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 interpretated 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. Enhacing the controls over emissions from vechicles 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 emisison control in the traffic and industry sectors would be not so effective as did in the non-heating period. This is a important message for regions, particularly less developed regions, to control emisisons 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 rewrite 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 achieved under real atmospheric conditions, particularly depending on the relative availability of NOx (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 $\Sigma_i X_i \times Y_i$, where X_i is the mass concentration ($\mu g\ m^{-3}$) 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 (NOx) (Ng et al., 2007), SOAFPs are typically calculated under low-NOx and high-NOx 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 beolw:

"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."

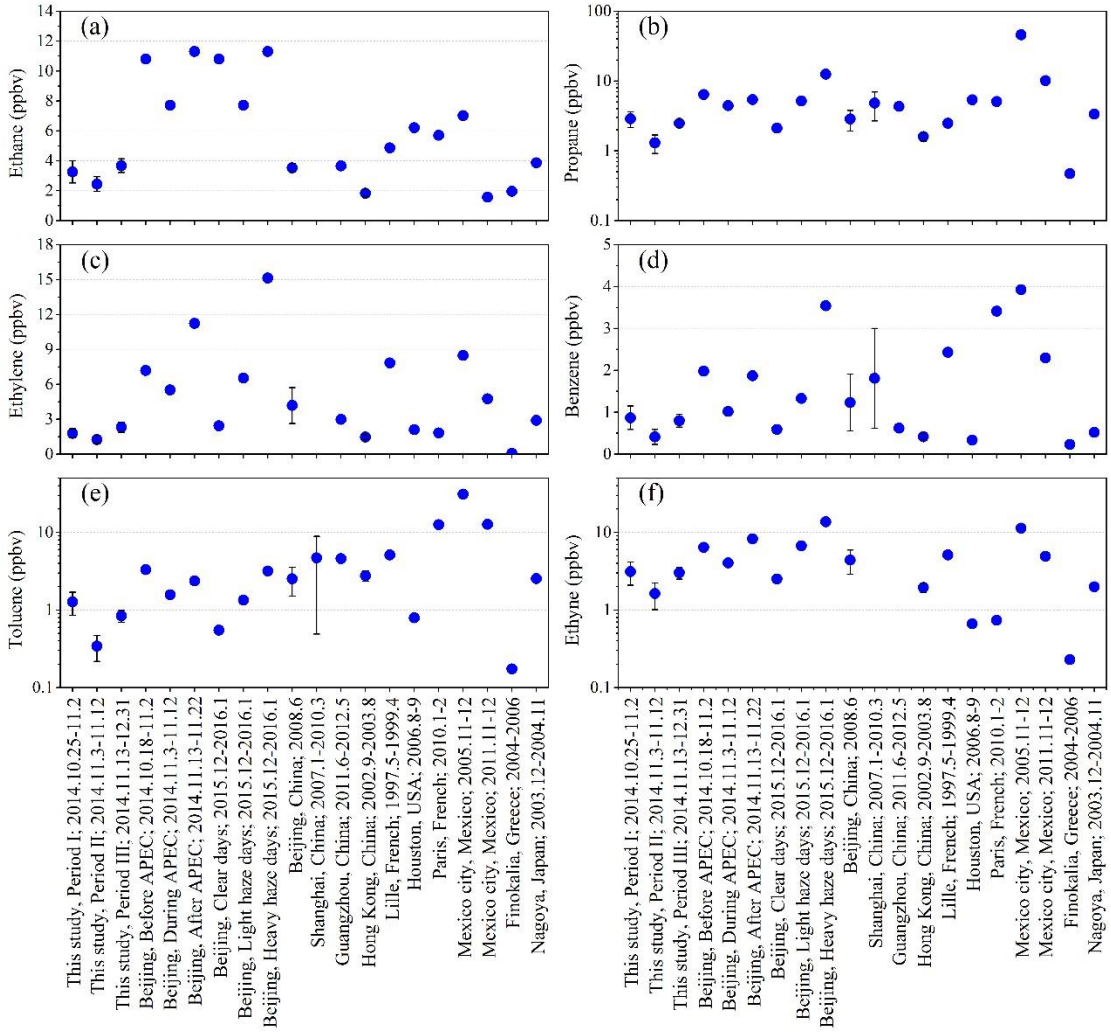

Figure S1. Comparison of (a) ethane, (b) propane, (c) ethylene, (d) benzene, (e) toluene and (f) ethyne observed at UCAS with those from other studies at metropolitan areas in the world.

[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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Author' Response to Referees' Comments

Anonymous Referee #2

Household air pollution from burning biomass and coal for cooking foods and heating rooms has long been a major environmental problem. Previous studies suggested that the uncontrolled and inefficient combustion of solid fuels for heating in winter also contributed substantially to outdoor $PM_{2.5}$, BC, OC, SO_2 and NOx in many regions, such as in the North China Plain (Liu et al., 2016, PNAS). The field observations at the rural site of Beijing in this study further demonstrated that the combustion of solid fuels for heating in winter made remarkable contribution to ambient volatile organic compounds (VOCs). The authors also took advantage of the temporary intervention measures for emission control during the APEC to evaluate the actual effect of the control measures on the ambient VOCs levels through reduction of the source contributions. The comparison between the heating and non-heating periods offered robust results indicating the influential emission from winter heating. Overall, the data quality of this manuscript is quite good, and the interpretation of the results is appropriate and convincing. Therefore, I strongly recommend publication of this manuscript.

Reply: Thanks for the comments. We have revised our manuscript with your constructive comments and suggestions as below.

Majors:

[1] As stated above, an important finding of this study is that residential coal burning, especially during winter heating period, could be a major contributor to the ambient VOCs. Apart from the emission factors available for residential coal burning, is it possible for the authors to have the amounts of coals consumed in the residential sector especially during winter and give an in-depth explanation why this source could contribute substantially?

Reply: Thanks for the suggestions. The information about coal consumptions and an in-depth explanation to the substantial contribution from residential coal burning have been added into the revised manuscript (section 3.3.2, line 443-459):

"Coal is consumed in residential, industrial and power sectors in Beijing. As showed in Fig. S5a, while annual total coal consumptions dropped rapidly during 2006-2015, the annual residential coal

consumptions remained almost unchanged with their percentages in total coal consumptions rising from 8.7% in 2006 to 23.4% in 2015 (Beijing Municipal Bureau of Statistics, 2016; Yu et al., 2018). As a matter of fact, over 60% of the residential coal consumption occurred in rural areas of Beijing (Fig. S5b), and residential coal is mainly burned in the cool winter season for house heating (Xue et al., 2016). While emission factors of VOCs from residential coal burning have been found to be a factor of 20 greater than those from coal-fired power plants (Liu et al., 2017), the differences in coal quality between the urban and rural areas augment emissions in rural areas: coal used in urban area was entirely anthracite with comparatively much lower emissions of volatiles than other types of coal (Xu et al., 2017); instead only 5-15% of coal used in rural area was anthracite (Xue et al., 2016). Consequently, residential coal combustion could have been a major contributor to the ambient VOCs in rural areas of Beijing during winter."

The coal consumptions in Beijing from 2006 to 2015 were also added to the supplement information as shown below (Fig. S5).

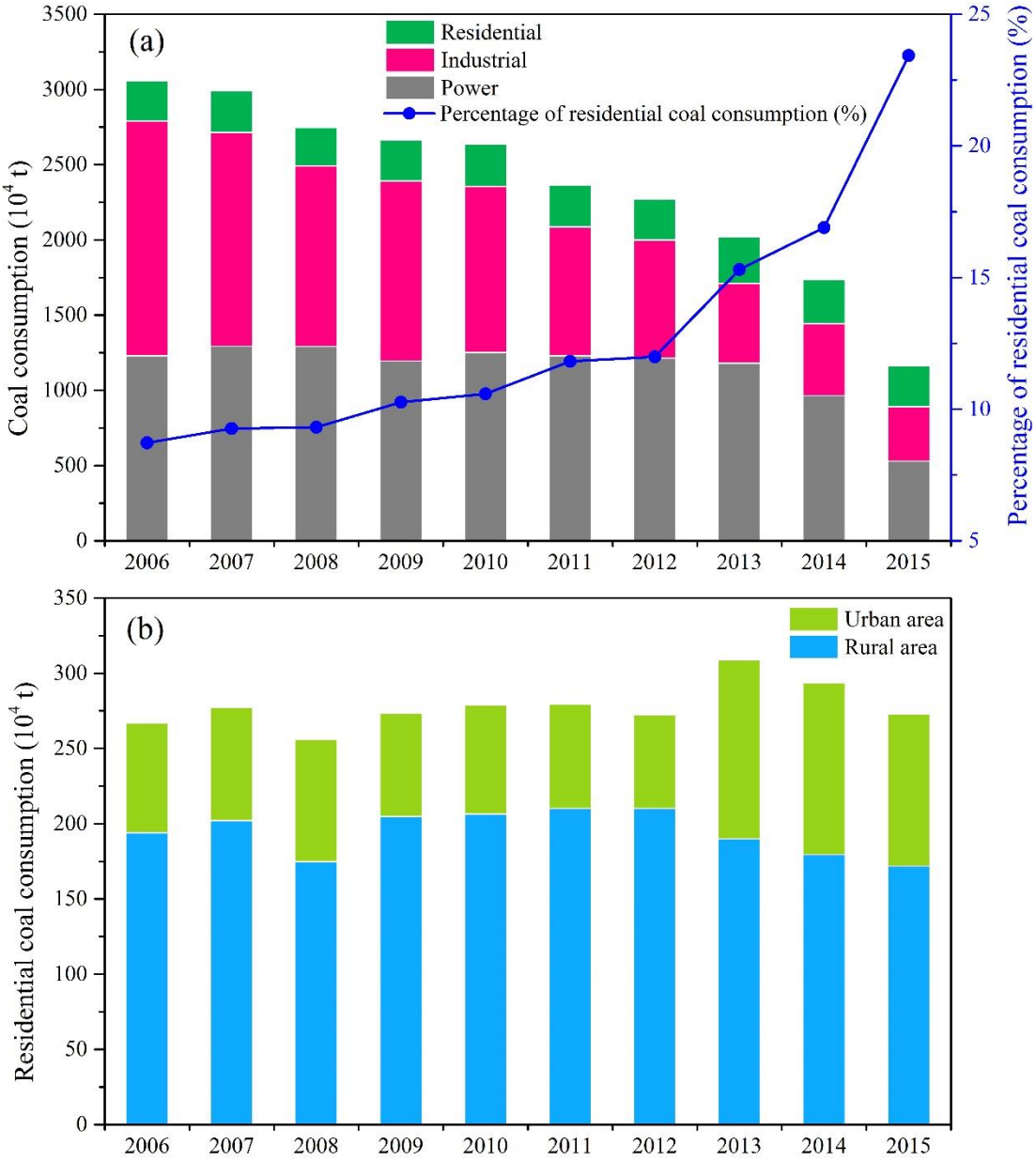

Figure S5. (a) The total coal consumption in residential, industrial and power generation sectors and the percentage of residential coal consumption in total coal consumption in Beijing during 2006-2015; (b) Residential coal consumption in urban and rural areas of Beijing during 2006-2015.

[2] The study suggests clean energy use in residential sector is vital for reducing VOCs in the heavily polluted winter. This aspect should be incorporated into the discussion or the conclusion part of the manuscript.

Reply: Thanks. In the revised manuscript we have re-write the introduction part to stress that residential burning of solid fuels for cooking and heating is not only a problem of indoor air

pollution, but also an important source of outdoor air pollutants. In the conclusion part, based on the results that residential burning of solid fuels contributed nearly halves of VOCs in ambient air during wintertime heating, we added:

"However, as observed in this study, even in megacities like Beijing, burning raw coal or biomass for household heating in winter could contribute near half of VOCs in ambient air. If the emission control over residential burning of solid fuels is underappreciated, the intervention measures targeted on traffic and industry sectors would be not so effective in the wintertime heating period as did in non-heating periods either to lower $PM_{2.5}$ as indicated by Liu et al. (2016) or to lower VOCs in ambient air as indicted by this study. If fact, a study by Yu et al. (2018) during the same field campaign of this study demonstrated that, without emission control over residential burning of solid fuels, ambient $PM_{2.5}$-bound toxic polycyclic aromatic hydrocarbons in rural Beijing during the 2014 APEC summit remained unchanged despite of the temporary intervention control measures, and they were largely aggravated after the start of wintertime heating. Therefore, cleaner energy use instead of poor-technology burning of solid fuels household heating would have tremendous health benefits in lowering both indoor and outdoor air pollution particularly in heavily polluted winter. It worth noting that this study was conducted in a rural area of the megacity Beijing. Emission from residential burning of solid fuels would be a source of greater importance and thus deserves more concern in less developed regions."

Minors:

Although I am not a native English speaker, I would say that there is still room for improving English writing of the manuscript. The authors better find a native English speaker to check the English.

Reply: Thanks for your careful check and your great patience in listing the errors/mistakes. For the revised manuscript, we have also asked a native English speaker to re-check the English writing.

Line 33-34: Change "during wintertime severe haze events" to "during severe wintertime haze events";

Reply: Revised as suggested.

Line 35: Change "comparatively much less" to "not well";

Reply: Revised as suggested.

Line 37: Change “inside” to “on”;

Reply: Revised as suggested.

Line 37: add “the” before “University”;

Reply: Revised as suggested.

Line 38: Change “northeast” to “northeastern”;

Reply: Revised as suggested.

Line 39: Remove “that”;

Reply: Revised as suggested.

Line 39: Change “during” to “on”;

Reply: Revised as suggested.

Line 40: Add “the” before “air quality”;

Reply: Revised as suggested.

Line 41: Change “in” to “on”;

Reply: Revised as suggested.

Line 41: Remove “that”;

Reply: Revised as suggested.

Line 41: Change “since” to “on”;

Reply: Revised as suggested.

Line 42: Change “it is” to “this sample collection period provided”;

Reply: Revised as suggested.

Line 43: Remove “the” before “temporary” and before “wintertime”;

Reply: Revised as suggested.

Line 44, 45: Add “the” before “temporary”;

Reply: Revised as suggested.

Line 46: Change “about” to “approximately”;

Reply: Revised as suggested.

Line 47: Change “that” to “the values”;

Reply: Revised as suggested.

Line 46-48: Change “that of 23.41 ppb before the APEC (25 October-2 November; Period I) or

21.71 ppb after the APEC (13 November-31 December; Period III)" to "the values of 23.41 ppb in Period I (25 October-2 November) before the APEC and 21.71 ppb in period III (13 November-31 December) after the APEC";

Reply: Revised as suggested.

Line 48: Change "Their" to "The";

Reply: Revised as suggested.

Line 49: Change "drop" to "decrease";

Reply: Revised as suggested.

Line 50: Change "of" to "over";

Reply: Revised as suggested.

Line 51: Remove "the" before "southerly";

Reply: Revised as suggested.

Line 52: Change "that in the northerly ones during period I, II and III" to "those in northerly air masses during periods I, II and III";

Reply: Revised as suggested.

Line 53: Remove "and";

Reply: Revised as suggested.

Line 54: Change "south" to "southern";

Reply: Revised as suggested.

Line 56: Change "changed" to "the altered";

Reply: Revised as suggested.

Line 57, 58: Remove "the" before "Period";

Reply: Revised as suggested.

Line 58: Change "emission" to "emissions";

Reply: Revised as suggested.

Line 59: Add "the" before "ambient";

Reply: Revised as suggested.

Line 60: Change "emission" to "emissions";

Reply: Revised as suggested.

Line 60: Remove "they";

Reply: Revised as suggested.

Line 61-62: Change “VOCs during the period I, II and III” to “the VOCs during periods I, II and III”;

Reply: Revised as suggested.

Line 62-63: Change “became the dominant source which accounted for 45.1% of the VOCs” to “became the largest source, accounting for 45.1% of the VOCs”;

Reply: Revised as suggested.

Line 64-65: Change “with a remarkably lower average contribution percentage (38.2%) in the southerly air masses than that of 48.8% in the northerly air masses” to “with a specifically lower average contribution percentage in southerly air masses (38.2%) than in northerly air masses (48.8%)”;

Reply: Revised as suggested.

Line 72: Change “emission” to “emissions”;

Reply: Revised as suggested.

Line 73: Change “benefit improving” to “improve the”;

Reply: Revised as suggested.

Line 74: Change “an extensive concern” to “a widespread concern”;

Reply: Revised as suggested.

Line 75, 79: Change “summertime” to “summer”;

Reply: Revised as suggested.

Line 75: Change “wintertime” to “winter”;

Reply: Revised as suggested.

Line 80: Remove “as well”;

Reply: Revised as suggested.

Line 82: Change “comparatively the role of VOCs in the wintertime with $PM_{2.5}$” to “comparatively, the effect of VOCs on wintertime $PM_{2.5}$”;

Reply: Revised as suggested.

Line 88: Change “in the control of air pollution by $PM_{2.5}$ in wintertime” to “in the control of $PM_{2.5}$ air pollution in winter”;

Reply: Revised as suggested.

Line 90: Change “under” to “on”;

Reply: Revised as suggested.

Line 92: Change “vehicle exhausts are” to “vehicle exhaust is an”;

Reply: Revised as suggested.

Line 96: Change “particularly in north China in wintertime” to “particularly in northern China in winter”;

Reply: Revised as suggested.

Line 99: Add “the” before “VOCs”;

Reply: Revised as suggested.

Line 100: Change “is widely occurring in the rural areas” to “widely occur in rural areas”;

Reply: Revised as suggested.

Line 101-102: Change “how the enhanced emission” to “how enhanced emissions”;

Reply: Revised as suggested.

Line 109: Change “north” to “northern”;

Reply: Revised as suggested.

Line 110: Add “the” before “air quality”;

Reply: Revised as suggested.

Line 111: Remove “so”;

Reply: Revised as suggested.

Line 111: Remove “when”;

Reply: Revised as suggested.

Line 112: Change “especially in wintertime with” to “especially in winter, with”;

Reply: Revised as suggested.

Line 116: Change “kind” to “type”;

Reply: Revised as suggested.

Line 118: Change “As for” to “For”;

Reply: Revised as suggested.

Line 121: Change “drops of” to “decreases in”;

Reply: Revised as suggested.

Line 123: Change “inside” to “on”;

Reply: Revised as suggested.

Line 124: Add “the” before “total”;

Reply: Revised as suggested.

Line 124: Add “were” before “reduced”;

Reply: Revised as suggested.

Line 125: Add “those in” before “the period”;

Reply: Revised as suggested.

Line 126: Change “about” to “of”;

Reply: Revised as suggested.

Line 127, 134: Remove “the” before “urban”;

Reply: Revised as suggested.

Line 127: Remove “entirely”;

Reply: Revised as suggested.

Line 128: Add “on” before “a regional scale”;

Reply: Revised as suggested.

Line 132-133: Change “The objectives of present study are” to “The objectives of the present study are as follows”;

Reply: Revised as suggested.

Line 135, 136: change “crucial” to “the major”;

Reply: Revised as suggested.

Line 136: Change “wintertime” to “winter”;

Reply: Revised as suggested.

Line 137: Add “the” before “APEC”;

Reply: Revised as suggested.

Line 141: Change “_” to “_”;

Reply: Revised as suggested.

Line 142: Change “inside the campus of” to “on the campus of the”;

Reply: Revised as suggested.

Line 142: Add “the” before “Huairou”;

Reply: Revised as suggested.

Line 143-144: Change “The UCAS is located about 60 km northeast of central Beijing and about 150 km northwest of the Tianjin city” to “UCAS is located approximately 60 km northeast of the center of Beijing and approximately 150 km northwest of the city of Tianjin”;

Reply: Revised as suggested.

Line 145-147: Change “16 meters above ground on the top of a four-story building, about 100 m west of a national road and only 1.5 km far away from the APEC main conference hall” to “16 meters above the ground on the top of a four-story building, approximately 100 m west of a national road and only 1.5 km away from the main APEC conference hall”;

Reply: Revised as suggested.

Line 152: Remove “of”;

Reply: Revised as suggested.

Line 153: Add “and” before “one”;

Reply: Revised as suggested.

Line 154: Add “was” before “less than”;

Reply: Revised as suggested.

Line 154: Add “a” before “relative”;

Reply: Revised as suggested.

Line 154: Add “of” before “less”;

Reply: Revised as suggested.

Line 158: Remove “the time span”;

Reply: Revised as suggested.

Line 163-164: Change “and average temperature was 11.4, 7.0, and 0.6°C during periods I, II and III” to “and the average temperature was 11.4, 7.0 and 0.6°C during periods I, II and III”;

Reply: Revised as suggested.

Line 224: Remove “the” before “period”;

Reply: Revised as suggested.

Line 226: Change “Total” to “The total”;

Reply: Revised as suggested.

Line 226: Change “inside” to “at”;

Reply: Revised as suggested.

Line 227: Change “in” to “on”;

Reply: Revised as suggested.

Line 229: Change “halves of 57.45, 36.17, and 56.56 ppb” to “half the values (57.45, 36.17, and 56.56 ppb)”;

Reply: Revised as suggested.

Line 231: Remove “both”;

Reply: Revised as suggested.

Line 234: Add “a” before “more than”;

Reply: Revised as suggested.

Line 234: Remove “the”;

Reply: Revised as suggested.

Line 234: Change “about” to “an approximately”;

Reply: Revised as suggested.

Line 237: Change “or” to “and the”;

Reply: Revised as suggested.

Line 238: Change “densities” to “density”;

Reply: Revised as suggested.

Line 240: Change “shared by” to “of”;

Reply: Revised as suggested.

Line 240: Remove “quite”;

Reply: Revised as suggested.

Line 243-244: Change “percentages shared by aromatics became lower during period II (12%) when compared to that in period I (21%) or period III (15%)” to “the percentage of aromatics was lower during period II (12%) than during period I (21%) and period III (15%)”;

Reply: Revised as suggested.

Line 246-247: Change “decreased by 49.0, 32.5, 72.8, and 48.1%, respectively, when compared to those during period I” to “were 49.0, 32.5, 72.8 and 48.1% lower than those during period I, respectively”;

Reply: Revised as suggested.

Line 247-248: Change “Aromatics evidently had a more substantial drop” to “Aromatics evidently

underwent a larger decrease";

Reply: Revised as suggested.

Line 249: Remove "as";

Reply: Revised as suggested.

Line 252: Change "ozone formation potentials (OFPs)" to "ozone formation potential (OFP)";

Reply: Revised as suggested.

Line 253: Change "in average during periods I, II and III were" to "on average during periods I, II and III was";

Reply: Revised as suggested.

Line 255: Change "Their" to "The";

Reply: Revised as suggested.

Line 255: Change "potentials (SOAFPs)" to "potential (SOAFP)";

Reply: Revised as suggested.

Line 257, 259: Add "the" to "total";

Reply: Revised as suggested.

Line 261: Change "VOCs" to "VOC";

Reply: Revised as suggested.

Line 262: Change "drop" to "decreases";

Reply: Revised as suggested.

Line 264: Change "changed contribution by aromatic" to "the altered contribution of aromatics";

Reply: Revised as suggested.

Line 266: Change "condition" to "conditions and from";

Reply: Revised as suggested.

Line 267: Change "condition" to "conditions";

Reply: Revised as suggested.

Line 270: Change "showed" to "shown";

Reply: Revised as suggested.

Line 271: Change "with the increase in" to "with an increase in the";

Reply: Revised as suggested.

Line 272: Change "like that" to "as those";

Reply: Revised as suggested.

Line 276: Add “the” before “wind”;

Reply: Revised as suggested.

Line 280: Change “showed” to “shows”;

Reply: Revised as suggested.

Line 281: Change “the” to “a”;

Reply: Revised as suggested.

Lines 282-285: “It clearly demonstrated that the mixing ratios of VOCs increased rapidly, and the back trajectories indicated that air masses changed from northerly to southerly and then declined sharply while the air masses changed back from southerly to northerly”, rewrite the sentences.

Reply: Revised as suggested.

Lines 285-286: Change “The southern areas of UCAS are the central Beijing with stronger emissions” to “The southern areas of UCAS are in central Beijing where emissions are stronger”;

Line 286: Add “that”;

Reply: Revised as suggested.

Line 287: Change “increase of” to “increase in the”;

Reply: Revised as suggested.

Line 288: Change “of source regions” to “in the source region”;

Reply: Revised as suggested.

Line 289: Change “showed” to “shown”;

Reply: Revised as suggested.

Line 291: Change “changed” to “altered”;

Reply: Revised as suggested.

Line 295: Add “and” before “2)”;

Reply: Revised as suggested.

Line 296: should be “: : :Mongolia and quickly: : :”;

Reply: Revised as suggested.

Line 297: Change “emission” to “emissions”;

Reply: Revised as suggested.

Line 302: Change “period” to “periods”;

Reply: Revised as suggested.

Line 303: Change “that” to “those”;

Reply: Revised as suggested.

Line 304: Change “OFPs in the southerly air masses were” to “the OFP in southerly air masses was”;

Reply: Revised as suggested.

Line 305: Change “and SOAFPs in the” to “and the SOAFP in”;

Reply: Revised as suggested.

Line 305: Change “were” to “was”;

Reply: Revised as suggested.

Line 308: Change “This indicates that the north and south” to “These results indicate that the northern and southern”;

Reply: Revised as suggested.

Line 313-314: Change “OFPs and SOAPFs” to “OFP and SOAFP”;

Reply: Revised as suggested.

Line 314: Add “that” before “the changes”;

Reply: Revised as suggested.

Line 315: Remove “to”;

Reply: Revised as suggested.

Line 316: Change “when compared to that during period I average” to “compared to that during period I, the average”;

Reply: Revised as suggested.

Line 319: Change “OFPs decreased by 48.1% and SOAFPs” to “the OFP decreased by 48.1% and the SOAFP”;

Reply: Revised as suggested.

Line 320: Change “when compared to that” to “compared to those”;

Reply: Revised as suggested.

Line 321: Add “the” before “average”;

Reply: Revised as suggested.

Line 323: Remove “when”;

Reply: Revised as suggested.

Line 323-324: Change “OFPs decreased by 48.9% and SOAFPs decreased by over 70% during period II relative to period I” to “the OFP decreased by 48.9%, and the SOAFP decreased by over 70% during period II relative to those in period I”;

Reply: Revised as suggested.

Line 325: Add “a” before “more”;

Reply: Revised as suggested.

Line 326: Change “emission control in” to “control over emissions from”;

Reply: Revised as suggested.

Line 327: Change “less changes in mixing ratios” to “decreased changes in the mixing ratios”;

Reply: Revised as suggested.

Line 328: Change “of” to “over”;

Reply: Revised as suggested.

Line 331: Change “that” to “those”;

Reply: Revised as suggested.

Line 331: Change “This difference in the increase rates” to “These different increases”;

Reply: Revised as suggested.

Line 332: Change “are” to “were”;

Reply: Revised as suggested.

Line 333: Change “heating supply was only available since” to “heat sources were only available after”;

Reply: Revised as suggested.

Line 334: Change “already” to “have”;

Reply: Revised as suggested.

Line 336: Change “apportioning” to “apportionment”;

Reply: Revised as suggested.

Line 338: Add “the” before “campaign”;

Reply: Revised as suggested.

Lines 338-339: Change “might be resulted from changed contribution by emission sources, such like” to “might have resulted from the altered contributions from emission sources, such as”;

Reply: Revised as suggested.

Line 341: add “the” before “characteristic”;

Reply: Revised as suggested.

Line 344: Change “in average during period” to “on average during periods”;

Reply: Revised as suggested.

Line 345: Change “were approaching” to “approached”;

Reply: Revised as suggested.

Line 347, 351: Remove “the” before “period”;

Reply: Revised as suggested.

Line 348: Remove “, which is characteristic of vehicular exhaust”;

Reply: Revised as suggested.

Line 349: Add “the” before “incomplete”;

Reply: Revised as suggested.

Line 354: Change “in” to “on”;

Reply: Revised as suggested.

Line 355: Change “that coal burning contributed more” to “an increased contribution of coal burning”;

Reply: Revised as suggested.

Line 357: Change “emission” to “emissions”**;**

Reply: Revised as suggested.

Line 359: Change “are mainly from” to “mainly originate from”;

Reply: Revised as suggested.

Line 361: Change “were” to “are”;

Reply: Revised as suggested.

Line 364: Change “when compared to that of” to “than the values of”;

Reply: Revised as suggested.

Line 365: Change “or” to “and of”;

Reply: Revised as suggested.

Line 366: Change “This drop in aromatics/CO ratios” to “This decrease in the ratios of aromatics to CO”;

Reply: Revised as suggested.

Line 367: Change “of” to “over”;

Reply: Revised as suggested.

Line 370, 371: Add “those in” before “period I”;

Reply: Revised as suggested.

Line 371-372: Change “Apparently larger decrease in TEX/CO ratios in the northerly air masses reflected” to “A larger decrease in the TEX/CO ratios in northerly air masses reflects the fact that”;

Reply: Revised as suggested.

Line 374: Change “3.3.2 Source Apportioning by PMF” to “3.3.2 Source Apportionment by PMF”;

Reply: Revised as suggested.

Line 375: Change “Thirty-five” to “The 35”;

Reply: Revised as suggested.

Line 375: Add “and” before “ethyne”;

Reply: Revised as suggested.

Line 376: Change “sources” to “source”;

Reply: Revised as suggested.

Line 377: Add “use with” before “the PMF”;

Reply: Revised as suggested.

Line 385: Change “the gasoline vehicle emission” to “gasoline vehicle emissions”;

Reply: Revised as suggested.

Line 386: should be “trichloroethylene and tetrachloroethylene”;

Reply: Revised as suggested.

Line 387: Change “of” to “by”;

Reply: Revised as suggested.

Line 388: Change “manufacturing industrials” to “industrial manufacturing”;

Reply: Revised as suggested.

Line 389-390: Change “by industries for make” to “in industry to prepare”;

Reply: Revised as suggested.

Line 390: Add “during the” before “production”;

Reply: Revised as suggested.

Line 392: Change “emission” to “emissions”;

Reply: Revised as suggested.

Line 393: Change “a larger percentage of the” to “larger percentages of”;

Reply: Revised as suggested.

Line 394: Chang “It is known that TEX are” to “TEX is known to be”;

Reply: Revised as suggested.

Line 396: Change “They are also” to “These compounds are also the”;

Reply: Revised as suggested.

Line 396-397: Change “auto factory painting and building coating” to “automobile factories, paint and building coatings”;

Reply: Revised as suggested.

Line 398: Change “as” to “to be”;

Reply: Revised as suggested.

Line 403-404: Change “top 3 species of” to “the top 3 species emitted during”;

Reply: Revised as suggested.

Line 405: Change “were” to “are”;

Reply: Revised as suggested.

Line 405-406: Change “and aromatics like benzene” to “as well as aromatics such as benzene”;

Reply: Revised as suggested.

Line 406-407: Change “So factor 5 is related to the coal/biomass burning” to “Thus, factor 5 is related to coal/biomass burning”;

Reply: Revised as suggested.

Line 408: Change “period” to “periods”;

Reply: Revised as suggested.

Line 409: Add “the” before “VOCs”;

Reply: Revised as suggested.

Line 411: Add the “the” before “temporary” and remove “the” before “period”;

Reply: Revised as suggested.

Line 412: Change “by” to “of”;

Reply: Revised as suggested.

Line 413: Change “drop” to “decrease”;

Reply: Revised as suggested.

Line 414: Change “by” to “from”;

Reply: Revised as suggested.

Line 415: Change “Quite similar” to “Similar”;

Reply: Revised as suggested.

Line 417: Remove “the”;

Reply: Revised as suggested.

Line 418: Change “from” to “on”;

Reply: Revised as suggested.

Line 419: Change “emission” to “emissions”;

Reply: Revised as suggested.

Line 420: Add “the” before “VOCs”;

Reply: Revised as suggested.

Line 421: Change “were showed” to “are shown”;

Reply: Revised as suggested.

Line 422: Change “by” to “of”;

Reply: Revised as suggested.

Line 422: Change “with the” to “with the increase in”;

Reply: Revised as suggested.

Line 423: Remove “instead”;

Reply: Revised as suggested.

Line 427: Change “consumptions” to “consumption”;

Reply: Revised as suggested.

Line 429: Change “The residential coal combustion is prevailing” to “Residential coal combustion is primarily carried out”;

Reply: Revised as suggested.

Line 429: Change “by using” to “with”;

Reply: Revised as suggested.

Line 430: Add “the” before “rural”;

Reply: Revised as suggested.

Line 431: Change “wintertime” to “winter”;

Reply: Revised as suggested.

Line 431: Remove “the”;

Reply: Revised as suggested.

Line 431: Change “accounts” to “accounted”;

Reply: Revised as suggested.

Line 433: Change “contribute predominately to” to “have been the predominant contributor to the”;

Reply: Revised as suggested.

Line 437, 438, 444, 446, 449: Remove “the” before “period”;

Reply: Revised as suggested.

Line 437, 440, 441: Change “by” to “from”;

Reply: Revised as suggested.

Line 441: Change “reduced” to “decreased”;

Reply: Revised as suggested.

Line 443: Change “showed” to “made”;

Reply: Revised as suggested.

Line 443: Change “period” to “periods”;

Line 447: Change “account” to “accounted”;

Reply: Revised as suggested.

Line 451: Change “period” to “periods”;

Reply: Revised as suggested.

Line 451: Remove “respectively”;

Reply: Revised as suggested.

Line 452: Change “emission (gasoline and diesel vehicles) was” to “emissions (gasoline + diesel) were”;

Reply: Revised as suggested.

Line 453: Change “VOCs during the period” to “the VOCs during periods”;

Reply: Revised as suggested.

Line 454: Remove “instead”;

Reply: Revised as suggested.

Line 456: Change “period” to “periods”;

Reply: Revised as suggested.

Line 459: Change “Contributions” to “The contributions”;

Reply: Revised as suggested.

Line 460: Change “were” to “are”;

Reply: Revised as suggested.

Line 460-461: Change “was mainly coming” to “mainly originated”;

Reply: Revised as suggested.

Line 467, 468, 470: Change “of” to “in”;

Reply: Revised as suggested.

Line 472: Change “emission” to “emissions”;

Reply: Revised as suggested.

Line 474: Change “3.3.3 Source contributions to SOAFPs” to “3.3.3 Source contributions to the SOAFP”;

Reply: Revised as suggested.

Line 475: Change “apportioning” to “apportionment”;

Reply: Revised as suggested.

Line 475: Change “SOAFPs by” to “the SOAFP of”;

Reply: Revised as suggested.

Line 476: Change “showed” to “shown”;

Reply: Revised as suggested.

Line 477: Change “condition” to “conditions”;

Reply: Revised as suggested.

Line 477: Change “SOAFPs by solvent use were much higher than that by” to “SOAFP of solvent use was much higher than that of”;

Reply: Revised as suggested.

Line 478: Change “were” to “was”;

Reply: Revised as suggested.

Line 479, 481: Change “period” to “periods”;

Reply: Revised as suggested.

Line 482: Change “of SOAFPs” to “in SOAFP”;

Reply: Revised as suggested.

Line 483: Change “by” to “from”;

Reply: Revised as suggested.

Line 485: Change “condition,” to “conditions, the”;

Reply: Revised as suggested.

Line 485: Change “of” to “in”;

Reply: Revised as suggested.

Line 486: Change “by” to “from”;

Reply: Revised as suggested.

Line 490: Change “or” to “and”;

Reply: Revised as suggested.

Line 490: Change “from” to “during”;

Reply: Revised as suggested.

Line 494: Change “SOAFPs” to “the SOAFP”;

Reply: Revised as suggested.

Line 494: Remove “only”;

Reply: Revised as suggested.

Line 496: Change “is a large of” to “are large”;

Reply: Revised as suggested.

Line 500-501: Change “SOA often shared higher factions in” to “SOAs often composed higher fractions of”;

Reply: Revised as suggested.

Line 502: Change “are much less” to “not well”;

Reply: Revised as suggested.

Line 504: Change “inside” to “on”;

Reply: Revised as suggested.

Line 505: Change “during” to “on”;

Reply: Revised as suggested.

Line 505, 506: Remove “and, in fact”;

Reply: Revised as suggested.

Line 507: Change “could take” to “took”;

Reply: Revised as suggested.

Line 509: Change “with” to “from”;

Reply: Revised as suggested.

Line 510: Change “could also compare” to “also compared”;

Reply: Revised as suggested.

Line 511: Add “use”;

Reply: Revised as suggested.

Line 512: Change “investigate” to “investigated”;

Reply: Revised as suggested.

Line 513: Change “the” to “a”;

Reply: Revised as suggested.

Line 514-515: Change “period II (3-12 November)” to “period (period II; 3-12 November), the”;

Reply: Revised as suggested.

Line 515: Change “when compared to that” to “compared to those”;

Reply: Revised as suggested.

Line 516: Change “And their” to “In addition, the”;

Reply: Revised as suggested.

Line 516: Change “potentials” to “potential”;

Reply: Revised as suggested.

Line 518: Change “drop” to “decrease”;

Reply: Revised as suggested.

Line 519: Change “of” to “over”;

Reply: Revised as suggested.

Line 520: Change “apportioning” to “apportionment”;

Reply: Revised as suggested.

Line 523: Chang “about” to “of”;

Reply: Revised as suggested.

Line 524: Change “With” to “Through”;

Reply: Revised as suggested.

Line 525: Change “of wind directions” to “in wind direction”;

Reply: Revised as suggested.

Line 526: Change “Total” to “The total”;

Reply: Revised as suggested.

Line 527: Change “that” to “those”;

Reply: Revised as suggested.

Line 531: Change “were” to “was”;

Reply: Revised as suggested.

Line 533: Change “by” to “of”;

Reply: Revised as suggested.

Line 534: Change “in average due to drops in the percentages by” to “on average due to decreases in the percentages of”;

Reply: Revised as suggested.

Line 535-536: Change “that accounted” to “accounting”;

Reply: Revised as suggested.

Line 537: Change “south” to “southern”;

Reply: Revised as suggested.

Line 538: Change “north” to “northern”.

Reply: Revised as suggested.

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households: A major and underappreciated ambient pollution source, P. Natl. Acad. Sci. USA., 113, 7756-7761, http://dx.doi.org/10.1073/pnas.1604537113, 2016.

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Volatile organic compounds at a rural site in Beijing: Influence of temporary emission control and wintertime heating

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Abstract

Secondary organic aerosols (SOA) contribute substantially to $PM_{2.5}$ during severe wintertime ~~severe~~ haze events in northern China, yet ambient volatile organic compounds (VOCs) as SOA precursors are ~~comparatively much less~~not well characterized in winter, especially in rural areas. In this study, ambient air samples were collected in 2014 from 25 October to 31 December at a rural site ~~inside~~ on the campus of the University of Chinese Academy of Sciences (UCAS) in northeastern Beijing for the analysis of VOCs. Since ~~that~~ temporary intervention measures were implemented ~~during~~ on 3-12 November to improve the air quality for the Asian-Pacific Economic Cooperation (APEC) summit held ~~in~~ on 5-11 November in Beijing, and ~~that~~ wintertime central heating started ~~since~~ on 15 November in Beijing after the APEC summit, ~~it is~~this sample collection period provided a good opportunity to study the influence of ~~the~~ temporary control measures and ~~the~~ wintertime heating on ~~the~~ ambient VOCs. As a result of the temporary intervention measures implemented during 3-12 November (period II), the total mixing ratios of non-methane hydrocarbons averaged 11.25 ppb, ~~about~~ approximately 50% lower than ~~that~~that the values of 23.41 ppb ~~before~~in period I ~~the APEC~~ (25 October-2 November~~; Period I~~) ~~or~~and 21.71 ppb ~~after the~~in period III ~~APEC~~ (13 November-31 December~~; Period III~~). The~~ir~~ ozone and SOA formation potentials decreased by ~50% and ~70%, respectively, with the larger ~~drop~~decrease in SOA formation potentials attributed to more effective control ~~of~~over aromatic hydrocarbons mainly from solvent use. Back trajectory analysis revealed that the average mixing ratios of VOCs in ~~the~~ southerly air masses were 2.3, 2.3 and 2.9 times ~~that~~those in ~~the~~ northerly ~~ones~~air masses during periods I, II and III, respectively; ~~and~~

all VOC episodes occurred under the influence of southerly winds, suggesting much stronger emissions in the southern urbanized regions than in the northern rural areas. Based on ~~the~~a positive matrix factorization (PMF) receptor model, the altered~~changed~~ contributions from traffic emissions and solvent use could explain 47.9% and 37.6% of the reduction in ambient VOCs, respectively, during ~~the~~ Period II relative to the Period I, indicating that the temporary control measures on vehicle emissions and solvent use were effective ~~in~~at lowering the ambient levels of VOCs. Coal/biomass burning, gasoline exhaust, and industrial emissions were among the vital sources, and ~~they~~ altogether contributed 60.3%, 78.6% and 78.7% of the VOCs during the periods I, II and III, respectively. Coal/biomass burning, mostly residential coal burning, became the dominant source~~, which~~ accounting~~ed~~ for 45.1% of the VOCs during the wintertime heating period, with a specifically~~remarkably~~ lower average contribution percentage ~~(38.2%)~~ in ~~the~~ southerly air masses (38.2%) than ~~that of 48.8%~~ in ~~the~~ northerly air masses (48.8%). The results suggests that emission control in the industry and traffic sectors is more effective in lowering ambient reactive VOCs in non-heating time; however, reducing emissions from residential burning of solid fuels for heating would be of greater importance and would have health co-benefits from lowing both indoor and outdoor air pollution.

1. Introduction

Volatile organic compounds (VOCs) are precursors of tropospheric ozone and secondary organic aerosols (SOA) (Forstner et al., 1997; Odum et al., 1997; Atkinson, 2000; O'Dowd et al., 2002; Sato et al., 2010). As ozone formation in urban areas is largely VOC-limited (Shao et al., 2009; Tang et al., 2010) and SOA are important components of fine particles or $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) (Cabada et al., 2004; Lonati et al., 2005; Huang et al., 2014), reducing emissions of VOCs would be very important for ~~benefit~~ improving~~ing~~ the air quality in megacities, such as China's capital city Beijing, where air pollution has become an ~~extensive~~widespread concern, with increasing surface ozone levels during summer~~time~~ and severe $PM_{2.5}$ pollution during winter~~time~~ (Streets et al., 2007; Ji et al., 2012; Wang et al., 2014).

While exposure to indoor air pollution from burning solid fuels affects nearly half of the world's population and household air pollution has long been a major environmental cause of death (Martin et al., 2011; Lim et al., 2012; Subramanian, 2014), emissions from residential energy use such as heating and cooking, prevalent in India and China, also have the largest impact on global premature mortality from outdoor air pollution (Lelieveld et al., 2015). In fact, Juda-Rezler et al. (2011) showed that coal combustion in residential boiler during winter was a major source of PM_{10} in four cities of central eastern European. A recent study revealed that even in Beijing and its surrounding regions, 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 (Liu et al., 2016). Since substantial amounts of VOCs are released from poor-technology burning of coal and biomass/biofuels (Yokelson et al., 2008; Shrivastava et al., 2015; Fang et al., 2017; Liu et al., 2017; Cheng et al., 2018), it is of wide concern how residential use of solid fuels, particularly for wintertime household heating, would influence ambient levels and compositions of VOCs. In residential areas of Izmir, Turkey, for example, household burning of coal on uncontrolled burners for domestic heating during winter was found to be a larger source of VOCs than the local traffic (Sari and Bayram, 2014).

Due to a wide variety of emission sources of VOCs and large uncertainties of the emission inventories of VOCs, to formulate emission control measures on reducing ambient VOCs is a highly challengeable task. More field measurements are therefore needed to characterize VOCs in ambient air and in emission sources for better source attribution. In Beijing, for example, since higher levels of ozone mostly occur during ~~summer and~~hot seasons ~~ozone formation in urban areas is largely VOC-limited (Shao et al., 2009; Tang et al., 2010)~~, many field measurements of VOCs ~~in Beijing~~ were conducted in summer~~time~~ with a focus on their sources (Song et al., 2007; Lu et al., 2007; Yuan et al., 2009; Wang et al., 2010a) and their mixing ratios (Liu et al., 2009; An et al., 2012; Zhang et al., 2012a; Liu et al., 2013) ~~as well~~, particularly during ozone episodes ~~(Liu et al., 2009; An et al., 2012; Zhang et al., 2012a; Liu et al., 2013).~~ ~~However, comparatively the role of VOCs in the wintertime with $PM_{2.5}$ pollution is much less understood~~. On the other hand, during extremely severe and persistent haze events in Beijing ~~in China~~, organic matter (OM) could contribute 30-70% of the total

$PM_{2.5}$ with higher fractions of SOA in OM (Guo et al., 2014; Huang et al., 2014; Zhang et al., 2014a). ~~Therefore~~However, the effect of VOCs on wintertime $PM_{2.5}$ pollution is much less understood, although the control of VOCs, as SOA precursors, is also of great importance in the control of $PM_{2.5}$ air pollution~~by $PM_{2.5}$time~~. A previous study already demonstrated that levels of aromatic hydrocarbons and carbonyls increased significantly ~~under~~on haze days in urban Beijing from 2008 to 2010 (Zhang et al., 2014b), yet few reports are available about wintertime precursor VOCs, especially about the potential contribution by burning solid fuels for household heating.

~~In urban areas, vehicle exhaust is an important sources of SOA precursors (McDonald et al., 2015; Liu et al., 2015a; Ortega et al., 2016; Deng et al., 2017; Gentner et al., 2017). However, biomass/biofuel burning and coal burning may also contribute substantially to SOA precursors (Yokelson et al., 2008; Shrivastava et al., 2015; Fang et al., 2017), particularly in northern China in winter when raw coal and biofuels are widely used for household heating (Liu et al., 2016; Zhang et al., 2016a; Liu et al., 2017). In fact, a study by Wang et al. (2013) in 2011-2012 revealed that even at an urban site in Beijing, coal combustion could account for 28-39% of the VOCs observed in ambient air. As raw coal and/or biofuel burning widely occur in rural areas in winter (Liu et al., 2016), it is necessary to investigate how enhanced emissions due to wintertime household heating would influence the levels and compositions of VOCs in rural areas, as forming SOA or ozone is an issue of regional scale.~~

Apart from health benefits from lowering indoor air pollution, controlling emissions in the residential sector would be of greater importance to further improve

outdoor air quality worldwide in the future (Liu et al., 2016), although previously efforts have been overwhelmingly targeted on reducing emissions from industrial and traffic sectors in many regions. In northern China, for example, ~~Due to a wide variety of emission sources of VOCs and large uncertainties of the emission inventories of VOCs, to assess the effect of emission control measures on reducing ambient VOCs is a highly challengeable task. The Chinese government has implemented long-term pollution control actions and~~ air quality has been greatly improved ~~in north China~~ in recent years due to the implementation of long-term pollution control actions (Hao and Wang, 2005; Wang et al., 2009; Zhang et al., 2012b; Liu et al., 2015a; Kelly and Zhu, 2016). However, the air quality there ~~in Beijing~~ is not ~~so~~ satisfactory ~~when~~ compared to that in cities in the United States and Europe, especially in winter~~,time~~ with frequent haze events and high $PM_{2.5}$ levels. Consequently, during critical international events such as the 2008 Olympic Games (Wang et al., 2010b; Huang et al., 2010) and the 2014 Asia-Pacific Economic Cooperation (APEC) summit, temporary intervention measures were adopted to guarantee better air quality. This ~~kind~~type of temporary intervention provided a good opportunity to assess the relatively importance of different sources and to study the effectiveness of various control measures on the reduction of ambient air pollutants including VOCs (Yao et al., 2013; Huang et al., 2017). ~~As for~~For the 21th Asia-Pacific Economic Cooperation (APEC) summit held in Beijing on 5-11 November 2014, temporary control measures in Beijing and its surrounding regions resulted in significant ~~drops~~decreased in ~~of~~ air pollutants, including $PM_{2.5}$ and NOx (Huang et al., 2015; Liu et al., 2015b; Wang et al., 2015; Xu et al., 2015; Zhang et al., 2016a). For the

VOCs in ambient air, as observed by Li et al. (2015) at an urban site ~~inside~~on the campus of Peking University, the total mixing ratios of VOCs were reduced by 44% during the APEC summit control period ~~when~~ compared to those in the period before. As the 2008 Olympic Games or the 2014 APEC were all held in the non-heating periods, it is not certain in what extent the temporary intervention measures mostly targeted on industrial and traffic emissions would take effect in the winter heating period.~~Since most observation-based evaluations about the effectiveness of temporary emission control measures were made with monitoring data in the urban areas, it is entirely necessary to further investigate the influence in rural areas or a regional scale.~~

~~In urban areas,~~ While vehicle exhaust is an important source of ~~SOA precursors~~VOCs in urban areas (McDonald et al., 2015; Liu et al., 2015c; Ortega et al., 2016; Deng et al., 2017; Gentner et al., 2017)~~. However~~, coal burning and biomass/biofuel burning ~~and coal burning~~ may also contribute substantially to ~~SOA precursors (Yokelson et al., 2008; Shrivastava et al., 2015; Fang et al., 2017),~~VOCs particularly ~~in northern China~~ in winter when raw coal and biofuels are widely used for household heating in regions like the northern China (Liu et al., 2016; Zhang et al., 2016b; Liu et al., 2017). In fact, a study by Wang et al. (2013) in 2011-2012 revealed that even at an urban site in Beijing, coal combustion could account for 28-39% of the VOCs observed in ambient air. As raw coal and/or biofuel burning widely occur in rural areas in winter (Liu et al., 2016), it is necessary to investigate extensively on how enhanced emissions due to wintertime household heating would influence ~~the levels and compositions of~~ambient VOCs particularly in rural areas, as forming SOA or ozone

is an issue of regional scale.

In this study, ambient air samples were collected at a rural site in the north of Beijing from 25 October to 31 December 2014, covering the period with ~~the~~ enhanced temporary emission control (3-12 November) for the APEC summit and the wintertime heating period starting from 15 November. The objectives of the present study are as follow: (1) to study changes in the mixing ratios and composition~~s~~ of VOCs at a rural site in Beijing in response to the emission control during the APEC summit and ~~the~~ wintertime heating; (2) to identify the crucial sources of VOCs in Beijing and their changes during the PM-polluted winter~~time~~; (3) to evaluate the impact of control measures implemented during the APEC summit on the reduction of VOCs in ambient air in rural areas; and (4) to assess the contribution of residential use of solid fuels for household heating to the ambient VOCs during winter.~~.~~

2. Methodology

2.1 Sampling Site and Field Sampling

The ambient air samples were collected at a site (40.41~~°~~° N, 116.68~~°~~° E; Fig. 1) ~~inside~~on the campus of the University of Chinese Academy of Science (UCAS) in the Huairou district of Beijing. ~~The~~ UCAS is located ~~about~~ approximately 60 km northeast of the central of Beijing and ~~about~~approximately 150 km northwest of the city of Tianjin ~~city~~. It is surrounded by several small villages and farmlands. The samples were collected 16 meters above the ground on the top of a four-story building, ~~about~~approximately 100 m west of a national road and only 1.5 km ~~far~~ away from the main APEC ~~main~~ conference hall.

Ambient air samples were collected from 25 October-31 December 2014 using cleaned and evacuated 2 L silica-lined stainless steel canisters. During field sampling, a model 910 canister sampler (Xonteck Inc., California, USA) with a constant flow rate of 66.7 ml min^{-1} was adopted to allow each canister to be filled in 60 min. Samples were collected at approximately 10:00 and 15:00 ~~of~~ local time (LT) on sunny days, and one or two more samples were collected at 12:00 and/or 18:00 LT on haze days when the visibility was less than 10 km at a relative humidity of less than 90% (Fu et al., 2016). A total of 153 samples were collected during sampling. According to the air pollution control measures, the field campaign was divided into periods I (25 October-2 November), II (3-12 November) and III (13 November-31 December). Period II was ~~the time span~~ when temporary control measures (Table 1; http://www.zhb.gov.cn/gkml/hbb/qt/201411/t20141115_291482.htm) implemented for better air quality. Wintertime heating started on 15 November just after the cease of temporary control measures on 13 November. During the sampling periods, the prevailing winds were mostly from north to northwest (315-360°);~~,~~ the average wind speeds were 3.5, 3.9, and 4.1 m s^{-1}~~,~~; and the average temperature was 11.4, 7.0, and 0.6°C during periods I, II and III, respectively.

2.2 Laboratory Analysis of VOCs and Carbon Monoxide

All ambient air samples were analyzed with a Model 7100 pre-concentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). Detailed cryogenically concentration steps are described

elsewhere (Zhang et al., 2012c). Briefly, 500 ml ambient air samples in the canister were first pumped into the primarily trap with glass beads and then concentrated with liquid-nitrogen cryogenic trap at -180°C. Following the primary trap was heated to 10°C, and all target compounds were transferred by pure helium to a secondary trap at -50°C with Tenax-TA as adsorbents. Majority of H_2O and CO_2 were removed through these two traps. The secondary trap then was heated to get VOCs transferred by helium to a third cryo-focus trap at -170°C. After the focusing step, the third trap was rapidly heated and the VOCs were transferred to the GC-MSD/FID system. The mixture were first separated by a DB-1 capillary column (60 m×0.32 mm×1.0 μm, Agilent Technologies, USA) with helium as carrier gas, and then split into two ways, one is a PLOT-Q column (30 m×0.32 mm×20.0 μm, Agilent Technologies, USA) followed by FID detector, another is to a 0.35 m×0.10 mm I.D. stainless steel line followed by MSD detection. The GC oven temperature was programmed to be initially at 10°C, holding for 3 min; next increased to 120°C at 5°C min^{-1}, and then 10°C min^{-1} to 250°C with a final holding time of 7 min. The MSD was selected ion monitoring (SIM) mode and the ionization method was electron impacting. Carbon monoxide (CO) in the ambient air samples were also analyzed with an Agilent model 6890 gas chromatography equipped with a FID and a packed column (5Å Molecular Sieve 60/80 mesh, 3 m×1/8 inch). CO was first separated by packed column, then converted to CH_4 by Ni-based catalyst and finally detected by FID (Zhang et al., 2016b).

2.3 Quality Control and Quality Assurance

Before sampling, all canisters were flushed at least five times by repeatedly filling

and evacuating humidified zero air. In order to check if there was any contamination in the canisters, all canisters were evacuated after the cleaning procedures, re-filled with pure nitrogen, stored in the laboratory for at least 24 h, and then analyzed the same way as field samples to make sure that all the target VOC compounds were not present.

Target compounds were identified based on their retention times and mass spectra, and quantified by external calibration methods. The calibration standards were prepared by dynamically diluting the Photochemical Assessment Monitoring Stations (PAMS) standard mixture and TO-14 standard mixture (100 ppbv, Spectra Gases Inc., New Jersey, USA) to 0.5, 1, 5, 15 and 30 ppb. The calibration curves were obtained by running the five diluted standards plus humidified zero air the same way as the field samples. The humidified zero air was initially analyzed every day to ensure the cleanness of system and then the analytical system was challenged daily with a one-point (typically 1 ppb) calibration before running air samples. If the response was beyond +/-10% of the initial calibration curve, recalibration was performed. The method detection limits (MDL) for each VOCs species were presented in Table 2.

2.4 Positive Matrix Factorization (PMF)

PMF is a multivariate factor analysis tool that decomposes a matrix of sample data into two matrices: factor contributions (G) and factor profiles (F). The method is reviewed briefly here and described in greater detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997). PMF uses both concentration and user-provided uncertainty associated with the data to weight individual points. Data values below the MDL were substituted with MDL/2; missing data values were substituted with median

concentrations. If the concentration is less than or equal to the MDL provided, the uncertainty is calculated using the equation of *Unc* = 5/6 × MDL; if the concentration is greater than the MDL provided, the uncertainty is calculated as *Unc* = [(Error faction× mixing ratio)^2 + (MDL)^2]$^{1/2}$. The number of factors in PMF was initially chosen based on the result of PCA/APCS model (Zhang et al., 2012c).

3. Results and discussion

3.1 Changing mixing ratios and compositions

As mentioned above, during ~~the~~ period II (3-12 November), temporary emission control measures were implemented to improve air quality during the 2014 APEC summit. The ~~T~~total mixing ratio~~s~~ of VOCs observed at the rural site ~~inside~~at UCAS during the period II was 11.25±3.22 ppb ~~in~~on average, significantly lower than ~~that~~the value of 23.41±5.76 ppb during period I and 21.71±2.97 ppb during period III (Fig. 2). These levels were less than ~~halves of~~half the values (57.45, 36.17, and 56.56 ppb) observed by Li et al. (2015) at an urban site in Beijing before, during and after the APEC summit, respectively. However, ~~both~~ our measurements at a rural site in this study and the measurements at an urban site by Li et al. (2015) consistently demonstrated that the temporary emission control resulted in a large decrease in ambient VOCs during the APEC summit, with a more than 30% reduction in ~~the~~ urban areas (Li et al., 2015) and ~~about~~an approximately 50% reduction in rural areas, as observed in this study. This reduced ambient mixing ratios of VOCs during the period II was also in line with the decreased $PM_{2.5}$ concentrations observed in Beijing during the APEC summit (Liu et al., 2015b), ~~or~~and the reduced NO_2 vertical column

densitiesdensity (VCD) and aerosol optical depth (AOD) in Beijing during the APEC summit based on remote sensing (Huang et al., 2015).

The percentages shared byof alkanes, alkenes, and ethyne in total VOCs were quite similar: alkanes accounted for 54, 57 and 54% of VOCs,; alkenes accounted for 12, 16 and 17%,; and ethyne accounted for 13, 14 and 14% of VOCs during periods I, II and III, respectively. Instead, the percentages shared byof aromatics becamewas lower during period II (12%) when compared to that inthan during period I (21%) orand period III (15%).

The mean mixing ratios of alkanes, alkenes, aromatics and ethyne during period II were 6.47, 1.83, 1.33, and 1.62 ppb (Fig. 2), and they decreased bywere 49.0, 32.5, 72.8, and 48.1% , respectively, when compared tolower than those during period I, respectively. Aromatics evidently hadunderwent a more substantial dropdecrease. Benzene, toluene, ethylbenzene, and m,p-xylene, which are the most abundant aromatics and usually collectively termed as BTEX, were 52.8, 73.1, 78.8, and 80.5% lower during period II than during period I, respectively.

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., 2010a), 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., 2010a) 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 to 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), meanwhile ethyne, a tracer of incomplete combustion, had mixing ratios 3-4 times higher than that in Houston.

The total ozone formation potential~~s~~ (OFP~~s~~), based on the simplified approach of MIR (maximum incremental reactivity) scale (Carter, 2009), ~~in~~on average ~~were~~was 60.64, 28.51, and 61.47 ppb (Table ~~S1~~S2) during periods I, II and III, respectively, with a 53.0% reduction during period II relative to the period I (Fig. 2). The~~ir~~ secondary organic aerosol formation potential~~s~~ (SOAFP~~s~~) under high-NOx and low-NOx

conditions (Ng et al., 2007; Lim and Ziemann, 2009) were also calculated (Table ~~S2~~S3). As ~~showed~~shown in Fig. 2, the total SOAFP~~s~~ under low-NOx conditions decreased by 71.0% from 8.77 μg m^{-3} during the period I to 2.54 μg m^{-3} during period II, and the total SOAFP~~s~~ under high-NOx conditions decreased by 64.4% from 4.02 μg m^{-3} during period I to 1.43 μg m^{-3} during period II. This significant decrease in OFP~~s~~ and SOAFP~~s~~ during period II is related to lowered VOC~~s~~ mixing ratios, especially larger ~~drop~~decreases in reactive alkenes and aromatics: alkenes and aromatics explain 26% and 52% of the reduction in total OFP~~s~~, respectively~~,~~; while the decrease in total SOAFP~~s~~ is mostly due to ~~changed~~the altered contribution ~~by~~of aromatics (Table ~~S2~~S3), whose SOAFP~~s~~ decreased from 7.30 μg m^{-3} during period I to 1.93 μg m^{-3} during period II under low-NOx conditions and from~~,~~ 2.39 μg m^{-3} during period I to 0.75 μg m^{-3} during period II under high-NOx conditions. The results suggest that enhancing the emission control of reactive alkenes and aromatics would be more ~~is especially~~ effective for reducing OFPs and SOAFPs of ambient VOCs ~~reduction~~.

3.2 Pollution episodes and influence of source regions

As ~~showed~~shown in Fig. 3d and 3e, a number of episodes with mixing ratios of VOCs over 30 ppb were recorded along with ~~the~~an increase in the CO and SO_2 concentrations (Fig. 3d) during the campaign, such ~~like~~as ~~that~~those on 4-5 November, 15-16 November, 18-21 November, 28-30 November, 17 December, and 26-28 December. During the episode on 3-5 November, for example, the total mixing ratio of VOCs was 14.30 ppb on 3 November, reached 31.96 ppb on 4 November, and then decreased again to 13.83 ppb on 5 November. As shown in Fig. 3a, the wind speeds

were all below 2 m s^{-1} during 3-5 November, and the planetary boundary layer (PBL) height on 4 November (477 m) was approximately 83% of that on 3 November (578 m) (Fig. 3c). This lower PBL height on 4 November could only partly explain the higher levels of VOCs. Figure ~~S1a~~ S2a ~~showed~~shows the 72-h back trajectories (HYSPLIT, ver. 4.0; http://www.arl.noaa. gov/ready/hysplit4.html) of air masses from 3-5 November at ~~the~~a height of 100 m in 12-h intervals and the corresponding mixing ratios of VOCs. It demonstrated that the mixing ratios of VOCs increased rapidly while air masses changed from ~~the~~ northerly to ~~the~~ southerly, and then declined sharply while the air masses turned back from ~~the~~ southerly to the northerly ~~again~~. The southern areas of UCAS are ~~the~~in central Beijing ~~with~~where ~~stronger~~ emissions are stronger;~~,~~ consequently, air masses that passed through these areas would carry higher levels of pollutants to the sampling site, leading to the quick increase ~~of~~in the mixing ratios of VOCs. This rapid change ~~of~~in the source region~~s~~ could reasonably explain more than the PBL height during the pollution episode of VOCs. As ~~showed~~shown in Fig. ~~S1b~~S2b, ~~1c~~2c, and ~~1d~~2d, back trajectories also suggested that the episodes on 18-21 November, 28-30 November and 26-28 December are related to the ~~changed~~altered source regions.

According to the 72-h back trajectories, air masses arriving at the sampling site could be categorized into two types (Fig. 4): 1) southerly (S) air masses, which passed through Hebei, Shandong, Tianjin, and central Beijing with high-density emissions before reaching UCAS, and~~;~~ 2) northerly (N) air masses, which originated from Mongolia and~~,~~ quickly passed through areas with less anthropogenic activity and low-density emissions before reaching UCAS. The pollution episodes with higher mixing

ratios of VOCs and CO, including the cases on 26-30 October, 4-5 November, 15-16 November, 18-20 November, 25-26 November and 26-28 December (Fig. 3d and 3e), all occurred under the influence of southerly air masses, also suggesting the impacts of emissions in the south.

During periods I, II and III, the average mixing ratios of VOCs for southerly air masses were 2.3, 2.3 and 2.9 times ~~that~~those for northerly air masses (Fig. 4), respectively; the OFPs in ~~the~~ southerly air masses ~~were~~was 2.0, 2.0 and 3.3 times that in ~~the~~ northerly air masses, respectively; and the SOAFPs in ~~the~~ air masses from the south ~~were~~was 1.7, 3.3, and 3.7 times that in ~~the~~ air masses from the north under low-NOx conditions~~,~~ and 1.9, 2.7, and 3.5 times that in ~~the~~ air masses from the north under high-NOx conditions, respectively. ~~This~~These results indicate~~s~~ that the northern and southern regions are completely different in their source strengths. ~~Developing strict~~ Stricter control measures in the southern region would be ~~is~~ an effective way for abating VOCs pollution in Beijing.

As mentioned above, the mixing ratios of VOCs, as well as their OFP~~s~~ and SOAPF~~s~~, decreased greatly during period II. ~~We can further see t~~The changes in the southerly and northerly air masses ~~to~~ indicate the changes in different source regions. In the southerly air masses, ~~when~~ compared to that during period I, the average mixing ratios of alkanes, alkenes, aromatics, and ethyne during period II were 8.32, 2.16, 1.93, and 2.23 ppb, with reduction rates of 46.0, 33.3, 64.3, and 44.7%, respectively; accordingly, the OFP~~s~~ decreased by 48.1% and the SOAFP~~s~~ decreased by 63.5 % (low-NOx conditions) and 57.6% (high-NOx conditions) during period II ~~when~~ compared to

~~that~~those during period I (Fig. 4). In the northerly air masses, the average mixing ratios of alkanes, alkenes, aromatics, and ethyne decreased 37.7, 4.8, 87.0, and 18.4% during period II ~~when~~ compared to that during period I, respectively; the OFP~~s~~ decreased by 48.9% and SOAFP~~s~~ decreased by over 70% during period II relative to those in period I (Fig. 4). As discussed below, a more drastic decrease in aromatics in both the northerly and southerly air masses implied more effective ~~emission~~ control over emissions ~~in~~from industrial solvent use during the APEC summit, and the much less changes in the mixing ratios of alkenes in the northerly air masses were related to the less effective control ~~of~~over domestic coal/biomass burning in the northern regions. The mixing ratios of VOCs in the southerly and northerly air masses during period III were 36.1% and 7.2% higher than ~~that~~those during period I, respectively. ~~This difference in the~~Those different increases rates might be explained by the fact that the urban areas in the south ~~are~~were largely central heating areas where heat~~ing supply was~~ sources were only available ~~since~~after 15 November~~,~~ and the northern areas were largely rural areas where individual household heating might ~~already~~have started during period I.

3.3 Source attribution and ~~apportioning~~apportionment

3.3.1 Indication from tracers

The great changes in the mixing ratios of VOCs during the campaign might ~~be~~have resulted from ~~changed~~the altered contributions ~~by~~from emission sources, such ~~like~~as enhanced emission control during the APEC summit or intensified emissions due to wintertime heating. These changes could be indicated by the characteristic fingerprints of different sources (Guo et al., 2007).

The toluene/benzene (T/B) ratio, a widely used indicator for sources of aromatics, was 1.09, 0.67 and 0.70 ~~in~~on average during periods I, II and III, respectively (Fig. ~~S2a~~S3a). While the T/B ratios during periods II and III ~~were approaching~~approached 0.6, which is characteristic of coal/biomass burning (Liu et al., 2008; Liu et al., 2015d), the ratios during ~~the~~ period I fell between that of coal/biomass burning (0.6) and vehicle exhaust (1.6)~~, which is characteristic of vehicular exhaust~~ (Wang et al., 2002; Liu et al., 2009; Zhang et al., 2013a). Carbon monoxide (CO), a typical tracer of the incomplete combustion of biomass or fossil fuels (Parrish et al., 2009; Zhang et al., 2015a), showed highly significant correlations with benzene during ~~the~~ period II (r^2=0.96, Fig. ~~S2b~~S3b) and ~~the~~ period III (r^2=0.88, Fig. ~~S2b~~S3b). SO_2, a good indicator of coal burning (Li et al., 2017), had similar concentrations during period II and period I, but its concentration~~s~~ increased 56.5% ~~in~~on average during period III compared to that during period I (Fig. 3d), suggesting ~~that~~an increased contribution of coal burning ~~contributed more~~ after the start of central heating. Methyl tert-butyl ether (MTBE), a specific indicator of gasoline related traffic emissions (Song et al., 2007; Cai et al., 2010), showed better correlation with benzene during period I (r^2=0.88, Fig. ~~S2c~~S3c) than during periods II and III.

As toluene, ethylbenzene and xylene (TEX)~~, are~~ mainly originate from solvent use in paint~~ing~~, decorations and coatings (Guo et al., 2007; Zhang et al., 2012c), the ratios of TEX to CO ~~were~~are widely used to examine the impact of solvent use relative to combustion emissions (Zhang et al., 2013a). The ratios of T/CO, E/CO and X/CO were 0.61±0.09, 0.23±0.06 and 0.35±0.07 (ppb/ppm) during period II, obviously lower ~~when~~

compared to that ofthan the values of 1.16±0.49, 0.59±0.24 and 0.99±0.41 during period I, or and of 1.34±0.27, 0.40±0.06 and 0.83±0.09 during period III (Fig. 5B), respectively. This dropdecrease in the ratios of aromatics to /CO ratios during period II also reflected more effective control ofover solvent use during the APEC summit.

If further categorized according to the air masses trajectories, the ratios of T/CO, E/CO and X/CO decreased 29.5, 45.7 and 45.7% in the southerly air masses during period II relative to those in period I,, and decreased 68.0, 80.3 and 83.0% in the northerly air masses during period II relative to those in period I, respectively (Fig. 5A). ApparentlyA larger decrease in the TEX/CO ratios in the northerly air masses reflectedreflects the fact that the control of solvent use was more effective in northern regions.

3.3.2 Source ApportioningApportionment by PMF

Thirty-fiveThe 35 most abundant VOCs, including alkanes, alkenes, aromatics, and ethyne, and sources tracers, such as chloromethane, trichloroethylene, tetrachloroethylene and MTBE, plus SO_2 and CO, were selected for use with the PMF receptor model. Figure 6 shows the 5 sources retrieved by the model.

Factor 1 has high values of MTBE and C_5-C_6 alkanes. MTBE is a common gasoline additive in China, and 2,2-dimethylbutane is used to enhance the octane levels of gasoline (Chang et al., 2004; Song et al., 2007; Cai et al., 2010).; Ethyne can be formed during fuel combustion (Blake and Rowland, 1995; Song et al., 2007; Suthawaree et al., 2010).; C_5-C_6 alkanes are associated with unburned vehicular emissions (Guo et al., 2004; Cai et al., 2010; Zhang et al, 2013b). Consequently factor

1 is related to ~~the~~ gasoline vehicle emissions.

Factor 2 is distinguished by a strong presence of trichloroethylene~~,~~ and tetrachloroethylene and moderate contributions ~~of~~by propene and butenes. Trichloroethylene and tetrachloroethylene are species from industrial manufacturing ~~industrials~~ (Yuan et al., 2013; Zhang et al., 2015b); propene and butenes are gases widely used ~~by industries~~in industry ~~for~~to ~~make~~prepare organic chemicals (Guo et al., 2007), such as during the production of synthetic rubber in the petrochemical industry (Lau et al., 2010). Thus, factor 2 was identified as industrial emissions.

Factor 3 accounts for ~~a~~ larger percentages of ~~the~~ toluene, ethylbenzene, m/p-xylene and o-xylene. ~~It~~TEX is known ~~that TEX are~~to be the primary constituent~~s~~ of solvent (Guo et al., 2004; Yuan et al., 2009; Zheng et al., 2013; Zhang et al., 2014c; Ou et al., 2015). ~~They~~These compounds are also the main components in emissions from automobile factories,~~y~~ paint~~ing~~ and building coatings (Liu et al., 2008; Yuan et al., 2010). Therefore, this source is considered ~~as~~to be solvent use related to painting and architecture.

Factor 4 is diesel exhaust, which is characterized by a significant amount of n-undecane and n-dodecane (Song et al., 2007; Zhang et al., 2012c).

Factor 5 is characterized by the presence of ethane, ethylene, CO, SO_2 and chloromethane. Chloromethane is the typical tracer of biomass burning (Liu et al., 2008; Cai et al., 2010; Zhang et al., 2014c). Ethylene, ethane and propene are the top 3 species ~~of~~emitted during rice straw burning (Zhang et al, 2013c; Fang et al., 2017). The VOC species from coal burning ~~were~~are mainly ethyne, C_2-C_3 alkenes and alkanes, and as

well as aromatics ~~like~~such as benzene (Liu et al., 2008). SO_2 is mainly from coal burning (Li et al., 2017). ~~So~~Thus, factor 5 is related to ~~the~~ coal/biomass burning.

Figure 7 shows the source contributions during periods I, II and III. During period I, gasoline exhaust was the largest source and accounted for 24.0% of the VOCs, while during period II, coal/biomass burning became the largest source. The most significant changes due to the temporary emission control during ~~the~~ period II were in the contribution percentages ~~by~~of coal/biomass burning (22.3% in period I and 42.4% in period II) and ~~by~~ solvent use (21.9% in period I and 5.8% in period II). The large ~~drop~~decrease in the contribution ~~by~~from solvent use was consistent with the above discussion about the TEX/CO ratios. ~~Quite similar contributions were observed for industrial emission and diesel exhaust.~~

In ~~the~~ period III (13 November-31 December), with ~~the~~ central heating starting ~~from~~on 15 November, coal/biomass burning became the largest source (45.1%), and industrial emission, solvent use, diesel exhaust and gasoline exhaust accounted for 25.2, 12.8, 8.7 and 8.2% of the VOCs, respectively. The time series of source contributions during the campaign ~~were showed~~are shown in Fig. ~~S3~~S4~~;~~ the contribution percentage~~s~~ ~~by~~ of coal/biomass burning increased gradually with the increase in ~~the~~ wintertime heating, while that of gasoline exhaust ~~instead~~ decreased.

Coal/biomass burning was an important source of VOCs during winter in Beijing, especially during period III with the start of central heating. In Beijing, coal consumption was greater than that of residential biomass (Liu et al., 2016). Coal is consumed in residential, industrial and power sectors in Beijing. As showed in Fig. S5a,

while annual total coal consumptions dropped rapidly during 2006-2015, the annual residential coal consumptions remained almost unchanged with their percentages in total coal consumptions rising from 8.7% in 2006 to 23.4% in 2015 (Beijing Municipal Bureau of Statistics, 2016; Yu et al., 2018). As a matter of fact, over 60% of the residential coal consumption occurred in rural areas of Beijing (Fig. S5b), and residential coal is mainly burned in the cool winter season for house heating (Xue et al., 2016). While emission factors of VOCs from residential coal burning have been found to be a factor of 20 greater than those from coal-fired power plants (Liu et al., 2017), the differences in coal quality between the urban and rural areas augment emissions in rural areas: coal used in urban area was entirely anthracite with comparatively much lower emissions of volatiles than other types of coal (Xu et al., 2017); instead only 5-15% of coal used in rural area was anthracite (Xue et al., 2016). Consequently, residential coal combustion could have been a major contributor to the ambient VOCs in rural areas of Beijing during winter.~~During 2008-2014 in Beijing the annual residential coal consumptions increased gradually while the total coal consumption decreased (Beijing Municipal Bureau of Statistics, 2015). The residential coal combustion is prevailing for heating and cooking by using domestic coal stoves in rural areas around urban Beijing particularly during wintertime. In 2014, although the annual residential coal consumption accounts for 17% (2.93×10^{9} kg a^{-1}) of the total coal consumption in Beijing (Beijing Municipal Bureau of Statistics, 2015), residential coal burning could contribute predominately to ambient VOCs from coal burning since the emission factors of VOCs from residential coal burning have been found to be a factor~~

~~of 20 greater than those from coal-fired power plants (Liu et al., 2017).~~

Compared with that in the period I (Fig. ~~S4~~S6), the contribution ~~by~~from solvent use during ~~the~~ period II was reduced to a greater extent than other sources; it became 4.29 ppb lower and could explain 37.6% of the reduction in ambient VOCs (Table ~~S3~~S4). The contribution ~~by~~from gasoline vehicles was 3.18 ppb lower and accounted for 27.9% of the total reductions. The contribution ~~by~~from diesel exhaust and industrial emissions ~~reduced~~decreased 2.28 ppb and 1.35 ppb~~,~~ and explained 20.0 and 11.8% of the total reduction, respectively. Coal/biomass burning ~~showed~~made similar contributions during periods I and II, with an elevated contribution percentage in ~~the~~ period II due to the reduction in other sources. This is consistent with the fact that during the APEC summit residential coal/biomass burning was not restricted in the rural areas. Traffic-related sources (gasoline and diesel vehicles) and solvent use accounted for 47.9 and 37.6% of the total reduction in ambient VOCs, indicating that control measures (Table 1) related to the control of traffic and solvent use were among the most effective ways to reduce the ambient VOCs.

Figure 8 shows the source contributions in the southerly and northerly air masses during periods I, II and III~~, respectively~~. In the southerly air masses, traffic related emission (gasoline and diesel vehicles) ~~was~~were the largest source, contributing 44.1 and 41.5% of the VOCs during ~~the~~ periods I and II, respectively,~~;~~ while coal/biomass burning ~~instead~~ was the largest source during period III, contributing 38.2% of the VOCs. In the northerly air masses, coal/biomass burning contributed 28.8, 51.6 and 48.8% of the VOCs during periods I, II and III, respectively. Overall, gasoline vehicle

exhaust contributed more VOCs in the southern regions (mostly densely populated urban areas) and coal/biomass burning and diesel exhaust accounted for more emissions of VOCs in northern regions (mostly rural areas). The ~~C~~contributions of different sources to most reactive alkenes and aromatics based on PMF ~~were~~was presented in Fig. 9. Alkenes ~~was~~ mainly ~~coming~~originated from coal/biomass burning, with shares of 31.2-68.0%, and gasoline exhaust ranked second, with contributions of 3.0-26.5%. Unlike alkenes, solvent use was the major contributor~~s~~ of aromatics, accounting for 77.5% during period I and 29.0% during period II in the northerly air masses; gasoline exhaust contributed 8.2-43.6% of the aromatics during the campaign. In the southerly air masses, the reductions in solvent use, gasoline exhaust, and diesel exhaust during ~~the~~ period II relative to ~~the~~ period I could explain 38.1, 31.1, and 15.8% of the total reduction ~~of~~in VOCs, respectively. In the northerly air masses, reductions ~~of~~in solvent use, diesel exhaust, and gasoline exhaust during ~~the~~ period II relative to the period I could explain 46.5, 35.8 and 11.9% of the total reduction ~~of~~in VOCs, respectively. Consequently, control measures related to solvent use and gasoline exhaust were more effective in the southern regions, while the control of solvent use and diesel exhaust emissions were more effective in the northern region.

3.3.3 Source contributions to the SOAFP~~s~~

With the PMF source ~~apportioning~~apportionment results, the contributions of the SOAFP~~s~~ ~~by~~of different sources were further estimated. As ~~showed~~shown in Fig. 10, under low-NOx conditions, the SOAFP~~s by~~ of solvent use ~~were~~was much higher than that ~~by~~of other sources, which ~~were~~was 4.88, 0.68 and 2.89 μg m^{-3}, accounting for 56.9,

27.2 and 54.7% of the total SOAFPs during periods I, II and III, respectively. Gasoline exhaust contributed 19.2, 29.5 and 10.9%, and diesel exhaust contributed 16.5, 26.8 and 11.3% of the SOAFPs during periods I, II and III, respectively. During the period II, with temporary intervention measures, the reduction ofin SOAFPs was mainly due to reduced contributions byfrom solvent use, gasoline exhaust and diesel exhaust, which could explain 69.1, 14.9 and 12.2% of the reduction in SOAFPs, respectively. Under high-NOx conditions, the calculated reduction ofin SOAFPs during the period II relative to the period I could largely be explained by the reduced contributions byfrom solvent use, diesel exhaust and gasoline exhaust, which accounted for 54.0, 25.8 and 16.8% of the reduction in SOAFPs, respectively.

It is worth noting that recent chamber studies revealed that aromatic hydrocarbons orand traditional VOCs could not fully explain the SOA formed fromduring atmospheric aging of source emissions (Zhao et al., 2014; 2015; Liu et al., 2015c; Deng et al., 2017; Fang et al., 2017), particularly for emissions from diesel vehicles or biomass burning (Zhao et al., 2015; Deng et al., 2017; Fang et al., 2017). Therefore the discussion on the SOAFPs in this study is only limited to traditional anthropogenic SOA precursor species (mainly aromatic hydrocarbons), and intermediate-volatility organic compounds (IVOCs), which is aare important SOA precursors large of secondary organic aerosol (Zhao et al., 2014), should be further considered in order to fully understand the influence of control measures on the ambient SOA.

4. Conclusions

During severe wintertime haze events in recent years in Beijing, SOA often

602 ~~shared~~composed higher fractions ~~in~~of organic aerosols, yet their precursor VOCs in
603 ambient air during winter are ~~much less~~not well understood, especially in ~~the~~ rural areas.
604 In this study, we collected ambient air samples from 25 October to 31 December in
605 2014 at a rural site ~~inside~~on the campus of UCAS in north Beijing. As the APEC summit
606 was held in Beijing ~~during~~on 5-11 November 2014, ~~and~~ temporary control measures
607 were adopted to improve the air quality, and ~~in fact~~ the so-called "APEC Blue" was
608 achieved due to the enhanced emission control. Therefore, we ~~could take~~took advantage
609 of this opportunity to see how the control measures influenced the ambient VOCs in
610 ~~the~~ rural areas. On the other hand, wintertime heating ~~with~~from coal burning has been
611 regarded as a major contributor to wintertime PM pollution and haze events; ~~,~~ thus, we
612 ~~could~~ also compared the ambient VOC levels and compositions ~~s~~ before and after the
613 start of central heating ~~–~~ on 15 November, and investigated the influence of wintertime
614 heating on ambient VOCs based on our observation at ~~the~~a rural site.
615 We observed that during the enhanced emission control period (period II; ~~(~~3-12
616 November), the average mixing ratios of VOCs decreased ~50% ~~when~~ compared to
617 ~~that~~those before or after that period. ~~And~~In addition, the~~ir~~ ozone and SOA formation
618 potential~~s~~ accordingly decreased by ~50% and ~70%, respectively, as a result of the
619 temporary intervention measures implemented during period II. The larger
620 ~~drop~~decrease in SOA formation potentials was attributable to more effective control
621 ~~of~~over aromatic hydrocarbons mainly from solvent use. Based on PMF source
622 ~~apportioning~~apportionment, the control of traffic-related emissions (gasoline and diesel
623 exhaust) and solvent use could explain 47.9 and 37.6% of the reduction in ambient

VOCs. This result thus offered an observation-based evaluation ~~about~~of the temporary emission control measures.

~~With~~Through back trajectory analysis, we could compare ambient VOCs with the change ~~of~~in wind direction~~s~~ and thus further investigate the source emission strength in different regions. The ~~T~~total mixing ratios of VOCs in ~~the~~ southerly air masses were 2.3, 2.3 and 2.9 times ~~that~~those in ~~the~~ northerly air masses before, during and after the period with temporary emission control for the APEC summit. VOC episodes during the campaign all occurred under southerly winds. This confirms that emission control in the southern urbanized regions is crucial for reducing ambient VOCs.

As residential coal/biomass burning ~~were~~was not controlled during the APEC summit, its contribution to the ambient mixing ratios of VOCs was similar between period I and period II, although the contribution percentages ~~by~~of coal/biomass burning became the largest ~~in~~on average due to ~~drops~~decreases in the percentages ~~by~~of other sources. During period III, with emissions from burning solid fuels for household heating, coal/biomass burning became the largest source, ~~that~~accounting~~ed~~ for 45.1% of the VOCs. Specifically, during period III, coal/biomass combustion contributed 38.2% of the VOCs in ~~the~~ southerly air masses (or in the southern regions), and 48.8% of the VOCs in ~~the~~ northerly air masses (or in the northern regions).

The finding of this study will provide useful information for the emission ~~on the direction of~~ control strategy~~ies~~ of VOCs ~~for abating both ozone and $PM_{2.5}$ pollution~~. A comparison of VOCs between period I (without intervention measures) and period II (with intervention measures) revealed that the temporary intervention measures mostly

targeted on the control in traffic and industry (industrial processes and solvent use) sectors are very effective to reduce reactive alkenes and aromatics and thereby to ~~The reduction~~ reduce ~~in total~~the OFPs and SOAFPs ~~during the APEC is largely due to the drop of reactive alkenes and aromatics, so adopting reactivity-based emission control would be the effective and economical way to lower the ozone and SOA formation potentials~~ of VOCs in ambient air. ~~As control measures related to solvent use and vehicle exhausts explained most of the reduction in both ambient VOCs and their ozone/SOA formation potentials,~~ Therefore, enhancing emission control for solvent use (especially solvents with aromatic hydrocarbons) and vehicle exhaust would benefit the VOC-related air pollution~~improving air quality in the future~~. ~~Moreover~~However, as observed in this study, even in megacities like Beijing, burning raw coal or biomass for household heating in winter could contribute near half of VOCs in ambient air. If the emission control over residential burning of solid fuels is underappreciated, the intervention measures targeted on traffic and industry sectors would be not so effective in the wintertime heating period as did in non-heating periods either to lower $PM_{2.5}$ as indicated by Liu et al. (2016) or to lower VOCs in ambient air as indicted by this study. If fact, a study by Yu et al. (2018) during the same field campaign of this study demonstrated that, without emission control over residential burning of solid fuels, ambient $PM_{2.5}$-bound toxic polycyclic aromatic hydrocarbons in rural Beijing during the 2014 APEC summit remained unchanged despite of the temporary intervention control measures, and they were largely aggravated after the start of wintertime heating. Therefore, cleaner energy use instead of poor-technology burning of solid fuels

household heating would have tremendous health benefits in lowering both indoor and outdoor air pollution particularly in heavily polluted winter. It worth noting that this study was conducted in a rural area of the megacity Beijing. Emission from residential burning of solid fuels would be a source of greater importance and thus deserves more concern in less developed regions.~~a cleaner way of wintertime household heating would help to lower both primary emission and secondary formation of air pollutants.~~

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Table 1. Enhanced temporary air pollution control measures during the 2014 Asian-Pacific Economic Cooperation (APEC) summit

Control types	Details	Control areas
Traffic	1. Yellow label vehicles were banned to run inside the sixth ring of Beijing and the Huairou urban area; 2. The number of private vehicles in operation reduced by 50% through an odd/even-number-plate rule throughout Beijing; 3. Trucks were limited to drive inside the sixth ring of Beijing between 6 am and 24 pm; 4. 70% of government cars also ordered off the roads in Beijing.	Inside the sixth ring of Beijing and the Huairou urban area
Industrial	1. 9289 enterprises were suspended, 3900 enterprises were ordered to limit production; 2. More than 40000 construction sites were shut down.	Beijing, some areas of Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia
Other fields	1. Open fire was completely controlled at North China Plain; 2. Increasing road cleaning and water spraying in Beijing; 3. Other relate control measures carried out in surrounding areas.	North China Plain Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia

Table 2. The mixing ratios, ranges and 95% confidence intervals (95% C.I.) of VOCs during period I, II and III at the rural site inside UCAS (in parts per trillion by volume, pptv).

Species	MDL[a]	Period I		Period II		Period III	
		Range	Mean (95% C.I.)	Range	Mean (95% C.I.)	Range	Mean (95% C.I.)
Ethane	39	1172-7855	3254(743)	910-5511	2442(491)	1082-12714	3674(465)
Propane	31	427-6145	2880(720)	270-4138	1296(384)	598-7604	2479(329)
i-Butane	14	53-2755	1121(312)	59-1400	474(187)	106-2741	754(129)
n-Butane	21	158-2947	1283(302)	83-1735	562(196)	174-3047	841(136)
i-Pentane	14	94-3729	1425(354)	39-1388	561(167)	72-12590	1018(279)
n-Pentane	8	47-1697	615(182)	30-910	247(106)	26-4808	456(112)
2,2-Dimethylbutane	14	15-68	30(6)	17-32	24(3)	BDL[b]-75	26(2)
Cyclopentane	12	13-135	64(15)	BDL-64	35(7)	13-274	50(8)
2,3-Dimethylbutane	12	13-140	45(15)	22-51	32(4)	13-235	38(6)
2-Methylpentane	8	13-679	171(68)	12-257	77(31)	9-1077	124(27)
3-Methylpentane	7	12-548	150(54)	14-220	68(26)	16-792	104(20)
n-Hexane	6	115-1033	505(97)	102-921	324(89)	108-7393	1400(257)
Methylcyclopentane	9	10-283	100(30)	13-195	59(23)	BDL-535	88(17)
2,4-Dimethylpentane	4	BDL-43	15(5)	BDL-15	10(2)	BDL-90	16(2)
Cyclohexane	6	10-458	167(51)	10-107	43(14)	7-646	76(17)
2-Methylhexane	6	10-304	68(27)	7-56	22(6)	7-318	51(10)
2,3-Dimethylpentane	9	BDL-139	31(12)	BDL-24	15(2)	BDL-102	28(3)
3-Methylhexane	6	12-436	93(38)	8-97	41(11)	9-367	70(12)
2,2,4-Trimethylpentane	9	12-126	44(12)	BDL-41	25(4)	BDL-127	38(5)
n-Heptane	10	12-358	89(33)	12-71	30(8)	13-441	82(14)
Methylcyclohexane	5	BDL-162	51(17)	BDL-66	21(7)	BDL-162	44(8)
2,3,4-Trimethylpentane	6	BDL-38	14(4)	BDL-12	9(1)	BDL-59	16(2)
2-Methylheptane	4	8-175	31(16)	BDL-31	13(3)	BDL-91	22(3)
3-Methylheptane	5	BDL-231	26(20)	BDL-15	8(1)	BDL-74	17(2)
n-Octane	6	8-104	42(11)	BDL-31	18(3)	BDL-160	40(6)
n-Nonane	6	9-99	40(11)	BDL-37	18(4)	BDL-171	38(6)
n-Decane	6	14-777	129(74)	8-110	36(14)	BDL-600	73(17)
n-Undecane	7	47-317	151(35)	27-206	66(20)	11-374	94(12)
n-Dodecane	7	9-646	129(57)	25-313	75(30)	8-316	63(9)
Ethylene	41	367-3495	1788(391)	553-3572	1254(352)	319-13911	2313(428)
Propene	31	117-1264	430(118)	170-766	371(67)	176-3222	820(128)
1-Butene	17	19-161	107(18)	BDL-100	55(12)	19-581	137(22)
1,3-Butadiene	20	21-403	154(44)	23-234	79(27)	BDL-2140	252(74)
trans-2-Butene	5	BDL-41	18(4)	BDL-35	12(4)	BDL-425	39(10)
cis-2-Butene	7	9-50	23(4)	BDL-38	14(5)	BDL-276	37(7)
1-Pentene	20	BDL-47	33(3)	21-25	23(1)	BDL-127	52(6)
Isoprene	13	BDL-623	163(56)	16-143	62(15)	17-765	200(24)
trans-2-Pentene	10	BDL-37	17(4)	BDL-19	15(3)	BDL-65	23(3)
cis-2-Pentene	6	BDL-24	11(3)	BDL-9	8(0)	BDL-46	15(2)
2-Methyl-2-butene	12	13-50	21(4)	17-20	18(1)	BDL-61	24(2)
Benzene	14	75-2695	868(279)	43-1465	410(179)	72-2916	795(151)
Toluene	9	120-3585	1273(419)	47-1186	343(126)	62-3425	840(146)
Ethylbenzene	6	25-2210	684(240)	12-611	145(67)	23-2450	317(75)
m/p-Xylene	9	39-2106	765(248)	16-620	149(67)	25-3285	422(91)
Styrene	8	15-578	167(71)	BDL-99	32(11)	10-1267	151(38)
o-Xylene	4	11-965	334(104)	9-284	71(31)	15-1224	178(36)
Isopropylbenzene	4	5-66	24(7)	BDL-21	11(2)	BDL-77	18(3)
n-Propylbenzene	4	6-231	71(27)	BDL-55	20(7)	5-239	38(8)
m-Ethyltoluene	3	13-593	136(67)	4-91	28(11)	4-854	85(23)
p-Ethyltoluene	3	6-295	61(29)	4-59	17(6)	4-245	41(9)
1,3,5-Trimethylbenzene	3	7-217	48(21)	BDL-35	12(4)	4-179	38(6)
o-Ethyltoluene	3	5-246	64(26)	4-58	17(6)	5-230	40(8)
1,2,4-Trimethylbenzene	6	22-984	220(93)	13-219	58(22)	8-803	127(26)
1,2,3-Trimethylbenzene	5	12-442	82(37)	BDL-92	24(9)	6-300	56(11)
1,3-Diethylbenzene	4	11-135	35(12)	BDL-26	15(3)	BDL-126	26(4)
1,4-Diethylbenzene	4	14-461	80(40)	5-69	23(7)	BDL-292	51(10)
1,2-Diethylbenzene	4	BDL-30	15(4)	BDL-8	6(1)	BDL-76	15(2)
Ethyne	57	406-10539	3128(1043)	290-6260	1625(615)	584-10378	3008(509)

[a] MDL, method detection limits, pptv; [b] BDL, bellowed detection limit.

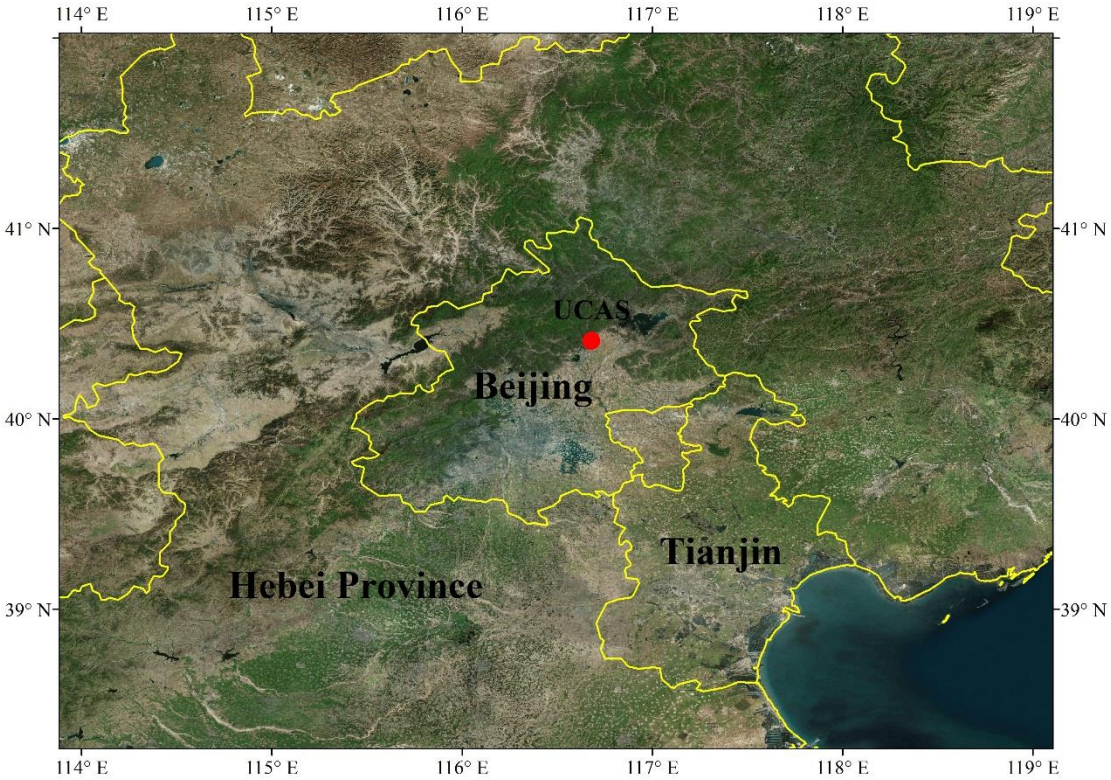


Figure1. Location of sampling site at a rural inside the campus of University of Chinese Academy of Science (UCAS).

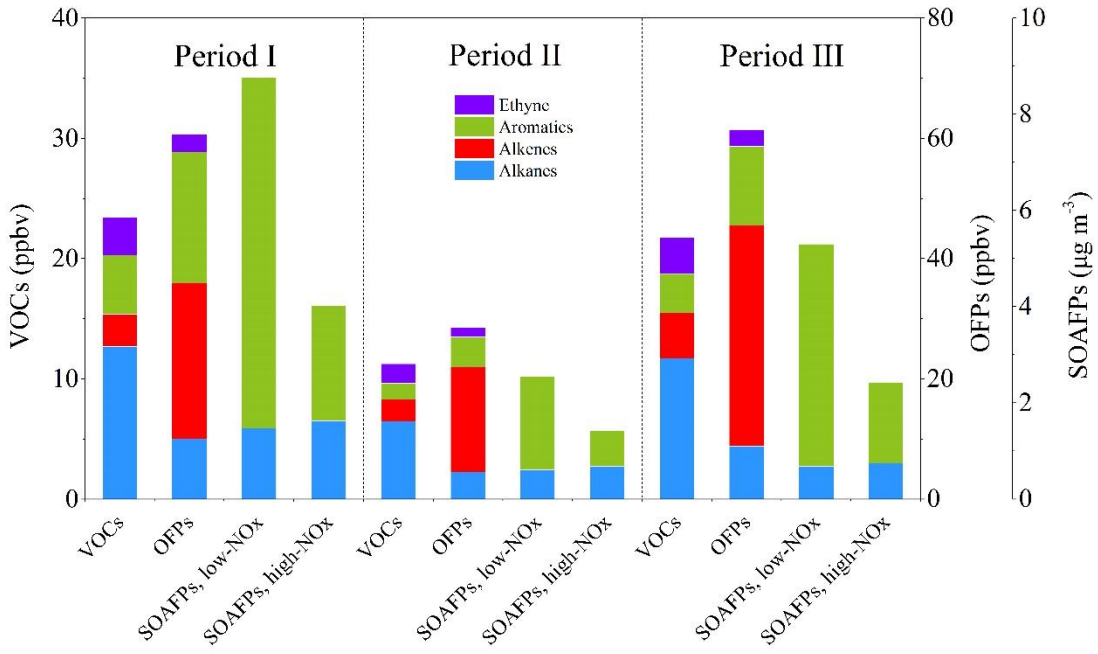


Figure 2. Mixing ratios of VOCs, ozone formation potentials (OFPs) and secondary organic aerosol formation potentials (SOAFPs) during period I, II and III at UCAS, respectively.

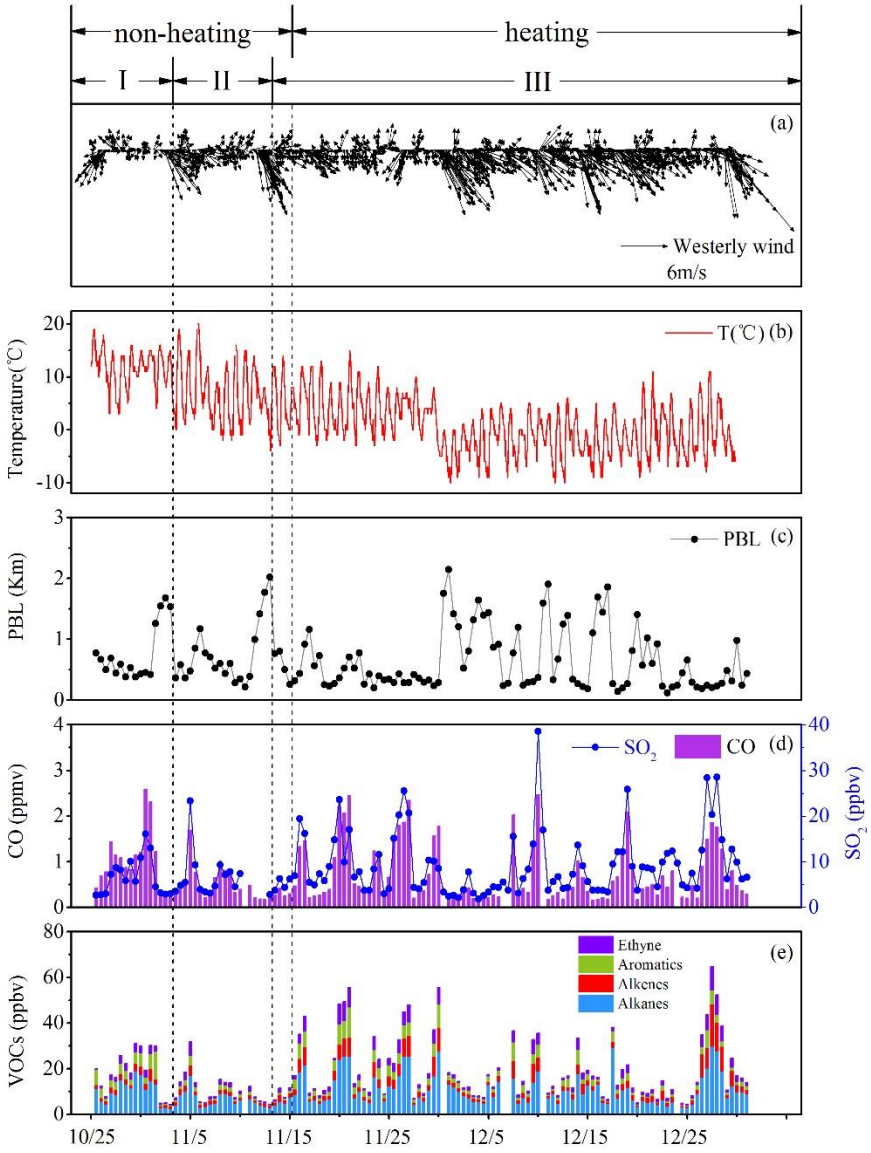


Figure 3. Time series of (a) wind speed and wind direction, (b) temperature, (c) planetary boundary layer height, (d) mixing ratios of CO and SO_2, (e) mixing ratios of VOCs, at the sampling site inside UCAS. The heating periods started on 15 November. Period I: 25 October-2 November; Period II: 3-12 November; Period III: 13 November-31 December.

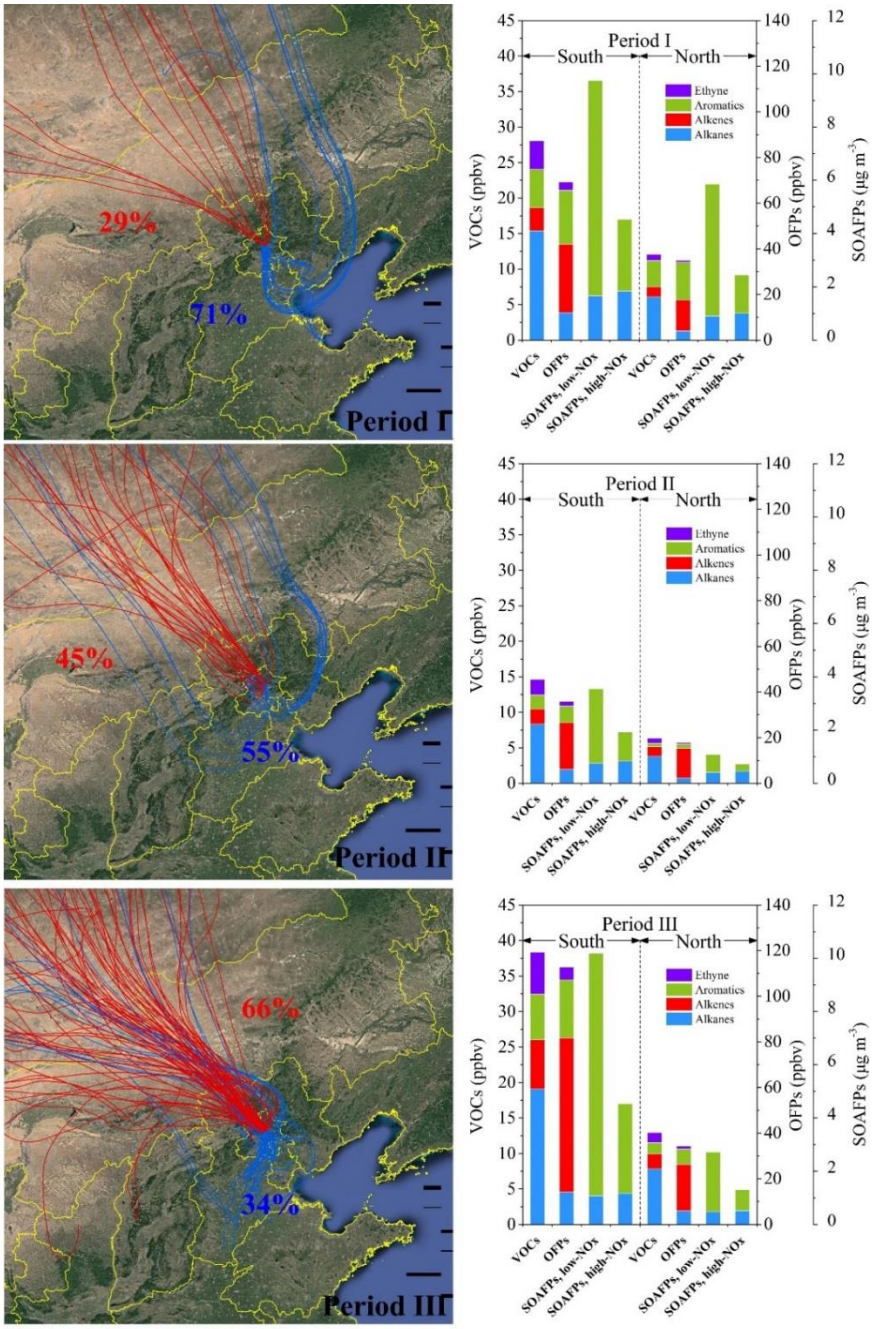


Figure 4. Mixing ratios of VOCs, ozone formation potentials (OFPs) and secondary organic aerosol formation potentials (SOAFPs) in the air masses from the south and north regions (right) and corresponding back trajectories at 100 meters above the ground level during period I, II and III, respectively (Left).

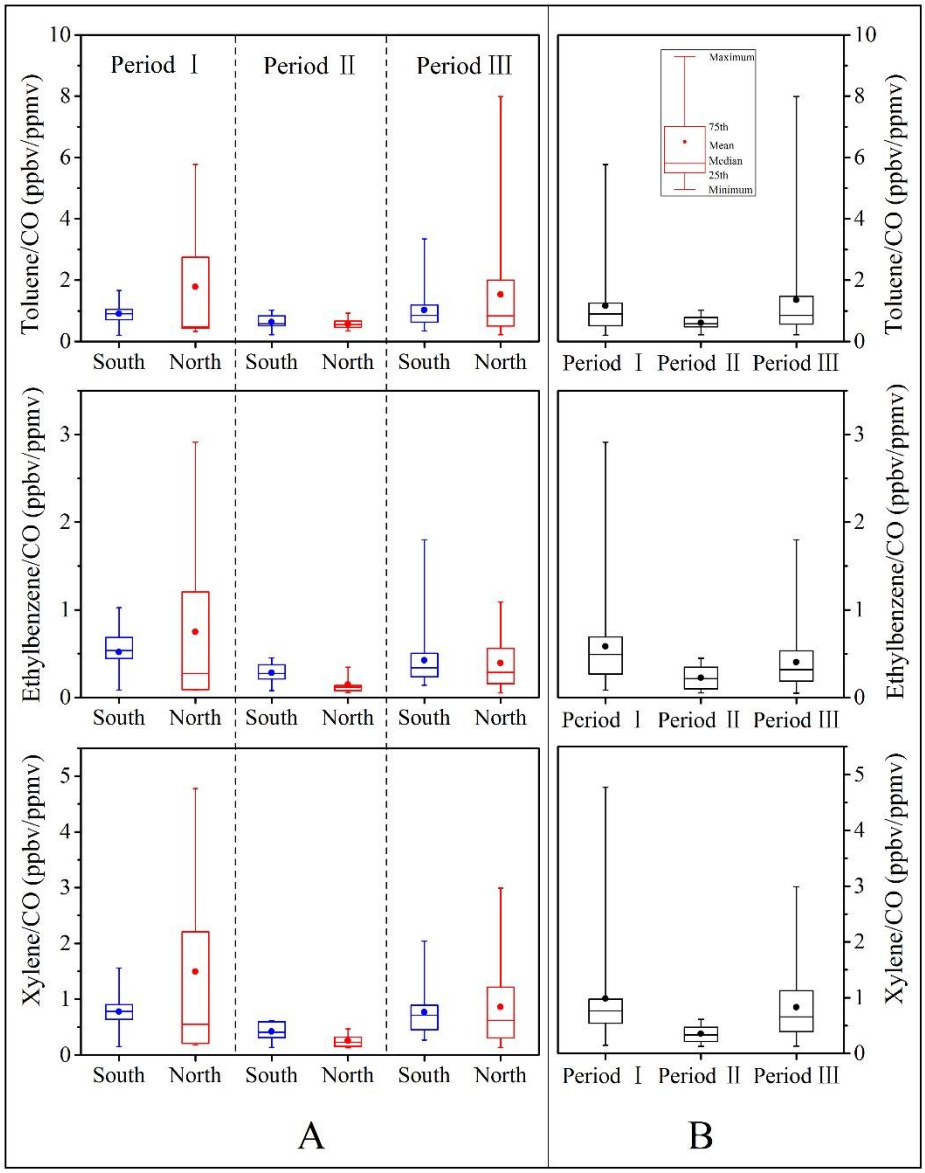


Figure 5. Ratios of aromatic hydrocarbons to carbon monoxide (CO) (A) in the air masses from the south and north regions and (B) in all samples during period I, II and III. (The lower and upper boundaries of the box represent the 25th and 75th percentiles, respectively; the whiskers below and above the box indicate the minimum and maximum, respectively; the line within the box marks the median; the dot represent the mean).

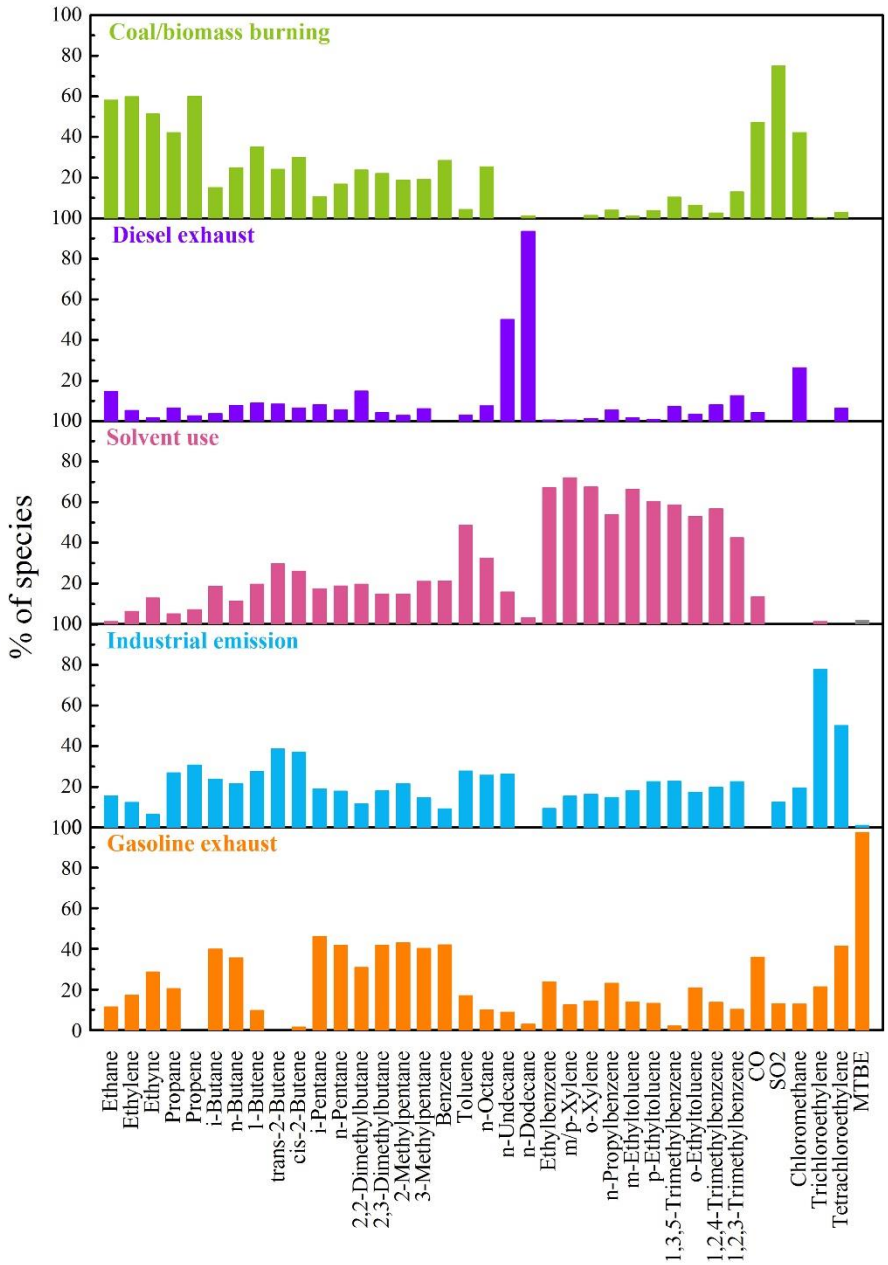


Figure 6. Source profiles revolved by PMF.

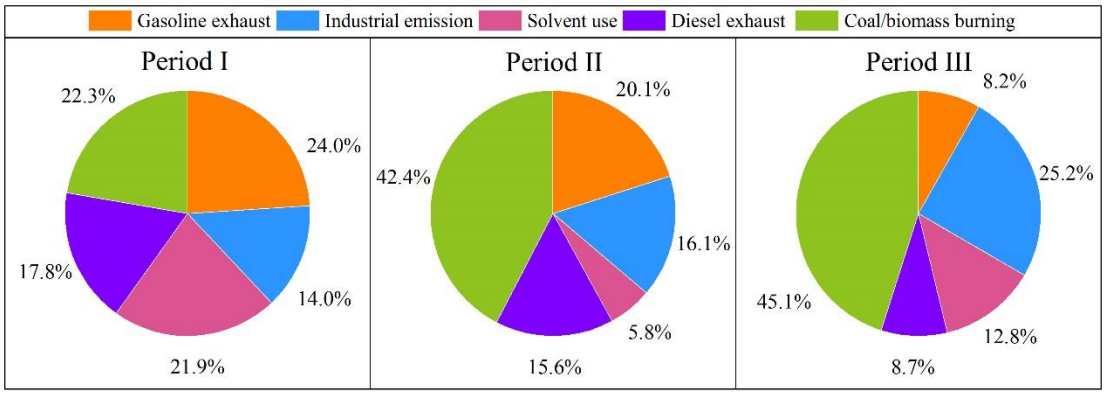


Figure 7. Contributions to VOCs in percentages (%) by different sources during period I, II and III.

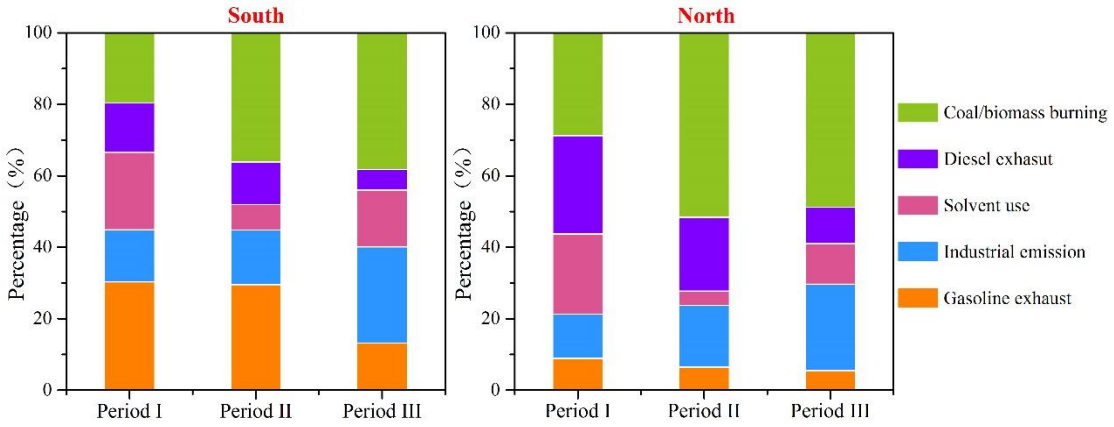


Figure 8. Sources contributions (%) to VOCs in the air masses from the south and north regions during period I, II and III.

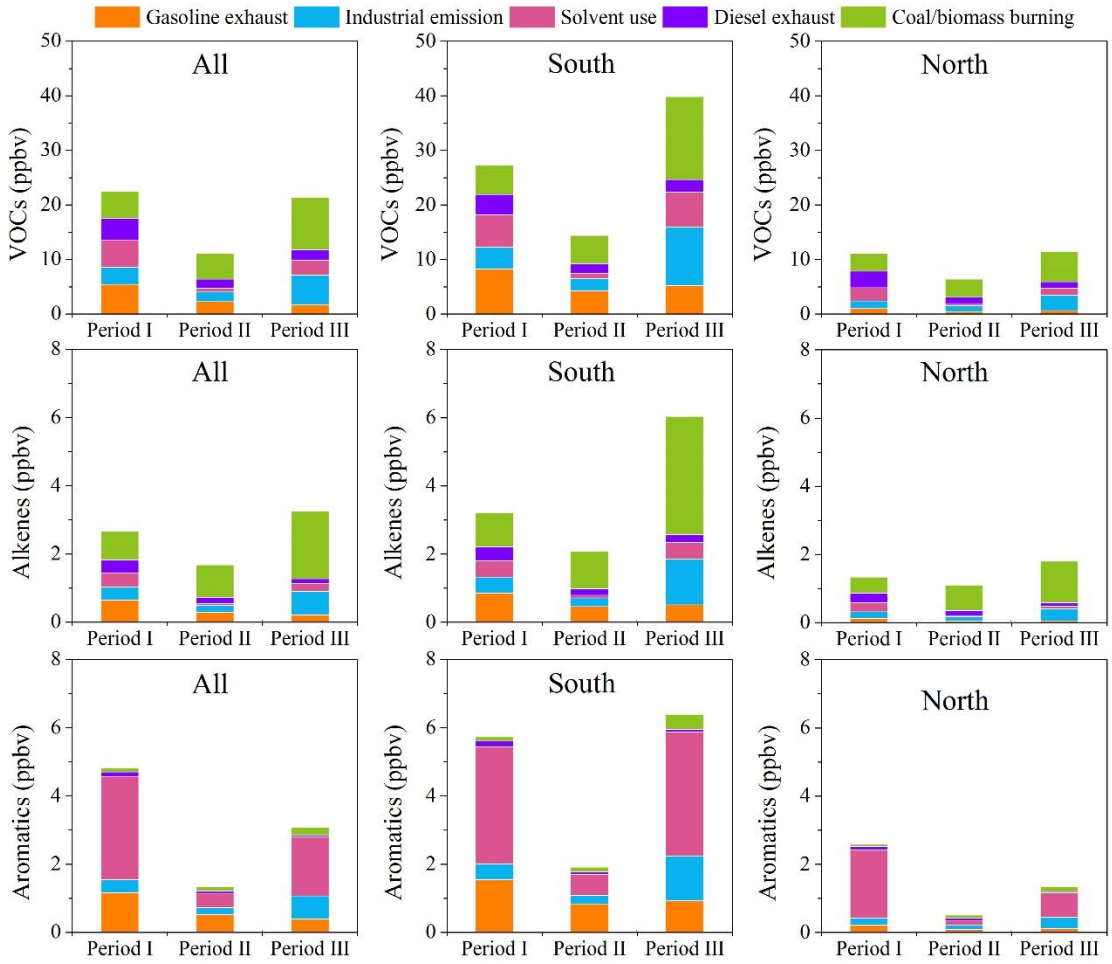
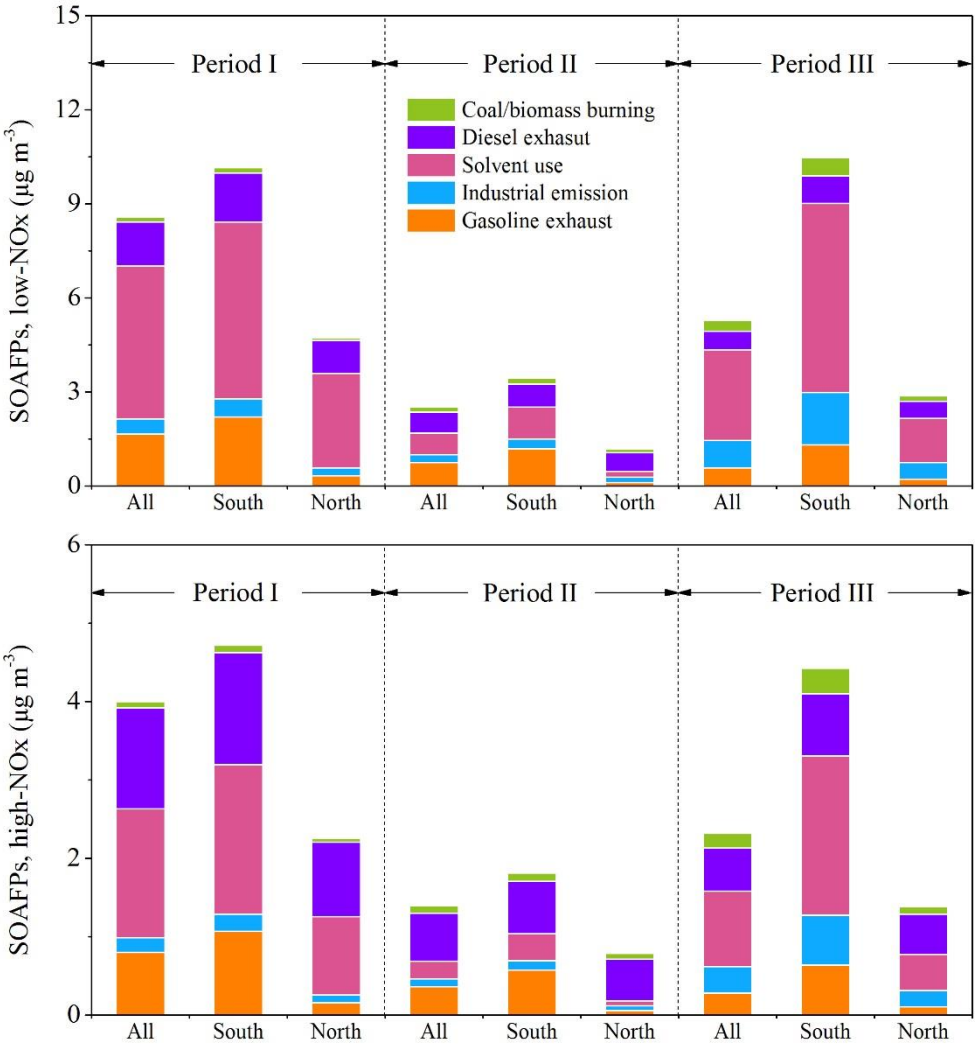


Figure 9. Sources contributions of VOCs and reactive alkenes/aromatics at UCAS, in all samples and in air masses from the south and north regions during period I, II and III.



1134

1135 Figure 10. Contributions to SOAFPs by different sources in the air masses from the

1136 south and north regions during period I, II and III.