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".

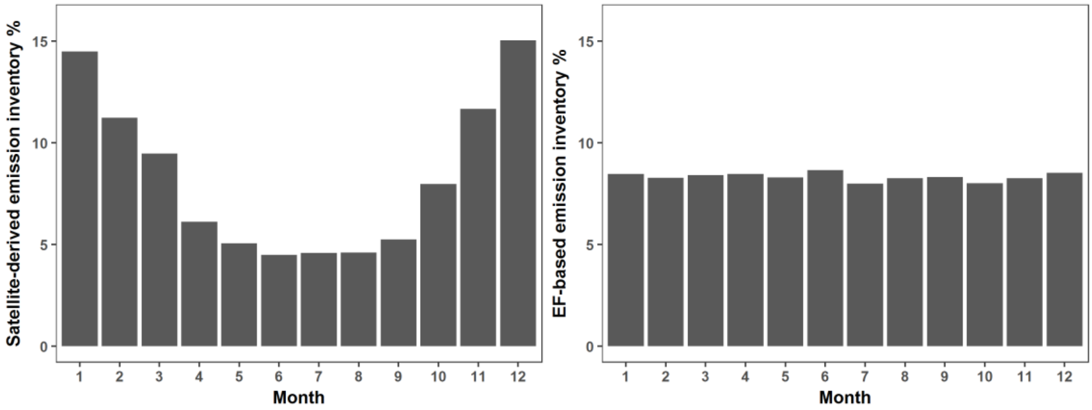


Figure 12. Monthly variability of VOC emissions from the satellite-derived and EF-based emission inventories.

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 emission inventory showed a considerably lower relative contribution than the value from the PMF analysis, especially in winter, the central heating season in Beijing."

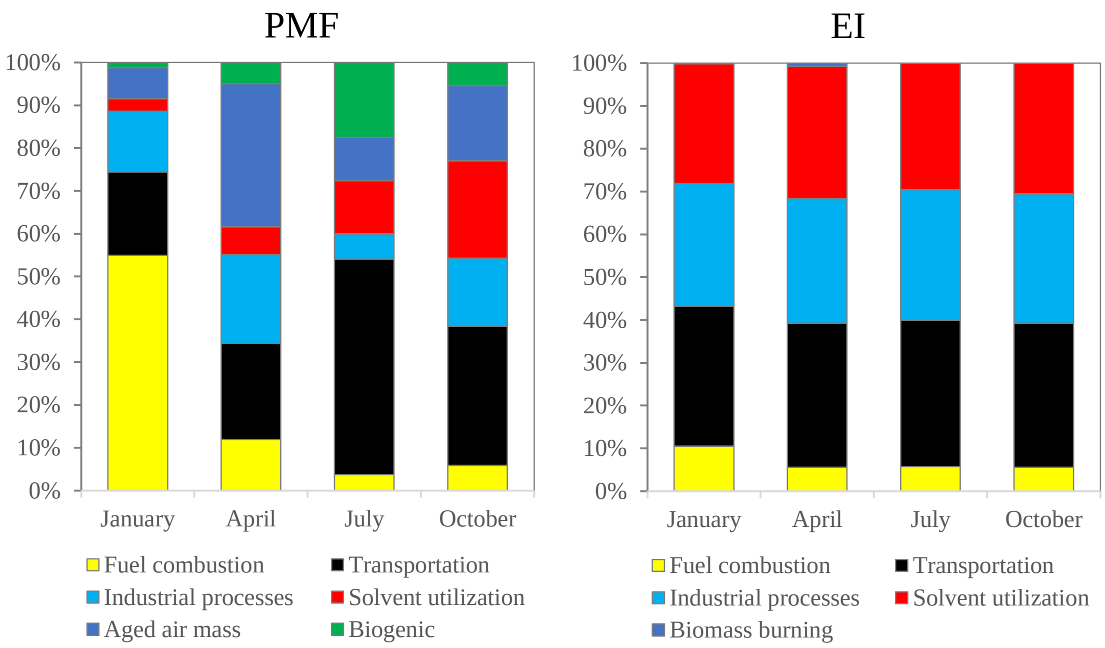


Figure 9.Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right).

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.

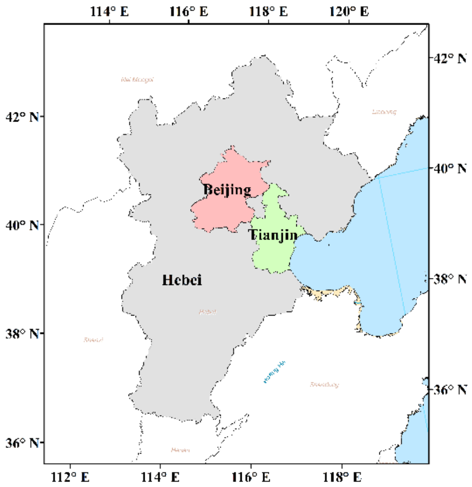
Zheng, J., Zhang, L., Che, W., Zheng, Z., and Yin, S.: A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment, Atmos. Environ., 43, 5112-5122, 10.1016/j.atmosenv.2009.04.060, 2009.

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" https://doi.org/10.1016/j.atmosenv.2005.06.029
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):

$$E_{VOC}=E_{Ref} \times ER_{VOC} \times MW_{VOC}/MW_{Ref} \qquad \text{Eq. (2)}$$

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 ° × 0.25 °. 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.

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

Li, J., Xie, S. D., Zeng, L. M., Li, L. Y., Li, Y. Q., and Wu, R. R.: Characterization of ambient volatile organic compounds and their sources in Beijing, before, during, and after Asia-Pacific Economic Cooperation China 2014, Atmos. Chem. Phys., 15, 7945-7959, 10.5194/acp-15-7945-2015, 2015.

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

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

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

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

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

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

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

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

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

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 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.”

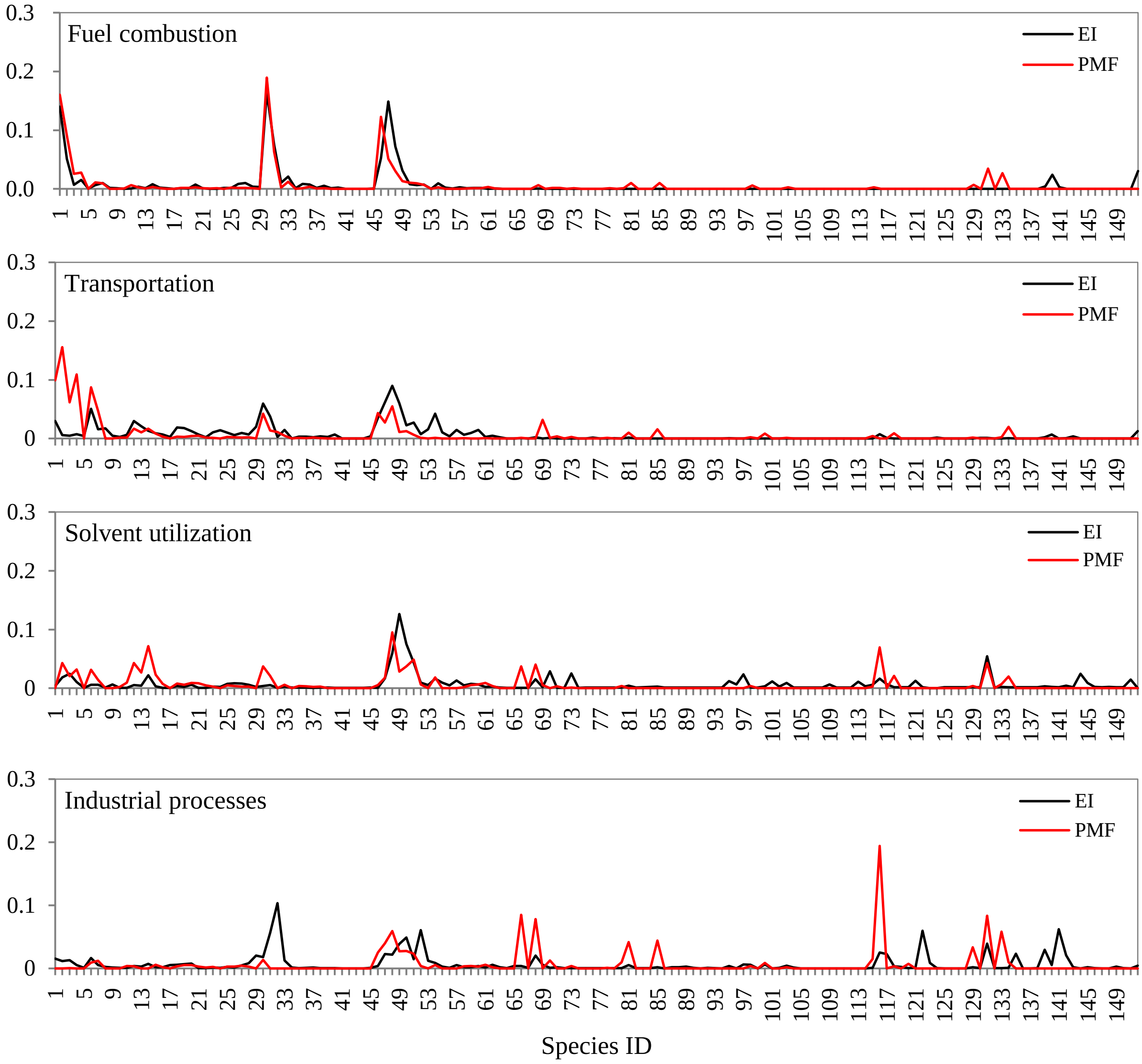


Figure 8. Source profiles for VOCs calculated by PMF and the emission inventory (Species name was shown in Table S4) .

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."

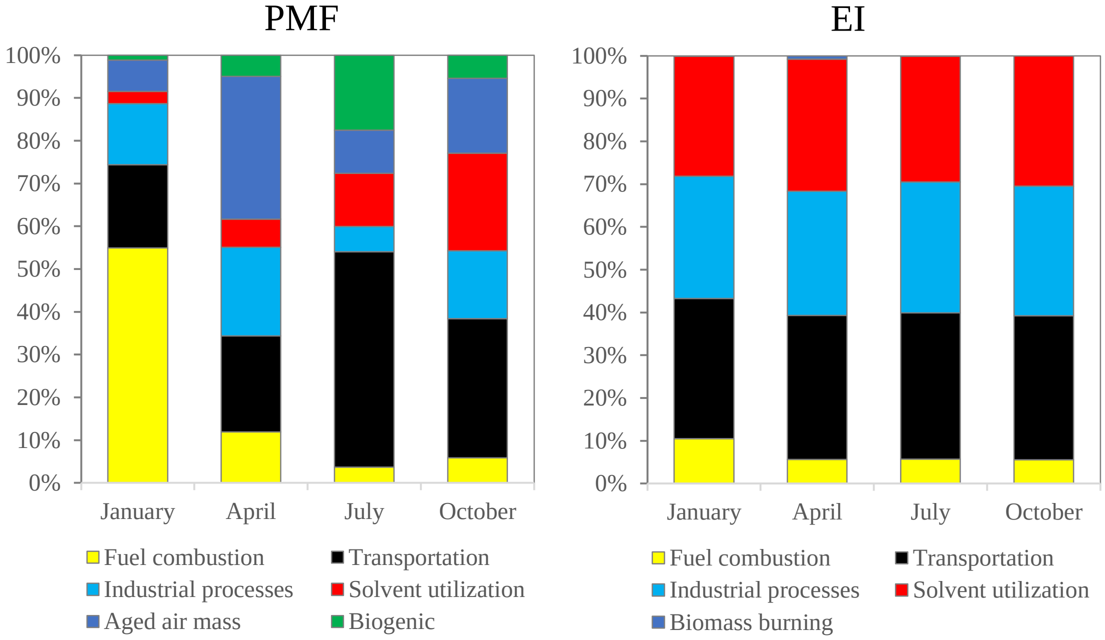


Figure 9. Monthly VOC source structure identified by the PMF analysis (left) and the emission inventory (right).

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."

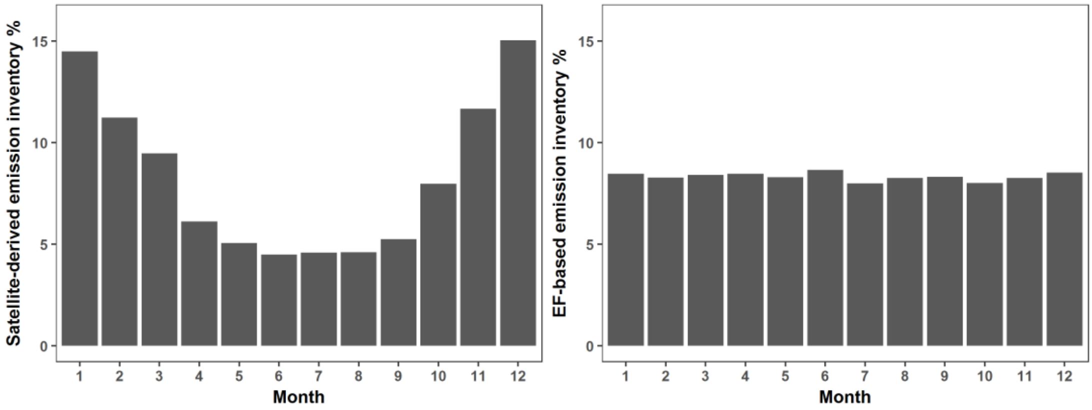


Figure 12. Monthly variability of VOC emissions from the satellite-derived and EF-based emission inventories.