Anonymous Referee #2

General description:

This manuscript presents work to verify anthropogenic emission inventories for the Beijing, Tianjing, Hebei area of China using a set of ambient VOC measurements made at a site in Beijing and satellite retrievals. They developed the inventory, performed a PMF analysis of the ambient data to evaluate the source structure and then evaluated the spatial distribution with satellite derived emissions. This is potentially important work a emission inventories are crucial as inputs for air quality models and thus for driving air pollution abatement strategies. It is therefore important that the inventories are accurate and comparison with emissions derived from measurements is an important tool to ensure this. The work is within the scope of ACP, however there some weaknesses that need to be addressed before final publication.

Response: Thanks a lot for your dedicated work. We really appreciate the careful reading and the useful suggestions, which help to improve the manuscript considerably. We have fully considered the comments and made revisions to our manuscript. The response and changes are listed below. The responses are in black, and revised portions are marked blue in the letter.

General comments:

1. The emission inventory was constructed using activity data but there is no discussion as to where this came from. More detail should be given as to the source of the activity data.

Response: Accepted. Thank you for your valuable suggestion. In the revised a table containing activity data for each source and for each category and the corresponding reference was provided in the Supplementary Information (Table S2).

2. Is there any temporal variation in the inventory? Presumably the activity data is time dependant (e.g. seasonal, hour of day). It would be important for the inventory to have temporal scaling factors in order for it to be used in models.

Response: Accepted. Thank you for your valuable suggestion. The monthly activity data is available. In the revised manuscript, we provided the monthly variability of the EF-based emission inventory.

The monthly VOC emissions of EF-based emission inventories can be calculated by monthly profile for each source, which usually developed based on monthly statistics (Li et al., 2017b). According to the method of Li et al. (2017b), Wu et al. (2018), and Zhang et al. (2009), we provided monthly profiles for every sources in the Table S3 of the Supplementary Information. In the revised manuscript, a table of monthly profiles used in this study was provided in the Supplementary Information (Table S3). Following sentences were added in section 2.1.2 to describe the method of temporal distribution, "The monthly variability of this VOC emission inventory was calculated based on the monthly profiles (Table S3). In summary, monthly profiles for industrial emissions were developed based on monthly output of industrial products (NBS, 2015). Power plant monthly profile was derived from monthly statistics of power generation (NBS, 2015). Monthly profiles of residential fossil fuel combustion were estimated based on household survey results (Guo et al., 2015;Zheng et al., 2014). Monthly profile of on-road vehicle emissions was derived from Li et al. (2017b). For field crop residue burning, the monthly profile was estimated based on the MODIS fire counts in croplands (Li et al., 2016). We

assumed that there was no monthly variation for the emissions from the other sources (Wu and Xie, 2018).” The monthly variability of the EF-based emission inventory obtained by this study was added in Figure 12, which didn’t exhibit obvious seasonal variations. The EF-based VOC emission inventories developed by the other studies (Li et al., 2017b; Wu and Xie, 2018) also didn’t exhibit obvious seasonal variations. The discrepancies among seasons were very small because of little monthly variation in emissions from industrial processes, transportation, and solvent utilization (Wu and Xie, 2018).

References:

Guo, J., Huang, Y., and Wei, C.: North–South debate on district heating: Evidence from a household survey, Energ. Policy, 86, 295-302, 10.1016/j.enpol.2015.07.017, 2015.

Li, J., Li, Y., Bo, Y., and Xie, S.: High-resolution historical emission inventories of crop residue burning in fields in China for the period 1990–2013, Atmos. Environ., 138, 152-161, 10.1016/j.atmosenv.2016.05.002, 2016.

Li, M., Zhang, Q., Kurokawa, J.-i., Woo, J.-H., He, K., Lu, Z., Ohara, T., Song, Y., Streets, D. G., Carmichael, G. R., Cheng, Y., Hong, C., Huo, H., Jiang, X., Kang, S., Liu, F., Su, H., and Zheng, B.: MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP, Atmos. Chem. Phys., 17, 935-963, 10.5194/acp-17-935-2017, 2017b.

NBS: China Economic Statistics Express, 2015.

Wu, R., and Xie, S.: Spatial Distribution of Secondary Organic Aerosol Formation Potential in China Derived from Speciated Anthropogenic Volatile Organic Compound Emissions, Environ. Sci. Technol., 52, 8146-8156, 10.1021/acs.est.8b01269, 2018.

Zheng, J., Zhang, L., Che, W., Zheng, Z., and Yin, S.: A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment, Atmos. Environ., 43, 5112-5122, 10.1016/j.atmosenv.2009.04.060, 2009.

Zheng, X., Wei, C., Qin, P., Guo, J., Yu, Y., Song, F., and Chen, Z.: Characteristics of residential energy consumption in China: Findings from a household survey, Energ. Policy, 75, 126-135, 10.1016/j.enpol.2014.07.016, 2014.

3. Could the authors comment on the representativeness of the PKU site for comparison with the 3kmx3km grid square of the inventory? It is difficult to use point measurements to compare to an emission rate for a much larger area so I wonder how use this comparison is?

Response: Accepted. Thank you for your comment. We are sorry for the unclear description about the sampling site and the method we used. In this study we used the “emission ratio” method to verify the VOC emissions. This method has been widely used to evaluate emission inventories of VOCs (Fu et al., 2007; Hsu et al., 2010; Shao et al., 2011; Borbon et al., 2013; Wang et al., 2014). The theory of this method is that the relative ratios between enhancements of VOCs and the increasing of a trace gas (such as CO) could reflect the ratios of their emission strength (Shao et al., 2011). The relative ratios can help reduce the influence of physical transformation processes. Thus, if the emissions of the trace gas can be determined, we can calculate out the emissions of VOC species (Eq. 2 of our manuscript). It should be noted that this approach for the calculation of VOC emissions based on ambient measurements has several limitations and uncertainties. First, in this study, we evaluated the emission inventory based on VOC measurement at one site, which limits the spatial representation of VOC measurement data relative to those observations in more sites. Secondly, we assume that the air mass over the site could respect the average emissions of the grid box, which will lead some uncertainties.

Since the online VOC measurement is difficult and costly, lots studies only use the VOC mixing ratios of one online sampling site to evaluate the emissions of a larger area. Wang et al. (2014)

measured the VOC mixing ratio during summer and winter in the PKU site, calculated the emissions of individual VOC species, and compared the emissions with the TRACE-P (Streets et al., 2003) and INTEX-B (Zhang et al., 2009) emission inventories. Borbon et al. (2013) compared the emission results of the "emission ratio" method with emission inventories of Los Angeles based on observations in one site. Shao et al. (2011) also use one site to represent the concentrations of one city. Offline VOC measurement for multiple sites is easier than online observations, but it limits the temporal representation of VOC measurement. The PKU site has been used to represent a typical urban environment in Beijing in many studies (Song et al., 2007; Yuan et al., 2012; Wang et al., 2015; Li et al., 2015; Wu et al., 2016). In this study, we assumed that the VOC concentrations of PKU site can represent the concentrations of the grid box.

In order to make it clear, in the revised manuscript, "This site has been used to represent a typical urban environment in Beijing in many studies (Song et al., 2007;Yuan et al., 2012;Li et al., 2015;Wang et al., 2015;Wu et al., 2016b)" was added in section 2.2.

The description about the method was revised and added in section 2.3.1: **"**VOC mixing ratios obtained from field observations cannot be directly compared with the VOC emissions due to physical and chemical transformation processes. One widely used approach to compare them is to estimate the emissions of individual VOC species by their emission ratios to a reference compound and the known emissions for the reference compound (Fu et al., 2007; Hsu et al., 2010; Shao et al., 2011; Borbon et al., 2013; Wang et al., 2014). The theory of this method is that the relative ratios between enhancements of VOCs and the increasing of a trace gas could reflect the ratios of their emission strength (Shao et al., 2011). The relative ratios can help reduce the influence of physical transformation processes".

The limitations of the approach and the single sampling site were added in section 2.3.1: "This approach for the calculation of VOC emissions based on ambient observations has several limitations. First, in this study, we evaluated the emission inventory based on VOC measurement at one site, which limits the spatial representation of VOC measurement data relative to those observations in more sites. Secondly, we assume that the air mass over the site could respect the average emissions of the grid box, which will lead some uncertainties. Thirdly, these approach relies on the assumption that the composition of urban emissions relative to CO. Thus, emissions based on VOC measurements on multiply sampling sites would be more reliable and some other method such as chemical transport model simulation maybe an ideal approach to verify emission inventories based on field observations in our future study".

References:

Borbon, A., Gilman, J. B., Kuster, W. C., Grand, N., Chevaillier, S., Colomb, A., Dolgorouky, C., Gros, V., Lopez, M., Sarda-Esteve, R., Holloway, J., Stutz, J., Petetin, H., McKeen, S., Beekmann, M., Warneke, C., Parrish, D. D., and de Gouw, J. A.: Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris, J. Geophys. Res.-Atmos., 118, 2041-2057, 10.1002/jgrd.50059, 2013.

Fu, T.-M., Jacob, D. J., Palmer, P. I., Chance, K., Wang, Y. X., Barletta, B., Blake, D. R., Stanton, J. C., and Pilling, M. J.: Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia and implications for ozone, J. Geophys. Res., 112, 10.1029/2006jd007853, 2007.

Hsu, Y.-K., VanCuren, T., Park, S., Jakober, C., Herner, J., FitzGibbon, M., Blake, D. R., and Parrish, D. D.: Methane emissions inventory verification in southern California, Atmos. Environ., 44, 1-7, 10.1016/j.atmosenv.2009.10.002, 2010.

Li, J., Xie, S. D., Zeng, L. M., Li, L. Y., Li, Y. Q., and Wu, R. R.: Characterization of ambient volatile organic compounds and their

sources in Beijing, before, during, and after Asia-Pacific Economic Cooperation China 2014, Atmos. Chem. Phys., 15, 7945-7959, 10.5194/acp-15-7945-2015, 2015.

Shao, M., Huang, D., Gu, D., Lu, S., Chang, C., and Wang, J.: Estimate of anthropogenic halocarbon emission based on measured ratio relative to CO in the Pearl River Delta region, China, Atmos. Chem. Phys., 11, 5011-5025, 10.5194/acp-11-5011-2011, 2011.

Song, Y., Shao, M., Liu, Y., Lu, S. H., Kuster, W., Goldan, P., and Xie, S. D.: Source apportionment of ambient volatile organic compounds in Beijing, Environ. Sci. Technol., 41, 4348-4353, 10.1021/es0625982, 2007.

Streets, D. G.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, J. Geophys. Res., 108, 10.1029/2002jd003093, 2003.

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 14, 5871-5891, 10.5194/acp-14-5871-2014, 2014.

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 14, 5871-5891, 10.5194/acp-14-5871-2014, 2014.

Wang, M., Shao, M., Chen, W., Lu, S., Liu, Y., Yuan, B., Zhang, Q., Zhang, Q., Chang, C. C., Wang, B., Zeng, L., Hu, M., Yang, Y., and Li, Y.: Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013, Atmos. Chem. Phys., 15, 1489-1502, 10.5194/acp-15-1489-2015, 2015.

Wu, R., Li, J., Hao, Y., Li, Y., Zeng, L., and Xie, S.: Evolution process and sources of ambient volatile organic compounds during a severe haze event in Beijing, China, Sci. Total. Environ., 560-561, 62-72, 10.1016/j.scitotenv.2016.04.030, 2016.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, n/a-n/a, 10.1029/2012jd018236, 2012.

Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C. C., and Liu, S. C.: Variations of ground-level O₃ and its precursors in Beijing in summertime between 2005 and 2011, Atmos. Chem. Phys., 14, 6089-6101, 10.5194/acp-14-6089-2014, 2014.

4. There are many parts of the manuscript where quite vague statements on the comparison between the inventory and the measured emissions are given. For example, the paragraph starting on line 274 states that a majority of NMHC agree within +- 100% with the inventory. What do the authors mean by a majority? How many agreed within 50% or 25%? Also in the paragraph starting on line 287 they state that annual emissions for alkenes, except ethene correlate well. What does 'well' mean in this case. Ingeneral the authors need to be a bit more quantitative in their statements of the degree of correlation between the inventories and the measured emissions.

Response: Accepted. We are sorry for the vague statements. There are 56 NMHC species measured by the GCMS/FID system in this study. The emissions for 51 NMHC species were agreed within ±100% in the emission inventory, 15 species were agreed within ±50%, and 10 species were agreed within ±25%. In the revised manuscript, Lines 275-277 was revised to "After the comparison with results obtained from measurements, the emissions for 51 of 56 kinds of non-methane hydrocarbon (NMHC) species were agreed within ±100% in the emission inventory, 15 species agreed within ±50%, and 10 species agreed within ±25%". Line 287 was revised to "The annual emissions for the alkenes, except ethene, were agreed within ±100%".

Besides, we revised other vague statements. Lines 282-283 was revised to "the annual emissions

for alkanes were agreed within ±100% between the two methods, except ethane and propane, which are important tracers of natural gas and LPG". Lines 407-408 was revised to "the annual emissions of 91% NMHCs derived from the measurements were agreed within ±100% with the results of the emission inventory". Lines 21-23 was revised to "The annual emissions for 51 of 56 kinds of non-methane hydrocarbon species derived from the measurements were agreed within ±100% with the results of the emission inventory".

Specific comments:

1. Line 37: Better to say 'production' rather than 'ambient concentrations' of secondary pollutants.

Response: Accepted. In the revised manuscript, "ambient concentrations" was revised to "production".

2. Line 99: Where do the emission factors (EFs) come from, please provide a reference.

Response: Accepted. The EFs for on-road vehicular VOC emissions were calculated by COPERT 4, a widely used software application for calculating emissions from road transport. The method has been explained in detail in previous studies (Cai and Xie, 2013). It has been descripted in following paragraph of Eq. (1).The EFs for the other VOC emission sources were from available literatures. The EFs and references were listed in Table S1.

3. Line 144: What international calibration scale is the standard used for calibrating the instrument tied to?

Response: Accepted. We are sorry for the unclear description. The sampling and analysis method of this study follow the US EPA Method TO-15 (USEPA, 1999).This method documents sampling and analytical procedures for measurement of VOCs. The concentration and drying steps are completed by the TH-PKU 300B instrument, which is a widely used VOC pre-concentration system (Yuan et al., 2012; Wang et al., 2013; Li et al., 2018). The analytical strategy for US EPA Method TO-15 was conducted by GC/MS-FID system. The GC/MS-FID system used in this study is provided from Shimadzu Co., Ltd., Japan (GCMS-QP2010). Method TO-15 provides specific method performance criteria to allow for alternative techniques and provides inherent quality control with criteria for internal standards, system verifications, method blanks, and compound identification. With the quality control tools, more assurances of good data are possible. In this study standard gases provided by the Environmental Technology Center, Canada and Linde Electronics and Specialty Gases Inc., USA were used to calibration the VOC mixing ratios, which are ideal for use with the TO-15 Calibration Standards (Linde Electronics and Specialty Gases, 2017).

In the revised manuscript, more information about the analysis method was added as follows "The sampling and analysis method of this study follow the US EPA Method TO-15 (USEPA, 1999). A custom-built online system was used to collect and analyze the ambient VOCs in a continuous and automatic manner (TH-PKU 300B, Wuhan Tianhong Instrument Co. Ltd., China). The system is a gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) with a time resolution of 1 hour (GCMS-QP2010, Shimadzu Co., Ltd., Japan). A total of 104 C2-C11 VOC species belonging to alkanes (27), alkenes (13), aromatics (16), halocarbons (29), alkynes (1), nitriles (1), and oxygenated VOCs (OVOCs, 17) were recognized and quantified by standard gases (source from the Environmental

Technology Center, Canada, and Linde Electronics and Specialty Gases Inc., USA). These standard gases are ideal for use with the TO-15 Calibration Standards (Linde Electronics and Specialty Gases, 2017). In addition, five concentrations of standard gases were used to perform monthly calibrations. The method detection limit (MDL) exhibited by the GC-MS/FID was in the range of 0.002 ppbv to 0.070 ppbv for each targeted species. A more detailed description of this system has been provided elsewhere (Li et al., 2015; Li et al., 2018). ”

Reference:

USEPA: Air Method, Toxic Organics-15 (TO-15): Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS), 1999.

Linde Electronics and Specialty Gases: Spectra VOC standards Method TO-15/TO-17, 2017.

4. Line 175: Please provide more information here. Is there a reference for the MarcoPolo project apart from the website? What chemical transport model is used?

Response: Accepted. Thank you for your suggestion. MarcoPolo project is a collaborative research projected by Chinese and European partners to study the emission sources using state-of-the-art techniques and to provide the latest air up-to-data emission inventories for China. Detailed information of the MarcoPolo emission inventory is described in (Hooyberghs et al., 2016). For the CO emission inventory, MarcoPolo project copied the Multi-resolution Emission Inventory for China (MEIC) emissions (Hooyberghs et al., 2016). The MEIC is a uniform emission model framework developed by Tsinghua University to estimate anthropogenic emissions over China (http://www.meicmodel.org/index.html). The CO emission inventory of MEIC has been validated by the chemical transport model (Hu et al., 2017), satellite observations (Yumimoto et al. 2014), and comparison with other studies (Li et al., 2017a). The chemical transport model used by Hu et al. (2017) is the Community Multiscale Air Quality (CMAQ) model with meteorological inputs from the Weather Research and Forecasting (WRF) model.

In the revised manuscript, appropriate references was added as follows: “The annual emission value of CO was obtained from the CO emission inventory of the MarcoPolo Project (http://www.marcopolo-panda.eu, Hooyberghs et al., 2016), which was copied from the Multi-resolution Emission Inventory for China (MEIC) emissions (http://www.meicmodel.org/index.html). This emission inventory has been validated by the chemical transport model (Hu et al., 2017), satellite observations (Yumimoto et al. 2014), and comparison with other studies (Li et al., 2017a)”.

References:

Hooyberghs, H., Veldeman, N., and Maiheu, B.: Marco Polo Emission Inventory for East-China: Basic Description, 2016.

Hu, J., Li, X., Huang, L., Ying, Q., Zhang, Q., Zhao, B., Wang, S., and Zhang, H.: Ensemble prediction of air quality using the WRF/CMAQ model system for health effect studies in China, Atmos. Chem. Phys., 17, 13103-13118, 10.5194/acp-17-13103-2017, 2017.

Li, M., Liu, H., Geng, G., Hong, C., Liu, F., Song, Y., Tong, D., Zheng, B., Cui, H., Man, H., Zhang, Q., and He, K.: Anthropogenic emission inventories in China: a review, National Science Review, 4, 834-866, 10.1093/nsr/nwx150, 2017a.

Yumimoto, K., Uno, I., and Itahashi, S.: Long-term inverse modeling of Chinese CO emission from satellite observations, Environ. Pollut., 195, 308-318, 10.1016/j.envpol.2014.07.026, 2014.

5. Section 3.2.1: Quite a lot of space is given to describing the time series of the VOC measurements here but it is not really put into context with the emissions. Maybe the section could be expanded to also describe how local meteorology and long range transport affects the concentration of the VOCs as well as their local emissions?

Response: Accepted. Thank you for your valuable suggestion. As we descripted in Section 3.2.1 "The VOCs accumulated in early October decreased sharply in the middle of the month, then began to accumulate again with the change of the diffusion condition". Local meteorology could impact the VOCs mixing ratios. Time series of wind speed and VOC mixing ratios in October 2015 can support the hypothesis. However, according to the comment of the other review, the point of using the observations is to validate the inventory and this section should be concise. In order to focus on the topic of this study, we expanded this section in the Supplementary Information.

Combined with reviewers' comments, in the revised manuscript, the second paragraph of Section 3.2.1 and Figure 6 was moved to the Supplementary Information. The impact of local meteorology on the mixing ratio of VOCs was added in the paragraph, which was revised to "Figure S2 presents the time series of VOC mixing ratios. The mixing ratios of VOCs in January were variable, with maximum value of 245.54 ppbv. There were lots of periods with high VOC mixing ratios in January. In April, the average VOC mixing ratio was not as high as in January but the mixing ratios of VOCs change a lot, a maximum value of 150.24 ppbv. The mixing ratios of VOCs in July were stable, with the highest level of 92.28 ppbv. The highest VOC mixing ratio in October was 201.10 ppbv. In early October, the VOCs accumulated when the wind speed was low (Fig. S3). Then VOCs decreased sharply when the wind speed became higher. And the VOC began to accumulate again with change of the wind speed. This shows that local meteorology could affect the mixing ratios of VOCs. "

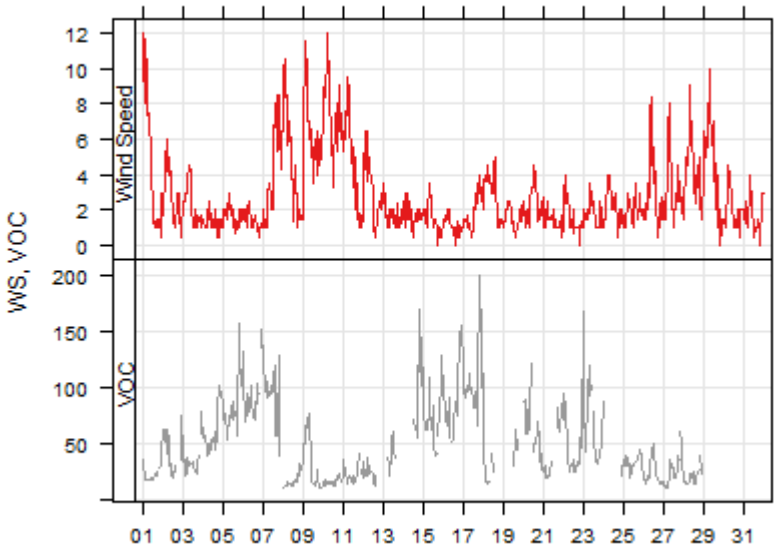

Figure S3. Time series of wind speed and VOC mixing ratios in October 2015.

6. Line 261: It is stated that all species except β-pinene and C2F2Cl3 were related to CO. Is this also true for other biogenic species such as isoprene?

Response: Accepted. Thank you for your comment. We stated that all species except β-pinene and

C2F2Cl3 were significantly related to CO ($p < 0.05$), which based on the p-value of the Pearson correlation. A p-value of less than 0.05 indicates there is a correlation relationship between CO and this species. The p-value for isoprene is less than 0.01, which means the Pearson correlation of isoprene and CO is significant at the 0.01 level (two-tailed). Isoprene is a topic biogenic species, however, Isoprene was detected at high percentage in vehicular exhaust as well (Liu et al., 2008). So isoprene was related to CO in urban area (Wang et al., 2014). Although most species were related to CO ($p < 0.05$), the R-values (correlation coefficients) for each species can be vary widely. Affected by the biogenic emissions, Isoprene had a strong correlation with CO in winter (R=0.77), and had a weaker correlation with CO in summer (R=0.18).

To make it clearer, in the revised manuscript, following sentence was added in section 3.2.2 "Affected by the biogenic emissions (Guenther et al., 2006), isoprene had a stronger correlation with CO in winter (R=0.77), and had a weaker correlation with CO in summer (R=0.18)".

References:

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, 2006.

Liu, Y., Shao, M., Fu, L. L., Lu, S. H., Zeng, L. M., and Tang, D. G.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42, 6247-6260, 10.1016/j.atmosenv.2008.01.070, 2008.

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 14, 5871-5891, 10.5194/acp-14-5871-2014, 2014.