NOTE: This file includes two sections. Section 1 presents comments from referees, the corresponding point-by-point responses, and the related changes in the manuscript. Section 2 is the marked-up manuscript.

Section 1: (the black font are comments from referees, the red font are authors' responses as well as the related change clarifications.)

Comment response to all referees:

Thanks very much for your comments, suggestions and recommendation with respect to improve our paper. The response to all your comments are listed below. There was an extensive discussion among the authors regarding how to revise the content, and this paper is subjected to a major revision including an update of all retrievals using new inputs (e.g., S_a based on standard deviation of a dedicated WACCM run from 1980 to 2020), re-plot all figures, condense/reorganize the content and focus more on the scientific topics. Thus, the response is delayed, and we are sorry for this.

(1) Detailed response to comments from referee #1:

General comments :

The authors have used a new FTIR dataset to infer tropospheric ozone seasonal evolution and photochemical production regime at Hefei in China. Comparisons of the new dataset with OMI observations, and the GEOS-Chem and WRF-chem model data have shown good agreements. Back trajectories analyses have been used to attribute the contribution regions, and seasonal variabilities, to the high ozone levels observed at Hefei. The chemical sensitivity to ozone production has been studied at Hefei by using proxies such as CO and HCOH.

Although the authors use a new dataset, the novelty of some results is hard to admit.

For instance, it is presented the fact that tropospheric ozone column is higher in spring/summer as a key result, which is a known scientific idea (same for better agreements comparing smoothed profiles relative to unsmoothed profiles). A reorganization of the paper’s structure is needed, with less focus on the know results and more thinking about what is the paper contribution to scientific progress. In addition, the goal of the comparisons of the new dataset with independent data (atmospheric models and satellite observations) is unclear, as well as the use of two different model (global and regional). The objectives of the paper should be clarified and listed in a concise way. The number of figures should be reduced to fit the main scientific results. Discussions about results, such as model and observations comparisons, are missing and would improve the scientific impact of the paper.

The thorough section describing the retrievals is well written and I would advise the authors to submit this paper to a more technical journal, such as Atmospheric Measurement Technique, if not addressing these comments.

Response: This paper has been subjected to a major revision based on the comments from three referees. All your comments are appreciated and have been addressed in the revised version. Main changes/improvements are listed as follows:

1) We have updated all retrievals with new S_a deduced from standard deviation of a dedicated WACCM run from 1980 to 2020, which should be more close to actual natural variation compared to the previous version. This improvement doesn't change the results of this paper.

2) We have reorganized the paper's structure, with less focus on known results and more describing about what is scientifically new. The objectives of the paper are clarified and listed in a concise way. The number of figures is reduced to focus more on the main scientific results. We have condensed quite a lot the descriptions of site/instrument, retrieval, theoretical basis but added many discussions/explanations regarding the observed results and photochemical regime. The figures and descriptions that are useful for understanding this paper but not scientific new are now shifted to the supplement (e.g., previous figures 2 - 5).

3) After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data, due to the following reasons:

a) The scientific topic of our manuscript is the investigation of the ozone seasonal evolution, source and photochemical production regime in polluted eastern China. The main interesting message we would like to present is the application of the FTS tools to determine if the tropospheric O_3 is produced by NOx or VOC, and give a recommendation about what could be done to mitigate the high O_3 levels. This can not only improve the understanding of regional photochemical O_3 production regime, but also contributes to the evaluation of O_3 pollution controls. In the revised version, we leads straightly to this recommendation. For things which are not important for the main message, especially the deviation or something which probably misleads a potential reader, are removed. Accordingly, we removed the comparison with the models and the satellite.

b) This topic regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data, is interesting, but it cannot be clarified clearly within a few sentences or paragraphs and is basically a separate paper. Considering that this paper is already very long (referee's comments), we keep the intention of investigating the ozone seasonal evolution, source and photochemical production regime and removed all comparison with the correlative data.

4) We have responded to all referees' comments point-by-point and revised the manuscript accordingly.

Related change: The changes/improvements listed above have been done in the revised paper.

Specific comments:

Concerning the structure of the paper, it needs to be reorganized with a shorter abstract focusing a key results, more detailed introduction about the proxies used to assess the chemical sensitivity to ozone production, more sub-sections and tables summarizing the results of the comparisons, less figures, and appropriate English language.

Response: We have reorganized the paper's structure, shortened the abstract to focus on a key results, and included more detailed introduction about the proxies used to assess the chemical sensitivity to ozone production. In addition, more sub-sections and tables are used, and the number of figures are reduced to focus on the main scientific results. The revised paper has been corrected by a copy-editing service to improve the language.

Related change: The changes/improvements listed above have been done in the revised paper.

Consistency is also needed across the paper: define once (NDACC has never been defined in the abstract but appears in the keyword section, same for HCOH and VOC in the abstract, …) and use them along the manuscript (ozone or O_3?). Change old references with newest and avoid Wikipedia as a reference.

Response: All acronyms are now defined when they are first mentioned and also used consistently along the manuscript. Most old references are replaced with the newest ones and the Wikipedia reference is removed.

Related change: All these problem have been addressed in the revised paper.

In the introduction section, more explanations about why using proxies such as CO and HCOH would help the reader understanding how to assess the chemical sensitivity to ozone production.

Response: We have added more detailed introduction about the proxies used to assess the chemical sensitivity to ozone production in the introduction section, which would help the reader understanding how to assess the chemical sensitivity to ozone production.

Related change: See introduction in the revised paper.

In the retrieval strategy section, you mention a meteorological station onsite. Do you correct the NCEP profiles with these data? If yes, it should be clarified.

Response: As done at the other FTIR sites of the network, we did not correct the NCEP profiles with these data because this step normally makes the a priori profile (pressure, temperature) inconsistent. The pressure/temperature profiles have to obey some rules and this is fulfilled in the model data. The correction is also not that crucial, because the layers chosen depend only to a small extent on the temperature. When creating HDF files for the NDACC database, people usually have a field for surface temperature. But it is optional.

Related change: None

Define the use of the coincidence criteria when comparing to OMI (Why 3 hours and 0.7 ?) and other independent data.

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now this problem doesn’t exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

In section 5.1, it is mentioned a trend analysis on a 4-years time series. The word “trend” needs to be changed.

Response: This has been done in the revised version.

Related change: Please check section 4.1 in the revised version.

Are back trajectories used to investigate the regions of influence of high tropospheric ozone at Hefei? If yes, it needs to be clarified and better structured in a sub-section. The end of section 5.1 needs to be better structured to emphasis on the scientific conclusions.

Response: The back trajectories are used to determine the origin of the air masses. This has been clarified and the previous section has been re-structured into two sub-sections.

Related change: Please check section 4 for details.

Concerning the comparisons with models, you may want to clarify their use; it is unclear if it is to assess the new dataset quality or investigate the model performances to reproduce observations. Explain the scientific interest of comparing the FTIR dataset with a global and a regional model. Discussions about results concerning comparisons between model/satellite and FTIR observations are missing and would raise the scientific level of the paper. Why is there a shift in the seasonal maximum in GEOS-Chem? Why do OMI and the FTS exhibit different seasonality? For WRF-Chem it is mentioned that the difference could be attributed to uncertainties in the input files, but what about the meteorological data, and/or the chemistry? This has to be further analyzed and explained.

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now all these problems don’t exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

Technical corrections :

- line 20 and 22 : define acronym CO, HCOH, and NO2

Response: We have defined these gases in the revised version.

Related change: Please check line 20 – 24 in the revised version.

- line 26 : by “the” FTS

- line27 : “occur” with no s

Response: This sentence has been removed when condensing the paper.

Related change: Please check the abstract in the revised version.

- line 32 and 33 : choose the precision, one or two decimal?

Response: Both are two decimal in the revised version.

Related change: Please check line 30 – 32 in the revised version.

- line 34 : by “atmospheric models” GEOS-Chem and WRF-Chem

Response: This sentence has been removed when condensing the paper.

Related change: Please check the abstract in the revised version.

- line 41-43 : rephrase the sentence

Response: We have rephrase it as “ Compared with SON/DJF season, the observed tropospheric O_3 levels in MAM/JJA are mainly influenced by transport of air masses from densely populated and industrialized areas while the broad and high O_3 level and variability in MAM/JJA is determined by the photochemical O_3 production.” Please check abstract for details.

Related change: Please check line 32 - 35 in the revised version.

- line 45-50 : state that HCHO is a VOC and define VOC

Response: We state that HCHO is a VOC and define VOC in the revised version. Please check the second sentence in the abstract for details.

Related change: Please check line 20 - 23 in the revised version.

- key words : NDACC never defined in the abstract

Response: As far as we know, the key words part is not a mandatory part of ACP, and thus we have removed the key words part in the revised version. The definition for NDACC has been done in the main text (introduction).

Related change: Please check line 135 in the revised version.

- line 55 : add a reference

- line 56 : add a reference

Response: This has been removed when condensing the paper.

Related change: Please check line 44 in the revised version.

- line 53-71 : references are old

Response: Some old references have been replaced by the references published recently.

Related change: Please check line 44-70 in the revised version.

- line 75-77 : why so many references? Are they all relevant? You may use the most relevant one.

Response: This paragraph focuses on descriptions of the NDACC network. In the revised version, I removed the whole paragraph since it doesn't have much contributions to the main point of this paper. According, all references (if not referred in elsewhere) are also removed.

Related change: Please check introduction in the revised version.

- line 78-79 : define all chemical species.

- line 84 : state the accuracy or use a reference

Response: The whole paragraph has been removed, see above.

- line 87 : avoid Wikipedia as a scientific reference

Response: This reference has been replaced by two scientific papers.

Related change: Please check line 118 in the revised version.

- line 88 : first time ozone is written O3. Be consistent across the manuscript

Response: In the revised version, all "ozone" are replaced by "O_3" . Now it is consistent across the paper.

- line 91 : "PM2.5"

- line 93 : "the" FTS

- line 96 : "Most NDACC sites"

Response: These have been done in the revised version.

Related change: Please check line 134-140 in the revised version.

- line 99 : Is the Hefei site a NDACC site? It is not clear here

Response: Hefei has ran both NDACC and TCCON conventions for more than 4 years, but is still a candidate site rather than an official one because of certain data publicity policy by Chinese government, and not because of the data quality. We are in progress to become an official TCCON site and we believe it will be also possible to be an official NDACC in near future.

Related change: Most site/instrument descriptions are removed and two reference are cited here.

- line 103 : add a reference for OMI

Response: A reference has been included in the revised version.

Related change: Please check line 138 in the revised version.

- line 105 : "the" site description
- line 107 : clarify the sentence "ozone related gases"
- line 114 : reference to Figure 1b
- line 114-115 : rephrase
- line 117 : clarify why it is an important region
- line 118 : add a reference
- line 119-120 : rephrase
- line 123-125 : rephrase
- line 125 : change "demonstrated" to "showed"
- line 126 : "typical observation day in August"

Response: All above related sentence has been removed when condensing the paper. Most site/instrument descriptions can be found in our previous paper (Yuan et al.,2017; Wei et al., 2017).

Related change: Please check section 2 in the revised version.

- line 121 : change "the same as" to "similar to"
- line 139 : define MIR
- line 143 : "for O3 measurements"

Response: These have been done in the revised version.

Related change: Please check section 2 in the revised version.

- line 144 : are you certain filters are used to avoid detector non-linearity? What about signal to noise ratios?

Response: Filters are used for both, avoid detector non-linearity and improve the signal to noise ratios. However, this sentence has been removed when condensing the paper.

Related change: Please check section 2 in the revised version.

- line 148 : clarify “ozone related gases”

Response: This has been changed to “FTS retrievals of O_3, CO and HCHO” in the revised version.

Related change: Please check line 163 in the revised version.

- line 151 : how much is an adequate accuracy?
- line 152-155 : is this sentence misplaced ? If not explain why it “confirms”
- line 155 : delete “so”
- line 157 : delete “overpass”

Response: To avoid misunderstanding, this paragraph has been removed when condensing the paper. Accuracy estimation can be found in section 3.3. The whole section 3 is used to confirm tropospheric O_3, CO and HCHO are robust in Hefei.

Related change: Please check section 3 in the revised version.

- line 161 : add a reference to SFIT4

Response: This has been done in the revised version.

Related change: Please check line 166 in the revised version.

- line 195 : use mathematical equations

Response: We have used mathematical equations in the revised version and shifted it to supplement.

Related change: Please check Supplement section A in the revised version.

- line 230 : “Figures 4 and 5”

Response: This has been done in the revised version. The two figures have been shifted to the supplement, now it is Figures S4 and S5.

Related change: Please check figures S4 and S5 in the revised version.

- line 252 : explain why two sets of models
- line 282 : how much is 0.7 in kilometers at Hefei?

- line 307 : add the GEOS-Chem general reference

- line 320 : what is the nearest grid in kilometer?

- line 345 : add a general reference for WRF-Chem

- line 347 : “Liu et al. (2016)”

- line 348 : “20 x 20 km”

- line 382-383 : add a reference

- line 395 : delete “global”

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now all these problems don’t exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

- line 430 : “air pollution”

- line 430-432 : rephrase the sentence

Response: This sentence has been replaced by many detailed explanations in the revised version.

Related change: Please check section 4.2 in the revised version for details.

- line 435 : state the percentage

Response: We have stated the percentage in the revised version.

Related change: Please check section 4.2 in the revised version for details.

- line 439 : “considering the fact”

Response: This sentence has been replaced by many detailed explanations in the revised version.

Related change: Please check section 4.2 in the revised version for details.

- line 441 : “air pollution”

Response: This has been done in the revised version.

Related change: Please check section 4.2 in the revised version.

- line 454 : “Obvious”. Why it is obvious?

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now this problem doesn’t exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

- line 465 : “not an emission pollutant” is not clear, rephrase

- line 466-467 : explain why the fact that it is complicated means that it shows regional representativeness?

Response: This sentence has been removed when condensing the paper.

Related change: Please check section 5.1 in the revised version.

- line 479 : “as a result”, explain further the link between the two sentences

Response: Many explanations have been included in the revised version.

Related change: Please check section 5.1 in the revised version for details.

- line 485 : stay at present

Response: This has been done in the revised version.

Related change: Please check line 340 in the revised version for details.

- line 497 : how much are a good and an adequate correlation?

Response: In previous version, we regard it as good correlation if the correlation is higher than 0.6, and regard it as moderate correlation if the correlation lies in between 0.4 and 0.6. However, in the revised version, we only present the numbers and don’t use the description such as “good” or “moderate” or “poor” to avoid controversy.

Related change: Please check the revised version for details.

- line 502 : “has taken”

Response: This sentence has been changed to “Sillman (1995a) and Tonnesen and Dennis (2000) found that in situ measurements of the $HCHO/NO_2$ ratio could be used to diagnose local photochemical regimes.” and shifted to introduction part.

Related change: Please check line 78 in the revised version for details.

- line 505-513 : this could go to the introduction section

Response: We have shifted these sentence to introduction section.

Related change: Please check line 95-105 in the revised version for details.

- line 525 : change “obtainment”

Response: Has been changed to “the measurement tool for HCHO in this study was not the same as that of…”

Related change: Please check line 386 in the revised version for details.

- line 554 : change “validate” since OMI, GEOS-Chem, and WRF-Chem, to my knowledge, have already been validated

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now this problem doesn’t exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check conclusion in the revised version.

- Figure 1 a : change to see star colors

- Figure 1 b : instead of showing SZA for 1 day, you may want to show the mean SZA for all the data involved in this study

- Figure 1 legend : is it relevant to point out the wetlands? Are the red hexagons SZA or azimuth angle?

Response: In order to present the objectives of this paper in a concise way, the content has been shortened quite a lot. We removed this figure in the revised version. Detailed site/instrument descriptions can be found in our previous paper (Yuan et al.,2017; Wei et al., 2017).

Related change: Please check section 2 in the revised version for details.

- Figure 2 : cut altitude at 60 or 80 km

Response: This has been done in the revised version and already shifted to supplement.

Related change: Please check the caption of figure S2 for details.

- Figure 3 : arrange the figure so that the text is readable and is not crossed by the lines. Figure 3 partial column averaging kernel of HCOH: explain what are the influences on retrieved column of a partial Avk of 12.

Response: This has been done in the revised version and is shifted to supplement. For partial column averaging kernel of HCOH, we find a bug in our previous plotting script. In the revised version, we fixed this bug and now this problem doesn’t exist. This bug has no influence on retrieval but on for PAVK plotting. Thus, every deduction is the same.

Related change: Please check figure S3 for details.

- Figure 4 and 5 : cut at 60 or 80 km and combine them in one Figure

Response: Both have been cut at 60 km, but we did not combine them in one figure because there are so much error components, and the combination is a big mess. We have shifted them to the supplement, please check for details.

Related change: Please check figures S4 and S5 for details.

- Figure 6, 8, and 10 : insert the number of points included in the comparison and insert the standard deviation of the mean
- Figure 7 and 9 a : insert error bars
- Figure 7 b : shift text
- Figure 11 b : why showing both biased and unbiased data?

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now this problem doesn't exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

- Figure 12 b : reduce y-axis scale

Response: This has been done in the revised version.

Related change: Please check figure 1b for details.

- Figure 15 : maybe plot all the measurements involved instead of daily means?

Response: Now all measurements were included in the revised version.

Related change: Please check figure 3 for details.

- Figure 16 : reduce the size of the dots. Do you consider error bars to fit the data?

Response: We have reduced the size of the dots and grouped them into different seasons in the revised version. The error bars were not included in the fit because the meteorological station data do not have uncertainties. We get the accuracy of each element from the user manual.

Related change: Please check figure 4 for details.

- Figure 18 : (a) all 3 panels should fit in one page. (b) Do you account for uncertainties when fitting the data? (c) R = 919 with 8 points, are you certain it is a robust statistic?

Response:

R(a): In the revise version, the 3 panels have been fitted in one page.

R(b): We account for both slope and correlation. Briefly, we iteratively altered the column HCHO/NO_2 ratio threshold and judged whether the sensitivities of tropospheric O_3 to HCHO or NO_2 changed abruptly. For example, in order to estimate the VOC-limited threshold, we first fitted tropospheric O_3 to HCHO that lies within column HCHO/NO_2 ratios < 2 (an empirical start point) to obtain the corresponding correlation/slope, and then we decreased the threshold by 0.1 (an empirical step size) and repeated the fit, i.e., only fitted the data pairs with column HCHO/NO_2 ratios $<$ 1.9. This has been repeated. Finally, we sorted out the transition ratio which shows an abrupt change in correlation/slope, and regarded this as the VOC-limited threshold. Similarly, the NO_x-limited threshold was determined by iteratively increasing the column HCHO/NO_2 ratio threshold till the sensitivity of tropospheric O_3 to NO_2 changed abruptly.

R(c): The previous figure (R = 919 with 8 points) is only used to demonstrate that PO_3 is more sensitive to VOC within VOC-limited region. Actually, the transition occurs close to about 0.6. At the transition ratio, there are much more points than 8. In the revised version, a detailed description for obtaining the transition threshold is presented, this kind of subfigures (only used for examples) are all removed.

Related change: Please check figure 6 for details

- Table 1 : enlarge the first column to adjust the word “regularization”. O3668 with exponent and index

Response: This has been done in the revised version.

Related change: Please check table 1 for details.

(2) Detailed response to comments from referee #2:

Summary:

The authors report on solar absorption FTIR measurements of tropospheric columns of O3, CO, and HCHO at a candidate NDACC IRWG observation station in Hefei, China. High spectral resolution measurements were conducted between 2014 and 2017 and fill a data gap within the NDACC observation network. The data shows higher tropospheric O3, also with higher variability, in spring and summer. The authors compare these O3 measurements to OMI satellite O3 (PROFOZ product), as well as GEOS-Chem (2 x 2.5 deg) and WRF-Chem (20 x 20 km) model O3 outputs. Comparisons are done in both profile and tropospheric partial column form.

Ozone FTS vs. GEOS-Chem model differences (481 coincidences) are attributed to uncertainties in GEOS-Chem input files ("ozone production loss rates and emission inventory"), it is concluded that GEOS-Chem is biased 13% lower (along profile), with r=0.5 for tropospheric column correlation plots.

Ozone FTS vs. WRF-Chem model differences (481 coincidences) are attributed to uncertainties in WRF-Chem input files ("ozone production and loss rates and MEIC inventory"), it is concluded that WRF-Chem is biased 12% lower (along profile), with r = 0.65 for tropospheric column correlation plots.

Comparisons to coincident OMI ozone profiles and partial (tropospheric) OMI columns were done on 53 coincident measurements after filtering for 0.7° spatial coincidence. Coincident FTS profiles were averaged in a 3 hour window around the OMI overpass at 13:30. OMI profiles were smoothed with FTIR averaging kernels. The OMI profiles are biased 2-13% lower than FTIR profiles, with r=0.73 for tropospheric column correlation plots, in which most OMI points sit below the 1:1 line, indicating also a low bias of OMI w.r.t. FTS.

Both sets of model ozone data are described as "smoother" than FTIR data and are "bias corrected" by adding a constant offset to the tropospheric O_3 columns throughout the year to shift the model data towards FTIR partial column values. GEOS-Chem partial columns are increased by ~100% while WRF-Chem partial columns are increase by ~33% to increase agreement with FTS. Finally, OMI ozone partial column data were increased by ~20% and only then were monthly mean ozone partial column differences calculated.

24-hour back trajectories were calculated arriving at Hefei at 3000 m.a.s.l. from

2014-2017, presumably for those days with FTS observations (?), and they were grouped into spring/summer (presumably MAM/JJA?) and autumn/winter (presumably SON/DJF?). Summer transport is less vigorous and more varied than winter transport, as expected, bringing more air from highly polluted areas, e.g., east China, and broadly accounting for higher O3 and higher O3 variability in the data in spring/summer.

Finally, the O3 production regime is analyzed by describing correlations to meteorological variables recorded at Hefei, as well as looking at O3 vs. CO, O3 vs NO2 (for ratios of HCHO/NO2 > 2.8, assumed to correspond to NOx-ltd O3 production) and O3 vs HCHO (for ratios of HCHO/NO2 < 1.3, assumed to correspond to VOC-ltd O3 production). The ratios to indicate the O3 production regime were found iteratively until the correlation between O3 and NO2 or O3 and HCHO was > 0.6. 106 days of observations (O3, HCHO, CO from FTS; NO2 from OMI) were identified and of those 60% were NOx-ltd, 11% were VOC-ltd, and the remainder were mixed.

Major comments:

The paper is generally well written and presents a thorough error budget and sensitivity analysis of FTIR retrievals (O_3, CO, HCHO) from a new candidate station in the NDACC network. The methods used here are well known and figures 2-5 should also move to the appendix, along with the Rodgers & Connor formulation, unless the authors highlight how their averaging kernels and error budget profiles differ from other similar published results. The paper presents a valuable new and growing observational dataset, however, this reviewer recommends major revisions in order to meet the ACP criteria of scientific significance and quality.

Response: This paper has been subjected to a major revision based on the comments from three referees. All your comments are appreciated and have been addressed in the revised version. Main changes/improvements are listed as follows:

1) We have updated all retrievals with new S_a deduced from standard deviation of a dedicated WACCM run from 1980 to 2020, which should be more close to actual natural variation compared to the previous version. This improvement doesn’t change the results of this paper.

2) We have reorganized the paper's structure, with less focus on known results and more describing about what is scientifically new. The objectives of the paper are clarified and listed in a concise way. The number of figures is reduced to focus more on the main scientific results. We have condensed quite a lot the descriptions of site/instrument, retrieval, theoretical basis but added many discussions/explanations regarding the observed results and photochemical regime. The figures and descriptions that are useful for understanding this paper but not scientific new are now shifted to the supplement (e.g., previous figures 2 - 5).

3) After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data, due to the following reasons:

a) The scientific topic of our manuscript is the investigation of the ozone seasonal evolution, source and photochemical production regime in polluted eastern China. The main interesting message we would like to present is the application of the FTS tools to determine if the tropospheric O_3 is produced by NOx or VOC, and give a recommendation about what could be done to mitigate the high O_3 levels. This can not only improve the understanding of regional photochemical O_3 production regime, but also contributes to the evaluation of O_3 pollution controls. In the revised version, we leads straightly to this recommendation. For things which are not important for the main message, especially the deviation or something which probably misleads a potential reader, are removed. Accordingly, we removed the comparison with the models and the satellite.

b) This topic regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data, is interesting, but it cannot be clarified clearly within a few sentences or paragraphs and is basically a separate paper. Considering that this paper is already very long (referee's comments), we keep the intention of investigating the ozone seasonal evolution, source and photochemical production regime and removed all comparison with the correlative data.

4) We have responded to all referees' comments point-by-point and revised the manuscript accordingly.

Related change: The changes/improvements listed above have been done in the revised paper.

The FTS O_3 measurements are higher than both models (global and regional) and the OMI measurements. The FTS measures a total column through a particular atmospheric slant column, and is expected to be less sensitive to local O3 events than an in situ sensor. We expect generally good agreement with downward-looking OMI, although coincidences are always a challenge. We also expect differences in the FTS vs. model comparisons because of different representativeness offered by a 20x20 km model vs. as 2.5 °x 2 °model. This is not discussed in the paper.

Also, for the 20x20 km WRF-Chem model, the profile up to 10 km could extend over two horizontal grid boxes for most SZAs > 45 °,depending on the location of Hefei within a model grid box. Has this been considered?

Without discussing representativeness, the authors attribute FTS vs. model differences to model "input files", e.g., "ozone production loss rates and emission inventory" which is superficial. As a consequence, we learn little, if anything, about specific model processes and emission inventories that may be responsible.

Also, why is the data from this candidate station considered as "truth" in the comparison to OMI and the models? The total errors are estimated as 10% but they are dominated by smoothing error and based on very tight Sa values for O_3 (10%), so (as the authors note), they are an underestimate.

If the authors plotted OMI vs. FTS trop O_3 column data with both data sets' error bars they would still not overlap, but presumably OMI data has been validated – is it generally found to be low compared to other data?

The addition of a simple offset to model O3 values before looking at fractional monthly mean differences w.r.t. FTS is problematic because it is evident in figures 9 and 11 that such a simple manipulation does not bring the data points onto the 1:1 line. Instead, we have the highest O3 values below the FTS measurements and the lowest values above. This is even more dramatic in GEOS-Chem data, presumably because of lower model resolution, which homogenizes high O_3 values over a large grid cell, while raising the background O3 values.

Since the highest values occur in spring/summer and the lowest in autumn/winter, the bias is seasonally dependent and therefore not just due to spatial representativeness. Is it due to incorrect emissions or chemistry?

What are the main chemistry and emissions differences between the two models being compared to FTS? WRF-Chem is running with the MEIC inventory, presumably optimized for China, as well as biogenic emissions from MEGAN – why does it only do a little bit better than GEOS-Chem?

About smoothing the OMI profile by the FTIR averaging kernels, this method is meant to be applied to high vertical resolution correlative data, which OMI is not. It has about ~1 DOF in the troposphere itself. This may explain why there is still a lot of “shape” left in the fractional difference between FTIR and smoothed OMI profiles. What do OMI kernels look like and where is its peak of sensitivity – is it the same as for FTS?

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now all these problems don’t exist in the revised version. Please check above clarification (page 4) for the reason.

Related change: Please check the revised version for details.

The trajectory cluster analysis is difficult to follow without familiarity with China’s geography. That can easily be fixed by adding the major city or region names referred to in the discussion to Figure 13. Without this information, it is hard to quickly judge if 1-day trajectories are long enough for transport to occur to Hefei. It is also not clear how the trajectories are clustered and the mean cluster trajectories (in color) are hard to see. Another way to represent this data would be to count trajectory elements crossing, e.g., 0.5 ° x 0.5 ° grid boxes. Also, why 3000 m? That seems much higher than the typical boundary layer height in winter, and probably also in summer. This choice will influence strongly both the speed and footprint of the pollution regions influencing Hefei. Have the authors tried 1500 m?

Response: In the revised version, all your comments regarding coincident trajectory cluster analysis have been addressed. Now we used 1500 m a.s.l. While the relative contribution/direction of each trajectory changes a little bit, the main point is still the same.

Related change: Now the height is 1500m, and China's geography is included. Please check figure 2 in the revised version for details.

Finally, regarding O3 production regimes, ratios of HCHO/NO2 were varied until the correlation was > 0.6 in plots of O3 vs. HCHO and O3 vs. NO2. The outcome is that the correlation for the NOx-ltd plot of O3 vs. NO2 is 0.66 (moderate) while the correlation for the VOC-ltd plot of O3 vs. HCHO is 0.92, with far fewer points remaining in the fit. This seems rather arbitrary and needs justification. Also of the 106 days available for this analysis, which are from spring/summer and which are from autumn/winter? Are all VOC-ltd days in winter?

Response: a) The previous figure (R = 0.919 with 8 points) was only used to demonstrate that PO_3 is more sensitive to VOC within VOC-limited region. Actually, the transition occurs close to about 0.6 (not 0.919). At the transition ratio, there are many more points than 8. In the revised version, a detailed description of obtaining the transition threshold is presented, this kind of subfigures (only used for demonstration) are all removed. Briefly, we iteratively altered the column $HCHO/NO_2$ ratio threshold and judged whether the sensitivities of tropospheric O_3 to HCHO or NO_2 changed abruptly. For example, in order to estimate the VOC-limited threshold, we first fitted tropospheric O_3 to HCHO that lies within column $HCHO/NO_2$ ratios < 2 (an empirical start point) to obtain the corresponding correlation/slope, and then we decreased the threshold by 0.1 (an empirical step size) and repeated the fit, i.e., only fitted the data pairs with column $HCHO/NO_2$ ratios < 1.9. This has been done iteratively. Finally, we sorted out the transition ratio which shows an abrupt change in correlation/slope, and regarded this as the VOC-limited threshold. Similarly, the NO_x-limited threshold was determined by iteratively increasing the column $HCHO/NO_2$ ratio threshold till the sensitivity of tropospheric O_3 to NO_2 changed abruptly.

The transition threshold estimation using this scheme exploits the fact that O_3

production is more sensitive to VOCs if it is VOCs-limited and is more sensitive to NO_x if it is NO_x limited, and it exists a transition point near the threshold (Martin et al., 2004). Su et al. (2017) used this scheme to investigate the O_3-NOx-VOCs sensitivities during the 2016 G20 conference in Hangzhou, China, and argued that this diagnosis of PO_3 could reflect the overall O_3 production conditions.

b) Table 4 and the last paragraph of section 5.3.2 present detailed description of classification for these 106 days measurements. Not all but ~ 75% VOC-ltd days are in winter.

Related change: This problem has been addressed in the revised version. Please check section 5.3 in the revised version for details.

When I look at the full O3 data in Figure 12, I wonder why there isn't a stronger signature of JJA O3 enhancements in Hefei? (Is it related to filtering out days affected by haze, App B?) Many high values seem to be in May, although the x-axis is hard to read and should really be changed to, Jan 1, June 1,etc., throughout the paper where dates are shown. Or possibly at boundaries between MAM, JJA, SON, DFJ, if these are the groupings for the seasons in the paper.

Response: a) Compared to other high resolution FTS sites, the O_3 measurement in Hefei in JJA are very high, and we observed higher day-to-day variations in summer than other seasons. Vigouroux et al. (2015) studied O_3 trends and variability with eight NDACC FTS stations that have a long-term time series of O_3 measurements, namely, Ny-Ålesund (79 ° N), Thule (77 ° N), Kiruna (68 ° N), Harestua (60 ° N), Jungfraujoch (47 ° N), Izaña (28 ° N), Wollongong (34 ° S) and Lauder (45 ° S). All these stations were located in non-polluted or relatively clean areas. The results showed a maximum tropospheric column in spring at all stations except at Jungfraujoch which extended into summer. This is because the stratosphere troposphere exchange (STE) is most effective during late winter and spring (Vigouroux et al. 2015). We don't think there isn't a stronger signature of JJA O_3 enhancements in Hefei is related to filtering criteria which are used to guarantee the data quality. It is most probably because the STE process is weaker in summer, though photochemical O_3 production is higher. Thus, tropospheric O_3 (STE fraction plus photochemical production fraction) in JJA is not the highest.

b) "June" and "MAM, JJA, SON, DFJ" have been used in the revised version.

Related change: "June" and "MAM, JJA, SON, DFJ" have been used in the revised version. Please check figure 1(b) in the revised version for details.

Have the FTS partial columns been compared to in situ O_3 monitors in Hefei to see if they also show enhancements in May/June 2015 and 2016? What about the low values in Jan 2015 and 2017 vs. the higher ozone in Jan 2016?

Response: We did not compared the FTS to in situ O_3 data due to a lack of co-existing in situ O_3 measurements. The O_3 variations in Jan 2016 are higher compared to Jan 2015 and 2017, most probably because of higher air pollution.

Related change: None

Finally, the Pearson coefficient of 0.35 – 0.6 was taken to mean "moderately correlated" in this work. Typically moderate correlation is associated with values of 0.5 – 0.8, since the lower bound would mean that the model fit to the data explains only 25% of the variations in the data. At 0.35 that drops to only 12%.

Response: In previous version, we regard it as good correlation if the correlation is larger than 0.6, and regard it as moderate correlation if the correlation lies in between 0.4 and 0.6. However, in the revised version, we only present the numbers and don't use a description such as "good" or "moderate" or "poor".

Related change: Please check section 5 in the revised version for details.

Further detailed technical comments:

Fig. 1a: most names in this figure are illegible. Use a cleaner map to reduce clutter.

Fig. 1b: no red hexagons are visible, but I assume the red arc is the azimuth and the un-described yellow circles are the SZA.

Response: In order to focus on the main objectives, the content has been shortened quite a lot. We removed this figure in the revised version. Detailed site/instrument descriptions can be found in our previous paper (Yuan et al.,2017; Wei et al., 2017).

Related change: Please check section 2 in the revised version for details.

Fig. 2: what does "with measured ILS" mean in this caption? Is the ILS characterized

with linefit and then fixed in the retrievals, or are some ILS parameters still being retrieved? Why is there a loss of sensitivity to HCHO right at the surface? Is this a priori related?

Response: a) In sfit4, the ILS can be treated with three options: one is assuming an ideal ILS, two is retrieving the ILS together with the trace gas retrieval, and three is using the measured ILS. We regularly used a low-pressure HBr cell to monitor the instrumental line shape (ILS) of the instrument, and included the measured ILS in the retrieval.

b) It is not a priori related but a characteristic of the HCHO retrieval. The sensitivity at the ground is low because of the very weak absorption feature of HCHO. The spectral signature at the ground is very broad, thus in the presence of noise very indistinguishable from the features created by the interfering species. The previous figures 2 and 3 have been shifted to supplement. Now is figures S2 and S3.

Related change: Please check section 3.1 in the revised version for details.

Fig. 3: the HCHO trop column AK seems unhealthy for growing so far past 1 quickly above ~3 km, even if there is little HCHO there. What is the reason for this shape?

Response: We find a bug in our previous plotting script. In the revised version, we fixed this bug and now this problem doesn’t exist. This bug only for PAVK plotting, and has no influence on retrieval. Thus, every deduction is the same as before. Thanks for point out this bug.

Related change: Please check figure S3 for details.

Fig. 4: What is the explanation for the peak in the CO error at around ~3 km?

Response: This is due to smoothing at around 3 km.

Related change: It has been shifted to supplement.

Fig. 5: Legend seems reversed for total random error and z shift for CO.

Response: We plot the three gases (O_3, CO, HCHO) using the same script, and after a careful check with our plotting script, we find there is no problem between the total random error and z shift for CO.

Related change: It has been shifted to supplement.

Fig. 9 and 11: it’s hard to judge seasons with the date labels as presented. Also, why do these figures not have the identical number of O3 data points if they are derived from the same data filtering applied to FTS data that is described in App B?

Fig. 14: is based on Fig 12, not 13 as the caption says. Again, what are the model process and inventory differences leading to this? Panel a) says smoothed model, but is OMI not also smoothed in this figure?

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now all these problems don't exist in the revised version. Please check above clarification (page 3) for the reason.

Related change: Please check the revised version for details.

Fig. 15: The wind sensor appears to be installed in a poor location as the wind speed never exceeds 0.3 m/s or ~1 km/h! If that is the case, then the wind direction data is also spurious. That's too bad, because I wanted to see a plot of Hefei O_3 vs. wind direction to see if O_3 is higher when winds blow from the city.

Response: The weather station gives an output every 10 seconds, but the previous figure 15 only presents the daily average data that coincident with O_3. The wind direction and wind speed are **vector**s, thus, the averages are quite different compared to the short term data. The changing wind direction is the reason why the daily averaged wind speed seems never exceeds 0.3 m/s or ~1 km/h, and not because the wind sensor in a poor location. The figure 3 in the revised version, which presents minutely, hourly, daily, and monthly averaged data, illustrates the features better. For minutely- averaged data, the wind speed can exceed 6 m/s.

Wind direction is also important because it affects pollution transport, giving rise to high O_3 in downwind locations (Wang et al., 2016). The city downtown locates in eastern of the observation site and the majority of the Chinese population lives in the eastern part of China, easterly winds (direction less than 180˚) could generally transport more pollutants to the observe area than westerly winds (direction larger than 180˚), resulting in a higher O_3 level.

Related change: Minutely, hourly, daily, and monthly averaged data are included. Please check figure 3 for details.

Fig 16: In spite of problems above, the highest O_3 values occur for the lowest of the low wind speeds, pointing to the accumulation of local pollution. There is a "moderate" negative correlation between O3 and RH – why? We could learn more if these data were colored according to spring/summer and autumn/winter.

Response: The data are now color coded into spring/summer (MAM/JJA) and autumn/winter (SON/DJF) groups in figure 4 in the revised paper. We have fitted the minutely, hourly and daily average data with the coincident O_3, and all of them showed weak negative correlation between O_3 and RH. Elevated O_3 concentrations generally occurs on days with dry condition, low pressure and low winds in Hefei probably because these conditions favor the accumulation of O_3 and its precursors.

Related change: Please check figure 4 in the revised paper.

Fig. 19: hard to judge seasons with x-axis labels. Panel b is based on data in panel a that does not seem to sample seasons evenly. This should be discussed.

Response: In the revised paper, we only present the time series of column HCHO/NO_2 ratios (figure 7), and the detailed discussion for PO_3 limitation is listed in table 4. The HCHO and O_3 are not retrieved within the same spectra, which means a measurement day that has a robust HCHO retrieval does not always has a robust O_3 retrieval, vice versa. The previous figure 19 (a) presents all days that have robust HCHO and NO_2, and figure 19 (b) presents the days that have robust HCHO, O_3 and NO_2. The criteria in figure 19 (b) is more stricter than figure 19 (a), and thus seems don't sample seasons evenly.

Related change: The previous figure 19 (b) is removed in the revised version and the detailed discussion for PO_3 limitation is listed in table 4. Please check figure 7 in the revised version for details.

Table 1: retrieved interfering gases →as columns, I presume, except for H2O, as noted? Also, WM →MW. I'm not sure what footnote b means, please clarify.

Response: The rows for H_2O has been deleted, WM is changed to MW. All footnotes has been removed because we think they are not necessary.

Related change: Please check table 1 for details.

Manuscript:

P1L74: sun spectra → solar absorption spectra

Response: This paragraph focuses on descriptions of the NDACC network. In the revised version, I removed the whole paragraph since it doesn't have much contributions to the main point of this paper.

Related change: This paragraph has been removed.

P1L3: replace wiki reference with something from the many, many refereed papers on Chinese modernization and growing air pollution problems.

Response: This sentence has been removed in the revised version.

P4L89: what are China's AQ standards in ppb for long- and short-term exposure?

Response: Tropospheric O_3 was already included in the new air quality standard as a routine monitoring component (http://www.mep.gov.cn, last access on 23 May 2018), where the limit for the maximum daily 8 h average (MDA8) O_3 in urban and industrial areas is 160µg/m^3 (~ 75 ppbv at 273 K, 101.3 kPa).

Related change: Please check line 122 in the revised version for details.

P4L95: greatly contribute to ozone pollution controls →contribute to the evaluation of O3 pollution controls

Response: This has been done in the revised version.

Related change: Please check line 140 in the revised version for details.

P4L117: … after it is itself validated as an NDACC site and it moves from candidate to regular status.

P5L129: then increases →then SZA increases

P5L129-133: what region influences the measurements depends on the azimuth of observation, yes, but also on the direction and wind speed pushing air masses above Hefei, especially for the lowest parts of the atmosphere. This could be significant when local pollution events are occurring as some events can be completely swept away from the FTS obs path.

Response: We agreed with your comment but we have removed these descriptions when condensing the paper. Detailed site/instrument descriptions can be found in our previous paper (Yuan et al.,2017; Wei et al., 2017).

Related change: Please check section 2 for details.

P6L173: cited references missing from references section

Response: This problem has been addressed in the revised version.

Related change: Please check the reference section.

P6L178: please explain deweighting more clearly. What are instrument SNR levels without deweighting?

Response: This sentence has been removed when condensing this paper. The standard deweighting stuff can be found in NDACC network or on request from the co-author Mathias Palm who is one of the SFIT4 developer. The instrument SNR level without deweighting is around 200 to 600.

Related change: Please check section 3 for details.

P7L187: how are the Sa diagonal element magnitudes chosen? WACCM?

Response: In the revised version, Sa diagonal element is based on standard deviation of WACCM simulations from 1980 to 2020.

Related change: Please check section 3 for details.

P7L191: is the ILS retrieved in all retrievals or is it done with LINEFIT and then held constant?

Response: We normally perform cell measurement once per month. For all measurements within this month, it is done with LINEFIT and then held constant. We included this clarification in the revised version.

Related change: Please check section 3 for details.

P11L315-317: tagged O3 runs are mentioned, which would be nice and would allow the attribution of pollution to various source regions, but these 3 lines are very unclear (i.e., also about restart files)

P14L393-4: basically reproduced … but with slight shifts in timing   July is wrong in both models; why are they low in August? When is the local Hefei smog season?

Response: In the revised version, these problems don't exist because we removed all comparisons with correlative data. By the way, in my impression, most smog occurs in winter season.

Related change: Please check section 4 for details.

P14L403: Logan (1985) “observed” →I presume this is a model study?

Response: This reference which based on both model simulation and observation has been replaced by some newly references in the revised version.

Related change: Please check section 4.2 for details.

P16L448: basically consistent throughout all seasons →it really doesn’t look like that to me; would be easier to think about if time series started with MAM as opposed to JFM.

P16L457-63: this really is a shallow explanation of what may be causing the differences, from which we learn nothing concrete. Also, how does larger air pollution increase uncertainty in either emission inventories or the photochemical regime? Isn’t the latter, especially, something that is diagnosed from the emission rates and relative abundances of NOx and VOCs?

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now all these problems don’t exist in the revised version. Please check above clarification (page 3) for the reason.

Related change: Please check the revised version for details.

P17L495/6: which emissions are being discussed here: biogenic? anthropogenic? What are the expected magnitudes and timing of each?

Response: In the revised version, this problem doesn’t exist because this sentence has been changed to “Pronounced tropospheric CO and NO_2 variations were observed but the seasonal cycles are not evident probably because of air pollution which is not constant over season or season dependent”.

Related change: Please check section 5.2 for details.

P18L528: straightly applied →straight forwardly applied

Response: This has been done in the revised version.

Related change: Please check line 389 for details.

P19L554: “validate OMI” →that’s a strong statement given the unproven nature of these particular FTIR measurements, and given there’s no reference to other OMI validation efforts and what they have typically revealed.

P19L560: WRF-Chem agreement is “better” →it has a lower “bias” but greater summer differences. It’s not clear if that is better given it is a high res model using optimized emissions for China

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now all these problems don’t exist in the revised version. Please check above clarification (page 3) for the reason.

Related change: Please check the revised version for details.

P22 L651: would not screening out hazy days eliminate a lot of JJA O_3 pollution days? Haze isn’t a problem for FTIR as much as non-constant intensity (e.g., clouds floating by during a ~20 minute observation time).

Response: This criterion that is used to eliminate bad spectra requires that the solar intensity variation (SIV) is less than 10%. Empirically, most of the variations are caused by floating clouds and some of them may be caused by other objects such as smog or unknown opaque object. The 10% empirical threshold keeps a reliable retrieval. We don’t think it eliminated a lot of JJA O_3 pollution days. Haze is not a key factor that cause the variation and we have removed the word “haze” in the revised version.

Related change: Please check supplement for details.

(3) Detailed response to comments from referee #3:

1 Overall remarks

The paper reports on about three years of tropospheric ozone and formaldehyde measurements from a new FTIR instrument in Heifei, China. The data are compared to a number of correlative data, including tropospheric NO2 from the OMI satellite instrument, and results from chemical transport models.

The authors give a very long and detailed description of their instrument and retrieval technique. They then analyse their observations using the correlative data mentioned above. Overall, their results, such as annual cycle, correlations, and trajectory analyses are plausible. However, the authors tend to discount differences and poor correlations, and to ignore the very coarse altitude resolution of their tropospheric ozone data, which average over a very wide altitude range, and have relatively little sensitivity to the planetary boundary layer, where a substantial part of the smog related ozone photo-chemistry takes place. Largely I concur with the comments by the other two reviewers. The paper does not present major new insights. However, it is important to report on new instruments and on tropospheric chemistry findings in China. Therefore, and also considering that this is a special issue for the last Quadrennial Ozone Symposium, I recommend publication after a few major deficits have been addressed.

Response: This paper has been subjected to a major revision based on the comments from three referees. All your comments are appreciated and have been addressed in the revised version. Main changes/improvements are listed as follows:

1) We have updated all retrievals with new S_a deduced from standard deviation of a dedicated WACCM run from 1980 to 2020, which should be more close to actual natural variation compared to the previous version. This improvement doesn't change the results of this paper.

2) We have reorganized the paper's structure, with less focus on known results and more describing about what is scientifically new. The objectives of the paper are clarified and listed in a concise way. The number of figures is reduced to focus more on the main scientific results. We have condensed quite a lot the descriptions of site/instrument, retrieval, theoretical basis but added many discussions/explanations regarding the observed results and photochemical regime. The figures and descriptions that are useful for understanding this paper but not scientific new are now shifted to the supplement (e.g., previous figures 2 - 5).

3) After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data, due to the following reasons:

a) The scientific topic of our manuscript is the investigation of the ozone seasonal evolution, source and photochemical production regime in polluted eastern China. The main interesting message we would like to present is the application of the FTS tools to determine if the tropospheric O_3 is produced by NOx or VOC, and give a recommendation about what could be done to mitigate the high O_3 levels. This can not only improve the understanding of regional photochemical O_3 production regime, but also contributes to the evaluation of O_3 pollution controls. In the revised version, we leads straightly to this recommendation. For things which are not important for the main message, especially the deviation or something which probably misleads a potential reader, are removed. Accordingly, we removed the comparison with the models and the satellite.

b) This topic regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data, is interesting, but it cannot be clarified clearly within a few sentences or paragraphs and is basically a separate paper. Considering that this paper is already very long (referee's comments), we keep the intention of investigating the ozone seasonal evolution, source and photochemical production regime and removed all comparison with the correlative data.

4) We have responded to all referees' comments point-by-point and revised the manuscript accordingly.

Related change: The changes/improvements listed above have been done in the revised paper.

Response to "the authors tend to discount differences and poor correlations, and to ignore the very coarse altitude resolution of their tropospheric ozone data, which average over a very wide altitude range, and have relatively little sensitivity to the planetary boundary layer, where a substantial part of the smog related ozone photo-chemistry takes place."

Briefly: Many scientists have proved that column technique (OMI, GOME, or airborne results) can be used to investigate PO_3 sensitivity (Martin et al. 2004a; Duncan et al. 2010; Choi et al., 2012; Witte et al., 2011; Jin and Holloway, 2015; Mahajan et al., 2015; Schroeder et al., 2017; Jin et al., 2017). The NO_2 used in this study is the same as most previous studies, the sensitivity/resolution of FTS O_3 is close to that of OMI (Liu et al., 2010), the FTS HCHO is verified to be robust in troposphere in view of future satellite validation (Vigouroux et al., 2018). Thus, column technique used in this study is reasonable. We do acknowledge the paper by

Schroeder et.al. (2017) which was published during the preparation of the manuscript. Schroeder et.al. (2017) question the usability of the column technique to infer PO3 sensitivity. However, this manuscript does take into account much of the criticism mentioned by Schroeder et.el (2017): we calculated the transition thresholds with the measurements in Hefei rather than straightly applied the thresholds estimated by either previous studies. The FTIR measurements have a much smaller footprint than the satellite measurements. Also we concentrate on measurements recorded during midday, when the mixing layer has largely been dissolved. And furthermore, the measurements are more sensitive to the lower parts of the troposphere, which can be inferred from the normalized AVK's. This reason is simply, that the AVK's show the sensitivity to the column, but the column per altitude decreases with altitude.

In detail: Over polluted areas, both HCHO and tropospheric NO_2 have vertical distributions that are heavily weighted toward the lower troposphere, indicating that tropospheric column measurements of these gases are fairly representative of near surface conditions. Many studies have taken advantage of these favorable vertical distributions to investigate surface emissions of NOx and VOCs from space (Boersma et al., 2009; Martin et al., 2004a; Millet et al., 2008; Streets et al., 2013). Martin et al. (2004a) and Duncan et al. (2010) used satellite measurements of column $HCHO/NO_2$ ratio to explore near-surface O_3 sensitivities from space and disclosed that this diagnosis of O_3 production rate (PO_3) is consistent with previous finding of surface photochemistry. Witte et al. (2011) used a similar technique to estimate changes in PO_3 to the strict emission control measures (ECMs) during Beijing Summer Olympic Games period in 2008. Recent papers have applied the findings of Duncan et al. (2010) to observe O_3 sensitivity in other parts of the world (Choi et al., 2012; Witte et al., 2011; Jin and Holloway, 2015; Mahajan et al., 2015; Schroeder et al., 2017; Jin et al., 2017).

Related change: Several references where the column technique (OMI, GOME, or airborne results) is used to investigate PO_3 sensitivity have been included in the revised version. Please check the introduction part for details.

2 Suggested Changes

The description of the FTIR technique and FTIR profile retrieval in lines 148 to 248, as well as the averaging kernel smoothing used for comparison (lines 249 to 279) is pretty much standard. This could all be omitted, or moved to an appendix. A short paragraph and a few references in the main text are enough.

Response: In the revised version, the previous lines 148 to 248 have been condensed dramatically. The previous figures 2 - 5 have been shifted to the supplement. Please check section 3 for details. We still keep some of them because this paper is the first time to present O_3, HCHO, and CO time series at Hefei site. We think a brief introduction regarding site/retrieval setting/error analysis is useful. The previous lines 249 to 279 are all removed when condensing this paper.

Related change: Please check section 3 for details.

lines 339 to 342, lines 367 to 370: I think these simple attributions to "model input files" are not valid. The wide averaging kernels and low sensitivity of the FTIR tropospheric ozone columns to boundary layer ozone, as well as the limited horizontal resolution of the model data could play a very large role here. Please reword or omit these parts.

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now this problem doesn’t exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

Appendix A: Basically this is textbook / Rogers (2000), right? So this could/ should be omitted.

Response: Appendix A is a textbook stuff but useful for understanding this paper. It has been shifted to the supplement in the revised paper.

Related change: Please check Supplement section A in the revised version.

Fig. 6: I am not sure how meaningful this comparison of ozone profiles is. Both have very poor altitude resolution, and profile shape is determined to a very large degree by a priori assumptions. Comparison with a real tropospheric ozone profile from ozone-sondes or lidar would be much more meaningful. Maybe drop this Figure

and its discussion? Similar considerations apply to Figs. 8 and 10.

Response: After an extensive discussion among the authors, we deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data. Now this problem doesn't exist in the revised version. Please check above clarification (page 2) for the reason.

Related change: Please check the revised version for details.

In most respects, I concur with the detailed recommendations by the other two reviewers. However, after shortening, and addressing the major comments, I think this manuscript is publishable in ACP.

Response: We have reorganized the paper's structure, with less focus on known results and more describing about what is the paper contribution to scientific progress. We have responded to all referees' comments point-by-point and revised the content accordingly. Thanks very much for your recommendation.

Section 2: marked up file, as follows

In brief, our paper has been subjected to a major revision based on the comments from three referees. In the marked up file, we only point out the main changes rather all revisions to avoid a big mess. Main changes/improvements are listed as follows:

1) We have updated all retrievals with new S_a deduced from standard deviation of a dedicated WACCM run from 1980 to 2020.

2) We have reorganized the paper's structure, with less focus on known results and more describing about what is scientifically new. The objectives of the paper are clarified and listed in a concise way. The number of figures is reduced to focus more on the main scientific results. We have condensed quite a lot the descriptions of site/instrument, retrieval, theoretical basis but added many discussions/explanations regarding the observed results and photochemical regime. The figures and descriptions that are useful for understanding this paper but not scientific new are now shifted to the supplement (e.g., previous figures 2 - 5).

3) We deleted all paragraphs and figures regarding comparisons with the correlative data, i.e., OMI, GEOS-Chem and WRF-Chem data.

The marked up file is as follow, please check the red underlined sentences for details:

Ozone seasonal evolution and photochemical production regime in polluted troposphere in eastern China derived from high resolution FTS observations

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Abstract:

The seasonal evolution of O_3 and its photochemical production regime in a polluted region of eastern China between 2014 and 2017 has been investigated using different observations and modelling. We used tropospheric ozone (O_3), carbon monoxide (CO) and formaldehyde (HCHO, a marker of VOCs (volatile organic compounds)) partial columns derived from high resolution Fourier transform spectrometry (FTS), tropospheric nitrogen dioxide (NO_2, a marker of NOx (nitrogen oxides)) partial column deduced from Ozone Monitoring Instrument (OMI), surface

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meteorological data, and a back trajectory cluster analysis technique. A broad O_3 maximum during both spring and summer (MAM/JJA) is observed; the day-to-day variations in MAM/JJA are generally larger than those in autumn and winter (SON/DJF). Tropospheric O_3 columns in June are, on average, 0.50×10^{18} molecules*cm^{-2} (47.6%) higher than those in December which has a mean value of 1.05×10^{18} molecules*cm^{-2}. Compared with SON/DJF season, the observed tropospheric O_3 levels in MAM/JJA are mainly influenced by transport of air masses from densely populated and industrialized areas while the broad and high O_3 level and variability in MAM/JJA is determined by the photochemical O_3 production. The tropospheric column HCHO/NO_2 ratio is used as a proxy to investigate the photochemical O_3 production rate (PO_3). The results show that the PO_3 is mainly nitrogen oxides (NO_x) limited in MAM/JJA, while it is mainly VOC or mix VOC-NO_x limited in SON/DJF. Statistics show that NO_x limited, mix VOC-NO_x limited, and VOC limited PO_3 accounts for 60.1%, 28.7%, and 11%, respectively. Considering most of PO_3 are NO_x limited or mix VOC-NO_x limited, reductions in NO_x would reduce most of the O_3 pollution in eastern China.

1 Introduction

Human health, terrestrial ecosystems, and materials degradation are impacted by poor air quality resulting from high photochemical ozone (O_3) levels (Wennberg and Dabdub, 2008; Edwards et al., 2013; Schroeder et al., 2017). In polluted areas, tropospheric O_3 generates from a series of complex reactions in the presence of sunlight involving carbon monoxide (CO), nitrogen oxides ($NO_x \equiv$ NO (nitric oxide) + NO_2 (nitrogen dioxide)), and volatile organic compounds (VOCs) (Oltmans et al., 2006; Schroeder et al., 2017). Briefly, VOCs first react with the hydroxyl radical (OH) to form a peroxy radical (HO_2 + RO_2) which increases the rate of catalytic cycling of NO to NO_2. O_3 is then produced by subsequent reactions between HO_2 or RO_2 and NO that lead to radical propagation (via subsequent reformation of OH). Radical termination proceeds via reaction of OH with NOx to form nitric acid (HNO_3) (reaction (1), referred to as LNOx) or by radical-radical reactions resulting in stable peroxide formation (reactions (2) – (4), referred to as LROx, where ROx $\equiv$ RO_2 + HO_2) (Schroeder et al., 2017):

$$OH + NO_2 \rightarrow HNO_3 \quad (1)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad (2)$$

$$HO_2 + RO_2 \rightarrow ROOH + O_2 \quad (3)$$

$$2RO_2 \rightarrow ROOR + O_2 \quad (4)$$

Typically, the relationship between these two competing radical termination processes (referred to as the ratio LRO_x/LNO_x) can be used to evaluate the photochemical regime. In high-radical, low-NO_x environments, reactions (2) – (4) remove radicals at a faster rate than reaction (1) (i.e., LROx $\gg$ LNOx), and the photochemical regime is regarded as "NOx limited". In low-radical, high-NOx environments the opposite is true (i.e., LROx $\ll$ LNOx) and the regime is regarded as "VOC limited". When the rates of the two loss processes are comparable (LNOx $\approx$ LROx), the regime is said to be at the photochemical transition/ambiguous point, i.e., mix VOC-NOx limited (Kleinman et al., 2005; Sillman et al., 1995a; Schroeder et al., 2017).

Understanding the photochemical regime at local scales is a crucial piece of information for enacting effective policies to mitigate O_3 pollution (Jin et al., 2017; Schroeder et al., 2017). In order to determine the regime, the total reactivity with OH of the myriad of VOCs in the polluted area has to be estimated (Sillman, 1995a; Xing et al., 2017). In the absence of such information, the formaldehyde (HCHO) concentration can be used as a proxy for VOC reactivity because it is a short-lived oxidation product of many VOCs and is positively correlated with peroxy radicals (Schroeder et al., 2017). Sillman (1995a) and Tonnesen and Dennis (2000) found that in situ measurements of the ratio of HCHO (a marker of VOCs) to NO_2 (a marker of NOx) could be used to diagnose local photochemical regimes. Over polluted areas, both HCHO and tropospheric NO_2 have vertical distributions that are heavily weighted toward the lower troposphere, indicating that tropospheric column measurements of these gases are fairly representative of near surface conditions. Many studies have taken advantage of these favorable vertical distributions to investigate surface emissions of NOx and VOCs from space (Boersma et al., 2009;

Martin et al., 2004a; Millet et al., 2008; Streets et al., 2013). Martin et al. (2004a) and Duncan et al. (2010) used satellite measurements of column HCHO/NO_2 ratio to explore near-surface O_3 sensitivities from space and disclosed that this diagnosis of O_3 production rate (PO_3) is consistent with previous finding of surface photochemistry. Witte et al. (2011) used the similar technique to estimate changes in PO_3 to the strict emission control measures (ECMs) during Beijing Summer Olympic Games period in 2008. Recent papers have applied the findings of Duncan et al. (2010) to observe O_3 sensitivity in other parts of the world (Choi et al., 2012; Witte et al., 2011; Jin and Holloway, 2015; Mahajan et al., 2015; Jin et al., 2017).

With in situ measurements, Tonnesen and Dennis (2000) observed a radical-limited environment with HCHO/NO_2 ratios < 0.8, a NOx-limited environment with HCHO/NO_2 ratios >1.8, and a transition environment with HCHO/NO_2 ratios between 0.8 and 1.8. With 3-d chemical model simulations, Sillman (1995a) and Martin et al. (2004b) estimated that the transition between the VOC- and NO_x-limited regimes occurs when the HCHO/NO_2 ratio is ~ 1.0. With a combination of regional chemical model simulations and the Ozone Monitoring Instrument (OMI) measurements, Duncan et al. (2010) concluded that O_3 production decreases with reductions in VOCs at column HCHO/NO_2 ratio < 1.0 and NO_x at column HCHO/NO_2 ratio > 2.0; both NO_x and VOCs reductions decrease O_3 production when column HCHO/NO_2 ratio lies in between 1.0 and 2.0. With a 0-D photochemical box model and airborne measurements, Schroeder et al. (2017) presented a thorough analysis of the utility of column HCHO/NO_2 ratios to indicate surface O_3 sensitivity and found that the transition/ambiguous range estimated via column data is much larger than that indicated by in situ data alone. Furthermore, Schroeder et al. (2017) concluded that many additional sources of uncertainty (regional variability, seasonal variability, variable free tropospheric contributions, retrieval uncertainty, air pollution levels and meteorological conditions) may cause transition threshold vary both geographically and temporally, and thus the results from one region are not likely to be applicable globally.

With the rapid increase in fossil fuel consumption in China over the past three decades, the emission of chemical precursors of O_3 (NO_x and VOCs) has increased dramatically, surpassing that of North America and Europe and raising concerns about worsening O_3 pollution in China (Tang et al., 2011; Wang et al., 2017; Xing et al., 2017). Tropospheric O_3 was already included in the new air quality standard as a routine monitoring component (http://www.mep.gov.cn, last access on 23 May 2018), where the limit for the maximum daily 8 h average (MDA8) O_3 in urban and industrial areas is 160μg/m^3 (~ 75 ppbv at 273 K, 101.3 kPa). According to air quality data released by the Chinese Ministry of Environmental Protection, tropospheric O_3 has displaced PM2.5 as the primary pollutant in many cities during summer (http://www.mep.gov.cn/, last access on 23 May 2018). A precise knowledge of O_3 evolution and photochemical production regime in polluted troposphere in China has important policy implications for O_3 pollution controls (Tang et al., 2011; Xing et al., 2017; Wang et al., 2017).

In this study, we investigate O_3 seasonal evolution and photochemical production regime in the polluted troposphere in eastern China with tropospheric O_3, CO and HCHO derived from ground-based high resolution Fourier transform spectrometry (FTS) in Hefei, China, tropospheric NO_2 deduced from the OMI satellite (https://aura.gsfc.nasa.gov/ omi.html, last access on 23 May 2018), surface meteorological data, and a back trajectory cluster analysis technique. Considering the fact that most NDACC (Network for Detection of Atmospheric Composition Change) FTS sites are located in Europe and Northern America, whereas the number of sites in Asia, Africa, and South America is very sparse, and there is still no official NDACC FTS station that covers China (http://www.ndacc.org/, last access on 23 May 2018), this study can not only improve our understanding of regional photochemical O_3 production regime, but also contributes to the evaluation of O_3 pollution controls.

This study is organized as below: in section 2 the location and the instrument is described, section 3 describes the retrieval of the gases. In section 4, the tropospheric evolution of O_3 in Hefei is investigated. In section 5, the production regimes are evaluated. The work concludes with a summary in section 6.

2 Site description and instrumentation

The FTS observation site (117°10′E, 31°54′N, 30 m a.s.l. (above sea level)) is located in the western suburbs of Hefei city (the capital of Anhui Province, 8 million population) in central-eastern China (Figure S1). Detailed description of this site and its typical observation scenario can be found in Tian et al. (2018). Similar to other Chinese megacities, serious air pollution is common in Hefei throughout the whole year (http://mep.gov.cn/, last access on 23 May 2018).

Our observation system consists of a high resolution FTS spectrometer (IFS125HR, Bruker GmbH, Germany), a solar tracker (Tracker-A Solar 547, Bruker GmbH, Germany), and a weather station (ZENO-3200, Coastal Environmental Systems, Inc., USA). The near infrared (NIR) and middle infrared (MIR) solar spectra were alternately acquired in routine observations (Wang et al., 2017). The MIR spectra used in this study are recorded over a wide spectral range (about 600 – 4500 cm^{-1}) with a spectral resolution of 0.005cm^{-1}. The instrument is equipped with a KBr beam splitter & MCT detector for O_3 measurements and a KBr beam splitter & InSb detector for other gases. The weather station includes sensors for air pressure (± 0.1hpa), air temperature (±0.3°C), relative humidity (±3%), solar radiation (±5%), wind speed (±0.2 m/s), wind direction (±5°), and the presence of rain.

3 FTS retrievals of O_3, CO and HCHO

3.1 Retrieval strategy

The SFIT4 (version 0.9.4.4) algorithm is used in the profile retrieval (Supplement section A; https://www2.acom.ucar.edu/irwg/links, last access on 23 May 2018). The retrieval settings for O_3, CO, and HCHO are listed in Table 1. All spectroscopic line parameters are adopted from HITRAN 2008 (Rothman et al., 2009). A priori profiles of all gases except H_2O are from a dedicated WACCM (Whole Atmosphere Community Climate Model) run. A priori profiles of pressure, temperature and H_2O are interpolated from the National Centers for Environmental Protection and National Center for Atmospheric Research (NCEP/NCAR) reanalysis (Kalnay et al., 1996). For O_3 and CO, we follow the NDACC standard convention with respect to micro windows (MW) selection and the interfering gases consideration (https://www2.acom.

ucar.edu/irwg/links, last access on 23 May 2018). HCHO is not yet an official NDACC species but has been retrieved at a few stations with different retrieval settings (Albrecht et al., 2002; Vigouroux et al., 2009; Jones et al., 2009; Viatte et al., 2014; Franco et al., 2015). The four MWs used in the current study are chosen from a harmonization project taking place in view of future satellite validation (Vigouroux et al., 2018). They are centered at around 2770 cm^{-1} and the interfering gases are CH_4, O_3, N_2O, and HDO.

We assume measurement noise covariance matrices $\mathbf{S}_\varepsilon$ to be diagonal, and set its diagonal elements to the inverse square of the signal to noise ratio (SNR) of the fitted spectra and its non-diagonal elements to zero. For all gases, the diagonal elements of *a priori* profile covariance matrices $\mathbf{S}_a$ are set to standard deviation of a dedicated WACCM run from 1980 to 2020, and its non-diagonal elements are set to zero.

We regularly used a low-pressure HBr cell to monitor the instrument line shape (ILS) of the instrument and included the measured ILS in the retrieval (Hase et al., 2012; Sun et al., 2018).

3.2 Profile information in the FTS retrievals

The sensitive range for CO and HCHO is mainly tropospheric, and for O_3 is both tropospheric and stratospheric (Figure S2). The typical degrees of freedom (DOFS) over the total atmosphere obtained in Hefei for each gas are included in Table 2: they are about 4.8, 3.5, and 1.2 for O_3, CO, and HCHO, respectively. In order to separate independent partial column amounts in the retrieved profiles, we have chosen the altitude limit for each independent layer such that the DOFS in each associated partial column is not less than 1.0. The retrieved profiles of O_3, CO, and HCHO can be divided into four, three, and one independent layers, respectively (Figure S3). The troposphere is well resolved by O_3, CO, and HCHO, where CO exhibits the best vertical resolution with more than two independent layers in the troposphere.

In this study, we have chosen the same upper limit for the tropospheric columns for all gases, which is about 3 km lower than the mean value of the tropopause (~15.1 km). In this way we ensured the accuracies for the tropospheric O_3, CO, and HCHO retrievals, and minimized the influence of transport from stratosphere, i.e., the so called STE process (stratosphere-troposphere exchange).

3.3 Error analysis

The results of the error analysis presented here based on the average of all measurements that fulfill the screening scheme, which is used to minimize the impacts of significant weather events or instrument problems (Supplement section B). In the troposphere, the dominant systematic error for O_3 and CO is the smoothing error, and for HCHO is the line intensity error (Figure S4). The dominant random error for O_3 and HCHO is the measurement error, and for CO is the zero baseline level error (Figure S5). Taken all error items into account, the summarized errors in O_3, CO, and HCHO for 0 –12 km tropospheric partial column and for the total column are listed in Table 3. The total errors in the tropospheric partial columns for O_3, CO, and HCHO, have been evaluated to be 8.7%, 6.8%, and 10.2%, respectively.

4 Tropospheric O_3 seasonal evolution

4.1 Tropospheric O_3 seasonal variability

Figure 1(a) shows the tropospheric O_3 column time series recorded by the FTS from 2014 to 2017, where we followed Gardiner's method and used a second-order Fourier series plus a linear component to determine the annual variability (Gardiner et al., 2008). While it failed to determine the secular trend of tropospheric O_3 column probably because the time series is much shorter than those in Gardiner et al. (2008), the observed seasonal cycle of tropospheric O_3 variations is well captured by the bootstrap resampling method (Gardiner et al., 2008). As commonly observed, high levels of tropospheric O_3 occur in spring and summer (hereafter MAM/JJA). Low levels of tropospheric O_3 occur in autumn and winter (hereafter SON/DJF). Day-to-day variations in MAM/JJA are generally larger than those in SON/DJF (Figure 1(b)). At the same time, it shows that the tropospheric O_3 column roughly increases over time at the first half of the year and reaches the maximum in June, and then decreases during the second half of the year. Tropospheric O_3 columns in June were, on average, 0.5×10^{18} molecules*cm^{-2} (47.6%) higher than those in December which have a mean value of 1.05×10^{18} molecules*cm^{-2}.

Vigouroux et al. (2015) studied the O_3 trends and variabilities at eight NDACC FTS stations that have a long-term time series of O_3 measurements, namely, Ny-Ålesund (79 ° N), Thule (77 ° N), Kiruna (68 ° N), Harestua (60 ° N), Jungfraujoch

(47 ° N), Izaña (28 ° N), Wollongong (34 ° S) and Lauder (45 ° S). All these stations were located in non-polluted or relatively clean areas. The results showed a maximum tropospheric O_3 column in spring at all stations except at Jungfraujoch where it extended into summer. This is because the STE process is most effective during late winter and spring (Vigouroux et al. 2015). In contrast, we observed a broader maximum in Hefei which extends over MAM/JJA season, and the values are higher than those studied in Vigouroux et al. (2015). This is because the observed tropospheric O_3 levels in MAM/JJA are more influenced by air masses originated from densely populated and industrialized areas (see section 4.2), and the MAM/JJA meteorological conditions are more favorable to photochemical O_3 production (see 6). The selection of tropospheric limits 3 km below the tropopause minimized but cannot avoid the influence of transport from stratosphere, the STE process may also contribute to high level of tropospheric O_3 column in spring. Particularly, there is no stronger signature of summer O_3 enhancements in Hefei is most probably because the STE process is weaker in summer than in spring (Vigouroux et al. 2015).

4.2 Regional contribution to tropospheric O_3 levels

In order to determine where the air masses came from and thus contributed to the observed tropospheric O_3 levels, we have used the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model to calculate the three-dimensional kinematic back trajectories that coincide with the FTS measurements from 2014 - 2017 (Draxler et al., 2009). In the calculation, the GDAS (University of Alaska Fairbanks GDAS Archive) meteorological fields were used with a spatial resolution of 0.25 °× 0.25 °, a time resolution of 6 h and 22 vertical levels from the surface to 250 mbar. All daily back trajectories at 12:00 UTC, with a 24 h pathway arriving at Hefei site at 1500 m a.s.l., have been grouped into clusters, and divided into MAM/JJA and SON/DJF seasons (Stunder, 1996). The results showed that air pollution in Jiangsu and Anhui Province in eastern China, Hebei and Shandong Province in northern China, Shaanxi, Henan and Shanxi Province in northwestern China, Hunan and Hubei Province in central China contributed to the observed tropospheric O_3 levels.

In MAM/JJA season (Figure 2(a)), 28.8% of air masses are east origin and arrived at Hefei through the southeast of Jiangsu Province and east of Anhui Province; 41.0% are southwest origin and arrived at Hefei through the northeast of Hunan and Hubei Province, and southwest of Anhui Province; 10.1% are northwest origin and arrived at Hefei through the southeast of Shanxi and Henan Province, and northwest of Anhui Province; 10.1% are north origin and arrived at Hefei through the south of Shandong Province and north of Anhui Province; 10.1% are local origin generated in south of Anhui Province. As a result, air pollution from megacities such as Shanghai, Nanjing, Hangzhou and Hefei in eastern China, Changsha and Wuhan in central-southern China, Zhenzhou and Taiyuan in northwest China, and Jinan in north China could dominate the contribution to the observed tropospheric O_3 levels.

In SON/DJF season, air masses are generally longer and originated in the northwest of the MAM/JJA ones (Figure 2(b)). The direction of east origin air masses shifts from the southeast to northeast of Jiangsu Province, and that of local origin air masses shifts from the south to the northwest of Anhui province. Trajectories of east origin, west origin, and north origin air masses in SON/DJF are 6.5%, 13.1%, and 0.7% smaller than the MAM/JJA ones, respectively. As a result, the air pollution outside Anhui province have 20.2% smaller contribution to the observed tropospheric O_3 levels in SON/DJF than in MAM/JJA. In contrast, trajectories of local origin air masses in SON/DJF are 20.2% larger than the MAM/JJA ones, indicating a more significant contribution of the air pollution inside Anhui province in SON/DJF.

The majority of the Chinese population lives in the eastern part of China, especially in the three most developed regions, the Jing-Jin-Ji (Beijing-Tianjin-Hebei), the Yangtze River Delta (YRD; including Shanghai-Jiangsu-Zhejiang-Anhui), and the Pearl River Delta (PRD; including Guangzhou, Shenzhen, and Hong Kong). These regions consistently have the highest emissions of anthropogenic precursors (Figure S6), which have led to severe region-wide air pollution. Particularly, the Hefei site located in the central-western corner of the YRD, where the population in the southeastern area is typically denser than the northwestern area. Specifically, the southeast of Jiangsu province and the south of Anhui province are two of the most developed areas in YRD, and human activities therein are very intense. Therefore, when the air masses originated from these two areas, O_3 level is usually very high. Overall, compared with SON/DJF season, the more southeastern air masses transportation in MAM/JJA indicated that the observed tropospheric O_3 levels could be more influenced by the densely populated and industrialized areas, which can be broadly accounting for higher O_3 level and variability in MAM/JJA.

5 Tropospheric O_3 production regime

5.1 Meteorological dependency

Photochemistry in polluted atmospheres, particularly the formation of O_3, depends not only on pollutant emissions, but also on meteorological conditions (Lei et al., 2008; Wang et al., 2016; Coates et al., 2016). In order to investigate meteorological dependency of O_3 production regime in the observed area, we analyzed the correlation of the tropospheric O_3 with the coincident minutely-averaged surface meteorological data. Figure 3 shows time series of temperature, pressure, humidity, wind direction, wind speed, and solar radiation recorded by the surface weather station. The seasonal dependencies of all these coincident meteorological elements show no clear dependencies except for the temperature and pressure which show clear reverse seasonal cycles. Generally, the temperatures are higher and the pressures are lower in MAM/JJA than those in SON/DJF. The correlation plots between FTS tropospheric O_3 column and each meteorological element are shown in Figure 4. The tropospheric O_3 column shows positive correlations with solar radiation and temperature, and negative correlations with pressure, humidity, wind direction and wind speed.

High temperature and strong sunlight primarily affects O_3 production in Hefei in two ways: speeding up the rates of many chemical reactions and increasing emissions of VOCs from biogenic sources (BVOCs) (Sillman and Samson, 1995b). While emissions of anthropogenic VOCs (AVOCs) are generally not dependent on temperature, evaporative emissions of some AVOCs do increase with temperature (Rubin et al., 2006; Coates et al., 2016). Elevated O_3 concentration generally occurs on days with dry condition, low pressure and low winds in Hefei probably because these conditions favor the accumulation of O_3 and its precursors. Wind direction is also important because it affects pollution transport, giving rise to high O_3 in downwind locations (Wang et al., 2016). The city downtown locates in eastern of the observation site and the majority of the Chinese population lives in the eastern part of China, easterly winds (direction less than 180°) could generally transport more pollutants to the observe area than westerly winds (direction larger than 180°), resulting in a higher O_3 level. Overall, MAM/JJA meteorological conditions are more favorable to O_3 production (higher sun intensity, higher temperature, lower pressure, and more easterly winds) than SON/DJF, which consolidates the fact that tropospheric O_3 in MAM/JJA are larger than those in SON/DJF.

5.2 PO_3 relative to CO, HCHO, and NO_2 changes

In order to determine the relationship between tropospheric O_3 production and its precursors, the chemical sensitivity of PO_3 relative to tropospheric CO, HCHO, and NO_2 changes was investigated. Figure 5 shows time series of tropospheric CO, HCHO, and NO_2 columns stay at present tropospheric O_3 counterparts, where tropospheric NO_2 was deduced from OMI product selected within the ±0.7° latitude/longitude rectangular area around Hefei site. The retrieval uncertainty for tropospheric column of is less than 30% (https://disc.gsfc.nasa.gov/datasets/OMNO2_V003/). Similar as tropospheric O_3, tropospheric HCHO exhibits a clear seasonal cycle and has a minimum in winter and a maximum in summer. Pronounced tropospheric CO and NO_2 variations were observed but the seasonal cycles are not evident probably because of air pollution which is not constant over season or season dependent.

Figure 6 shows the correlation plot between the FTS tropospheric O_3 column and the coincident tropospheric CO, HCHO, and NO_2 columns. The tropospheric O_3 column shows positive correlations with tropospheric CO, HCHO, and NO_2 columns. Generally, the higher the tropospheric CO concentration, the higher the tropospheric O_3, and both VOCs and NO_x reductions decrease O_3 production. As an indicator of regional air pollution, the good correlation between O_3 and CO (Figure 6(a)) indicates that the enhancement of tropospheric O_3 is highly associated with the photochemical reactions which occurred in polluted conditions rather than due to the STE process. Since the sensitivity of PO_3 to VOCs and NO_x is different under different limitation regimes, the relative weaker overall correlations to HCHO (Figure 6 (b)) and NO_2 (Figure 6 (c)) indicates that the O_3 pollution in Hefei can neither be fully attributed to NO_x pollution nor VOCs pollution.

5.3 O_3-NOx-VOCs sensitivities

5.3.1 Transition/ambiguous range estimation

Referring to previous studies, the chemical sensitivity of PO_3 in Hefei was investigated using the column $HCHO/NO_2$ ratio (Martin et al., 2004; Duncan et al., 2010; Witte et al., 2011; Choi et al., 2012; Jin and Holloway, 2015; Mahajan et al., 2015; Schroeder et al., 2017; Jin et al., 2017). The methods have been adapted to the particular conditions in Hefei. In particular the findings of Schroeder et.al (2017) have been taken into account.

First, previous studies either based on space or airborne column $HCHO/NO_2$ ratios (Martin et al., 2004; Duncan et al., 2010; Witte et al., 2011; Schroeder et al., 2017), both ground-based remote sensing (O_3, CO, and HCHO) and results measured from space (NO_2) were used here. Both products have the same viewing geometry, i.e. they measure the whole troposphere. The ground-based products in Hefei are verified to be robust in troposphere (section 3) and the HCHO product is dedicated to future satellite validation (Vigouroux et al., 2018).

Second, while in most previous studies tropospheric NO_2 and total HCHO have been chosen as the proxy (Martin et al., 2004; Duncan et al., 2010; Witte et al., 2011; Jin and Holloway, 2015; Jin et al., 2017), we used the same tropospheric limits for all gases to calculate tropospheric columns. The AVK's of the measurements show, that all three gases are sensitive throughout the troposphere (compare figure S2).

Third, most previous studies used chemical transport model to estimate the transition threshold (Martin et al., 2004a; Duncan et al., 2010; Witte et al., 2011; Jin and Holloway, 2015; Schroeder et al., 2017; Jin et al., 2017). We used the observation results plus an empirical iterative scheme to calculate the transition threshold (Su et al., 2017). Schroeder et al. (2017) showed, that the transition threshold depends on the particular conditions of the site under study and no global value can be obtained.

Since the measurement tools for O_3 and HCHO, the pollution characteristic and the meteorological condition in this study were not the same as those of previous studies, the transition thresholds estimated in either previous studies were not straightly applied here (Martin et al., 2004a; Duncan et al., 2010; Witte et al., 2011; Choi et al., 2012; Jin and Holloway, 2015; Mahajan et al., 2015; Schroeder et al., 2017; Jin et al., 2017). In order to determine transition thresholds applicable in Hefei, China, we iteratively altered the column HCHO/NO_2 ratio threshold and judged whether the sensitivities of tropospheric O_3 to HCHO or NO_2 changed abruptly. For example, in order to estimate the VOC-limited threshold, we first fitted tropospheric O_3 to HCHO that lies within column HCHO/NO_2 ratios < 2 (an empirical start point) to obtain the corresponding correlation/slope, and then we decreased the threshold by 0.1 (an empirical step size) and repeated the fit, i.e., only fitted the data pairs with column HCHO/NO_2 ratios < 1.9. This has been done iteratively. Finally, we sorted out the transition ratio which shows an abrupt change in correlation/slope, and regarded this as the VOC-limited threshold. Similarly, the NO_x-limited threshold was determined by iteratively increasing the column HCHO/NO_2 ratio threshold till the sensitivity of tropospheric O_3 to NO_2 changed abruptly.

The transition threshold estimation using this scheme exploits the fact that O_3 production is more sensitive to VOCs if it is VOCs-limited and is more sensitive to NO_x if it is NO_x limited, and it exists a transition point near the threshold (Martin et al., 2004). Su et al. (2017) used this scheme to investigate the O_3-NOx-VOCs sensitivities during the 2016 G20 conference in Hangzhou, China, and argued that this diagnosis of PO_3 could reflect the overall O_3 production conditions.

5.3.2 PO_3 limitations in Hefei

The FTS retrievals within ± 1 h of OMI overpass time (13:30 local time (LT)) were used for investigation of PO_3 limitations. While the FTS instrument can measure throughout the whole day, if not cloudy, OMI measures only during midday. For Hefei, this coincidence criterion is a balance between the accuracy and the number of data points. Through the above empirical iterative calculation, we observed a VOC-limited regime with column HCHO/NO_2 ratios < 1.3, a NOx-limited regime with column HCHO/NO_2 ratios > 2.8, and a mix VOC-NO_x-limited regime with column HCHO/NO_2 ratios between 1.3 and 2.8. Schroeder et. al. (2017) argued, the column measurements from space have to be used with care because of the high uncertainty and the inhomogeneity of the satellite measurements. This has been mitigated in this study by the following:

The FTIR measurements have a much smaller footprint than the satellite measurements. Also we concentrate on measurements recorded during midday, when the mixing layer has largely been dissolved.

The measurements are more sensitive to the lower parts of the troposphere, which can be inferred from the normalized AVK’s. This reason is simply, that the AVK’s show the sensitivity to the column, but the column per altitude decreases with altitude.

Figure 7 shows time series of column HCHO/NO_2 ratios which varied over a wide range from 1.0 to 9.0. The column HCHO/NO_2 ratios in summer are typically larger than those in winter, indicating that the PO_3 is mainly NO_x limited in summer and mainly VOC limited or mix VOC-NO_x limited in winter. Based on the calculated transition criteria, 106 days of observations that have coincident O_3, HCHO, and NO_2 counterparts in the reported period are classified, where 57 days (53.8%) are in MAM/JJA season and 49 days (46.2%) are in SON/DJF season. Table 4 listed the statistics for the 106 days of observations, which shows that NO_x limited, mix VOC-NO_x limited, and VOC limited PO_3 accounts for 60.3% (64 days), 28.3% (30 days), and 11.4% (12 days), respectively. The majority of NO_x limited (70.3%) PO_3 lies in MAM/JJA season, while the majorities of mix VOC-NO_x limited (70%) and VOC limited (75%) PO_3 lie in SON/DJF season. As a result, reductions in NO_x and VOC could be more effective to mitigate O_3 pollution in MAM/JJA and SON/DJF season, respectively. Furthermore, considering most of PO_3 are NO_x limited or mix VOC-NO_x limited, reductions in NO_x would reduce most O_3 pollution in eastern

China.

6 Conclusion

We investigated the seasonal evolution and photochemical production regime of tropospheric O_3 in eastern China from 2014 – 2017 by using tropospheric O_3, CO and HCHO columns derived from Fourier transform infrared spectrometry (FTS), tropospheric NO_2 column deduced from Ozone Monitoring Instrument (OMI), the surface meteorological data, and a back trajectory cluster analysis technique. A pronounced seasonal cycle for tropospheric O_3 is captured by the FTS, which roughly increases over time at the first half year and reaches the maximum in June, and then it decreases over time at the second half year. Tropospheric O_3 columns in June are, on average, 0.50×10^{18} molecules*cm^{-2} (47.6%) higher than those in December which has a mean value of 1.05×10^{18} molecules*cm^{-2}. A broad maximum within both spring and summer (MAM/JJA) is observed and the day-to-day variations in MAM/JJA are generally larger than those in autumn and winter (SON/DJF). This differs from tropospheric O_3 measurements in Vigouroux et al. (2015). However, Vigouroux et al. (2015) used measurements at relatively clean sites.

Back trajectories analysis showed that air pollution in Jiangsu and Anhui Province in eastern China, Hebei and Shandong Province in northern China, Shaanxi, Henan and Shanxi Province in northwest China, Hunan and Hubei Province in central China dominate the contributions to the observed tropospheric O_3 levels. Compared with SON/DJF season, the observed tropospheric O_3 levels in MAM/JJA are mainly influenced by transport of air masses from densely populated and industrialized areas while the broad and high O_3 level and variability in MAM/JJA is determined by the photochemical O_3 production. The tropospheric column HCHO/NO_2 ratio is used as a proxy to investigate the chemical sensitivity of O_3 production rate (PO_3). The results show that the PO_3 is mainly nitrogen oxide (NO_x) limited in MAM/JJA, while it is mainly VOC or mix VOC-NO_x limited in SON/DJF. Reductions in NO_x and VOC could be more effective to mitigate O_3 pollution in MAM/JJA and SON/DJF season, respectively. Considering most of PO_3 are NO_x limited or mix VOC-NO_x limited, reductions in NO_x would reduce most O_3 pollution in eastern China.

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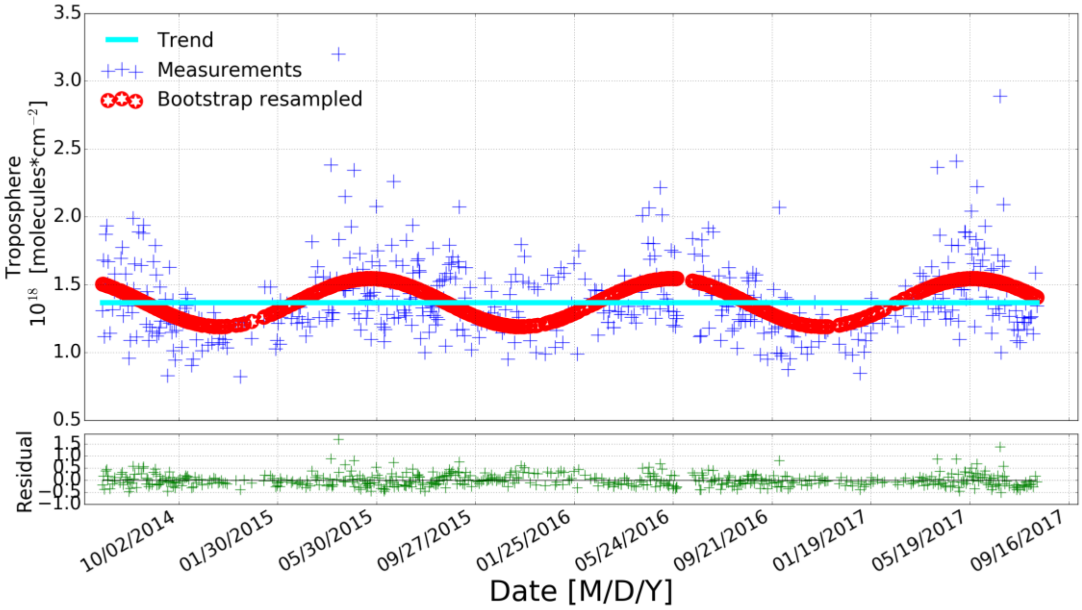
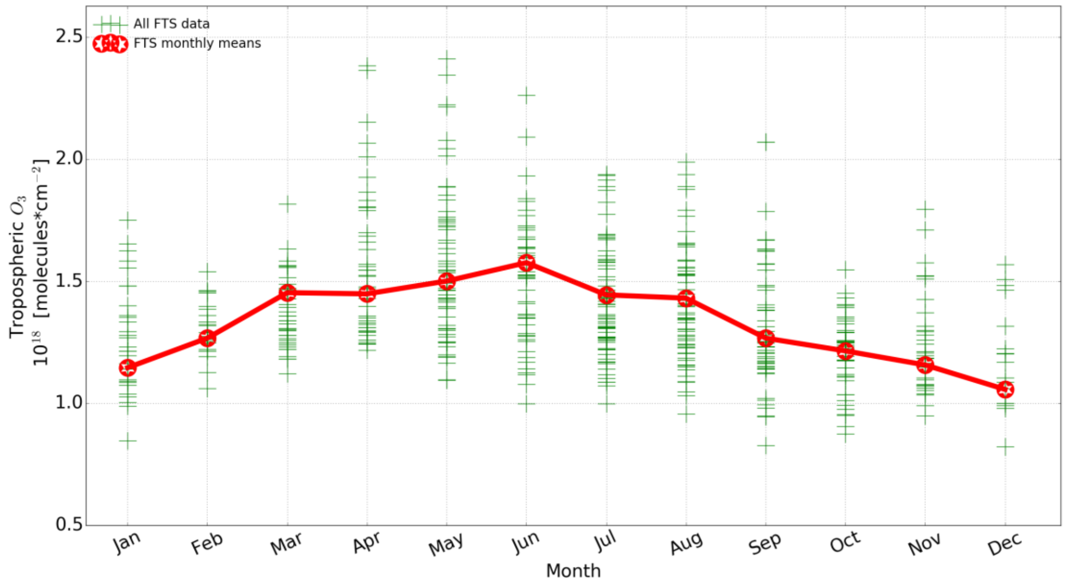
Figs

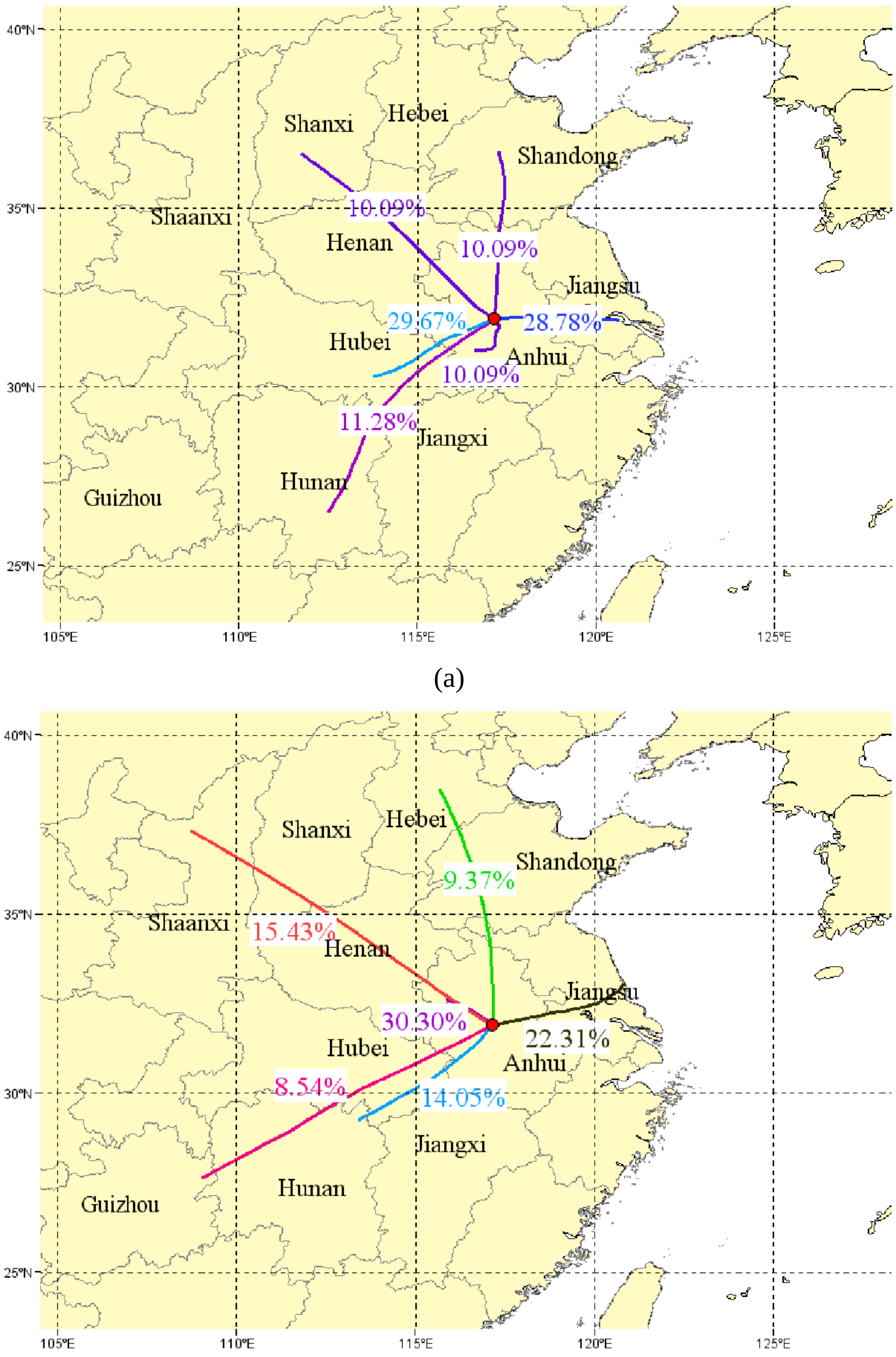


(a)



(b)

Figure 1. (a): FTS measured and bootstrap resampled tropospheric O_3 columns at Hefei site. The linear trend and the residual are also shown. (b): Tropospheric O_3 column monthly means derived from (a).



(a)

(b)

Figure 2. One-day HYSPLIT back trajectory clusters arriving at Hefei at 1500 m a.s.l that are coincident with the FTS measurements from 2014 - 2017. (a) Spring and summer (MAM/JJA), and (b) Autumn and winter (SON/DJF) season. The base map was generated using the TrajStat 1.2.2 software (http://www.meteothinker. com).

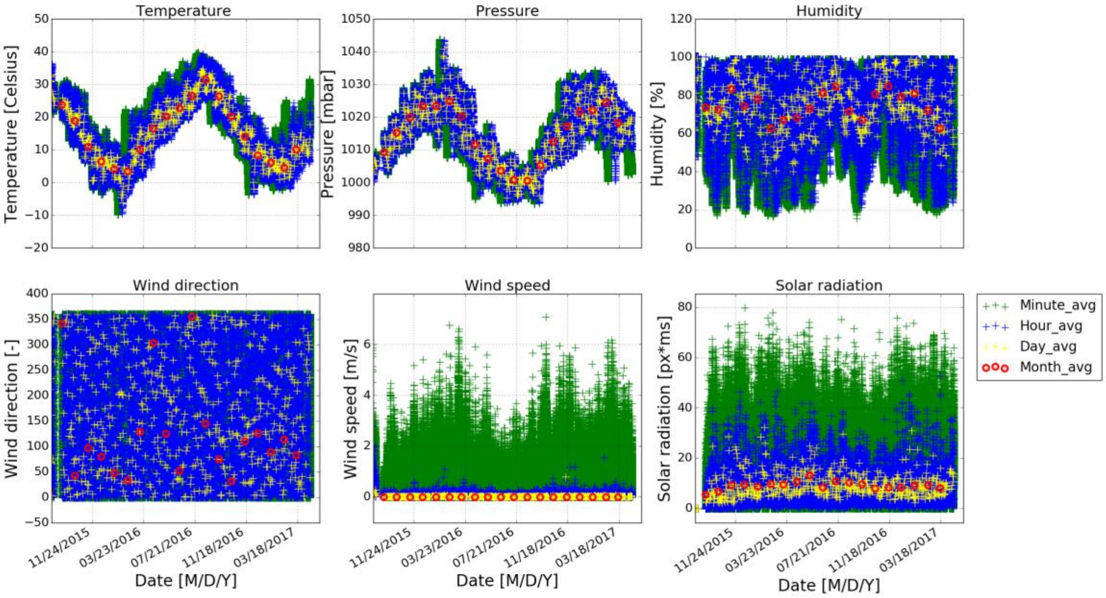


Figure 3. Minutely, hourly, daily, and monthly averaged time series of temperature, pressure, humidity, wind direction, wind speed, and solar radiation recorded by the surface weather station.

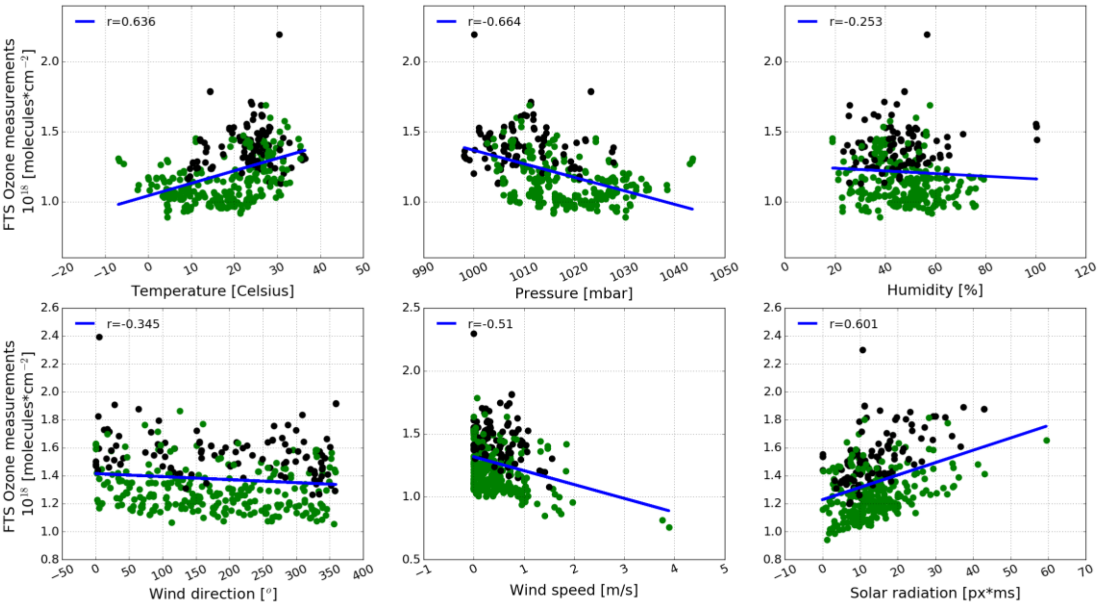


Figure 4. Correlation plot between the FTS tropospheric O_3 column and the coincident minutely-averaged surface meteorological data. Black dots are data pairs within MAM/JJA season and green dots are data pairs within SON/DJF season.

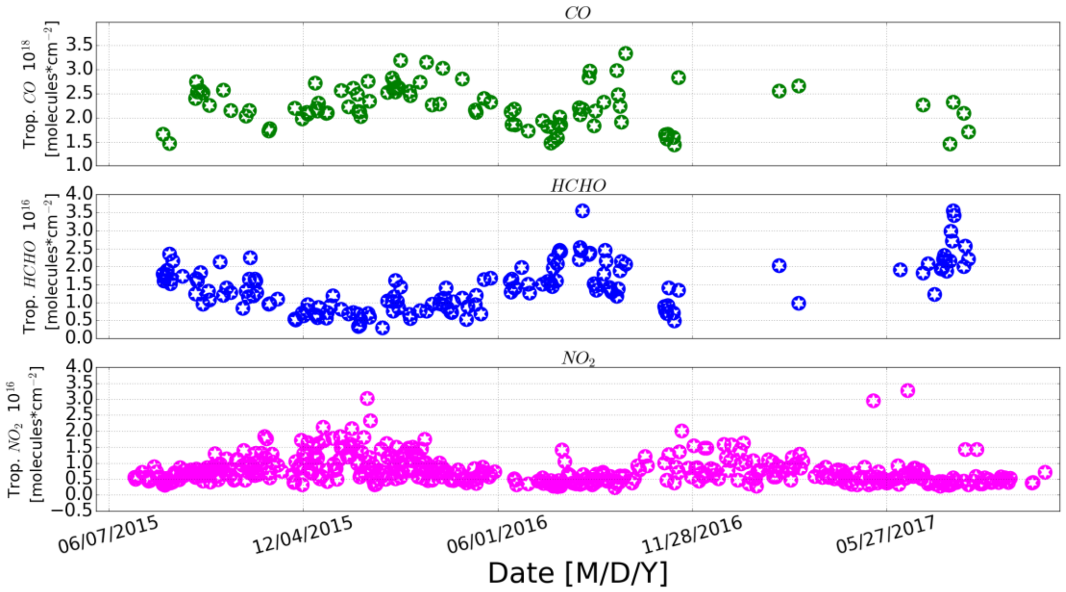


Figure 5. Time series of tropospheric CO, HCHO, and NO_2. Tropospheric CO and HCHO were derived from FTS observations which is the same as tropospheric O_3 and tropospheric NO_2 is derived from OMI data.

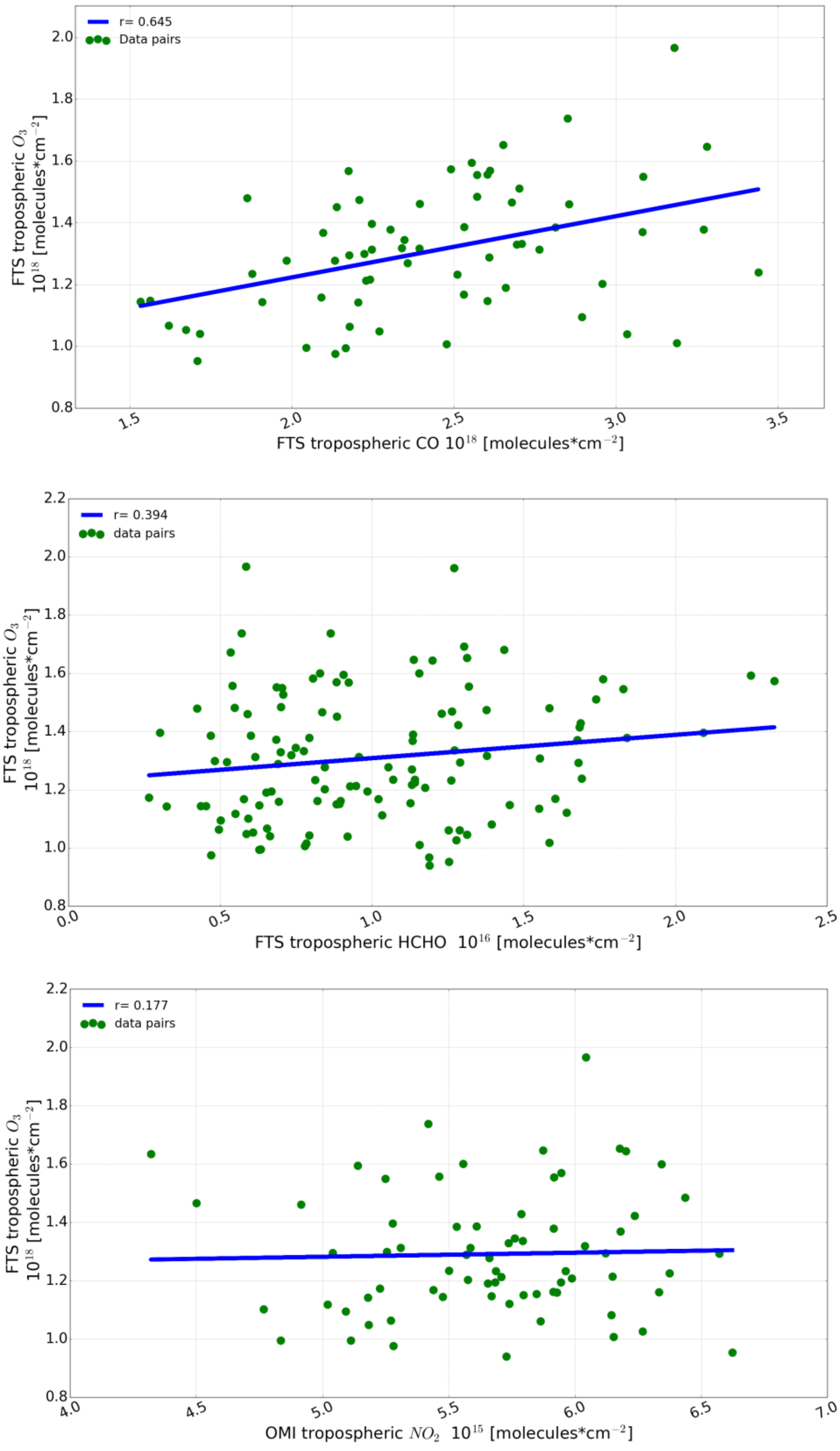


Figure 6. Correlation plot between the FTS tropospheric O_3 column and coincident tropospheric CO (upper), HCHO (middle), and NO_2 (bottom) columns. The CO and HCHO data are retrieved from FTS observations and the NO_2 data were deduced from OMI product.

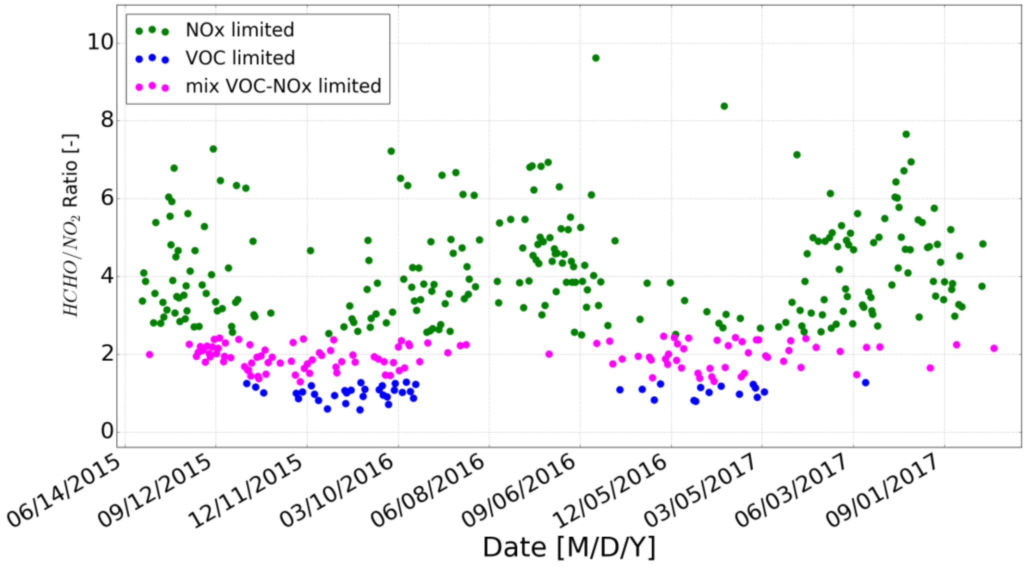


Figure 7. Time series of column HCHO/NO_2 ratios.

Tables

Table 1. Summary of the retrieval parameters used for O_3, CO, and HCHO. All micro windows (MW) are given in cm^{-1}.

Gases		O_3	CO	HCHO
Retrieval code		SFIT4 v 0.9.4.4	SFIT4 v 0.9.4.4	SFIT4 v 0.9.4.4
Spectroscopy		HITRAN2008	HITRAN2008	HITRAN2008
P, T, H_2O profiles		NCEP	NCEP	NCEP
A priori profiles for target/interfering gases except H_2O		WACCM	WACCM	WACCM
MW for profile retrievals		1000-1004.5	2057.7-2058 2069.56-2069.76 2157.5-2159.15	2763.42-2764.17 2765.65-2766.01 2778.15-2779.1 2780.65-2782.0
Retrieved interfering gases		H_2O, CO_2, C_2H_4, $^{668}O_3$, $^{686}O_3$	O_3, N_2O, CO_2, OCS, H_2O	CH_4, O_3, N_2O, HDO
SNR for de-weighting		None	500	600
Regularization	**S_a**	Diagonal: 20% No correlation	Diagonal: 11% ~ 27% No correlation	Diagonal: 10% No correlation
	S_ε	Real SNR	Real SNR	Real SNR
ILS		LINEFIT145	LINEFIT145	LINEFIT145
Error analysis		Systematic error: -Smoothing error (smoothing) -Errors from other parameters: Background curvature (curvature), Optical path difference (max_opd), Field of view (omega), Solar line strength (solstrnth), Background slope (slope), Solar line shift (solshft), Phase (phase), Solar zenith angle(sza), Line temperature broadening (linetair_gas), Line pressure broadening (linepair_gas), Line intensity(lineint_gas)		
		Random error: -Interference errors: retrieval parameters (retrieval_parameters), interfering species (interfering_species) -Measurement error (measurement) - Errors from other parameters: Temperature (temperature), Zero level (zshift)		

Table 2. Typical degrees of freedom for signal (DOFs) and sensitive range of the retrieved O_3, CO, and HCHO profiles at Hefei site.

Gas	Total column DOFs	Sensitive range (km)	Tropospheric partial column (km)	Tropospheric DOFs
O_3	4.8	Ground - 44	Ground - 12	1.5
CO	3.5	Ground - 27	Ground - 12	2.7
HCHO	1.2	Ground - 18	Ground - 12	1.1

Table 3. Errors in % of the column amount of O_3, CO, and HCHO for 0 –12 km tropospheric partial column and for the total column.

Gas	O_3		CO		HCHO	
Altitude (km)	0 – 12	Total column	0 – 12	Total column	0 – 12	Total column
Total random	3.2	0.59	3.8	0.66	3.3	0.97
Total systematic	8.1	4.86	5.7	3.9	9.6	5.7
Total errors	8.7	5.0	6.8	3.95	10.2	5.8

Table 4. Chemical sensitivities of PO_3 for the selected 106 days of observations that have coincident O_3, HCHO, and NO_2 counterparts

Items	Proportion		Autumn and winter		Spring and summer	
	days	percentage	days	percentage	days	percentage
NOx limited	64	60.3%	19	29.7%	45	70.3%
Mix VOC-NOx limited	30	28.3%	21	70%	9	30%
VOC limited	12	11.4%	9	75%	3	25%
Sum	106	100%	49	46.2%	57	53.8%