Authors' Response to Referees' Comments

Anonymous Referee #3

This manuscript describes NMHCs measurements at an urban site in Beijing city in winter in order to identify their levels, variation characteristics, and their sources. Therefore, the authors applied a widely-used receptor model, PMF, to investigate sources of NMHCs in winter at this site. The concentrations and their temporal variation were analyzed according to different meteorological situations (clear days and haze days). The overall analysis shows the important contribution of coal combustion emissions to the NMHCs in winter especially in haze days. The paper is well written and organized. I would however, like to see some revisions before it is accepted for publication in ACP.

Answer: We appreciate your positive comments about our manuscript. The questions raised by you were responded point by point as followings.

Major revisions

1-Page 4, line 1: specify how the detection limit is determined.

Answer: The method detection limits (MDLs) of 0.02-0.10 ppbv for the NMHCs were estimated based on the signal to noise ratio of 3 and enrichment volume of 400 ml. The detail information about the MDLs could be referenced in our previous publication (Liu et al., 2016). The sentence in Page 4, line 1 was revised as following:

The method detection limits (MDLs) of 0.02-0.10 ppbv for the NMHCs were estimated based on the signal to noise ratio of 3 and enrichment volume of 400 ml (Liu et al., 2016a).

2-Add a table with all the measured NMHCs (average, median, standard deviation, and detection limit) and indicate which compounds were selected for PMF analysis. The table can be added to supplementary material.

Answer: According to your valuable suggestion, the average, standard deviation, and detection limit of the measured NMHCs are listed in Table 2, and the compounds selected for PMF analysis were marked as *.

Table 2 The method detection limit (MDL), mean concentrations and standard deviations of NMHCs during clear days, light haze days and heavy haze days (ppbv)

Compund	Clear days	Light haze days	Heavy haze days	MDL
Ethylene*	2.43±3.32	6.54±5.02	15.14±7.01	0.08
Propene*	0.89±1.52	2.35±2.31	4.51±2.42	0.09
1-Butene	0.19±0.19	0.44±0.29	0.78±0.38	0.05
Trans-2-Butene	0.11±0.03	0.12±0.04	0.15±0.08	0.05
Cis-2-Butene	0.12±0.02	0.12±0.05	0.17±0.07	0.05

1-penene	0.07±0.04	0.11±0.05	0.19±0.09	0.05
Isoprene	0.07±0.04	0.12±0.05	0.16±0.05	0.05
Trans-2-Pentene	0.06±0.02	0.07±0.03	0.09±0.04	0.05
Cis-2-Pentene	0.16±0.23	0.22±0.21	0.51±0.34	0.05
1-Hexene	0.11±0.01	0.11±0.02	0.14±0.05	0.03
Ethane*	3.71±2.79	8.03±4.66	17.63±8.48	0.09
Propane*	2.12±2.02	5.18±3.37	12.52±6.01	0.08
n-Butane*	0.73±0.81	1.76±1.26	3.71±2.14	0.06
n-Pentane*	0.26±0.22	0.54±0.31	1.31±0.78	0.05
n-Hexane*	0.93±0.79	0.81±0.86	1.04±0.69	0.03
n-Heptane*	0.07±0.06	0.15±0.08	0.35±0.18	0.03
n-Octane	0.03±0.02	0.05±0.03	0.09±0.05	0.02
Nonane	0.03±0.02	0.05±0.03	0.09±0.04	0.02
n-Decane	0.02±0.01	0.03±0.02	0.06±0.03	0.02
n-Undecane	0.03±0.02	0.03±0.01	0.04±0.01	0.03
Dodecane	0.05±0.04	0.05±0.03	0.05±0.03	0.09
Isobutane*	0.44±0.41	0.91±0.59	2.05±1.04	0.07
Isopentane*	0.39±0.38	0.83±0.51	1.76±0.88	0.05
2,2-Dimethylbutane	0.06±0.04	0.08±0.07	0.13±0.1	0.04
Cyclopentane	0.07±0.05	0.16±0.08	0.29±0.13	0.05
2,3-Dimethylbutane	0.03±0.03	0.07±0.05	0.09±0.05	0.04
2-Methylpentane*	0.16±0.14	0.36±0.26	0.59±0.33	0.04
3-Methylpentane	0.18±0.13	0.24±0.18	0.42±0.26	0.03
Methylcyclopentane	0.21±0.15	0.32±0.24	0.65±0.38	0.03
2,4-Dimethylpentane	0.03±0.01	0.04±0.01	0.05±0.02	0.03
Cyclohexane	0.07±0.05	0.13±0.13	0.24±0.13	0.03
2-Methylhexane	0.05±0.03	0.09±0.05	0.18±0.08	0.03
3-Methylhexane	0.07±0.08	0.14±0.09	0.36±0.21	0.03
2,2,4-Trimethylpentane	0.06±0.05	0.14±0.07	0.22±0.09	0.02
Methylcyclohexane	0.05±0.04	0.11±0.07	0.26±0.14	0.03
2,3,4-Trimethylpentane	0.02±0.02	0.05±0.03	0.07±0.03	0.03
2-Methylheptane	0.03±0.01	0.05±0.03	0.08±0.03	0.02
3-Methylheptane	0.02±0.01	0.03±0.02	0.05±0.02	0.02
Benzene*	0.59±0.72	1.33±0.96	3.54±1.76	0.03
Toluene*	0.55±0.66	1.34±0.83	3.18±1.72	0.03

Ethylbenzene*	0.1±0.14	0.27±0.18	0.68±0.34	0.02
m,p-Xylene*	0.24±0.35	0.66±0.45	1.56±0.81	0.02
Styrene	0.06±0.06	0.13±0.09	0.25±0.14	0.03
o-Xylene*	0.09±0.12	0.24±0.16	0.57±0.29	0.03
Isopropylbenzene	0.01±0.01	0.02±0.01	0.02±0.01	0.02
n-Propylbenzene	0.02±0.01	0.02±0.01	0.04±0.02	0.03
m-Ethyltoluene	0.04±0.03	0.08±0.04	0.14±0.06	0.02
1,3,5-Thrimethylbenzene	0.02±0.01	0.04±0.02	0.06±0.02	0.03
o-Ethyltoluene	0.02±0.01	0.03±0.02	0.06±0.03	0.03
1,2,4-Thrimethylbenzene	0.04±0.04	0.11±0.06	0.19±0.09	0.03
1,2,3-Thrimethylbenzene	0.02±0.01	0.03±0.02	0.06±0.04	0.03
m-Diethylbenzene	0.02±0.01	0.03±0.01	0.03±0.01	0.03
p-Diethylbenzene	0.02±0.02	0.02±0.01	0.03±0.01	0.03
acetylene*	2.51±2.86	6.72±4.71	13.69±6.09	0.10
alkenes	3.67±1.78	10.01±3.21	21.84±6.12	
alkanes	9.52±2.61	20.17±4.90	44.83±16.33	
aromatics	1.58±0.67	3.84±1.08	9.63±3.28	
TNMHCs	17.05±5.87	40.46±10.92	89.98±28.40	

* the compounds selected for PMF analysis

3-Page 4, line 5-6: the authors cited 4 PMF studies in China but there are earlier and more authoritative studies, as the PMF is widely-used and not limited to a specific place. It would be good to integrate some of these as well.

Answer: According to your valuable suggesting, the earlier and more authoritative references about application of the PMF analysis were cited as following:

The US PMF 5.0 was applied to identify major emission sources of NMHCs sources (Sowlat et al., 2016). PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices-factor contributions and factor profiles which can be interpreted by an analyst as to what sources are represented based on observations at the receptor site (Guo et al., 2010; Ling et al., 2014; Ou et al., 2015; Shao et al., 2016; Shi et al., 2009;Xie et al., 2008;Lanz et al., 2007;Zhang et al., 2013).

4-I suggest to add wind direction and ozone concentrations in figure 1 and to add analysis accordingly in section 3.1. In addition, pollution roses of some specific compounds can be shown.

Answer: According to your valuable suggesting, wind direction and ozone concentrations were

added in Fig. 1, and the analysis of the pollutants was revised as following:

In contrast to NMHCs and $PM_{2.5}$, ozone concentrations approached to zero during each haze events and reached to the maximum of about 35 ppbv in daytime just after the haze events followed by strong winds from northwest directions. Although strong winds from northwest directions occurred during the period of 12-14 January 2016, ozone concentrations didn't evidently increase during daytime, implying that ozone formation depended on the pollution levels of its precursors (NMHCs and NOx).

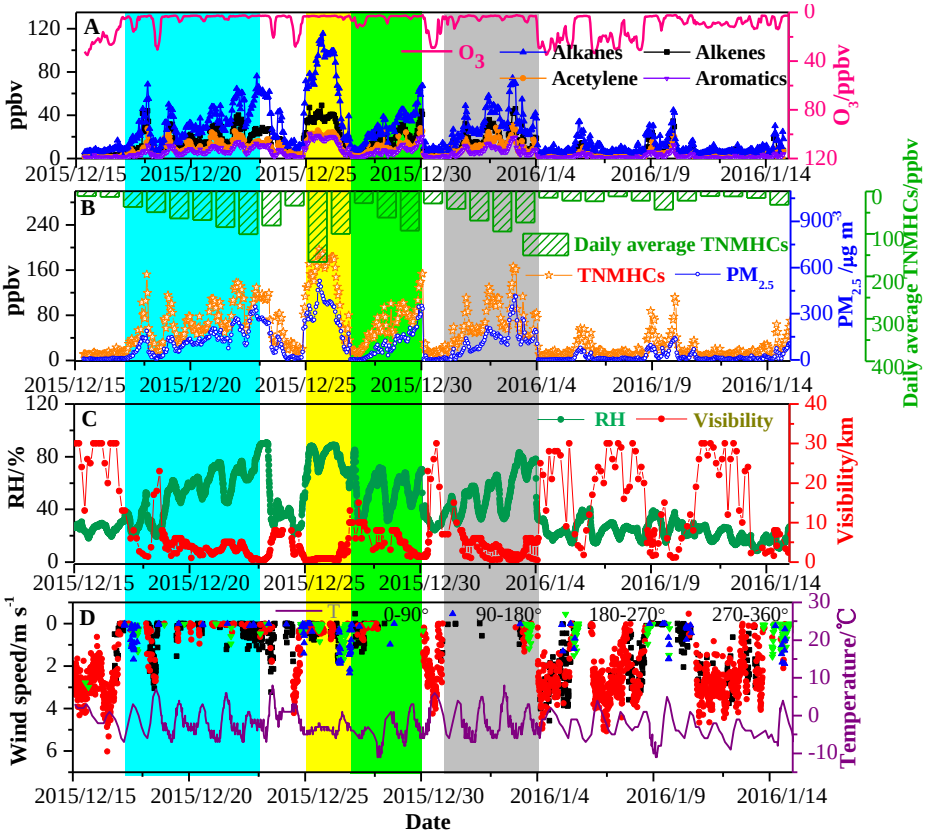

Fig. 1 Time series of measured NMHCs, $PM_{2.5}$, O_3, visibility, relative humidity, temperature and wind speed. The shaded areas indicate pollution episodes: 17-22 December (Cyan), 25-26 December (Yellow), 27-29 December (Green) and 31 December-3 January (LT Gray).

5-Page 6, section 3.2.2: Please explain more, in the beginning of the paragraph, why you selected these compounds (propene and propane) because referring to table 4, we can see that the correlation between combustion related specsies such as benzene/toluene (r2=0.96) and between ethylene/acetylene (r2=0.91) is better than between propane/propene (r2=0.8). Knowing that toluene is more reactive than benzene, and ethylene is more reactive than acetylene.

Answer: Considering the large difference of the reactivity between propane and propene towards NO_3 and OH radicals, the diurnal variations of propane/propene ratios were analyzed for revealing the nighttime and daytime reaction processes. Although toluene is more reactive than benzene, and ethylene is more reactive than acetylene towards OH radicals, the small difference of the reaction

reactivity towards NO_3 between the two hydrocarbon pairs ($k_{(toluene+NO3)}/k_{(benzene+NO3)}$ = 3.1; $k_{(ethylene+NO3)}/k_{(acetylene+NO3)}$ =2.1) could not reflect the nighttime NO_3 chemistry. In addition, the difference of the reaction reactivity towards OH radicals between propane and propene ($k_{(propene+OH)}/k_{(propane+OH)}$ =23.58) is remarkably greater than between the hydrocarbon pairs of benzene/toluene ($k_{(toluene+OH)}/k_{(benzene+OH)}$ =4.61) and ethylene/acetylene ($k_{(ethylene+OH)}/k_{(acetylene+OH)}$ =9.36). According to your valuable suggestion, the sentence of "Considering the large difference of the reactivity between propane and propene towards NO_3 and OH radicals, the diurnal variations of propane/propene ratios were analyzed for revealing the nighttime and daytime reaction processes." was added in the beginning of the paragraph.

6-Page 7, line 7: add O2 to the reaction (8) : O3 + NO2 -> NO3 + O2

Answer: According to your valuable suggesting, O_2 were added in the reaction (8).

7-Page 8, section 3.3.1: why did you select the cis-2-butene/trans-2-butene ratio? These species weren't even included in PMF analysis. It seems that these two compounds don't have the same behavior in clear/haze days (figure 4).

Answer: Previous studies have used the cis-2-butene/trans-2-butene ratio as the indicator for gasoline vehicle emissions, and hence the ratio was also analyzed in this study for comparison. Because the levels of cis-2-butene and trans-2-butene during clear days were close to the detection limits (0.05 ppbv) of the instrument, the large uncertainties of the data measured in clear days might be the reason for the different behaviors of the two compounds between clear days and haze days. Therefore, the species were not included in PMF analysis.

8-Page 8, line 10: do you mean gasoline vehicle exhaust or gasoline evaporation related to vehicles?

Answer: Sorry for the unclear description, and the sentence was revised as following:

The ratios of o-xylene/m,p-xylene and cis-2-butene/trans-2-butene have been widely used as the indicators for gasoline vehicle exhaust emissions.

9-Page 8, the first paragraph (line 10 – 29): It will be better if the ratios from literature are shown in figure 4 as it is the case of figure 5.

Answer: According to your valuable suggesting, the slopes from literature are shown in Fig. 4.

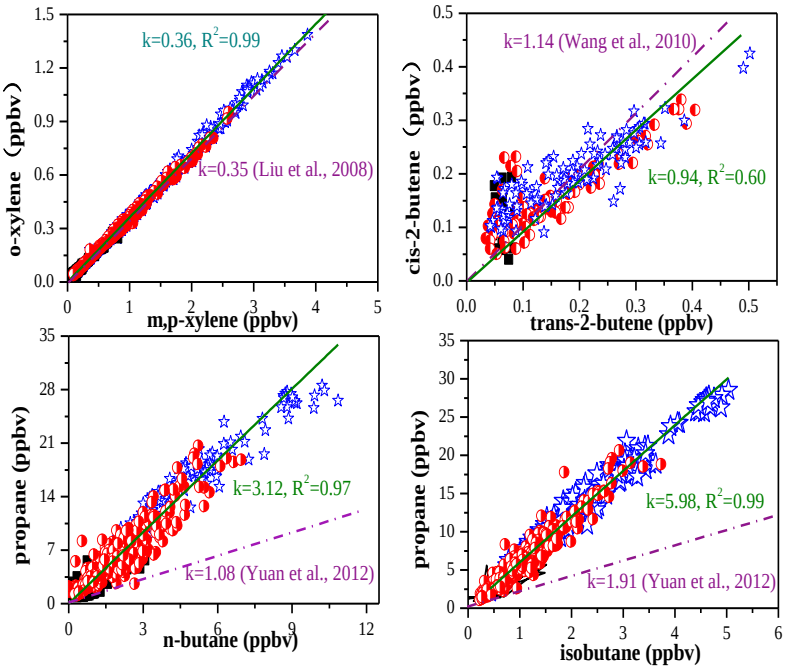

Fig. 4 Ratios and linear correlation coefficients (R^2) between (A) o-xylene and m,p-xylene, (B) cis-2-butene and trans-2-butene, (C) propane and n-butane, and (D) propane and isobutane during clear days (in black), light haze days (in red) and heavy haze days (in blue)

10-Page 9, section 3.3.2: the source attribution must be consolidated and more detailed. It will be nice to see diurnal variation of the different factors as well as the time series in different conditions (clear sky, haze days). The PMF results should be also consolidated by using the air quality indicators (like ozone and PM2.5). Adding to that, an analysis of all the factors with wind direction can add more information about the sources and can reveal some point sources such as industries.

Answer: According to your valuable suggestions, the diurnal variation of the different factors as well as the time series in different conditions were analyzed in the revised manuscript as followings: The time series of the contributions from the five factors to atmospheric NMHCs are shown in Fig. 7. In general, the variation trends of the contributions from gasoline related emissions (gasoline exhaust and evaporation), diesel exhaust, coal combustion emissions and acetylene-related emissions to atmospheric NMHCs were closely related with the variation trend of atmospheric NMHCs measured, while the contribution from the consumer and household products had less correlation with the atmospheric NMHCs measured. The daily emissions from gasoline related sources (gasoline exhaust and evaporation), diesel exhaust, coal combustion sources and acetylene-related sources are usually stable, and hence, the similar variation trends of their contributions to atmospheric NMHCs were mainly ascribed to the variation of meteorological condition. The sources of consumer and household products were suspected to be irregular for explaining the abnormal variation trends of their contributions to atmospheric NMHCs. It should be mentioned that the contribution from coal combustion was the maximum during the most serious pollution episode II (25-26 December 2015) when the wind direction was from southwest, implying that the air parcel

transportation from southern was an important source for NMHCs in Beijing (Wang et al., 2013). The diurnal variations of the contributions from the five factors to atmospheric NMHCs are shown in Fig. 8. Compared with the sources of coal combustion, acetylene-related emissions and consumer and household products, the contributions of the vehicle emissions (gasoline and diesel exhaust) to atmospheric NMHCs during the morning and evening rush hours indeed evidently increased during the clear days and light haze days, but slightly decreased in the morning rush hours during the heavy haze days. The remarkably higher contributions of diesel exhaust than gasoline emissions during the midnight for haze days well reflected the traffic situation, namely, heavy diesel vehicles being only permitted on the road during the midnight in Beijing. The relatively high contributions of consumer and household products to atmospheric NMHCs mainly occurred in clear days during daytime when temperature was relatively high. No distinct diurnal variations of the contributions from coal combustion and acetylene-related emissions to atmospheric NMHCs were found.

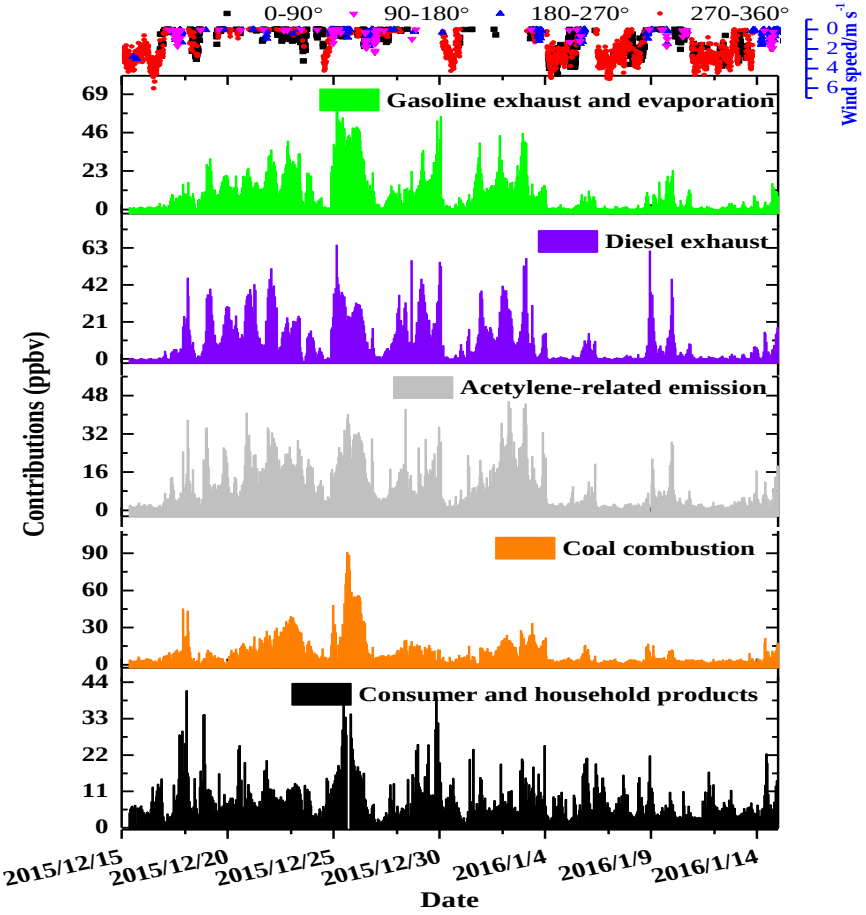

Fig.7 The time series of the contributions from gasoline related emissions, diesel exhaust, coal combustion, acetylene-related emission and consumer and household products to atmospheric NMHCs

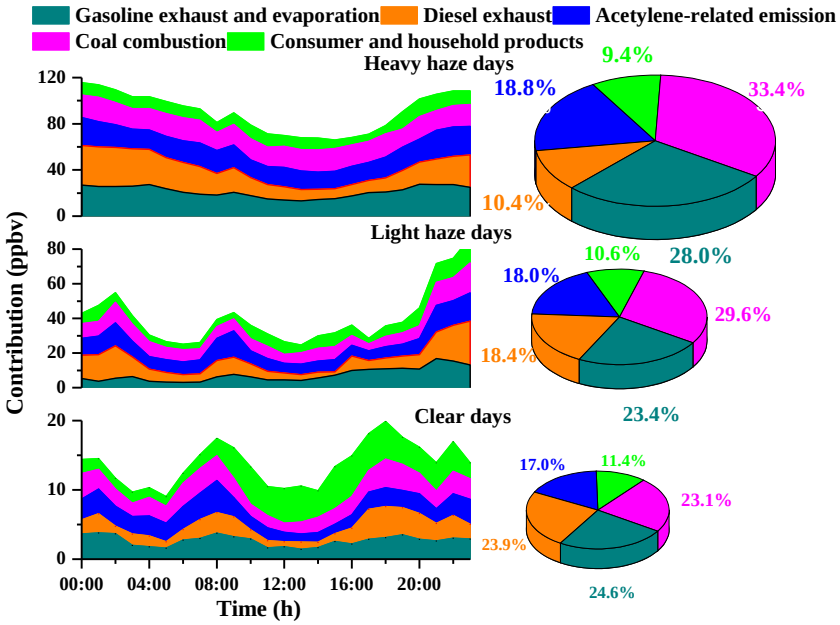

Fig. 8 The diurnal variations of the contributions from the five factors to atmospheric NMHCs (left) and source apportionment of NMHCs (right) in Beijing during clear days, light haze days and heavy haze days

11-Page 9, line 15: It is not true that highly reactive NMHCs were excluded because xylenes, ethylene, etc. were included in the PMF analysis so please put other arguments.

Answer: Yes, you are right. According to your valuable comment, the sentence was revised as following:

The PMF model was performed based on the data of 740 air samples and the NMHCs species with high uncertainties of the measurement were excluded to reduce the possible bias of the modeling results.

12-Page 10, line 1 - 5: how can you explain the correlation of aromatic > C7 with benzene which is a combustion tracer as it correlates also with ethylene and acetylene.

Answer: Yes, your suspicion is logical. The sentence was revised as following:

It is known that these species can be emitted from coal combustion, vehicular exhaust or associated with the solvent emissions of paints, inks, sealant, varnish and thinner for architecture and decoration (Borbon et al., 2002; Guo et al., 2011a). Coal combustion and gasoline exhaust could be excluded as the main contributors to source 4, because aromatics emissions from the two sources are usually accompanied by high emissions of various species with carbon numbers less than six. Solvent emissions could also be excluded due to the relatively high contribution of small molecules such as ethylene and propene in source 4. Based on the PMF analysis for the diurnal variation characters, source 4 is finally attributed to diesel exhaust.

13-Page 10, section 4: please make a brief introduction about the work at the beginning of the

paragraph.

Answer: According to your valuable suggestion, a brief introduction was added at the beginning of the paragraph: Atmospheric non-methane hydrocarbon compounds (NMHCs) were measured at a sampling site in Beijing city from 15 December 2015 to 14 January 2016.

Minor revisions:

1- Page 6, line 10 – 12: please rephrase. I think the word "concentration" is lacking.

Answer: Sorry! We have corrected the mistake in the revised manuscript.

2- Page 6, line 16-17: rephrase: ". . .indicated that vehicle exhaust was an important source of NMHCs. . ."

Answer: Sorry! We have corrected the mistake in the revised manuscript.

3- Page 6, line 24: ". . .which favors accumulation. . ." remove "the"

Answer: Sorry! We have corrected the mistake in the revised manuscript.

4-Keep the same name of compounds in all the manuscript like (propene or propylene; ethane or ethylene. . .)

Answer: Sorry! We have corrected the mistake in the revised manuscript.

5-Page 7, line 27-28: Put this sentence as an explanation before the equations, at line 14.

Answer: Yes! We have put the sentence before the equations.

6-Page 8, line 3: "which is close to. . ."

Answer: Sorry! We have corrected the mistake in the revised manuscript.

7-Page 8, line 23: ". . . in winter of Beijing are close to those. . ." and not "closed to"

Answer: Sorry! We have corrected the mistake in the revised manuscript.

8-Page 8, line 27: ". . .could also be confirmed. . ." not "been"

Answer: Sorry! We have corrected the mistake in the revised manuscript.

9-Page 9, line 15: "with highly reactive", remove "with".

Answer: Sorry! We have corrected the mistake in the revised manuscript.

10-Page 9, line 23: "which was in consistent. . ." please clarify, do you mean "inconsistent"?

Answer: Sorry! We have corrected the mistake in the revised manuscript.

11-Page 10, line 11: “it is clear. . .” not “clearly”

Answer: Sorry! We have corrected the mistake in the revised manuscript.

12-Page 11, line 1: “significant fluctuation. . .” not “significantly”

Answer: Sorry! We have corrected the mistake in the revised manuscript.

13-Page 15 and 21, table 1 title: “status” not “statues”

Answer: Sorry! We have corrected the mistake in the revised manuscript.

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