Anonymous Referee #1

General Description of manuscript:

The authors developed an emission inventory of anthropogenic non-methane volatile organic compounds for Beijing-Tianjin-Hebei (BTH) region of China for 2015 using emission factor approach. Their estimate of total anthropogenic VOCs emissions over BTH in 2015 is 3277.66 Gg. The authors reported that their emission inventory shows significant consistence with both ambient measurements and satellite-derived emission inventory. PMF analysis of online measurements and their emission inventory show that vehicle emissions dominate the anthropogenic VOCs in Beijing. This study is interesting, and within the general scope of ACP. However, there are some weaknesses in current version. For example, many key statements come without citation; some references are inappropriate; some conclusions are not fully supported by their figures and numbers; some discussions are not quantitative. Therefore, I think this manuscript needs a major revision before it become suitable for 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. Activity data is quite important in EF-based emission inventory. Where did the activity data come from? Can you please provide a table of activity data for each source and for each category?

Response: Accepted. Thank you for your valuable suggestion. In the revised manuscript, 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. What is the monthly variability of the EF-based emission inventory? And what's the difference between your monthly emissions and the satellite-derived monthly emissions?

Response: Accepted. Thank you for your comment. 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 source in the Table S3 of the Supplementary Information.

In the revised manuscript, we provided the monthly variability of the EF-based emission inventory and discussed the difference between our monthly emissions and the satellite-derived monthly emissions. 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 the 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 shown 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 tiny because of little monthly variation in emissions from industrial processes, transportation, and solvent utilization (Wu and Xie, 2018). Monthly variations of the satellite-derived VOC emissions exhibit obvious seasonal characteristics, with the maximum in winter and minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios. Thus, the satellite-derived emission inventories may better reflect the monthly characteristics of VOC emissions.

In the revised manuscript, Figure 12 was revised and comparison between the monthly variations of the satellite derived emission inventory and EF-based emission inventory was added in section 3.4 as follows, "The temporal resolution of the satellite-derived emission inventory is one month. As shown in Fig. 12, monthly variations of VOC emissions exhibit obvious seasonal characteristics, with the maximum in winter and minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios (Fig. 5). However, monthly profiles for the EF-based emission inventory, which developed based on monthly statistics, didn't exhibit seasonal variations. EF-based VOC emission inventories developed by the other studies (Li et al., 2017; Wu and Xie, 2018) also didn't exhibit obvious seasonal variations because of little monthly variation in emissions from transportation, industrial processes, and solvent utilization (Wu and Xie, 2018). The satellite-derived emission inventories may better reflect the monthly characteristics of VOC emissions and be used to allocate monthly emissions". In addition, the subtitle of this part was changed to "Verification of spatial and temporal distributions."





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. Can you please add comparison between source structure from PMF analysis and that from your emission inventory for each season? As there might be a seasonal variability in source structure of your emission inventory.

Response: Accepted. Thank you for your suggestion. As we described in the response to your General Comment No.2, monthly profiles for EF-based emission inventories usually didn't exhibit seasonal variations.

In the revised manuscript, we added comparison between source structure from PMF analysis and that from our emission inventory for each season in Figure 9, and the following sentences were added in section 3.3.2 "Compared with the seasonal PMF results, the emissions from industrial processes, transportation, and solvent utilization of the emission inventory didn't exhibit obvious seasonal variations (Fig. 9). It is because the monthly profiles of these sources, which developed on monthly statistics, have little monthly variations (Wu and Xie, 2018). The emissions from fuel combustion of the emission inventory exhibit similar seasonal variations with the PMF results with much higher emissions in winter than the other seasons. However, the relative contribution of fuel combustion for each season in the emission inventory was significantly lower than the contribution in the PMF results, especially for winter. On the basis of the above comparisons of the VOC source structure, we inferred that: (1) the annual contributions of the vehicles, solvent utilization, and industrial processes from the emission inventory and the PMF results were similar, but the monthly profiles of these sources cannot replicate the temporal variations; and (2) the fuel combustion in the PMF analysis, especially in winter, the central heating season in Beijing."



Figure 9.Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right).

Specific Comments:

1. Line 33: "Their direct emission sources include biogenic and anthropogenic sources". Forest fire emissions are also worth to mention here. In addition, please include some appropriate citations here. **Response: Accepted.** Thank you for your suggestion. Forest fire emissions were mentioned and some appropriate citations were added here. In the revised manuscript, this sentence was revised to "Their direct emission sources include biogenic sources, forest fires, and anthropogenic sources (Guenther et al., 2006; Kansal et al., 2009; Simpson et al., 2011).

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.

Kansal, A.: Sources and reactivity of NMHCs and VOCs in the atmosphere: a review, J. Hazard. Mater., 166, 17-26, 10.1016/j.jhazmat.2008.11.048, 2009.

Simpson, I. J., Akagi, S. K., Barletta, B., Blake, N. J., Choi, Y., Diskin, G. S., Fried, A., Fuelberg, H. E., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Wennberg, P. O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R. J., and Blake, D. R.: Boreal forest fire emissions in fresh Canadian smoke plumes: C1-C10 volatile organic compounds (VOCs), CO2, CO, NO2, NO, HCN and CH3CN, Atmos. Chem. Phys., 11, 6445-6463, 10.5194/acp-11-6445-2011, 2011.

2. Line 42-46: Zhang et al. (2009) and Li et al. (2014) have done a lot work in compiling anthropogenic VOCs emissions over China. They are also worth to cite here.Response: Accepted. These studies were cited here.

3. Line 63-66: Both Karplus et al. (2018) and Henne et al. (2016) are not appropriate references here, because Karplus et al. (2018) talks about SO2 and Henne et al. (2016) talks about methane. Please include some NMVOC-related references here.

Response: Accepted. We are sorry for the inappropriate references. Fu et al. (2007) constrained the NMVOC emissions from multiple sources over East and South Asia by analyzing the spatiotemporal variability in the observed formaldehyde columns. Cao et al. (2018) used satellite retrievals along with a chemical transport model to constrain NMVOC emissions from China.

In the revised manuscript, the sentence was revised to "Since the satellite data possess the advantage of reflecting the spatial characteristics of VOCs (Fu et al., 2007), satellite-derived anthropogenic VOC emission estimations obtained from the chemical transport model can be utilized to evaluate the spatial distribution of the EF based emission inventories (Cao et al., 2018)". References:

Cao, H., Fu, T.-M., Zhang, L., Henze, D. K., Miller, C. C., Lerot, C., Abad, G. G., De Smedt, I., Zhang, Q., van Roozendael, M., Hendrick, F., Chance, K., Li, J., Zheng, J., and Zhao, Y.: Adjoint inversion of Chinese non-methane volatile organic compound emissions using space-based observations of formaldehyde and glyoxal, Atmos. Chem. Phys., 18, 15017-15046, 10.5194/acp-18-15017-2018, 2018. 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.

4. Line 67-69: Please include some references here to denote "Earlier studies" and "most studies". **Response:** Accepted. Gaimoz et al. (2011) evaluated the source structure of VOC emission inventories by source appointment with one month ambient measurements; Borbon et al. (2013) and Wang et al. (2014) evaluated the species-specific emissions by the emission ratios to an inert tracer; Cao et al. (2018) evaluate the spatial distribution by satellite retrievals. Gaimoz et al. (2011), Borbon et al. (2013) and Wang et al (2014) were based on the data from one, one, and two-month ambient measurements, respectively. In the revised manuscript, the references to denote "Earlier studies" and "most studies" were added as follows, "Earlier studies by various research groups applied only one of these methods to evaluate either the source structure or species-specific emissions of VOC emission inventories (Gaimoz et al., 2011; Borbon et al., 2013; Wang et al. 2014; Cao et al., 2018). Moreover, most studies have been based on the data from one or two-month ambient measurements, which cannot accurately represent the annual emissions (Gaimoz et al., 2011; Borbon et al., 2014; Cao et al., 2013; Wang et al., 2014)". 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.

Cao, H., Fu, T.-M., Zhang, L., Henze, D. K., Miller, C. C., Lerot, C., Abad, G. G., De Smedt, I., Zhang, Q., van Roozendael, M., Hendrick, F., Chance, K., Li, J., Zheng, J., and Zhao, Y.: Adjoint inversion of Chinese non-methane volatile organic compound emissions using space-based observations of formaldehyde and glyoxal, Atmos. Chem. Phys., 18, 15017-15046, 10.5194/acp-18-15017-2018, 2018.

Gaimoz, C., Sauvage, S., Gros, V., Herrmann, F., Williams, J., Locoge, N., Perrussel, O., Bonsang, B., d'Argouges, O., Sarda-Estève, R., and Sciare, J.: Volatile organic compounds sources in Paris in spring 2007. Part II: source apportionment using positive matrix factorisation, Environ. Chem., 8, 91, 10.1071/en10067, 2011.

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.

5. Line 105: what is "COPERT 4" short for? Please give a full name of this software when you first mention it.

Response: Accepted. "COPERT" is short for "COmputer Programme to calculate Emissions from Road Transport". In the revised manuscript, the full name of the software was added as "EFs were calculated by COmputer Programme to calculate Emissions from Road Transport version 4 (COPERT 4)".

6. Line 122-123: Where did "county-level", "city-level", and "provincial-level" data come from? Please include corresponding references here.

Response: Accepted. We are sorry for the unclear descriptions. In the revised manuscript, a table containing activity data and corresponding reference for each source and for each category was added in the supplementary information (Table S2).

7. Line 132: Please give the source profile of Wu and Xie (2017), you can put it in the supplementary information.

Response: Accepted. The source profile used in this study was added in the supplementary information (Table S4). In the revised manuscript, "The source profile database used in this study was listed in Table S4." was added.

8. Line 137: Please also give the height of roof site.

Response: Accepted. In the revised manuscript, the height of the roof site was added as follow: "The roof of the Technical Physics Building at Peking University, with a height of approximately 15 m above the ground (PKU, 39.99 N, 116.33 E, Fig. 1) was selected as the sampling site".

9. Line 169-170: Please give the emission ratios of VOC species relative to CO you obtained from the linear fit model.

Response: Accepted. The emission ratios of VOC species relative to CO obtained from the linear fit model were listed in Table S5.

10. Line 171-172: Please include references to support "(1) CO has similar sources as that of anthropogenic VOC and (2) CO emissions show lower uncertainty compared with VOC emissions". **Response: Accepted.** Thank you for your suggestion. A lot of studies have chosen CO as the reference compound to study the emission ratios for many cities in the world (Warneke et al., 2007; Coll et al., 2010; Borbon et al., 2013; Wang et al., 2014). Wang et al. (2014) calculated the emission ratios for Beijing and described that CO has similar sources as that of anthropogenic VOC in Beijing and the uncertainty of CO emissions are lower than that of VOC emissions in detailed. In the revised manuscript, references were added as follows "In this study, we selected CO as a reference compound considering that: (1) CO has similar sources as that of anthropogenic VOC and (2) CO emissions show lower uncertainty compared with VOC emissions (Warneke et al., 2007; Wang et al., 2014). Thus, CO was a suitable reference compound (Coll et al., 2010;Borbon et al., 2013;Wang et al., 2014)". 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.

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.

Coll, I., Rousseau, C., Barletta, B., Meinardi, S., and Blake, D. R.: Evaluation of an urban NMHC emission inventory by measurements and impact on CTM results, Atmos. Environ., 44, 3843-3855, 10.1016/j.atmosenv.2010.05.042, 2010.

Warneke, C., McKeen, S. A., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Holloway, J. S., Williams, E. J., Lerner, B. M., Parrish, D. D., Trainer, M., Fehsenfeld, F. C., Kato, S., Atlas, E. L., Baker, A., and Blake, D. R.: Determination of urban volatile organic compound emission ratios and comparison with an emissions database, J. Geophys. Res., 112, 10.1029/2006jd007930, 2007.

11. Line 177: Please include appropriate references on validation of CO emission inventory of MarcoPolo Project.

Response: Accepted. Thank you for your suggestion. MarcoPolo project is a collaborative research project 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. 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 Tsinghua University to estimate anthropogenic emissions China by over (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).

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.

12. Line 186-187: Can you please give a brief description (or formulas) on how your sampled VOCs uncertainties were calculated?

Response: Accepted. The observed uncertainty file was set following the method proposed by Polissar et al. (1998), which was recommended by the user guide of the PMF model. In the revised manuscript, the description was added as follows: "The observed uncertainty file was set following the method proposed by Polissar et al. (1998), which was recommended by the user guide of the PMF model. The uncertainty is calculated by Eq. (3), if the mixing ratio is equal to or less than the MDL; the uncertainty is calculated using Eq. (4), if mixing ratio if larger than the MDL (USEPA, 2014a).

Uncertainty
$$=\frac{5}{6} \times MDL$$
 Eq. (3)

Uncertainty =
$$\sqrt{(Error \ Fraction \ \times \ mixing \ ratio)^2 + (0.5 \ \times \ MDL)^2}$$
 Eq. (4)

References:

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol over Alaska: 2. Elemental composition and sources, J. Geophys. Res.-Atmos., 103, 19045-19057, 10.1029/98jd01212, 1998.

USEPA: Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, US Environmental Protection Agency, Office of Research and Development, Washington, D.C, 2014a.

13. Line 198: "...limited..." should be "...constrained..." **Response: Accepted.** "limited" was changed to "constrained".

14. Line 199-200: "HCHO is a high-yield product of VOCs species oxidation" should be "HCHO is a high-yield product of many VOCs species oxidation". Also, please include some appropriate references to support this sentence. Such as Millet et al. (2006), Stavrakou et al. (2015).

Response: Accepted. "HCHO is a high-yield product of VOCs species oxidation" was revised to "HCHO is a high-yield product of many VOCs species oxidation". And some appropriate references such as Millet et al. (2006), Stavrakou et al. (2015) were added.

15. Line 200: ". . . relative to. . ." should be ". . . against. . ." **Response: Accepted.** "relative to" was changed to "against".

16. Line 235: ". . . in January, with an average value of 62.26 ppbv"? But figure 5 shows that the January average was less than 60 ppbv.

Response: Accepted. Thank you for your comment. Figure 5 does not show the distribution of the data well. The following box-plot shows the distributions of the VOC mixing ratios in January, April, July, and October 2015. As shown in this figure, the January average was larger than 60 ppbv (red dot). In the revised manuscript, the box-plot was added in the Supplementary Information as Fig. S4.



Figure S4. Box-plot of VOC mixing ratios in in January, April, July, and October 2015.

17. Line 237: "In October, the average mixing ratio of VOCs was 50.64 ppbv". Again, the October average in figure 5 seems to be less than 50 ppbv.

Response: Accepted. Please refer to the figure shown in the response to the **specific comment #16**. The October average was larger than 50 ppbv (red dot).

18. Line 246: "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". Can you please provide some meteorological analysis or some references to support this sentence?

Response: Accepted. Thank you for your valuable comment. Time series of wind speed and VOC mixing ratios in October 2015 was shown in the following figure, which can support this sentence. In early October, the VOCs accumulated when the wind speed was low. Then VOCs decreased sharply when the wind speed became higher. And the VOC began to accumulate again with change of the wind speed. According to the comment of the other review, this paragraph is meaningless in this manuscript. The point of using the observations is to validate the inventory and this section should be concise.

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 paragraph 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"



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

19. Line 265: ". . .a few different emission sources from CO" should be ". . .a few emission sources different from CO sources"

Response: Accepted. "a few different emission sources from CO" was changed to "a few emission sources different from CO sources".

20. Line 275-277: "After the comparison with results obtained from measurements, the emissions for a majority of the non-methane hydrocarbon (NMHC) species were agreed within $\pm 100\%$ in the emission inventory". Can you please quantify the "a majority"?

Response: Accepted. There are 56 NMHC species measured by the GCMS/FID system in this study. The emissions for 51 NMHC species were agreed within $\pm 100\%$ in the emission inventory. In the revised manuscript, this sentence was revised to "the emissions for 51 of 56 kinds of non-methane hydrocarbon (NMHC) species were agreed within $\pm 100\%$ in the emission inventory, 15 species agreed within $\pm 50\%$, and 10 species agreed within $\pm 25\%$ ".

21. Line 277: "The emissions for acetonitrile came from the two methods were similar" doesn't seem to be supported by the acetonitrile emissions values (0.21 Ton yr-1 vs 16.52 Ton yr-1) listed in Table S2.

Response: Accepted. We are sorry for the mistake in Table S2. 0.21 was the ER value for acetonitrile instead of the emissions determined by the measurements (ER method). As shown in Fig. 6 and Fig.7, the acetonitrile emission value determined by the measurements be 106.7 Ton yr⁻¹. The acetonitrile emissions determined by the measurements (106.7 Ton yr⁻¹) is around 5 times the acetonitrile emissions determined by the emission inventory (16.52 Ton yr⁻¹).

In the revised manuscript, Table S2 is corrected. In addition, this sentence was revised to "The acetonitrile emissions determined by the measurements is around 5 times the acetonitrile emissions determined by the emission inventory".

22. Line 282-283: "The annual emissions for alkanes were in agreement between the two methods". Can you please quantify the "agreement"? As the detailed emission values of many alkanes in Table S2 have large difference between these two methods.

Response: Accepted. It is not appropriate to use "agreement" here. There are 27 alkane species measured by the GCMS/FID system in this study. The emissions for 25 alkane species were agreed within $\pm 100\%$ in the emission inventory, 8 species were agreed within $\pm 50\%$, and 6 species were agreed within $\pm 25\%$.

In the revised manuscript, this sentence was revised to "the annual emissions for alkanes were agreed within $\pm 100\%$ between the two methods, except ethane and propane, which are important tracers of natural gas and LPG".

23. Line 287: "The annual emissions for the alkenes, except ethene, correlated well". Again, please quantitatively state the "correlate well".

Response: Accepted. It is not appropriate to use "correlated well" here. In the revised manuscript, this sentence was revised to "The annual emissions for the alkenes, except ethene, were agreed within $\pm 100\%$ ".

24. Line 288-289: "Ethene and acetylene are mainly emitted through an incomplete combustion process". Please include appropriate references for this sentence.

Response: Accepted. We are sorry for the lack of references. Liu et al. (2008) experimentally determined the profiles of major VOC sources in China, and Mo et al. (2016) complied a database of VOC profiles for 75 species in China by measuring and available literature. Both of them indicated that ethene and acetylene are mainly emitted through an incomplete combustion process. In the revised manuscript, the references were added.

References:

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.

Mo, Z., Shao, M., and Lu, S.: Compilation of a source profile database for hydrocarbon and OVOC emissions in China, Atmos. Environ., 143, 209-217, 10.1016/j.atmosenv.2016.08.025, 2016.

25. Line 293-297: What's the local VOC emission standards? Can you please give a reference?

Response: Accepted. We are sorry for the lack of references. Beijing had issued local VOC emission standards for many solvent utilization sources since 2015. These emission standards included "Emission standard of volatile organic compounds for printing industry (DB11/1201-2015)", "Emission standard of air pollutants for wood furniture (DB11/1202-2015)", "Emission standard of air pollutants for industrial surface coating (DB11/1226-2015)", "Emission standard of air pollutants for printing industry (DB11/1227-2015)", and "Emission standard of air pollutants for vehicle maintenance and repair industry (BD11/1228-2015)". In the revised manuscript, the code names for these emission standards were added "The common character of these sources is that Beijing had issued local VOC emission standards for the above sources since 2015 (DB11/1201-2015; DB11/1202-2015; DB11/1226-2015; DB11/1227-2015;

BD11/1228-2015)".

26. Line 303: "...reaction..." should be "reactivity".Response: Accepted. "reaction" was changed to "reactivity".

27. Line 316: "appointment" should be "apportionment"?Response: Accepted. "appointment" was changed to "apportionment".

28. Line 323-335: Can you please add some comparison between your PMF analysis with PMF analysis from other studies during these seasons?

Response: Accepted. Thank you for your suggestion. We compared the PMF result in this study with PMF analysis from other studies conducted in Beijing during these seasons.

In the revised manuscript, Comparison of the relative contributions of sources of VOC emissions in Beijing calculated by the PMF model in this study and results from the other studies was added in Table S7 of the Supplementary Information. Following descriptions were added in section 3.3.1 "Comparison of the relative contributions of VOC emission sources in Beijing calculated by the PMF model of this study and results from the other studies during these seasons was listed in Table S7. Results of this and other studies have shown that the fuel combustion was the largest VOC contributor in winter. The contribution proportions of fuel combustion in winter were ranged from 45% - 55% (Li et al., 2015, Yang et al., 2018). Results of this and other studies have shown that vehicle-related source was the largest VOC contributor in summer and winter, with the contribution ranged from 50% - 57%, and 33% - 42%, respectively. The contribution proportion of summer biogenic emission in this study was larger than that in the other studies".

Table S7. Comparison of the relative contributions of sources of VOC emissions in Beijing calculated by the PMF model in this study and results from the other studies.

Reference	Sampling period			Cita tama	Source categories					
	Year	Period	Season	Site type	Vehicle	Industrial	Solvent	Fuel	Biogenic	Others ^a
This study	2015	April	Spring	Urban	22%	21%	7%	12%	5%	33%
This study	2015	July	Summer	Urban	50%	6%	12%	4%	18%	10%
Song et al.,2007	2005	1–26 August	Summer	Urban	55%	20%	5%	5%	2%	11%
Li et al.,2016	2015	11–19 August	Summer	Urban	57%	4%	14%	10%	1%	14%
Yuan et al., 2009	2006	15 August to 10 September	Summer to Autumn	Urban	62%		16%	6%	3%	13%
Yuan et al., 2009	2006	15 August to 10 September	Summer to Autumn	Rural	39%		14%	3%	8%	37%
This study	2015	October	Autumn	Urban	33%	16%	23%	6%	5%	18%
Wu et al., 2016	2014	1–15 October	Autumn	Urban	49%	11%	9%	22%		9%
Li et al.,2015	2014	18-31 October	Autumn	Urban	43%	22%	12%	9%		14%
Yang et al.,2018	2014	25 October–2 November	Autumn	suburban	42%	14%	22%	22%		0%
This study	2015	January	Winter	Urban	19%	14%	3%	55%	1%	7%
Li et al.,2015	2014	13–22 November	Winter	Urban	20%	14%	11%	45%		10%
Yang et al.,2018	2014	13 November-13 December	Winter	suburban	17%	25%	13%	45%		0%

^a The source categories of different PMF studies are different. Except for some comment categories (vehicle, industrial processes, solvent utilization, fuel combustion, and biogenic), there are some other categories such as aged air mass, long-lived species, biomass burning,

background, secondary formation, LPG, NG, which were defined as others in Table S7.

References:

Li, J., Wu, R., Li, Y., Hao, Y., Xie, S., and Zeng, L.: Effects of rigorous emission controls on reducing ambient volatile organic compounds in Beijing, China, Sci. Total. Environ., 557-558, 531-541, 10.1016/j.scitotenv.2016.03.140, 2016.

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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.

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.

Yang, W., Zhang, Y., Wang, X., Li, S., Zhu, M., Yu, Q., Li, G., Huang, Z., Zhang, H., Wu, Z., Song, W., Tan, J., and Shao, M.: Volatile organic compounds at a rural site in Beijing: influence of temporary emission control and wintertime heating, Atmos. Chem. Phys., 18, 12663-12682, 10.5194/acp-18-12663-2018, 2018.

Yuan, Z., Lau, A. K. H., Shao, M., Louie, P. K. K., Liu, S. C., and Zhu, T.: Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing, J. Geophys. Res., 114, 10.1029/2008jd011190, 2009.

29. Line 384: Can you please make markers of Xingtai and Handan on the maps of figure 13? **Response: Accepted.** The name of each city was added in figure 13 as follows:



30. Line 386-391: The subtitle of this part is "Verification of spatial distribution", but here you are discussing the monthly variabilities of satellite-derived emissions and another bottom-up emission inventory (Li et al., 2017) at length. It seems a little odd. If you want to discuss monthly variation, can you please provide the comparison between your monthly VOCs emissions and satellite-derived monthly emissions? And also, please keep the subtitle consistent with your text.

Response: Accepted. Thank you for your suggestion. Because EF-based VOC emission inventories usually didn't exhibit obvious seasonal variations for little monthly variation in monthly statistics (Li et al., 2017; Wu and Xie, 2018). So we discussing the monthly variabilities of satellite-derived emissions and another bottom-up emission inventory (Li et al., 2017). I agreed it seems odd.

In the revised manuscript, we compared the monthly profiles between the satellite-derived emission inventory and our EF-based emission inventory in Figure 12. And the subtitle of this part was changed to "Verification of spatial and temporal distributions". For the detailed method and comparison about the monthly distribution please refer to the response to the **General Comment #2**.

31. Line 392-393: Again, Geng et al. (2017) talks about NO2 and NOx emissions. Can you please include some appropriate references on top-down VOCs emissions and OVOC satellite observations? Such as Palmer et al. (2006), Fu et al. (2007), Marais et al. (2014), Stavrakou et al. (2015), Bauwens et al. (2016).

Response: Accepted. Thanks a lot for providing these appropriate references. In the revised manuscript, these references were added as follows: "The satellite-derived emission inventory possesses the advantage of efficiently reflecting the spatial and monthly characteristics of the VOC emissions (Palmer et al., 2006; Fu et al., 2007; Marais et al., 2014; Stavrakou et al., 2015; Bauwens et al., 2016).".

32. Line 407-408: Again, can you please quantify the consistence between the NMHCs emissions derived from online measurements and those from your emission inventory?

Response: Accepted. In the revised manuscript, it was revised to "the annual emissions of 91% NMHCs derived from the measurements were agreed within $\pm 100\%$ with the results of the emission inventory".

33. Table 1.: What are "1,1,2,2-" and "1,2-" in the last 3 rows? **Response: Accepted.** We are sorry for the wrong format of Table 1. In the revised manuscript, Table 1 is corrected.

34. Figure 2.: The unit "Ton/grid" should be "Ton year⁻¹ grid⁻¹". **Response: Accepted.** The unit "Ton/grid" was revised to "Ton year⁻¹ grid⁻¹".

35. Figure 4.: What's the difference between "Other VOCs" and "Others" in the bar plot? What's "Other thenes"? Why is "Others" the largest contributor in bar plot, while it is the smallest one in the pie plot?

Response: Accepted. We are sorry for the misleading descriptions. VOCs consist thousands of compounds. We determined a unified species list for source profiles (Table S4). These species were measurable, abundant, or highly reactive in the atmosphere (Wu et al., 2017), which can be group into alkanes, alkenes, alkynes, aromatics, halocarbons, OVOCs, nitriles, and others.

The pie plot in Fig.4 showed the contributions of each VOC groups. Because the measured VOC species from identical sources typically varied among different studies, there are some VOC species didn't belong to the VOC groups (alkanes, alkenes, alkynes, aromatics, halocarbons, OVOCs, and nitriles). These species were group into "**Others**" in the pie plot. The name of species in the bar plot is consistent with the source profile database (Table S4). Because the space is limit, we only displayed the top 35 VOC species with the largest VOC emissions. The emission of all the other VOC (except the top 35 VOC species) added together was defined as emission from "**Others**" in the bar plot. Thus,

the "Others" is the largest contributor in bar plot, while it is the smallest one in the pie plot.

The name of top 35 VOC species in the bar plot is consistent with the species name in the source profile database. The source profile database consisted of 152 individual species in total. In the database, there are 16 abundant alkenes, and the other alkenes except the 16 abundant alkenes were defined as **"Other alkenes"**. We tried our best to determine VOC species according to available source profiles, however, there are some VOC species were defined as "**Other VOC**" in some source profiles. So we defined the "unknown" or "other VOC" as **"Other VOCs"** in the database. In the revised manuscript, we changed the "Other VOCs" in the database to "**Unspecific VOCs**".

In order to make it clearer, Figure 4 and related description were revised as follows: "Figure 4 illustrates the chemical compositions of VOC emissions in the BTH region. Emissions of a total of 152 VOC species (Table S4) bellowing to alkanes, alkenes, alkynes, aromatics, halocarbons, OVOCs, nitriles, and others were calculated in this study. The emissions of aromatics, alkanes, OVOCs, and alkenes accounted for 34%, 32%, 17%, and 11% of total anthropogenic VOC emissions, respectively."



Figure 4. The top 30 VOC species with the highest emissions (bar plot) and the contributions of VOC groups to the total emsssions (pie plot) in the BTH region, China.

References:

Wu, R., and Xie, S.: Spatial Distribution of Ozone Formation in China Derived from Emissions of Speciated Volatile Organic Compounds, Environ. Sci. Technol., 51, 2574-2583, 10.1021/acs.est.6b03634, 2017.

36. Line 580-586: ". . .Sci Total Environ . . ." in line 582, and ". . .Journal Of Geophysical Research-Atmospheres. . ." in line 585. The formats of references are not unified. Please unify the reference format throughout the whole references.

Response: Accepted. The reference format throughout the whole references was checked and corrected.

Review References:

Bauwens, M., Stavrakou, T., Müller, J.-F., De Smedt, I., Van Roozendael, M., van der Werf, G. R., Wiedinmyer, C., Kaiser, J. W., Sindelarova, K., and Guenther, A.: Nine years of global hydrocarbon emissions based on source inversion of OMI formaldehyde observations, Atmos. Chem. Phys., 16, 10133-10158, <u>https://doi.org/10.5194/acp-16-</u>10133-2016, 2016.

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Marais, E. A., Jacob, D. J., Guenther, A., Chance, K., Kurosu, T. P., Murphy, J. G., Reeves, C. E., and Pye, H. O. T.: Improved model of isoprene emissions in Africa using Ozone Monitoring Instrument (OMI) satellite observations of formaldehyde: implications for oxidants and particulate matter, Atmos. Chem. Phys., 14, 7693-7703, https://doi.org/10.5194/acp-14-7693-2014, 2014

Millet, D. B., Jacob, D. J., Turquety, S., Hudman, R. C., Wu, S., Fried, A., Walega, J., Heikes, B. G., Blake, D. R., Singh, H. B., Anderson, B. E., and Clarke, A. D.: Formaldehyde distribution over North America: Implications for satellite retrievals of formaldehyde columns and isoprene emission, J. Geophys. Res., 111, D24S02,https://doi.org/10.1029/2005jd006853, 2006.

Palmer, P. I., Abbot, D. S., Fu, T.-M., Jacob, D. J., Chance, K., Kurosu, T. P., Guenther, A., Wiedinmyer, C., Stanton, J. C., Pilling, M. J., Pressley, S. N., Lamb, B., and Sumner, A. L.: Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column, J. Geophys. Res., 111, D12315, https://doi.org/10.1029/2005jd006689, 2006.

Stavrakou, T., Müller, J.-F., Bauwens, M., De Smedt, I., Van Roozendael, M., De Mazi ère, M., Vigouroux, C., Hendrick, F., George, M., Clerbaux, C., Coheur, P.-F., and Guenther, A.: How consistent are top-down hydrocarbon emissions based on formaldehyde observations from GOME-2 and OMI?, Atmos. Chem. Phys., 15, 11861–11884, https://doi.org/10.5194/acp-15- 11861-2015, 2015.

Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emis- sions in 2006 for the NASA INTEX-B mission, Atmos. Chem. Phys., 9, 5131–5153, https://doi.org/10.5194/acp-9-5131-2009, 2009.

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.

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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.

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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.

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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 $\pm 100\%$ in the emission inventory, 15 species were agreed within $\pm 50\%$, and 10 species were agreed within $\pm 25\%$. 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 $\pm 100\%$ in the emission inventory, 15 species agreed within $\pm 50\%$, and 10 species agreed within $\pm 25\%$ ". Line 287 was revised to "The annual emissions for the alkenes, except ethene, were agreed within $\pm 100\%$ ".

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

for alkanes were agreed within $\pm 100\%$ 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 $\pm 100\%$ 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 $\pm 100\%$ with the results of 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 Tsinghua University to estimate anthropogenic emissions China by over (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.

Anonymous Referee #3

Summary and recommendation

Li et al. compile a new VOC emissions inventory for the Beijing-Tianjin-Hebei metro area, and validate it against in-situ VOC concentrations and satellite-derived emissions within the region. The new VOC observations and emission inventory are within the scope specified by ACP, representing a contribution to "substantial new data." In the present version of the manuscript there are some weaknesses in the analysis comparing the new inventory to the validation datasets. I will recommend publication once these issues are addressed.

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. As the first reviewer said, the activity data is important for the construction of the inventory, and it is also not clear to me where this is sourced from. This information definitely needs to be provided in the main manuscript.

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. In section 3.2, much of the focus was comparing the speciation of the emission inventory based on CO ratios at the PKU site. This ultimately depends on how representative the PKU site is at the spatiotemporal scale of comparison. The PMF results remove a lot of these complications by decomposing the variability into a set of dominant modes corresponding to source types that can more easily be compared to the sector-based speciation in the inventory. This is likely a more quantitative comparison of the skill of the inventories speciation, and thus should be a greater focus.

Response: Accepted. Thank you for your valuable suggestion. The approach for calculation of VOC emissions based on ambient measurements has several limitations and uncertainties. The description of the method was unclear. In the revised manuscript, we revised the description of the method and added some discussion about the evaluation method in section 2.3.1.Please refer to the response to **specific comment #6** for detailed changes. We agreed that PMF results are a reliable test on the inventory speciation. According to your suggestion, we also compared the source profiles derived from the PMF against their attributed sources from the inventory to test on the inventory speciation. Please refer to the response to specific comment #8 for detailed changes.

3. I also so no temporal validation of the emissions inventory. The discussion of Fig. 14 in section 3.4 seems to indicate there is no temporal variation in the emissions inventory, which would be a major weakness considering the seasonal variation showed by the top-down satellite inventory. If there is no seasonality then I believe this must be included before final publication. The seasonality in total VOC emissions must be validated against the satellite inventory, and the sector based emissions can be

assessed by comparing against the PMF source factor weightings.

Response: Accepted. Thank you for your valuable suggestion. Because EF-based VOC emission inventories usually didn't exhibit obvious seasonal variations for little monthly variation in monthly statistics (Li et al., 2017; Wu and Xie, 2018). Therefore, we discussed the monthly variabilities of satellite-derived emissions and another bottom-up emission inventory (Li et al., 2017). In the revised manuscript, we provided the monthly variability of our EF-based emission inventory and it was validated against the satellite inventory. We also validated the seasonal source structure of our EF-based emissions against the PMF source factor results.

The monthly profile can calculate the monthly VOC emissions of EF-based emission inventories 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 source 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 the 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 shown in Figure 12, which didn't exhibit apparent 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 tiny because of little monthly variation in emissions from industrial processes, transportation, and solvent utilization (Wu and Xie, 2018). Monthly variations of the satellite-derived VOC emissions exhibit obvious seasonal characteristics, with the maximum in winter and minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios. Thus, the satellite-derived emission inventories may better reflect the monthly characteristics of VOC emissions.

In the revised manuscript, Figure 12 was revised, and comparison between the monthly variations of the satellite-derived emission inventory and EF-based emission inventory was added in section 3.4 as follows "The temporal resolution of the satellite-derived emission inventory is one month. As shown in Fig. 12, monthly variations of VOC emissions exhibit obvious seasonal characteristics, with the maximum in winter and minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios (Fig. 5). However, monthly profiles for the EF-based emission inventory, which developed based on monthly statistics, didn't exhibit seasonal variations. EF-based VOC emission inventories developed by the other studies (Li et al., 2017; Wu and Xie, 2018) also didn't exhibit obvious seasonal variations because of little monthly variation in emissions from transportation, industrial processes, and solvent utilization (Wu and Xie, 2018). The satellite-derived

emission inventories may better reflect the monthly characteristics of VOC emissions and be used to allocate monthly emissions". In addition, the subtitle of this part was changed to "Verification of spatial and temporal distributions".



Figure 12. Monthly variability of VOC emissions from the satellite-derived and EF-based emission inventories.

In the revised manuscript, we added comparison between source structure from PMF analysis and that from our emission inventory for each season in Figure 9. The following sentences were added in section 3.3.2, "Compared with the seasonal PMF results, the emissions from industrial processes, transportation, and solvent utilization of the emission inventory didn't exhibit obvious seasonal variations (Fig. 9). It is because the monthly profiles of these sources, which developed on monthly statistics, have little monthly variations (Wu and Xie, 2018). The emissions from fuel combustion of the emission inventory exhibit similar seasonal variations with the PMF results with much higher emissions in winter than the other seasons. However, the relative contribution of fuel combustion for each season in the emission inventory was significantly lower than the contribution in the PMF results, especially for winter. On the basis of the above comparisons of the VOC source structure, we inferred that: (1) the annual contributions of the vehicles, solvent utilization, and industrial processes from the emission inventory and the PMF results were similar, but the monthly profiles of these sources cannot replicate the temporal variations; and (2) the fuel combustion in the PMF analysis, especially in winter, the central heating season in Beijing."



Figure 9.Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right).

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.

Specific Comments

1. Figure 1: Please indicate the Beijing, Tianjin, and Hebei regions separately on the middle panel of the figure, as these are referenced individually throughout the text.

Response: Accepted. Thank you for your comment. In the revised manuscript, the middle panel of Figure 1 was revised as follow:



2. Line 201: "Its [HCHOs] column concentration is directly related to emissions" This also depends on the lifetime of the precursor VOC.

Response: Accepted. Thank you for your comment and we are sorry for the inappropriate description. In the revised manuscript, the sentence was revised to "Its column concentration is directly related to the emission of reactive VOCs (De Smedt et al., 2015)".

Reference:

De Smedt, I., Stavrakou, T., Hendrick, F., Danckaert, T., Vlemmix, T., Pinardi, G., Theys, N., Lerot, C., Gielen, C., Vigouroux, C., Hermans, C., Fayt, C., Veefkind, P., Müller, J. F., and Van Roozendael, M.: Diurnal, seasonal and long-term variations of global formaldehyde columns inferred from combined OMI and GOME-2 observations, Atmos. Chem. Phys., 15, 12519-12545, 10.5194/acp-15-12519-2015, 2015.

3. Line 233: "Figure 5 presents the averaging mixing ratios..." Also indicate in the text that Figure 5 is showing observations at the PKU site.

Response: Accepted. In the revised manuscript, the sentence was revised to "Figure 5 presents the average mixing ratios and chemical compositions of VOCs measured at the PKU site in January, April, July, and October 2015".

4. Line 241: "Figure 6 presents the time series of VOC mixing ratios . . ." I am not sure what this paragraph/figure is getting at. There are a range of factors driving the variability in the instantaneous observations, including stability of the boundary layer, diurnal/seasonal variation in emissions, transport to the site etc. The point of using the observations is to validate the inventory. For instance, one could put the inventory into a chemical transport model and test if it can replicate the site variability in VOC concentrations. Short of doing something like this, I am not sure what the Figure is trying to show.

Response: Accepted. Thank you for your comment. We agree that this paragraph/figure is meaningless. In the revised manuscript, this paragraph was removed, and figure 6 was moved to the Supplementary Information.

5. Line 251: "Benzene and toluene were important VOC..." Barletta et al. (2005) discussion

Benzene/Toluene ratios of different combustion sources from a survey of Chinese cities. Perhaps your discussion here can reference this in relation to the different sources. Reference Barletta et al. (2005) "Volatile organic compounds in 43 Chinese cities" <u>https://doi.org/10.1016/j.atmosenv.2005.06.029</u>

Response: Accepted. Thank you for your suggestion. Barletta et al. (2005) can support our discussion here. The reference was added in the revised manuscript as follow: "Benzene and toluene were important VOC species. During combustion processing, the emissions of benzene are much higher than toluene (Barletta et al., 2005)".

6. Line 266: "Table 2 lists the emission ratios for individual VOCs. . ." The following 2 paragraphs make the implicit assumption that emission ratios of the VOCs in the 0.25x0.25 degree grid box surround the PKU site are representative of the concentration ratios of VOCs within the site. In general I think it is difficult to assess this in a quantitative way without modelling. For instance, transport from surrounding grid boxes may be important. Also the diurnal structure of emissions will also play a role - sources that have relatively higher night-time emissions will have an outsized impact on the concentration ratio, due to the higher boundary layer stability and reduction in chemical processing. It is for reasons such as these that I find a comparison of the concentration ratios vs. emission ratios difficult.

Response: Accepted. Thank you for your comment. We are sorry for the unclear description of the method we used. We agreed that the VOC concentrations obtained from field observations could not be directly compared with the VOC emissions of the grid box due to some physical (pollutant transport, change of boundary layer height or sedimentation) and chemical transformation processes. There are some commonly used methods can help to compare the VOC concentrations and emissions, including chemical transport model simulation, satellite inversion, receptor modelling, and the "emission ratio" method (Borbon et al., 2013).

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). In order to reduce the influence of the chemical process, the ratios should be calculated excluding or correcting the effect of photochemical processing on measured VOC (Wang et al., 2014). A commonly used method to determine emission ratios is to utilize a linear regression fit, and temporal filters (nighttime) can be applied to account for the influence of chemistry (Borbon et al., 2013).

In this study, we choose CO as the trace gas, and we use the nighttime linear regression fit method to determine the emission ratios, then we calculated the emissions of individual VOC species based on the emission ratios and CO emissions. According to Wang et al. (2014), the local time period 03:00 to 07:00 was set as a temporal filter to reduce the impact of photochemical processing. 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., 2014; Li et al., 2015; Wu et al., 2016). 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. 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. 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. Although the online VOC measurement is difficult and costly; we recommend more online VOC measurements be conducted.

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. In addition, this approach relies on the assumption that the composition of urban emissions relative to CO. Chemical transport model simulation is an ideal approach to verify emission inventories based on field observations. We will recommend and try to use this approach to verify the emissions in future study. According to your suggestion, we also compared the source profiles derived from the PMF against their attributed sources from the inventory to test on the inventory speciation. Please refer to the response to specific comment # 8.

In order to make it clear, in the revised manuscript, more detailed description of the method and the limitation was added in section 2.3.1 as follows:

2.3.1 Species VOC emissions based on ambient measurements.

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 calculation of annual emissions for individual VOC species is performed based on Eq. (2):

$$E_{VOC} = E_{Ref} \times ER_{VOC} \times MW_{VOC} / MW_{Ref}$$

Eq. (2)

where, EVOC denotes the emission of a particular VOC species per year (Gg); E_{Ref} denotes the emission of the reference compound per year (Gg); MW_{VOC} denotes the molecular weight of a particular VOC species; MW_{Ref} denotes the molecular weight of the reference compound; and ER_{VOC} denotes the emission ratio of VOC species relative to the reference compound (ppbv (ppmv Ref)⁻¹).

Photochemical processing is an important factor influencing the chemical compositions of VOCs in ambient air. Thus, the way in which photochemical processing impacts the measured VOC ratios should be excluded or corrected using a temporal filter (Borbon et al., 2013). The local time period 03:00 to 07:00 was set as a temporal filter to reduce the impact of photochemical processing (Wang et al., 2014). The emission ratios of VOC species to the reference compound (ERVOC) from 03:00 to 07:00 local time were estimated using the linear fit model.

In this study, we selected CO as a reference compound considering that: (1) CO has similar

sources as that of anthropogenic VOC and (2) CO emissions show lower uncertainty compared with VOC emissions (Warneke et al., 2007; Wang et al., 2014). Thus, CO was a suitable reference compound (Coll et al., 2010; Borbon et al., 2013; Wang et al., 2014). The CO levels in the ambient air were obtained from the Wanliu National Air Quality Monitoring Station (http://zx.bjmemc.com.cn). 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 based on the chemical transport model (Hu et al., 2017), satellite observations (Yumimoto et al., 2014), and comparison with other studies (Li et al., 2017a) and measurement data. The spatial resolution of this CO emission inventory is $0.25 \circ \times 0.25 \circ$. To obtain reasonable results, we compared the VOC emissions of the grid where the PKU site was located (Fig. S1).

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 multiple sampling sites would be more reliable and some other method such as chemical transport model simulation may be 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.

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7. Line 277: "the annual emissions of many OVOCs and halocarbons were much lower..." Here it is suggested that OVOCs are underestimated by the emission inventory. However secondary production through the oxidation of precursor VOCs will have a similar impact.

Response: Accepted. Thank you for your comment. As described in section 2.3.1, in order to reduce the impact of secondary production, the local time period 03:00 to 07:00 was set as a temporal filter. The emission ratios of VOC species to the reference compound (ERVOC) from 03:00 to 07:00 local time were estimated using the linear fit model.

While we try to reduce the impact of secondary production, but it still will have some impact. In the revised manuscript, following sentence was added in section 3.2.2 "In addition, secondary production through the oxidation of precursor VOCs might impact the accuracy of OVOC emission estimated from the observations".

8. Line 317: "The PMF receptor model. . ." Here in Figure 9 I would like to see a comparison between the source profiles derived from the PMF against their attributed sources from the inventory. I believe this is a more reliable test on the inventory speciation.

Response: Accepted. Thank you for your valuable suggestion. In the revised manuscript, Figure 9 was removed to the Supplementary Information as Figure S5. Comparison of source profiles for VOCs calculated by PMF and the emission inventory was presented in Figure 8. The following sentences were added "Figure 8 illustrates the comparison between source profiles derived from the PMF against their attributed sources from the emission inventory. The source profiles for fuel combustion agreed between the two methods. For the source profiles of transportation, the contributions of C2 – C4 alkanes derived from the PMF were larger than contributions from the emission inventory. Aromatics were the dominant group in the source profiles for solvent utilization derived from the two methods. For the source profiles of some halocarbons OVOCs from the PMF were larger than proportions from the emission inventory. The finding agreed with the results of section 3.2.2 that the proportions of OVOCs and halocarbons in the source profile database may be



Figure 8. Source profiles for VOCs calculated by PMF and the emission inventory (Species name was shown in Table S4) .

9. Line 323: "Figure 10 illustrates source contributions percentages..." In Figure 10 it would be useful to compare the source contribution percentages derived from the PMF to those from the inventory, to address whether the inventory can or cannot replicate the temporal variations in source categories. Instead of using the Pie charts you could make a bar graph like the one in Fig. 5, putting the results of the inventory next to the observations, or just show the absolute VOC source totals as coloured lines for the four months. Doing this, you probably don't need to make the yearly comparison (Fig 11).

Response: Accepted. Thank you for your valuable suggestion. In the revised manuscript, Figure 10 was revised accordingly. Figure 11 was moved to the Supplementary Information, and the following sentences were added in section 3.3.2 "Compared with the seasonal PMF results, the emissions from industrial processes, transportation, and solvent utilization of the emission inventory didn't exhibit obvious seasonal variations (Fig. 9). It is because the monthly profiles of these sources, which developed on monthly statistics, have little monthly variations in the monthly profiles (Wu and Xie, 2018). The emissions from fuel combustion of the emission inventory exhibit similar seasonal

variations with the PMF results with much higher emissions in winter than the other seasons. However, the relative contribution of fuel combustion for each season in the emission inventory was significantly lower than the contribution in the PMF results, especially for winter. On the basis of the above comparisons of the VOC source structure, we inferred that: (1) the annual contributions of the vehicles, solvent utilization, and industrial processes from the emission inventory and the PMF results were similar, but the monthly profiles of these sources cannot replicate the temporal variations; and (2) the fuel combustion in the emission inventory showed a considerably lower relative contribution than the value from the PMF analysis, especially in winter, the central heating season in Beijing."



Figure 9.Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right).

10. Line 385: "The temporal resolution of the satellite-derived emissions inventory. . ." It would be useful to compare the temporal resolution of the EF-inventory to the satellite. If it is not there then it needs to be considered.

Response: Accepted. Thank you for your valuable suggestion. Because EF-based VOC emission inventories usually didn't exhibit obvious seasonal variations because of little monthly variation in monthly statistics (Li et al., 2017; Wu and Xie, 2018). Therefore, we discussed the monthly variabilities of satellite-derived emissions and another bottom-up emission inventory (Li et al., 2017). In the revised manuscript, we provided the monthly variability of our EF-based emission inventory, and it was validated against the satellite inventory.

The monthly VOC emissions of EF-based emission inventories can be calculated by the 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 source 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 the 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 shown 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 tiny because of little monthly variation in emissions from industrial processes, transportation, and solvent utilization (Wu and Xie, 2018). Monthly variations of the satellite-derived VOC emissions exhibit obvious seasonal characteristics, with the maximum in winter and minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios. Thus, the satellite-derived emission inventories may better reflect the monthly characteristics of VOC emissions.

In the revised manuscript, Figure 12 was revised and comparison between the monthly variations of the satellite derived emission inventory and EF-based emission inventory was added in section 3.4 as follows, "The temporal resolution of the satellite-derived emission inventory is one month. As shown in Fig. 12, monthly variations of VOC emissions exhibit obvious seasonal characteristics, with maximum the in winter and minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios (Fig. 5). However, monthly profiles for the EF-based emission inventory, which developed based on monthly statistics, didn't exhibit seasonal variations. EF-based VOC emission inventories developed by the other studies (Li et al., 2017; Wu and Xie, 2018) also didn't exhibit obvious seasonal variations because of little monthly variation in emissions from transportation, industrial processes, and solvent utilization (Wu and Xie, 2018). The satellite-derived emission inventories may better reflect the monthly characteristics of VOC emissions and be used to allocate monthly emissions". In addition, the subtitle of this part was changed to "Verification of spatial and temporal distributions."



Figure 12. Monthly variability of VOC emissions from the satellite-derived and EF-based emission inventories.
List of all relevant changes made in the manuscript

Position in					
the revised	Previous Version	Revised Version			
manuscript					
Line 18	spatial	spatial and temporal			
	The annual emissions for of non-methane				
Lina 21 22	hydrocarbon species (NMHCs) derived from the	The annual emissions for 51 of 56 kinds of non-methane hydrocarbon species derived from			
Line 21-25	measurements were significantly consistent with	the measurements were agreed within $\pm 100\%$ with the results of the emission inventory.			
	the results of the emission inventory.				
Line 24	clearly	Deleted			
Line 24 25	Their direct emission sources include biogenic and	Their direct emission sources include biogenic sources, forest fires, and anthropogenic			
Line 34-35	anthropogenic sources.	sources (Guenther et al., 2006;Kansal, 2009;Simpson et al., 2011).			
Line 39	ambient concentrations	production			
Line 42	important	essential			
Line 45-47	(Tonooka et al., 2001;Streets, 2003;Klimont et al., 2002;Ohara et al., 2007;Bo et al., 2008; Zheng et al., 2009;Wu et al., 2016a;Huang et al., 2017;Janssens- Maenhout et al., 2015)	(Tonooka et al., 2001;Streets, 2003;Klimont et al., 2002;Ohara et al., 2007;Bo et al. 2008;Zhang et al., 2009;Zheng et al., 2009;Li et al., 2014;Wu et al., 2016a;Huang et al. 2017;Janssens-Maenhout et al., 2015)			
Line 55	VOCs is key for effectively controlling and reducing air pollution in the future.	VOCs is key to effectively control and reduce air pollution in the future.			
Line 64-67	Since the satellite data possess the advantage ofreflectingthe spatial characteristics of VOCs(Karplusetal.,2018),satellite-derived	Since the satellite data possess the advantage of reflecting the spatial characteristics of VOCs (Fu et al., 2007), satellite-derived anthropogenic VOC emission estimations			

	anthropogenic VOC emission estimations obtained	obtained from the chemical transport model can be utilized to evaluate the spatial
	from the chemical transport model can be utilized to	distribution of the EF based emission inventories (Cao et al., 2018).
	evaluate the spatial distribution of the EF based	
	emission inventories (Henne et al., 2016).	
Line 68-72	Earlier studies by various research groups applied only one of these methods to evaluate either the source structure or species-specific emissions of VOC emission inventories. Moreover, most studies have been based on the data from one or two-month ambient measurements, which cannot accurately represent the annual emissions	Earlier studies by various research groups applied only one of these methods to evaluate either the source structure or species-specific emissions of VOC emission inventories (Gaimoz et al., 2011; Borbon et al., 2013; Wang et al. 2014; Cao et al., 2018). Moreover, most studies have been based on the data from one or two-month ambient measurements, which cannot accurately represent the annual emissions (Gaimoz et al., 2011; Borbon et al., 2013; Wang et al., 2013; Wang et al., 2011; Borbon et al., 2013; Wang et al., 2013; Wang et al., 2014; Cao et al., 2014; Cao et al., 2014; Cao et al., 2014; Cao et al., 2018).
Line 83	spatial	Spatial-temporal
Line 107	COPERT	COmputer Programme to calculate Emissions from Road Transport version 4 (COPERT 4)
Line 126		Add Table S2
Line 135-136		The source profile database used in this study was listed in Table S4.
Line 137-144		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 the 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).				
Line 147-148	The roof of the Technical Physics Building at Peking University	The roof of the Technical Physics Building at Peking University, with a height of approximately 15 m above the ground				
Line 150-151	This site selected represents the typical urban environment of Beijing and is far from strong direct emissions	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)				
Line 153		The sampling and analysis method of this study follow the US EPA Method TO-15 (USEPA, 1999).				
Line 155		(TH-PKU 300B, Wuhan Tianhong Instrument Co. Ltd., China).				
Line 156		(GCMS-QP2010, Shimadzu Co., Ltd., Japan)				
Line 159-161	(source from the Environmental Technology Center, Canada, and Linde Electronic)	(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, 2017).				
Line 173-180	Based on the ambient measurements of VOCs, the calculation of annual emissions for individual VOC species is performed based on Eq. (2):	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 calculation of annual emissions for individual VOC species is performed based on Eq. (2):				

Line 192-194	(1) CO has similar sources as that of anthropogenicVOC and (2) CO emissions show lower uncertaintycompared with VOC emissions.	(1) CO has similar sources as that of anthropogenic VOC and (2) CO emissions show lower uncertainty compared with VOC emissions (Warneke et al., 2007;Wang et al., 2014).
Line 195-200	The annual emission value of CO was obtained from the CO emission inventory of the MarcoPolo Project (http://www.marcopolo-panda.eu), which has been validated based on the chemical transport model and measurement data.	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).
Line 202-209		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 multiple sampling sites would be more reliable and some other method such as chemical transport model simulation may be an ideal approach to verify emission inventories based on field observations in our future study.
Line 218-223		which was recommended by the user guide of the PMF model. The uncertainty is calculated by Eq. (3), if the mixing ratio is equal to or less than the MDL; the uncertainty is calculated using Eq. (4), if mixing ratio if larger than the MDL (USEPA, 2014b). Uncertainty = $\frac{5}{6} \times MDL$ Eq. (3) Uncertainty = $\sqrt{(Error Fraction \times mixing ratio)^2 + (0.5 \times MDL)^2}$ Eq.(4)

Line 233	limited	constrained				
Line 234-235	HCHO is a high-yield product of VOCs species oxidation.	HCHO is a high-yield product of many VOC species oxidation (Millet et al., 2006;Stavrakou et al., 2015).				
Line 236	relative to	against				
Line 236-237	Its column concentration is directly related to the emission.	Its column concentration is directly related to the emission of reactive VOCs.				
Line 257-259		Emissions of a total of 152 VOC species (Table S4) bellowing to alkanes, alkenes, alkynes, aromatics, halocarbons, OVOCs, nitriles, and others were calculated in this study.				
Line 270-271	Figure 5 presents the average mixing ratios and chemical compositions of VOCs in January, April, July, and October 2015.	Figure 5 presents the average mixing ratios and chemical compositions of VOCs measured at the PKU site in January, April, July, and October 2015.				
Line 278-279		Detailed time series and box-plot of VOC mixing ratios observed in this study are shown in Fig. S2 and Fig. S4, respectively.				
Line 295-299	The correlation coefficients between some halocarbons/ketones and CO were lower as halocarbons and ketones have a few different emission sources from CO.	The correlation coefficients between some halocarbons/ketones and CO were lower as halocarbons and ketones have a few emission sources different from CO sources. 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).				
Line 309-313	After the comparison with results obtained from measurements, the emissions for a majority of the non-methane hydrocarbon (NMHC) species were agreed within $\pm 100\%$ in the emission inventory. The emissions for acetonitrile came from the two methods were similar	After the comparison with results obtained from measurements, the emissions for 51 o kinds of non-methane hydrocarbon (NMHC) species were agreed within $\pm 100\%$ in emission inventory, 15 species agreed within $\pm 50\%$, and 10 species agreed within ± 2 The acetonitrile emissions determined by the measurements is around five times acetonitrile emissions determined by the emission inventory.				
Line 317	Correlated well	were agreed within ±100%				

Line 323 324	Ethene and acetylene are mainly emitted through an	Ethene and acetylene are mainly emitted through an incomplete combustion process (Liu		
Line 525-524	incomplete combustion process.	et al., 2008;Mo et al., 2016).		
Line 220 221		(DB11/1201-2015; DB11/1202-2015; DB11/1226-2015; DB11/1227-2015; BD11/1228-		
Line 550-551		2015).		
1. 225.226		In addition, secondary production through the oxidation of precursor VOCs might impact		
Line 555-550		the accuracy of OVOC emission estimated from the observations.		
Line 340	reactions	reactivity		
Line 352	appointments	apportionments		
Line 260	Figure 10 illustrates source contribution	Source contribution percentages in January, April, July, and October was shown in Table		
Line 300	percentages in January, April, July, and October.	S6.		
		Comparison of the relative contributions of VOC emission sources in Beijing calculated by		
		the PMF model of this study and results from the other studies during these seasons was		
		listed in Table S7. Results of this and other studies have shown that the fuel combustion		
		was the largest VOC contributor in winter. The contribution proportions of fuel combustion		
Line 373-379		in winter were ranged from 45% - 55% (Li et al., 2015; Yang et al., 2018). Results of this		
		and other studies have shown that vehicle-related source was the largest VOC contributor		
		in summer and winter, with the contribution ranged from 50% - 57%, and 33% - 42%,		
		respectively. The contribution proportion of summer biogenic emission in this study was		
		larger than that in the other studies.		
		Figure 8 illustrates the comparison between source profiles derived from the PMF against		
		their attributed sources from the emission inventory. The source profiles for fuel		
Line 381-388		combustion agreed between the two methods. For the source profiles of transportation, the		
		contributions of $C2 - C4$ alkanes derived from the PMF were larger than contributions from		
		the emission inventory. Aromatics were the dominant group in the source profiles for		

		solvent utilization derived from the two methods. For the source profiles of industrial processes, the proportions of some halocarbons OVOCs from the PMF were larger than proportions from the emission inventory. The finding agreed with the results of section 3.2.2 that the proportions of OVOCs and halocarbons in the source profile database may be unreliable.
Line 400-407	According to the seasonal PMF result (Fig. 10), the relative contribution of fuel combustion in winter was 55%, significantly higher than the contributions in the spring (12%), summer (4%), and fall (6%). However, the relative contributions of fuel combustion in the spring, summer, and fall were similar to the value obtained from the emission inventory. Therefore, the difference between the contributions of PMF and the emission inventory may be caused by the large difference of the contributions in winter.	Compared with the seasonal PMF results, the emissions from industrial processes, transportation, and solvent utilization of the emission inventory didn't exhibit obvious seasonal variations (Fig. 9). It is because the monthly profiles of these sources, which developed on monthly statistics, have little monthly variations (Wu and Xie, 2018). The emissions from fuel combustion of the emission inventory exhibit similar seasonal variations with the PMF results with much higher emissions in winter than the other seasons. However, the relative contribution of fuel combustion for each season in the emission inventory was significantly lower than the contribution in the PMF results, especially for winter.
Line 407-409	(1) the contributions of the vehicles, solvent utilization, and industrial processes from the emission inventory and the PMF results were similar;	(1) the annual contributions of the vehicles, solvent utilization, and industrial processes from the emission inventory and the PMF results were similar, but the monthly profiles of these sources cannot replicate the temporal variations;
Line 425	Verification of spatial distributions	Verification of spatial and temporal distributions
Line 443-445		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 because of little monthly variation in emissions from transportation, industrial processes, and solvent utilization (Wu

		and Xie, 2018).			
Line 448-450	The satellite-derived emission inventory possesses the advantage of efficiently reflecting the spatial	The satellite-derived emission inventory possesses the advantage of efficiently reflecting the spatial and monthly characteristics of the VOC emissions (Palmer et al. 2006; Fu et al.			
	and monthly characteristics of the VOC emissions.	2007;Marais et al., 2014;Stavrakou et al., 2015;Bauwens et al., 2016).			
Line 464-465	The annual emissions of NMHCs derived from the measurements were consistent with with the results of the emission inventory.	The annual emissions of 91% NMHCs derived from the measurements were agreed within $\pm 100\%$ with the results of the emission inventory.			
Line 477-479		Fourthly, monthly profiles of the EF-based emission inventory developed based on monthly statistics cannot replicate the temporal variations of VOC emissions well.			
Table 1		Revised			
Figure 1		Revised			
Figure 2		Revised			
Figure 4		Revised			
Figure 8	Figure 9.Source profiles for VOCs in the PKU site calculated by PMF (bars: mixing ratio of species; dots: % of species).	Figure 8.Source profiles for VOCs calculated by PMF and the emission inventory (Species name was shown in Table S4).			
Figure 9	Relative contributions (%) of the six sources identified by PMF analysis in January, April, July, and October of 2015.	Figure 9.Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right).			
Figure 11		Revised			
Figure 12	Figure 14. Monthly profiles of VOC emissions from the satellite-derived emission inventory.	Figure 12. Monthly variability of VOC emissions from the satellite-derived and EF-based emission inventories.			

Verification of anthropogenic VOC emission inventory through ambient measurements and satellite retrievals

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- Abstract. Improving the accuracy of the anthropogenic volatile organic compound (VOC) emission inventory is essential for reducing air pollution. In this study, we established an emission inventory of anthropogenic VOCs in the Beijing–Tianjin–Hebei (BTH) region of China for 2015 based on the emission factor (EF) method. Online ambient VOC observations were conducted in one urban area of Beijing in January, April, July, and October, which respectively represented winter, spring, summer, and autumn in 2015. Furthermore, the developed emission inventory was evaluated by a comprehensive verification system based on the measurements and satellite retrieval
- 15 results. Firstly, emissions of the individual species of the emission inventory were evaluated according to the ambient measurements and emission ratios versus carbon monoxide (CO). Secondly, the source structure of the emission inventory was evaluated using source appointment with the Positive Matrix Factorization (PMF) model. Thirdly, the spatial and temporal distribution of the developed emission inventory was evaluated by a satellite-derived emission inventory. According to the results of the emission inventory, the total anthropogenic VOC
- 20 emissions in the BTH region were 3277.66 Gg in 2015. Online measurements showed that the average mixing ratio of VOCs in Beijing was approximately 49.94 ppbv in 2015, ranging from 10.67 ppbv to 245.54 ppbv. The annual emissions for 51 of 56 kinds of of non-methane hydrocarbon speciess (NMHCs) derived from the measurements were significantly consistent agreed within ±100% with the results of the emission inventory. Based on the PMF results and the emission inventory, it is clearly evident that vehicle-related emissions dominate the composition of anthropogenic VOCs in Beijing. The spatial correlation between the emission inventory and
- 25 composition of anthropogenic vOCs in Beijing. The spatial correlation between the emission inventory and satellite inversion result was significant (p < 0.01) with a correlation coefficient of 0.75. However, there were discrepancies between the relative contributions of fuel combustion, emissions of oxygenated VOCs (OVOCs), and halocarbons from the measurements and inventory. To obtain a more accurate emission inventory, we propose the investigation of the household coal consumption, the adjustment of EFs based on the latest pollution control policies, and the verification of the source profiles of OVOCs and halocarbons.</p>
 - 1 Introduction

Ambient volatile organic compounds (VOCs) encompass of various kinds of chemical substances that predominantly help to form the ground-level ozone (O_3) and the secondary organic aerosol (SOA) (Toro et al., 2006). Their direct emission sources include biogenic <u>sources</u>, forest fires, and anthropogenic sources_(Guenther et al., 2006;Kansal, 2009;Simpson et al., 2011). Most VOCs are emitted naturally on a global scale; however, in

urbanized areas, they are mainly emitted anthropogenically (Guenther et al., 2012; Janssens-Maenhout et al., 2015).

In addition, some VOC species have adverse effects on human health (Bari et al., 2016;Weichenthal et al., 2012). Therefore, it is essential to acquire reliable knowledge of anthropogenic VOC emissions to develop strategies for reducing the emissions and ambient concentrationsproduction of secondary pollutants.

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The emission inventory is a widely used method for calculating the emissions of VOCs, through which the magnitude, strength, spatial and temporal distribution, source structure of VOC emissions, and other related information can be provided (Wang et al., 2014). Moreover, emission inventories are important essential input data for the chemical transport model (Hodzic et al., 2010;Coll et al., 2010). Since the pioneering study by (Piccot et al., 1992), the "Emission factor (EF) method" has been widely used to establish emission inventories, which estimates the emissions of VOC sources by multiplying the corresponding activities and detailed EFs (Tonooka et al., 2001;Streets, 2003;Klimont et al., 2002;Ohara et al., 2007;Bo et al., 2008;Zhang et al., 2009;Zheng et al., 2009;Li et al., 2014;Wu et al., 2016a;Huang et al., 2017;Janssens-Maenhout et al., 2015). The characterization

and quantification of VOC emissions are highly complicated as the emission sources of VOCs exhibit complexity

and diversity (Borbon et al., 2013). Although great progress has been made in the establishment of VOC emission inventories, there are still a number of limitations (Wu et al., 2016a). Based on the results of the Monte Carlo 50 simulation, the uncertainty of the VOC emission inventory was more than 100% (Bo et al., 2008). The chemical transport model simulation studies found that existing VOC emissions inventories cannot accurately assess air quality, which makes it ineffective for meeting the management needs of developing emission reduction policies (Carmichael, 2003;Coll et al., 2010;Kim et al., 2011). Thus, developing an accurate emission inventory of 55 anthropogenic. VOCs is key for to effectively controlling and reducing reduce air pollution in the future.

Emission inventories can be verified and evaluated based on the ambient measurements of VOCs or-on satellite retrievals. However, the concentration of VOCs is measured after the emission undergoes physical and chemical transformations. One method for assessing regional emissions is to perform source appointments with receptor models that can calculate different sources' contributions and assess the VOC source structures, in terms

60 of the accuracy of the emission inventories, accordingly (Gaimoz et al., 2011; Morino et al., 2011; Wang et al., 2014). In addition, the calculation of the anthropogenic emission of individual VOC species can be performed according to two indicators, (1) the emission ratios to an inert tracer (reference compound) and (2) the known emissions for the inert tracer (Borbon et al., 2013). Subsequently, the results can be used for the verification of the species-specific emissions of the EF-based inventory. Since the satellite data possess the advantage of 65 reflecting the spatial characteristics of VOCs (Fu et al., 2007), satellite-derived anthropogenic VOC emission estimations obtained from the chemical transport model can be utilized to evaluate the spatial distribution of the EF based emission inventories (Cao et al., 2018).

Earlier studies by various research groups applied only one of these methods to evaluate either the source structure or species-specific emissions of VOC emission inventories_(Gaimoz et al., 2011;Borbon et al., 70 2013; Wang et al., 2014; Cao et al., 2018). Moreover, most studies have been based on the data from one or twomonth ambient measurements, which cannot accurately represent the annual emissions_(Gaimoz et al., 2011;Borbon et al., 2013;Wang et al., 2014). Also, there is a lack of systematic analysis of the qualities and uncertainties of anthropogenic VOC emission inventories. Therefore, we took the VOC emissions of the Beijing-Tianjin-Hebei (BTH) region as a case for the verification of a method for establishing an anthropogenic VOC emission inventory. The BTH region is the political center of China, a developed cluster of large cities, and one of the most polluted areas in China (Jiang et al., 2015). In recent years, severe haze events have occurred frequently

in the BTH region (Zhu et al., 2016), and the mixing ratios of O_3 have increased significantly (Ma et al., 2016). There is an urgent need for effective pollution control measures in the area.

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In this study, the emission inventory of anthropogenic VOCs in 2015 in the BTH region of China was developed at a 3 km × 3 km spatial resolution based on the EF method. We conducted online measurements of ambient VOCs at an interval of 1 h in January, April, July, and October 2015 at an urban site in Beijing. We extracted the VOC emissions of the BTH region from a satellite-derived anthropogenic VOC emission inventory. The source structure, species-specific VOC emissions, and spatial<u>-temporal</u> distribution of the emission inventory were evaluated based on online measurements and satellite retrievals.

85 2 Methodology

2.1 Establishment of the anthropogenic VOC emission inventory

Through a systematic literature review, we found that the anthropogenic VOC emission inventory methodologies are similar, but the source classification and EFs used in some studies are different. So, this study combined the existing source classification system, EF databases, and source profile databases, followed by establishing the emission inventory in the BTH region (Bo et al., 2008;Wu et al., 2016a;Huang et al., 2017;Zhao et al., 2017;Zhong et al., 2017). A detailed description of the method is provided below.

2.1.1 Source classification

According to the actual state of VOC emissions in the BTH region, a four-level categorization was used to classify the anthropogenic VOC sources (Wu et al., 2016a). Level 1 has five sub-levels in total: transportation, the stationary combustion of fossil fuel, biomass burning, solvent utilization, and industrial processes. For example, transportation, a Level 1 source, was further divided into off-road transportation and on-road vehicles in Level 2. On-road vehicles can be divided into buses, passenger cars, motorcycles, light-duty vehicles, as well as heavy-duty vehicles in Level 3 based on the fleet type. Level 3 sources can be further divided into Level 4 sources based on fuels. Table S1 lists these classifications in detail.

100 **2.1.2 Emission estimation and allocation**

Calculation of on-road vehicular VOC emissions was performed taking into account the EFs, number of vehicles, and the corresponding average mileage for each vehicle category per year, following Eq. (1).

Eq. (1)

$$E_V = \sum P_{i,j} \times VMT_{i,j} \times EF_{i,j}$$

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where E_v is the vehicular VOC emission (Gg); $P_{i,j}$ denotes the number of vehicles in category *i* under emission standard *j*; *VMT*_{*i,j*} denotes the average mileage per year in km for vehicles in category *i* under emission standard *j*; and $EF_{i,j}$ denotes the emission factor in g km⁻¹ for vehicles in category *i* under emission standard *j*. EFs were calculated by <u>COmputer Programme to calculate Emissions from Road Transport version 4 (COPERT 4)</u>, a widely used software application for calculating emissions from road transport. The input parameters included the fuel information, monthly ambient temperature, average speeds and so on. The method has been explained in detail in previous studies (Cai and Xie, 2013). Furthermore, the vehicles were classified into different categories according

110 previous studies (Cai and Xie, 2013). Furthermore, the vehicles were classified into different categories according to COPERT 4.

The Level 2 sources of biomass burning include biofuel combustion and crop field residue burning. Multiplying the activity data by corresponding EFs yields the emissions estimate of biomass burning. For crop residue burning in fields, the activity data was the total mass of crop residues burned in fields, which can be

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calculated based on the crop production, the grain-to-straw ratio of each crop type, the proportion of field crop residue burning, the burning efficiency, and the proportion of dry matter in the crop residue. Li et al. (2016) described in detail the method used to obtain the activity data. The EFs of biomass burning were obtained from local experimentally measurements, as shown in Table S1.

- The emission estimation of other VOC sources, including off-road transportation, the stationary combustion of fossil fuel, industrial processes, and solvent utilization, were estimated by multiplying the corresponding 120 activities and detailed EFs. The EFs used in this study were obtained from locally measured EFs, recently discharge EPA published literature. national or local standards. the AP42 Report (http://www3.epa.gov/ttnchie1/ap42/) and the EEA Air Pollutant Emission Inventory Guidebook 2013. The detailed sub-sources and the EFs of each sub-source are listed in Table S1.
- 125 In the current study, selected county-level statistical data were prioritized to calculate the VOC emissions. For the sources without county-level data, either city-level or provincial-level statistical data were selected (Table <u>S2</u>)._ Further, the VOC emissions estimated based on the statistical data were allocated to county-level by the most related surrogates. GDP, population, and cultivation area were used as the surrogates for allocating industrial sources, residential sources, and biomass burning sources, respectively. The county-level emissions were further
- 130 divided into 3 km × 3 km grids based on a population density map (http://www.geodoi.ac.cn/WebCn/Default.aspx). For field crop residue burning, the allocation of emissions was carried out according to the fire counts in croplands. The MODIS Thermal Anomalies/Fire gridded level-3 product (MOD/MYD14A1) was selected to determine fire counts. The CCI-LC Map was used to identify croplands (http://maps.elie.ucl.ac.be/CCI/viewer/index.php). Multiplying the total VOC emission by the corresponding weight percentage from the source profile database
- 135 yielded the emission of individual VOC species. The source profile database used in this study was listed in Table S4.-The study by Wu and Xie (2017) described the source profile database used in this study in detail.

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 the 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

140 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).

145 2.2 VOC sampling and analysis

The online observations of ambient VOCs were conducted at an interval of 1 h in January, April, July, and October 2015, representing winter, spring, summer, and fall, respectively. The roof of the Technical Physics Building at Peking University, with a height of approximately 15 m above the ground (PKU, 39.99 N, 116.33 E, Fig. 1) was selected as the sampling site. During this study, a total of 2174 valid measurements were obtained. No large industrial point sources are around to the monitoring site. This site has been used to represent a typical urban

environment in Beijing in many studies This site selected represents the typical urban environment of Beijing and is far from strong direct emissions (Song et al., 2007; Yuan et al., 2012; Li et al., 2015; Wang et al., 2015; Wu et al., 2016b).

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) (*TH-PKU 300B, Wuhan Tianhong Instrument Co. Ltd., China*). A total of 104 C2-C11 VOC species (see Table S32) 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., USALinde Electronic*). These standard gases are ideal for use with the TO-15 Calibration Standards (Linde, 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).

2.3 Emission inventory verification system

— The validation of the emission inventory was conducted based on ambient VOC measurements and satellite retrieval results. Firstly, emission strengths of VOCs on the basis of emission ratios relative to CO were estimated, and the results were compared with the emission inventory developed here to evaluate the species-specific emissions. Secondly, the positive matrix factorization (PMF) receptor model was applied to evaluate the VOC source structure with regard to its accuracy in the emission inventory. Thirdly, the study compared the emission inventory developed here with a satellite-based anthropogenic VOC emission inventory to evaluate the spatial distribution and annual VOC emissions.

2.3.1 Species VOC emissions based on ambient measurements-

- 175 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
- 180 <u>a trace gas could reflect the ratios of their emission strength (Shao et al., 2011). The relative ratios can help reduce</u> the influence of physical transformation processes. Based on the ambient measurements of VOCs, tThe calculation of annual emissions for individual VOC species is performed based on Eq. (2):

$$E_{VOC} = E_{Ref} \times ER_{VOC} \times MW_{VOC} / MW_{Ref}$$

Eq. (2)

where, E_{VOC} denotes the emission of a particular VOC species per year (Gg); E_{Ref} denotes the emission of the reference compound per year (Gg); MW_{VOC} denotes the molecular weight of a particular VOC species; MW_{Ref} denotes the molecular weight of the reference compound; and ER_{VOC} denotes the emission ratio of VOC species relative to the reference compound (ppbv (ppmv Ref)⁻¹).

Photochemical processing is an important factor influencing the chemical compositions of VOCs in ambient

air. Thus, the way in which photochemical processing impacts the measured VOC ratios should be excluded or

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corrected using a temporal filter (Borbon et al., 2013). The local time period 03:00 to 07:00 was set as a temporal filter to reduce the impact of photochemical processing (Wang et al., 2014). The emission ratios of VOC species to the reference compound (ER_{VOC}) from 03:00 to 07:00 local time were estimated using the line<u>ar</u> fit model.

In this study, we selected CO as a reference compound considering that: (1) CO has similar sources as that of anthropogenic VOC and (2) CO emissions show lower uncertainty compared with VOC emissions_(Warneke et al., 2007;Wang et al., 2014). Thus, CO was a suitable reference compound (Coll et al., 2010;Borbon et al., 2013;Wang et al., 2014). The CO levels in the ambient air were obtained from the Wanliu National Air Quality Monitoring Station (*http://zx.bjmemc.com.cn*). 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*). which-This emission inventory has been validated based onby the chemical transport model_(Hu et al., 2017), satellite observations (Yumimoto et al., 2014), and comparison with other studies (Li et al., 2017a)and measurement data. The spatial resolution of this CO emission inventory is 0.25 ° × 0.25 °. To obtain reasonable results, we compared the VOC emissions of the grid where the PKU site was located (Fig. S1).

205 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 210 CO. Thus, emissions based on VOC measurements on multiply multiple sampling sites would be more reliable and some other method such as chemical transport model simulation may be an ideal approach to verify emission

2.3.2 Source apportionments

inventories based on field observations in our future study.

The U.S.EPA PMF 5.0 model (USEPA, 2014b) was applied to the ambient VOC source apportionments. 215 More information about the PMF model can be seen elsewhere (Paatero and Tapper, 1994), while the section below gives a brief discussion on some related concepts that enable a better understanding of the analysis in this study. Since the PMF model is a mathematical approach to quantify the contribution of sources, it is necessary to use a large number of samples to ensure the reliability of the results. During the collection period, a total of 2174 valid measurements were obtained for 104 VOC species. The PMF required two input files: (1) concentration values of sample species and (2) the uncertainty values of sample species. The observed uncertainty file was set following the method proposed by Polissar et al. (1998)=, which was recommended by the user guide of the PMF model. The uncertainty is calculated by Eq. (3), if the mixing ratio is equal to or less than the MDL; the uncertainty is calculated using Eq. (4), if mixing ratio if larger than the MDL (USEPA, 2014b).

Uncertainty
$$=\frac{5}{6} \times MDL$$
 Eq. (3)

225 Uncertainty = $\sqrt{(Error \ Fraction \ \times \ mixing \ ratio)^2 + (0.5 \ \times \ MDL)^2}$ Eq. (4)

The PMF model can calculate each species' signal to noise ratio (S/N) according to the input files. Species

were categorized as "Bad" when the S/N ratio was < 0.2 and "Weak" when the S/N ratio was > 0.2 but < 0.5. Two to ten factors solutions were calculated by <u>the PMF</u> model. The most appropriate number of factors were selected by some mathematical indicators calculated following the PMF model, including the coefficient of determination, Q value, a possible explanation of the sources, and the residual distribution.

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2.3.3 Satellite-derived emission inventory

To evaluate the spatial distribution of the EF based VOC emission inventory and the VOC annual emissions, we compared the emission inventory established in our study with satellite-derived anthropogenic VOC emission estimations. The satellite-derived estimations were obtained from the Global Emission project (*http://tropo.aeronomie.be/datapage_BIRA.php?species=TNMVOC*). The anthropogenic VOC emissions were derived based on source inversion with the IMAGESv2 model (Stavrakou et al., 2009) which is <u>constrainedlimited</u> by the column densities of tropospheric HCHO from OMI satellite instrument (De Smedt et al., 2015). HCHO is a high-yield product of <u>many_VOC</u> species oxidation_(Millet et al., 2006;Stavrakou et al., 2015). Its atmospheric lifetime is relatively short (only a few hours) <u>against relative to</u> photolysis and oxidation. Its column concentration is directly related to <u>the emission of reactive VOCs</u> (De Smedt et al., 2015)s. Therefore, satellite observations of formaldehyde column concentrations can provide a "top-down" constraint for better quantitation of high spatial-temporal resolution of VOCs. The spatial resolution of the satellite-derived emissions was $0.25-^{\circ} 0.25-^{\circ}$ and the

temporal resolution was one month. To facilitate the spatial distribution verification, the emissions of the 3 km \times 3 km emission inventory established in this study were weighted and summed in the 0.25 ° \times 0.25 ° grid, so that

the spatial resolution was consistent with the satellite inversion emission inventory.

3 Results and discussion

3.1 VOC emission inventory in the BTH region in 2015

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A total of 3277.66 Gg of anthropogenic VOC were emitted in BTH region in 2015, accounting for about 10% of the national VOC emissions (Wu et al., 2016a). Emissions in the Beijing, Tianjin, and Hebei provinces were 411.72 Gg, 666.53 Gg, and 2199.41 Gg, respectively. The spatial distribution of VOC emissions is shown in Fig. 2. The emissions were lower in the northern part of the BTH region, and the emission density was higher in the southeast. Moreover, the southwestern part of Beijing, the southeastern part of Tianjin, and the eastern part of Shijiazhuang displayed high VOC emissions.

Figure 3 illustrates the contribution of each source to the total VOC emissions. For the BTH region, industrial processes were the largest source, accounting for 39% of the total VOC emissions. The next was transportation with emissions of 1080.62 Gg, accounting for 33% of the total emissions. Emissions from solvent utilization, biomass burning, and fuel combustion contributed 18%, 6%, and 4 % of total VOC emissions, respectively. The primary source of VOC emissions in Beijing was transportation, while in the Tianjin and Hebei provinces it was industrial processes.

260 Figure 4 illustrates the chemical compositions of VOC emissions in the BTH region. Emissions of a total of 152 VOC species (Table S4) bellowing to alkanes, alkenes, alkynes, aromatics, halocarbons, OVOCs, nitriles, and others were calculated in this study. The emissions of aromatics, alkanes, OVOCs, and alkenes accounted for 34%, 32%, 17%, and 11% of total anthropogenic VOC emissions, respectively. Aromatics and alkanes were the main compound groups of anthropogenic VOCs, with annual emissions of 1412.6 Gg and 1058.6 Gg, respectively.

- 265 Emissions of alkynes, halocarbons, other VOCs and nitrile were much lower, accounting for 2.2%, 2.2%, 1.4%, and 0.2% of total anthropogenic VOC emissions, respectively. The species with the highest emissions are listed in Fig. 4. The top ten species are m/p-xylene, toluene, ethylbenzene, ethylene, n-hexane, benzene, ethanol, o-xylene, and isopentane with annual emissions of 227.0 Gg, 216.9 Gg, 154.5 Gg, 142.1 Gg, 140.8 Gg, 138.1 Gg, 113.3 Gg, 102.2 Gg, 94.7 Gg and 91.1 Gg, respectively. Among the 10 species, five belonged to aromatics, three
- 270 to alkanes, one to ethene, and one to OVOCs.

3.2 Verification of species-specific VOC emissions

3.2.1 VOC mixing ratios

Figure 5 presents the average mixing ratios and chemical compositions of VOCs measured at the PKU site in January, April, July, and October 2015. The average mixing ratio of VOCs was about 49.94 ppbv in 2015, varying 275 from 10.67 ppbv to 245.54 ppbv. The highest VOC mixing ratio was occurred in January, with an average value of 62.26 ppbv. The VOC mixing ratios were relatively lower in April and July, with average values of 41.09 ppbv and 41.77 ppbv, respectively. In October, the average mixing ratio of VOCs was 50.64 ppbv. The VOCs species varied dramatically across the four seasons. Overall, alkanes dominated total VOCs during all seasons, accounting for 31.2%–39.5% on average. In January, alkanes constituted the largest group of VOCs (39.5%), and the next 280 one was alkenes (22.6%). In other months, the highest VOC group was also alkanes, followed by OVOCs. Detailed time series and box-plot of VOC mixing ratios observed in this study are shown in Fig. S2 and Fig. S4,

respectively.

Figure 6 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, 285 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 ppby. 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. The highest VOC mixing ratio in October was 201.10 ppbv.

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The VOC species showing the highest mixing ratios in January, April, July, and October (top 20) are listed in Table 1. Ethane exhibited the largest proportion during all the four months. Ethene, acetylene, propene, and benzene are considered typical combustion tracers (Liu et al., 2008). Compared with the other months, the mixing ratios of combustion sources tracers were much higher in January. Benzene and toluene were important VOC species. During combustion processing, the emissions of benzene are much higher than toluene (Barletta et al., 295 2005). As shown in Table 1, benzene showed a higher mixing ratio than toluene in January. In contrast, the benzene

showed a lower mixing ratio compared with toluene in the other three months. Combustion may be an important source in winter. During July, the levels of acetone, methyl methacrylate, and 2-butanone were much higher, which may be influenced by secondary formation process. The mixing ratios of n-butane and i-pentane were also very high in July, which may be influenced by the evaporation of gasoline in summer.

300 3.2.2 Verification of individual VOC species emissions

Here, we selected CO as a reference compound for anthropogenic VOC species. For verifying the rationale of setting CO as the reference compound, this study analyzed the mutual influence of mixing ratios of individual VOC species and CO levels. All VOC species, except β -pinene and C₂F₃Cl₃, were significantly related to CO (p < 0.05). Acetylene, ethane, and ethene were the most obviously related to CO (R⁺ > 0.8), and benzene, propene,

- 305 tran-2- butane, 2,3-dimethyl butane, and i-butane also displayed strong correlations with CO ($\mathbf{R}_{\mathbf{F}} > 0.6$). The correlation coefficients between some halocarbons/ketones and CO were lower as halocarbons and ketones have a few different emission sources different from CO sources. 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).
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Table S325 listed the emission ratios for individual VOC species measured in this study and compared the individual emissions estimated from the emission ratios and emission inventory. Based on the annual emissions derived from the measurements, the top fifteen species with the highest emissions were ethane, ethene, propane, acetylene, acetone, toluene, dichloromethane, n-butane, benzene, methyl methacrylate, ethyl acetate, propene, ipentane, i-butane, and 2-butanone. Based on the annual emissions derived from the emission inventory, the top 315 fifteen species with higher emissions were m-/p-xylene, toluene, ethylbenzene, benzene, ethylene, o-xylene, i-

pentane, ethane, tetrachloroethylene, ethyl acetate, 1,2, 4-trimethylbenzene, propylene, pentane, n-butane, and nhexane.

The emissions of individual VOC species determined by the measurements and emission inventory for the sampling site in 2015 were displayed in Fig. 76. After the comparison with results obtained from measurements, 320 the emissions for 51 of 56 kinds of a majority of the non-methane hydrocarbon (NMHC) species were agreed within $\pm 100\%$ in the emission inventory, 15 species agreed within $\pm 50\%$, and 10 species agreed within $\pm 25\%$. The acetonitrile emissions determined by the measurements is around five times the acetonitrile emissions determined by the emission inventory. for acetonitrile came from the two methods were similar, however, Tthe annual emissions of many OVOCs and halocarbons were much lower in the emission inventory than that in the 325 measurements results. Moreover, the emission levels of some aromatics in the emission inventory were higher

than thoseat of the measurements.

Figure 8-7 makes a direct comparison between the emissions of individual VOC species from the measurements and emission inventory. The annual emissions for alkanes were in agreement agreed within $\pm 100\%$ between the two methods, except ethane and propane, which are important tracers of natural gas and LPG (Katzenstein et al., 2003). The emission inventory may underestimate the VOC emissions from the utilization of natural gas and LPG. This conclusion was consistent with the study by Wang et al. (2014), which compared the emission ratios of 27 sites in Beijing to the INTEX-B emission inventory.

The annual emissions for the alkenes, except ethene, correlated wellwere agreed within $\pm 100\%$. The acetylene in the emission inventory showed a lower annual emission compared with that from the measurements. Ethene and acetylene are mainly emitted through an incomplete combustion process (Liu et al., 2008;Mo et al., 335 2016). The lower emissions of the two species in the emission inventory indicated that the emission inventory might have underestimated the VOC emissions from combustion sources. Emissions of some aromatics like toluene, o-xylene, and m/p-xylene in the emission inventory were higher compared with that from the

measurements. Toluene and xylene were mainly emitted from various solvent utilization sources, such as 340 automobile coatings, building coatingsprinting, and furniture manufacturing. The common character of these sources is that Beijing had issued local VOC emission standards for the above sources since 2015 (DB11/1201-2015; DB11/1202-2015; DB11/1226-2015; DB11/1227-2015; BD11/1228-2015). The enactment of local VOC emission standards decreases the emission of some aromatics. However, the influence of those standards on EFs has not been considered before, which might lead to higher emissions of toluene, o-xylene, and m/p-xylene in the emission inventory than in measurements.

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OVOC and halocarbons showed a much lower emission in the emission inventory compared with that from the observations, which might be due to the lack of reliable source profiles. In addition, secondary production through the oxidation of precursor VOCs might impact the accuracy of OVOC emission estimated from the observations. The VOC source profiles obtained from the local measurements mainly focused on the monitoring 350 of NMHC species, and fewer studies have been conducted on the measurement of OVOCs and halocarbons (Mo et al., 2016). Moreover, the extensively used VOC source profiles database, USEPA SPECIATE, excludes VOC species with very low atmospheric photochemical reactivityreactions, such as methylene chloride, methyl chloroform, and fluorochemicals (USEPA, 2014a). For instance, both acetone and 2-butanone are carbonyl compounds. Vehicle exhaust, biomass combustion, food flue gas, surface coating, and industrial exhaust gas are 355 the sources of carbonyl compounds, while only 45 of the more than 150 sources profiles included acetone and 38 source profiles contained 2-butanone. Another example is that of esters, which are used as tracers of industrial emissions and are emitted by most of the industrial processes and surface coating processes. However, only 12 sources in the source profile database contained methyl acetate, 6 sources contained methyl methacrylate, 29 sources contained ethyl acetate, and 14 sources contained butyl acetate. Halocarbons are also vital tracers of

industrial sources. Of all the source profile databases collected in this study, only 33 sources profiles contained 360 methyl chloride, 28 sources contained chloroform, 35 sources contained 1,2-dichloroethane, and 26 sources contained 1,2-dichloropropane. Consequently, more source emission monitoring investigations need to be carried out to obtain reliable source profiles of VOC emissions.

3.3 Verification of source structures

365 3.3.1 Source apportionments appointments

The PMF receptor model was used to conduct dynamic source apportionment according to the measured VOCs. The following analysis adopted 63 strong and 5 weak species, accounting for more than 90% of the total VOC mixing ratios. In the following, six sources were identified, including (1) vehicle-related sources, (2) fuel combustion, (3) aged air mass and biomass burning, (4) industrial processes, (5) biogenic source, (6) solvent

370 utilization. Figure 9-85 shows the source profiles of individual sources, and the source identification is described in the supplemental file.

Figure 10 illustrates Source contribution percentages in January, April, July, and October was shown in Table S6. In January, fuel combustion made the largest most significant contribution (55%) to VOC mixing ratios. Emissions from vehicle-related source and industrial processes contributed 19%, and 14% to total VOC mixing ratios, respectively. The contributions from aged air mass, solvent utilization, and biogenic were relatively low at 7%, 3%, and 1%, respectively. In April, aged air mass made the largest contribution (33%) to VOCs, followed by

vehicle-related sources (22%) and industrial processes (21%). The contribution proportion of fuel combustion, solvent utilization, and biogenic respectively was 12%, 7%, and 5% of the total VOC mixing ratios. In July, vehicle-related sources accounted for 50% of the total VOCs. Meanwhile, the biogenic source elevated from 5%
in April to 18% in July. Emissions from solvent utilization, aged air mass, industrial processes, and fuel combustion respectively contributed 12%, 10%, 6%, and 4% of total VOCs. In October, vehicle-related sources were also the most important source, accounting for 33% of the total VOC mixing ratios, followed by solvent utilization (23%), aged air mass (18%), and industrial processes (16%). Contributions from fuel combustion and biogenic sources were relatively low, with values of 6% and 5%, respectively.

385 Comparison of the relative contributions of VOC emission sources in Beijing calculated by the PMF model of this study and results from the other studies during these seasons was listed in Table S7. Results of this and other studies have shown that the fuel combustion was the largest VOC contributor in winter. The contribution proportions of fuel combustion in winter were ranged from 45% - 55% (Li et al., 2015; Yang et al., 2018). Results of this and other studies have shown that vehicle-related source was the largest VOC contributor in summer and winter, with the contribution ranged from 50% - 57%, and 33% - 42%, respectively. The contribution proportion of summer biogenic emission in this study was larger than that in the other studies.

3.3.2 Comparison between the emission inventory and PMF results

Figure 8 illustrates the comparison between source profiles derived from the PMF against their attributed sources from the emission inventory. The source profiles for fuel combustion agreed between the two methods. For the source profiles of transportation, the contributions of C2 – C4 alkanes derived from the PMF were larger than contributions from the emission inventory. Aromatics were the dominant group in the source profiles for solvent utilization derived from the two methods. For the source profiles of industrial processes, the proportions of some halocarbons OVOCs from the PMF were larger than proportions from the emission inventory. The finding agreed with the results of section 3.2.2 that the proportions of OVOCs and halocarbons in the source profile database

400 <u>may be unreliable.</u>

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This study compared the annual average and seasonal PMF results with the VOC source structures of the emission inventory established (Fig. <u>11S6 and Fig. 9</u>). The <u>annual</u> results of PMF demonstrated that transportation made the largest contribution to VOCs, which accounted for 36% of the total anthropogenic VOC emissions. On the other hand, the results of the emission inventory also showed that transportation was the largest contributor to VOCs-(<u>33 %</u>). The contribution of industrial processes (<u>20%</u>) from PMF results was comparable with the result from emission inventory (<u>30%</u>). The contribution for of the solvent utilization obtained from the PMF result was <u>19%</u>, which was higher than the value of the emission inventory (<u>30%</u>). The relative contribution of the fuel combustion source from the PMF result was <u>25%</u>, which was significantly lower than that in the emission

inventory (8%). According to the PMF results and the emission inventory, the vehicle-related emissions were the
 primary source in urban area in Beijing. Solvent utilization and industrial processes also contributed significantly.
 However, large differences were observed in the stationary combustion of fossil fuel consistent with the
 comparison results shown in section 3.2.2.

Compared with the seasonal PMF results, the emissions from industrial processes, transportation, and solvent utilization of the emission inventory didn't exhibit obvious seasonal variations (Fig. 9). It is because the monthly

415 profiles of these sources, which developed on monthly statistics, have little monthly variations (Wu and Xie, 2018).

The emissions from fuel combustion of the emission inventory exhibit similar seasonal variations with the PMF results with much higher emissions in winter than the other seasons. However, the relative contribution of fuel combustion for each season in the emission inventory was significantly lower than the contribution in the PMF results, especially for winter.

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According to the seasonal PMF result (Fig. 10), the relative contribution of fuel combustion in winter was 55%, significantly higher than the contributions in the spring (12%), summer (4%), and fall (6%). However, the relative contributions of fuel combustion in the spring, summer, and fall were similar to the value obtained from the emission inventory. Therefore, the difference between the contributions of PMF and the emission inventory may be caused by the large difference of the contributions in winter.

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On the basis of the above comparisons of the VOC source structure, we inferred that: (1) the annual contributions of the vehicles, solvent utilization, and industrial processes from the emission inventory and the PMF results were similar, but the monthly profiles of these sources cannot replicate the temporal variations; and (2) the fuel combustion in the emission inventory showed a considerably lower relative contribution than the value from the PMF analysis, especially -in winter, - the central heating season in Beijing. The emission inventory

- 430 was established by multiplying statistical data and EFs. Table S1 lists the EFs of fossil fuel combustion sources used here, which were referenced from local measurement studies and were comparable with EFs reported by the US government or the European Union (USEPA, 1995; EEA, 2013). Hence, we attributed the large difference between fuel combustion contributions from the PMF analysis and emission inventory to the uncertainties of activity data obtained from statistical information. For industrial-related activity data, the statistical data was 435

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relatively reliable; however, uncertainty in the statistical data was very high for residential-related activity data. For instance, it is very difficult challenging to quantify the consumption of coal briquettes and chunks, the major fossil fuel for heating and cooking in Chinese households, since such coal for household often goes unreported in official statistics (Liu et al., 2016). Moreover, it is suspected that actual residential coal consumption is much higher than it reported in official statistics (Andersson et al., 2015). We speculate that the underestimation of the emissions from stationary combustion of fossil fuel by the emission inventory can be explained by the incomplete statistical data of residential coal consumption. In future studies, it is necessary to estimate the exact activity data and emissions of residential fossil fuel combustion through scientific approaches.

3.4 Verification of spatial and temporal distributions

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The satellite-derived emission inventory revealed that the VOC emissions in the BTH region were 4368.50 Gg, while the annual emissions according to the EF-based emission inventory were 3277.66 Gg. The deviation of the emissions calculated by the two methods is 30%, within a reasonable error range. The two types of emission inventory shown similar distributions (Fig. 12a10a) and comparable emissions (Figure-Fig. 13.a10b) for the gridded emissions. The spatial distributions of VOC emissions derived from the emission inventory and satellite data are shown in Fig. 1311. The gridded VOC emissions of the emission inventory displayed significant 450 correlations with the emissions derived from the satellite (p < 0.05), with a correlation coefficient of 0.75. The areas with higher and lower VOC emissions in the two emission inventories are also consistent. The areas with higher emissions were concentrated in the urban areas of Beijing and Tianjin, whereas areas with lower emissions were concentrated in the north of the BTH region, including Zhangjiakou and Chengde. The emissions of EFbased emission inventory present some positive biases compared to the satellite-derived emissions for the grids

455 located in the south (Fig. <u>12b10b</u>). The eEmissions calculated by the EF-based emission inventory were higher than those calculated by the satellite-derived emission inventory for Xingtai and Handan (Fig. 1311), two heavy industrial cities in Hebei province.

The temporal resolution of the satellite-derived emission inventory is one month. As shown in Fig. 1412, monthly variations of VOC emissions exhibit obvious seasonal characteristics, with a maximum in winter and a 460 minimum in summer, which are consistent with the seasonal characteristics of the ambient VOC mixing ratios (Fig. 5). However, monthly profiles for the EF-based emission inventories inventory, which -usually-developed based on monthly statistics, didn't exhibit seasonal variations. 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 because of little monthly variation in emissions from transportation, industrial processes, and solvent utilization (Wu and Xie,

2018). - The satellite-derived emission inventories can-may better reflect the monthly characteristics of VOC 465 emissions and be used to allocate monthly emissions.

The satellite-derived emission inventory possesses the advantage of efficiently reflecting the spatial and monthly characteristics of the VOC emissions (Palmer et al., 2006;Fu et al., 2007;Marais et al., 2014;Stavrakou et al., 2015;Bauwens et al., 2016). The significant correlation between the emission inventory established here

470 and the satellite-derived emission inventory is indicative of the reliability of the spatial allocation method and the spatial emissions of the emission inventory. The satellite-derived emission inventory can provide constrains to improve the existing understanding of monthly profiles of VOC emissions.

4 Conclusions

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An emission inventory of anthropogenic VOCs was established for the BTH region in China at a 3 km \times 3 km spatial resolution based on the EF method. We conducted VOC online observations selecting a site in the urban area of Beijing. Based on the measurements, we estimated the annual emission strengths of VOCs according to their emission ratios relative to CO, and then compared these results with the emission inventory established in this study to verify the species-specific VOC emissions. The PMF model was used to qualify the relative contribution made by each source. The result was compared with the emission inventory to evaluate the source 480 structure of the VOCs. We also compared the emission inventory established in our study with a satellite-derived anthropogenic VOC emission inventory for verification of the spatial distribution and VOCs annual emissions.

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According to the PMF results and the emission inventory, the vehicle-related emissions dominate the composition of anthropogenic VOCs in Beijing. The annual emissions of 91% NMHCs derived from the measurements were agreed within $\pm 100\%$ consistent with with the results of the emission inventory. The total amount of anthropogenic VOC emissions of the emission inventory was similar to the satellite inversion result, with a deviation of 30%. The spatial correlation between the emission inventory and the satellite inversion result was significant (p < 0.01) with a correlation coefficient of 0.75.

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Our results showed that the vehicle-related VOC emissions estimated by the emission inventory based on the EF method were reliable. The emissions of NMHCs estimated by the emission inventory were accurate, and the method of spatial distribution was feasible. Nevertheless, there are a few limitations of the existing method for establishing an anthropogenic VOC emission inventory based on EFs. Firstly, there is a large difference between the relative contributions of fuel combustion, and the method underestimated the emissions from fuel combustion sources, especially in winter. Secondly, the emissions of OVOCs and halocarbons estimated in the emission inventory appeared much lower than those derived from the measurements due to the lack of reliable source

- 495 profiles. Thirdly, emissions of some aromatics estimated in the emission inventory were higher than the values derived from the measurements due to the enactment of some local emission standards. <u>Fourthly, monthly profiles</u> of the EF-based emission inventory developed based on monthly statistics cannot replicate the temporal variations of VOC emissions well.
- To acquire a more accurate VOC emission inventory, we propose the following improvements to the future 500 emission inventories: (1) the investigation of household coal consumption to improve the accuracy of activity data; (2) the adjustment of EFs based on the latest pollution control policies to establish dynamic emissions inventories; and (3) the verification of OVOCs and halocarbons emissions and (4) the performance of more source emission monitoring studies to obtain reliable source profiles of VOC emissions.

Author contributions.

505 SDX designed the study, JL performed the data analysis and wrote the paper. YFH contributed to the online measurements. MS contributed to the development of the emission inventory. YQS and ZYX assisted with data collection. All authors assisted with interpretation of the results and the writing of the paper.

Competing interests.

The authors declare that they have no conflict of interest.

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Figure and Table captions:

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Table 1. The VOC species showing the highest mixing ratios (ppbv) in January, April, July, and October 2015 (top 20).

Figure 1. The location of the BTH region in China (shaded area) and the sampling site (black dot).

Figure 2. The spatial distribution of VOC emissions in the BTH region at a 3 km × 3 km resolution.

Figure 3. Source contributions to the total VOC emission in the Beijing, Tianjin, Hebei provinces (a) and the BTH region (b), China.

Figure 4. The top 30 VOC species with the highest emissions (bar plot) and the contributions of VOC groups to the total emissions (pie plot)VOC emissions in the BTH region, China.

Figure 5. Mixing ratios and compositions of VOCs (ppbv) measured at the PKU site during the four seasons and throughout the study period.

Figure 6. Time series of mixing ratios of VOCs in January, April, July, and October 2015.

Figure 7<u>6</u>. Comparisons of VOC annual emissions (ton) derived from the ambient measures and emission inventory for the PKU site ($0.25 \circ \times 0.25 \circ \text{grid}$).

Figure <u>87</u>. Comparisons of individual species emissions (ton) derived from the ambient measures and emission inventory for the PKU site ($0.25 \circ \times 0.25 \circ$ grid).

Figure 98. Source profiles for VOCs in the PKU site calculated by PMF-<u>and the emission inventory (Species name was shown in Table S4). (bars: mixing ratio of species; dots: % of species).</u>

Figure 109.<u>Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory</u> (right).<u>Relative contributions (%) of the six sources identified by PMF analysis in January, April, July, and October of</u> 2015.

Figure 11. Comparison of VOC source structure in the emission inventory (left) and the PMF results (right).

Figure <u>1210</u>. Comparisons between the emissions from the EF-derived emission inventory and the satellite-derived emission inventory.

Figure 1311. Comparision between spatial distribution of VOC emissions obtained from the EF-derived emission inventory and the satellite-derived emission inventory with a $0.25^{\circ} \times 0.25^{\circ}$ spatial resolution.

Figure 12. Monthly variability of VOC emissions from the satellite-derived and EF-based emission inventories. Figure 14. Monthly profiles of VOC emissions from the satellite-derived emission inventory.

January		April		July		October	
Ethane	11.66	Ethane	5.67	Ethane	4.18	Ethane	5.63
Ethene	10.70	Acetone	5.53	Acetone	4.18	Propane	4.54
Acetylene	6.98	Propane	3.49	Methylmethacrylate	3.75	Acetone	4.42
Propane	5.48	Ethene	2.58	Propane	2.98	Ethene	3.73
CF2Cl2	2.58	Acetylene	2.41	Acetylene	2.47	Acetylene	3.09
Propene	2.45	Dichloromethane	2.34	Dichloromethane	2.04	Dichloromethane	2.41
n-Butane	2.10	n-Butane	1.29	Ethene	1.82	n-Butane	1.95
Acetone	1.82	Ethyl acetate	1.13	Toluene	1.55	Methylmethacrylate	1.89
i-Butane	1.45	Toluene	1.06	n-Butane	1.54	Toluene	1.66
Benzene	1.30	2-Butanone	1.04	2-Butanone	1.00	Chloroform	1.40
Toluene	1.28	Chloromethane	1.03	i-Penpane	1.00	Chloromethane	1.40
i-Penpane	1.13	i-Penpane	0.88	i-Butane	0.86	i-Penpane	1.39
Dichloromethane	1.12	i-Butane	0.87	Benzene	0.80	i-Butane	1.10
2-Butanone	0.95	methylmethacrylate	0.85	1,2- Dichloroethane	0.78	Ethyl acetate	1.03
Ethyl acetate	0.89	Chloroform	0.78	Chloromethane	0.76	Benzene	1.01
Chloromethane	0.81	Benzene	0.76	Chloroform	0.66	Propene	0.87
Penpane	0.68	Penpane	0.59	Acetonitrile	0.61	Penpane	0.82
Methylmethacrylate	0.53	Propene	0.57	1,1,2,2- Detrachloromethane	0.57	n-Hexane	0.74
Butyl acetate	0.49	Acetonitrile	0.5 <u>0</u>	Penpane	0.5 <mark>0</mark>	1,2- Dichloropropane	0.6 <mark>0</mark>
n-Hexane	0.44	Menthyl acetate	0.48	1,2-Dichloropropan	0.49	1,2-Dichloroethane	0.59

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770 Table 1. The VOC species showing the highest mixing ratios (ppbv) in January, April, July, and October 2015 (top 20).



Figure 1. The location of the BTH region in China (shaded area) and the sampling site (black dot).





Figure 2. The spatial distribution of VOC emissions in the BTH region at a 3 km $\times 3$ km resolution.



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785 Figure 5. Mixing ratios and compositions of VOCs (ppbv) measured at the PKU site during the four seasons and throughtout the entire study period.



Figure 76. Comparisons of VOC annual emissions (ton) derived from the ambient measures and emission inventory for the PKU site ($0.25 \circ \times 0.25 \circ$ grid).





791Figure 87. Comparisons of individual species emissions (ton) derived from the ambient measures and emission792inventory for the PKU site (0.25 °× 0.25 ° grid).






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803 Figure 9.Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right). Figure
804 10. Relative contributions (%) of the six sources identified by PMF analysis in January, April, July, and October of
805 2015.

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Figure <u>1210</u>. Comparisons between emissions from the EF-derived emission inventory and the satellite-derived emission inventory.



810 Figure 1311. Comparision between spatial distribution of VOC emissions obtained from the EF-derived emission inventory and the satellite-derived emission inventory with a 0.25 °×0.25 ° spatial resolution.



Figure 1412. <u>Monthly variability</u><u>Monthly profiles</u> of VOC emissions from the satellite-derived <u>and EF-based</u> emission 815 inventor<u>iesy</u>.

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