

Response to Referee #2

Thank you very much for your thoughtful and constructive comments on our manuscript. We have revised the manuscript accordingly. [The detailed responses are given below point by point \(in blue\)](#), and the [revised manuscript is shown in red](#).

This paper reported one year VOC measurements in high frequency at oil-gas station area in China. High frequency VOC data enable to show diurnal variations of VOCs in the sampling site and strong influence of meteorological condition for VOC concentrations was elucidated. Using PMF analysis, VOC emission was successfully categorized into five sources. Further, CPF analysis gave more information about the direction of the VOC emission sources. Also, backward trajectory based analysis (PSCF, CWT) were applied.

[General comments]

Similar VOCs measurement and analysis were already demonstrated in urban area, but the detailed VOC observation at oil-gas station area will be important in view point of source area information. Because strong VOC emission sources are close to the measurement site, the analyzed results would be simpler and seems to be reasonable. But I am not sure about the validity of PSCF and CWT analysis in this measurement. When there is a strong source very close to the measurement site (like 2 km from Oil refinery and 6km from Oil-gas field in Fig 1c), the backward trajectories passed the near emission source will be counted as high concentration over its whole trajectory route. Therefore, the raster analysis (distinguish local and regional area) would be reasonable trial. (But I am afraid that the influence of very close emission sources cannot be excluded, because that 12h radius will be still long and concentration of each grid was estimated from CWT.)

[We thank the reviewer for the valuable comments. All of them have been addressed in the revised manuscript. Please see our itemized responses below.](#)

[Explanation for the validity of PSCF and CWT](#)

Despite the potential source contribution function (PSCF) method has deficiencies such as the determination of the statistical significance of its outcome is difficult (Stohl, 1996). The PSCF (Polissar et al., 1999; Hsu et al., 2003) and concentration weighted trajectory (CWT) are frequently used to figure out the direction and sources of air pollution at a receptor site. To reduce the uncertainty and increase the confidence of the results, a weighted function is widely used (Wang et al., 2016). Grid cells for which high PSCF values are calculated from the arrival of air parcels at a receptor site with pollutant concentrations higher than a given value. In this study, the 75th percentiles of each source contribution were set as the criterion (Bressi et al., 2014; Wang et al., 2015). The detailed information about the PSCF and CWT calculation can be found in Appendix B.

The PSCF results represent potential source directions rather than locations because PSCF modeling evenly distributes weight along the path of trajectories as the referee mentioned. This even weighting results in a trailing effect so that areas upwind and downwind of the sources are likely to be identified as sources as well (Hsu et al., 2003). Therefore, in this study, we simply define a circle with 12 h radius area as the local areas and the outer areas of this circle is regional. The reasons are listed below:

(1) The duration of *m, p*-xylene decreasing from highest concentrations (at 02:00 LT) to lowest (14:00 LT) was 12 h (section 3.4). The atmospheric lifetime of *m, p*-xylene is about 11.8 h assuming that the OH radical equals to 10^6 rad cm^{-3} . The compounds with atmospheric lifetime longer than *m, p*-xylene can be transported from long distance or accumulated in the local area.

(2) The endpoint of every 2 h backward trajectories in the first 24 h was tested to find the optimum range of “local and nearby” area (Fig. C1). As the backward time increasing from 2 h to 24 h, the area covered by the long air masses increased significantly. Before the first 5 h, the air masses were mainly from the northwest and the east of the sampling site. From 7 h to 12 h, air masses from the northeast, southeast and southwest reached the receptor site and

the “shape of local area” formed. After 12 h, the air masses, especially for the trajectories from the west transported for long distance reached the sampling site, indicating the regional conditions.

As the referee mentioned, the 12 h radius to define the local and regional transport was still long that the very close emission sources cannot be excluded. The method used in this study was a trial to give the quantitative information of the local and regional transport despite flaws existed.

Reference

Bressi, M., Sciare, J., Gherzi, V., Mihalopoulos, N., Petit, J.-E., Nicolas, J. B., Moukhtar, S., Rosso, A., Féron, A., Bonnaire, N., Poulakis, E. and Theodosi, C.: Sources and geographical origins of fine aerosols in Paris (France), *Atmos. Chem. Phys.*, 14(16), 8813–8839, doi:10.5194/acp-14-8813-2014, 2014.

Hsu, Y.-K., Holsen, T. M. and Hopke, P. K.: Comparison of hybrid receptor models to locate PCB sources in Chicago, *Atmos. Environ*, 37(4), 545–562, doi:10.1016/S1352-2310(02)00886-5, 2003.

Stohl, A.: Trajectory statistics-A new method to establish source-receptor relationships of air pollutants and its application to the transport of particulate sulfate in Europe, *Atmos. Environ*, 30(4), 579–587, doi:10.1016/1352-2310(95)00314-2, 1996.

Wang, L., Liu, Z., Sun, Y., Ji, D. and Wang, Y.: Long-range transport and regional sources of PM_{2.5} in Beijing based on long-term observations from 2005 to 2010, *Atmos. Res*, 157, 37–48, doi:10.1016/j.atmosres.2014.12.003, 2015.

Wang, Q., Liu, M., Yu, Y. and Li, Y.: Characterization and source apportionment of PM_{2.5}-bound polycyclic aromatic hydrocarbons from Shanghai city, China, *Environ. Pollut*, 218, 118–128, doi:10.1016/j.envpol.2016.08.037, 2016.

[Detailed comments]

Fig. 1: What is 2 type green area in Fig 1(a)? What is blue area in Fig1(b)? Exact location of the sampling site is difficult to see in Fig1 (b) (because of blue color). Is the sampling site located in Region 1? What is the rose figure

in Fig1c? Wind speed or VOC concentration from each direction? If this rose figure shows wind direction, figure caption will be incorrect (“Northwesterly and northeasterly wind prevailed”).

Fig. 1 has been revised. Fig. 1a shows the spatial distribution of oil and gas bearing basins in China in different colors (yellow: gas well, red: oil well, and green: depositional basin). In the Fig. 1b, the sampling site is located in region 1

Fig. 1c shows the wind rose and the prevailing wind.

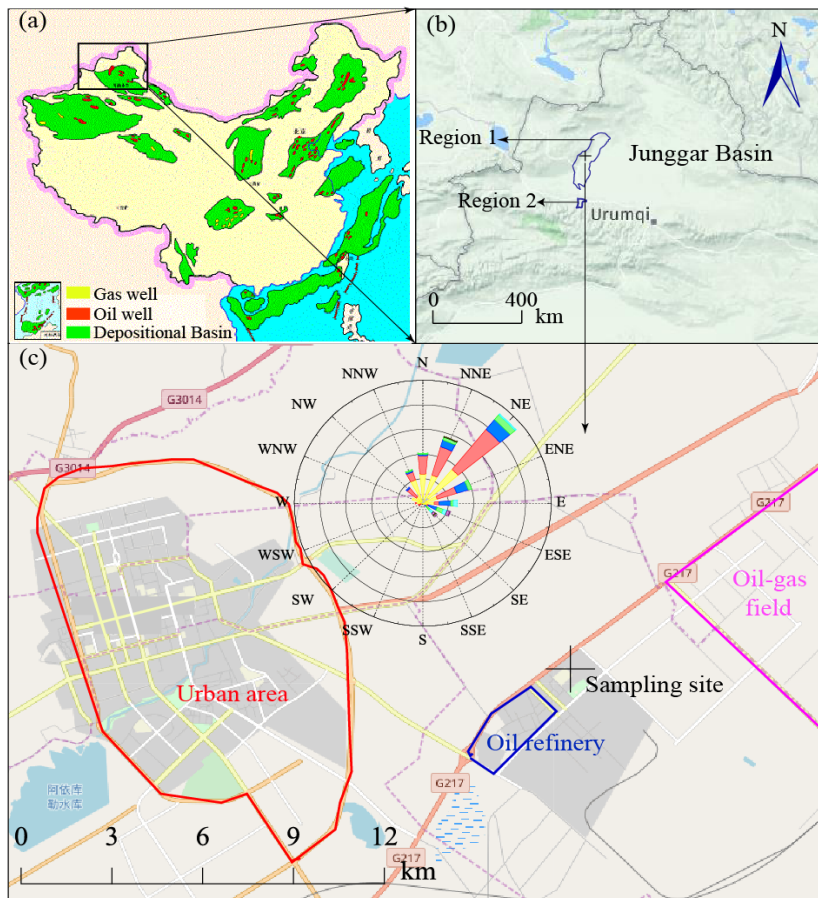


Figure 1. The spatial distribution of oil gas bearing basins in China (a) and the terrain of the study area (b). The sampling site is about 11 km away from the urban area and located in the northeast of an oil refinery plant and southwest of an oil gas field. The northeasterly winds prevailed during the sampling periods (c)

Page4 L3: PLOT column will be used for C₂-C₄ separation in GC. For C₂-C₄ trap, some absorbent (tenax etc) would be used. Please check the explanation about VOC measurement system.

The VOCs analysis method has been checked and some technic errors have been corrected.

Briefly, two-channels were installed to analyze VOCs separately. The water and carbon dioxide in the sampled air was firstly removed at a cold trap maintaining at $-80\text{ }^{\circ}\text{C}$ and then concentrated at $-150\text{ }^{\circ}\text{C}$ at another cold trap. After the purification and concentration, the VOCs were desorbed by rapid heating to $100\text{ }^{\circ}\text{C}$. The $\text{C}_2\text{--C}_5$ VOCs were separated with a PLOT column (diameter: 0.32 mm , thickness of membrane: $1.5\text{ }\mu\text{m}$, length: 60 m) and were quantified by the gas chromatograph-flame ionization detector (GC-FID, Agilent 7890). $\text{C}_5\text{--C}_{12}$ were separated by a DB-624 column (diameter: 0.25 mm , thickness of membrane: $3\text{ }\mu\text{m}$ and length: 60 m) and were quantified using mass spectrometer detector (MSD, Agilent 5975).

Table 1: Please explain “MDL” (method detection limit). “KOH” will be better to write in small characters.

Thanks for your suggestion and we have revised it.

Fig3: Is the colors in Fig. 3(e) same as Fig. 3(a)-(d)? (In Fig. 3(e), blue (acetylene?) seems larger contribution.)

Thanks for your reminder, the color in Fig. 3(e) is the same as Fig. 3(a)-(d) and we find some errors in Fig. 3e and therefore it has been revised. After correction, the contribution of aromatics (magenta) is greater than acetylene (blue).

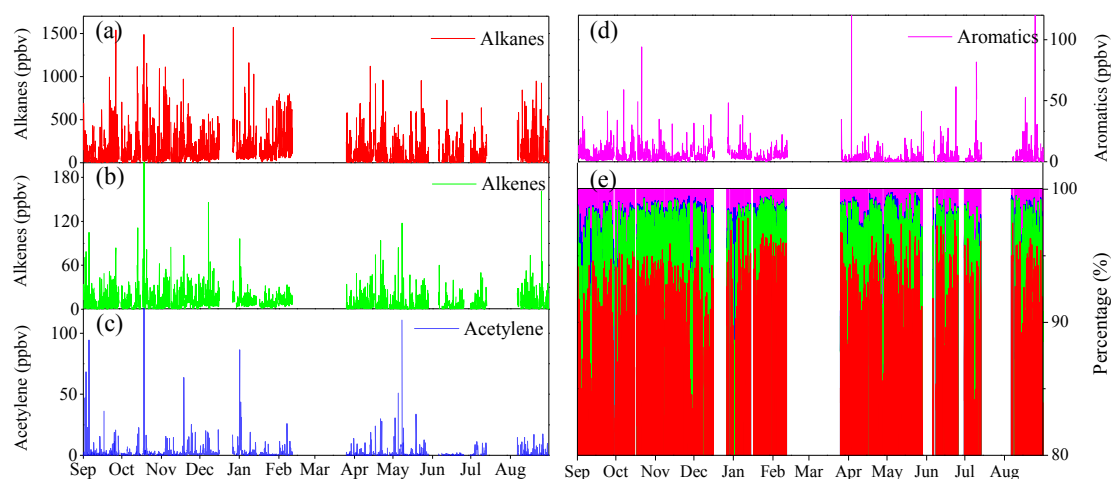


Figure 3. Time series of the hourly concentrations (expressed in ppbv) of four categories of VOCs including alkanes (a), alkenes (b), acetylene (c), aromatics (d), and their fractions (e) during the sampling period.

Fig. 6 and text: Are O_3 , BLH etc 24-hour average or only daytime average? There are strong diurnal variations in BLH, O_3 and VOCs, so these plots would be different when you use whole day or only daytime data.

Yes, the O₃, BLH etc. are 24-hour average in the original Fig. 6. In this part, we want to discuss the temporal variation of VOCs in different timescales. For daily variation patterns (Fig. 6), we used the 24-h average values to discuss. Of course, we agree with the referee's opinion that the concentrations of O₃, VOC and NO₂ concentrations and BLH would be different during the daytime and nighttime. So, we discussed the diurnal variation of these factors using the 95% confidence interval of gases (VOCs, O₃ and NO₂) and average \pm standard deviation of BLH as shown in Fig. 7.

Therefore, we revised the Fig. 6 and Fig. 7 as below:

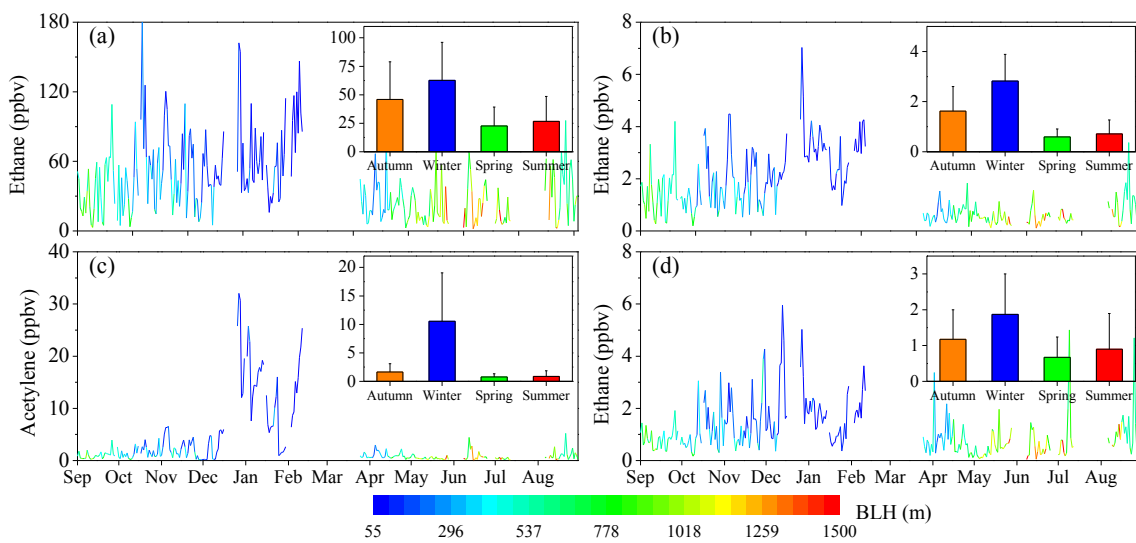


Figure. 6 Seasonal and daily variations of ethane (a), ethylene (b), acetylene (c), and benzene (d) during the sampling period.

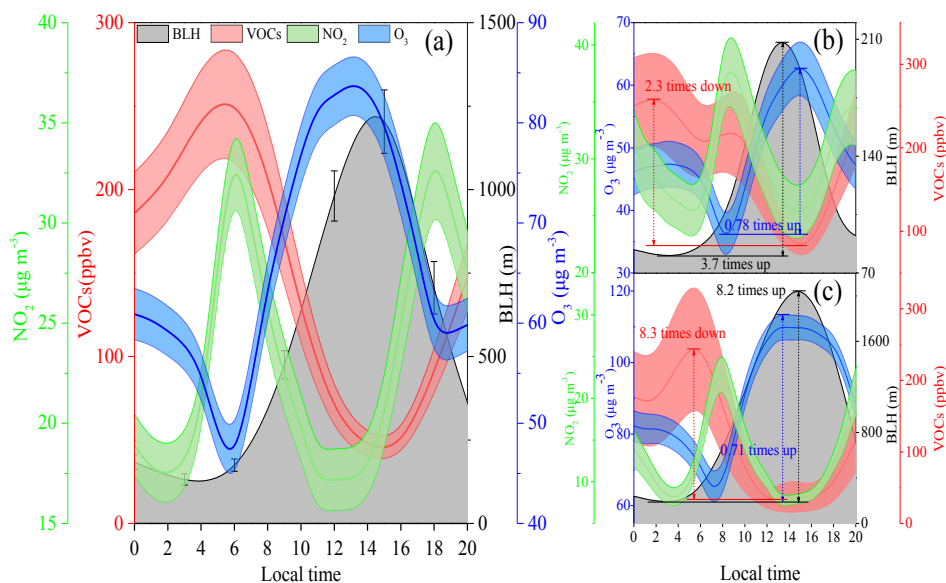


Figure 7. Diurnal variation of boundary layer height (BLH), VOCs, NO₂ and O₃ concentrations in different timescale: annual (a), winter (b) and summer (c). Solid line represents the average value and filled area indicates the 95th confidence intervals of the mean.

Fig12 (d): Is it correct “F1-F4” ? (Is it “CO-F4” ?)

Yes, it is corrected as “F1-F4” in Fig. 12d. To avoid the vague description, the Fig. 12 was revised. For instance, the F1 (Oil refinery), F2 (NG), F3 (Combustion), F4 (Asphalt) and F5 (Fuel evaporation) were added in x-axis. In addition, the color maps of different metrological data were unified.

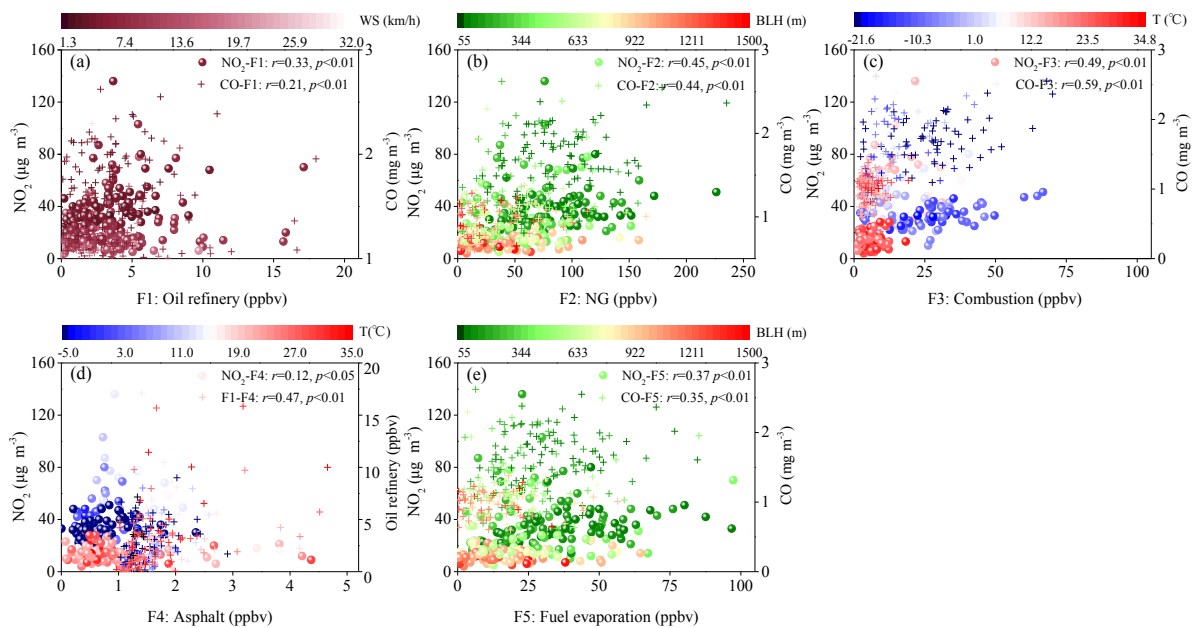


Figure 12. Scatter plots of daily concentrations of trace gas and source contributions including oil refinery (a), NG (b), combustion (c), asphalt (d), and fuel evaporation (e) under different meteorological conditions (wind speed (WS), boundary layer height (BLH) and temperature (T))

Fig13: Please explain MCH and MCP. In the right axis of (a), (b), (e), "/" will be better to show as ",". They are not ratio, but just concentration. “Cyclohexane” etc would be better to show as dot and line.

Thanks for your suggestion. This figure has been revised.

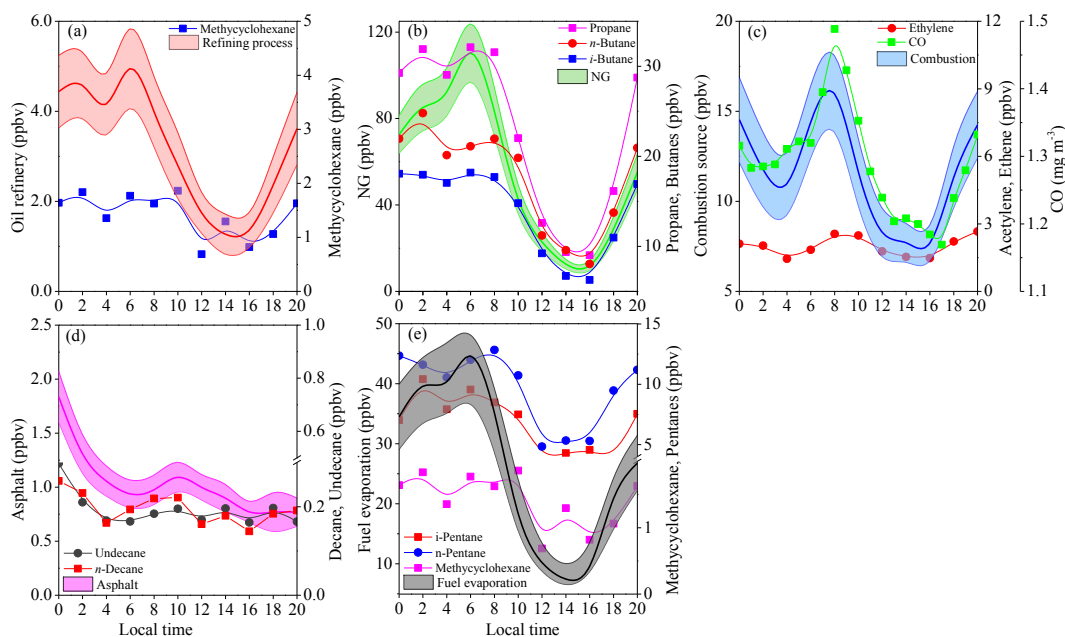


Figure 13. Diurnal variations of the contributions (expressed in ppbv) of five identified sources including oil refining process (a), NG (b), combustion source (c), asphalt (d) and fuel evaporation (e), and specific compounds with high loadings in each source profile. Note that the CO in combustion source was expressed in mg m^{-3}

P12 L24-2: Diurnal pattern of acetylene seems to be different. (Acetylene did not decrease during daytime.)

Yes, we agree with the referee's idea and this expression has been revised.

The diurnal variation of combustion source was in accordance with the diurnal pattern of ethylene and CO with Pearson correlation coefficients as 0.71 ($p < 0.05$) and 0.84 ($p < 0.01$), respectively.

P15 L20-22: "Northeast to Southwest" Is this "Southeast to Southwest"?

Yes, thanks for your correction.

P15 L23-24: Fig.14(b), highest peak is in east direction.

Thanks for your correction, we also find that there were some grids with high PSCF value in the east direction of the sampling site. So, we have revised this sentence as following:

Indeed, high values of CPF, PSCF and CWT were found in the east direction (Fig. 14b, Fig. 15b and Fig. 16b), which indicated that the potential geographic origins of NG.