed VOCs are completely oxidized in the atmosphere.

In the present study, we put our focus mainly on how the control measures or human activities would impact the VOCs occurring in the ambient air, so we just followed the widely adopted approaches to indicate their ozone and SOA formation potentials, although they are simplified and even scientifically not solid enough.

[3] I recommend expanding discussion at least to compare VOC speciation from other locations in the region and other metropolitan areas in the world.

Reply: Thanks for the suggestion. In the revised manuscript, we have added the comparison as below:

“Table S1 shows a comparison of VOCs from our study with those observed at other metropolitan areas in the world. Mixing ratios of VOCs from this study at a rural site in Beijing during period I (23.41 ppb) and period III (21.71 ppbv) were comparable to that in urban Shanghai from January 2007 to March 2010 (Cai et al., 2010), but lower than those in Beijing during June 2008 (Wang et al., 2010), Guangzhou from June 2011 to May 2012 (Zou et al., 2015), Lille, French from May 1997 to April 1999 (Borbon et al., 2002) and Houston in August-September 2006 (Leuchner and

Rappengluck, 2010). Average mixing ratios of VOCs during period II (11.25 ppbv) with enhanced emission control in the present study were significantly lower than those reported in other metropolitan areas. As for the most abundant VOC species including ethane, propane, ethylene, benzene, toluene and ethyne, the mixing ratios of ethane and ethylene at UCAS were similar to that at Beijing during June 2008 (Wang et al., 2010) and urban Guangzhou from June 2011 to May 2012 (Zou et al., 2015), but significantly lower than that in urban Beijing during 2014 APEC (Li et al., 2015). Propane in present study are comparable with that in Hong Kong from September 2002 to August 2003 (Guo et al., 2007) and Lille, French from May 1997 to April 1999 (Borbon et al., 2002), but factors of 2-3 lower than that reported in urban Shanghai from January 2007 to March 2010 (Cai et al., 2010) and Guangzhou from June 2011 to May 2012 (Zou et al., 2015). Mixing ratios of benzene and toluene in Lille, French from May 1997 to April 1999 (Borbon et al., 2002) were over 2 times higher than that in present study. Mixing ratios of ethylene, benzene and toluene in present study were comparable to those observed in Houston during August-September 2006 (Leuchner and Rappengluck, 2010), while ethyne, a tracer of incomplete combustion, had mixing ratios 3-4 times higher than that in Houston.”

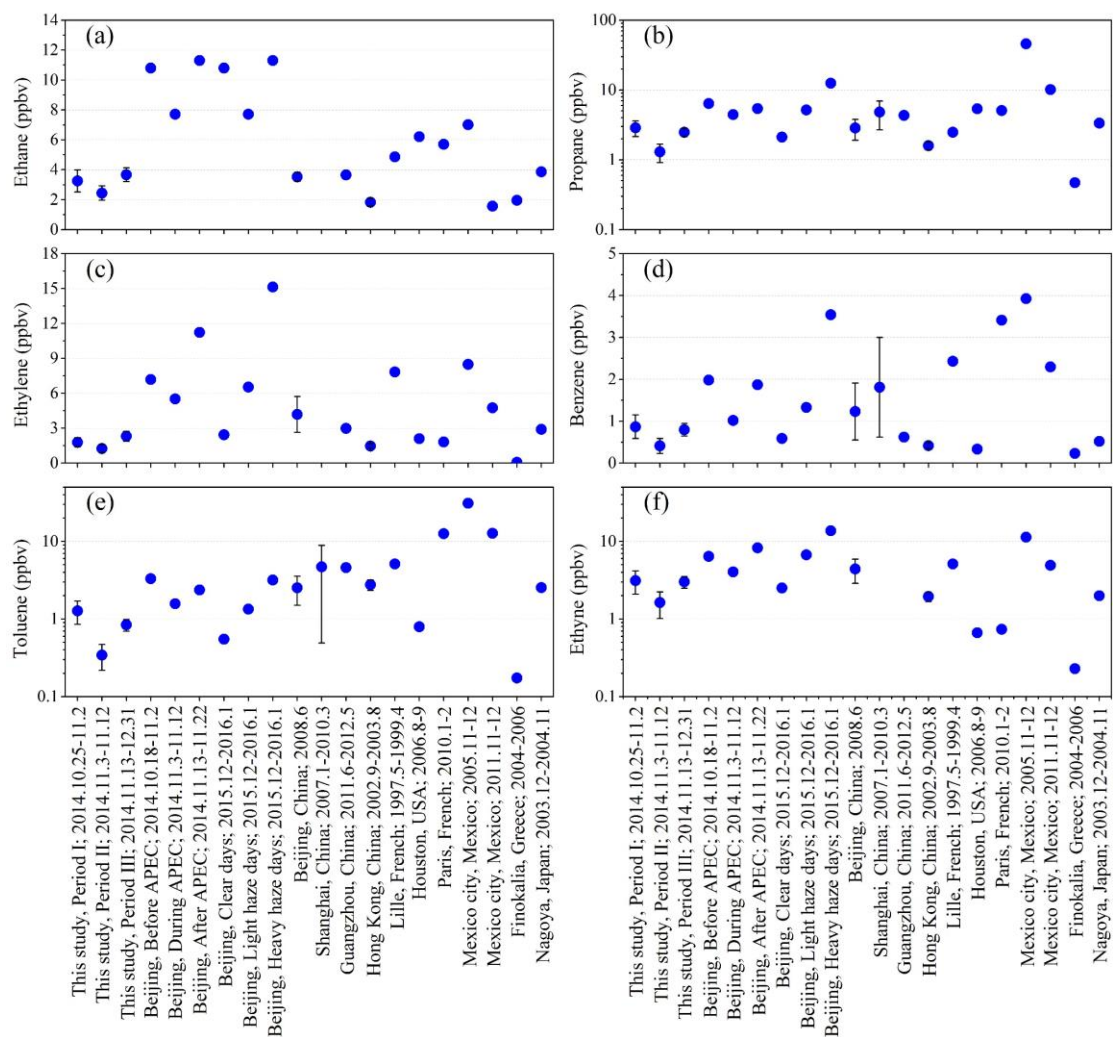


Figure S1. Comparison of (a) ethane, (b) propane, (c) ethylene, (d) benzene, (e) toluene and (f) ethyne observed at UCAS with those from other studies at metropolitan areas in the world.

[4] In addition, I would recommend more thorough descriptions on ozone formation potential and SOA formation potential particularly in the context of whether the metrics are relevant in this photochemical environment.

Reply: As responding to comment [2] above, we fully agree that we should consider if the metrics are relevant in a specific photochemical environment. However, in the present study since we put our focus mainly on how the control measures or human activities would impact the VOCs occurring in the ambient air, so we just followed the widely adopted approaches to indicate their ozone and SOA formation potentials, although they are over simplified and even scientifically not solid enough.

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