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Atmospheric Chemistry and Physics Discussions

Interactive comment on "MAX-DOAS measurements of tropospheric NO_2 and HCHO in Nanjing and the comparison to OMI observations" *by* Ka Lok Chan et al.

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We thank reviewer #1 for the comments. Some of these comments are useful for improving our manuscript. We understand that the comments on the scientific content of the manuscript in general are positive, however, several clarifications are necessary. We have addressed the reviewer's comments on a point to point basis as below for consideration. All page and line numbers are refer to the marked-up version of the manuscript.

General comments

In this paper, Chan et al. presented the long-term MAX-DOAS measurements of NO2 and HCHO profiles in Nanjing. The data are used to validate OMI NO2 and HCHO products, discuss the effects of a-priori profiles on OMI retrievals, analyze effects of regional transports, and effects of pollution control measures during the Youth Olympic Games. In general the scientific topic is meaningful, and the MAX-DOAS data quality is well proved. However the authors need to give more deep discussions in many parts to firmly prove the conclusions. Generally I have three major concerns below:

1) Regarding the comparisons with the OMI data in section 3.2, the authors should also show the comparisons of a-priori profile shapes of OMI NO2 retrievals with the NO2 profiles measured by MAX-DOAS for the discussion on the effect of a-priori profiles. In addition, the authors also need to discuss the a-priori effect for HCHO even in the case that a good agreement is found. It is very important to see if good agreements of HCHO profile shapes can been also seen between MAX-DOAS and OMI a-priori.

The underestimation of OMI NO2 VCDs is up to 50% compared to MAX-DOAS data shown in Fig. 2. However the previous study in Wuxi, see Wang et al. 2017, shows the underestimation is âĹij20%. One major difference is that the NO2 product is from NASA in your study, but from DOMINO v2 in Wang et al., 2017. Are there big differences of both OMI NO2 data sets? Why are there big differences? In order to answer the questions, the author needs to do comparisons also with the DOMINO v2 product. Meanwhile DOMINO v2 is an official product which is well known and widely used. In addition the author demonstrates that "Measurements with such large spatial coverage are probably difficult to capture the spatial gradient of NO2 and resulted in an underestimation over pollution hot spots due to the averaging of large OMI footprint. This effect is especially significant over Nanjing, as it is a local pollution hot spot surrounded by rather clean areas". If it is true, the NO2 measured by the MAX-DOAS is dominated by local emission. However the discussion on regional pollution transport in section 3.4, the author concludes that "the air quality of Nanjing is significantly influenced by the air pollution transportation, especially during winter.". The two elaborations are contradic-

tive. Therefore the authors need to carefully discuss the reason of the underestimations of the OMI NO2 data.

Response: The reviewer compares our estimation to previous study in Wuxi, China. We think that these studies cannot be compared directly for several reasons. There are major differences in satellite products used, measurement time and locations. In this study, we compare our MAX-DOAS measurements result to the NASA OMI NO2 standard product version 3 while the previous study in Wuxi used OMI NO2 product produced by KNMI. These products are processed with different algorithms, for example, there are significant differences in the spectral analysis, stratospheric and tropospheric NO2 separation methods, radiative transfer simulation and a priori profiles. Different versions of NASA OMI NO2 products even show a difference up to 40% (Krotkov et al., 2017), let alone the differences between two completely different algorithms. In addition, the differences in measurement time and location also make a big difference in the comparison. Measurements taken at the city center and several tens kilometer away in the suburban can already show a big difference.

To answer the reviewer question, whether the two OMI NO2 products are so different, we have also plotted the DOMINO version 2 data together with the NASA NO2 standard product in Figure 4. The result shows the NO2 VCD from the KNMI product is a factor of 2 higher than that of the NASA product. The result shows that the KNMI OMI product underestimated the NO2 VCDs by $\sim$30% compared to the MAX-DOAS observations. This observation is consistence with the previous study. Further discussion is included in the manuscript (page 13, line 24-34).

We mentioned that regional transportation of pollutants has 'significant' impact on the local air quality which does not implies that regional transport is the 'major' source. Therefore, these sentences do not contradict with each other. Despite the strong local contribution, regional transportation of pollutants can also influence the local air quality. We have further clarified the confusion and rephrase the sentences in section 3.4 (page 18, line 20-21).

2) In section 3.4, the authors used the reconstructed maps to quantitatively validate the satellite maps. Therefore a speculated life time is used to scale MAX-DOAS VCD in the reconstruction of maps. However are the quantitative comparisons reasonable? Because the authors assume that all the pollutants measured by the MAX-DOAS instrument are from emissions in an area corresponding to the starting location of a trajectory. However emissions in different grids along the trajectory route should be mixed up and contribute to the pollutants measured by the MAX-DOAS in reality. The emissions from different distances should be scaled differently. But do we know the proportions of the different emissions? I think the reasonable comparisons of the re-constructed maps with the satellite maps are the relative distributions, but not the absolute values.

The reconstructed maps should depend on the selected backward time of trajectories. The author should show the maps with different trajectory backward time and compare them with the satellite maps in order to see which time is reasonable. And the suitable backward time depends on actual lifetime. Since the lifetime effect is already implied if different backward time is tested, the scaling with lifetime might be not needed and do not give any meaningful results. In addition, transports of pollutants can occur during night time and day time. Lifetime only matters for transports during day time. Nighttime transports can reach a far distance and contribute to concentrations of pollutants during day time. This is another reason why lifetime should not be applied.

The backward propagation method has been applied to long lifetime pollutants and also trace gases measured from MAX-DOAS in previous studies. Some references should be cited in the paper. Meanwhile the sentence "We developed a new technique to assemble the source contribution map using backward trajectory analysis" in the abstract might be inappropriate.

Response: We have to clarify that we did not perform any quantitative comparison between the MAX-DOAS and OMI datasets. We just wanted to remind the reader that there is a large difference in the MAX-DOAS and OMI VCDs. Therefore, the absolute value is expected to be different. Our discussion mainly focused on the spatial distribu-

tion of pollutant. We have rephrased the sentences to avoid any confusion (page 18, line 7-9).

I think there might be some misunderstandings with our approach. In our approach, NO2 and HCHO do not decay along the backward trajectory. The assumed lifetimes are only used to compute the weighting factors for the reconstruction of spatial distribution of NO2 and HCHO. As data are more reliable with shorter backward time, therefore, we give higher weight for data with shorter backward time. In order to avoid confusion, we have changed the term 'lifetime weight factor' to 'age weighting factor'. The age weighting approach is useful when multiple trajectories overlapping with each other within a single grid point. In addition, we did not mention that the pollutants measured by the MAX-DOAS are coming from primary emissions. They can also be secondary formed. We have only reconstructed the spatial distribution of pollutants, but not emission maps. In order to avoid the misunderstanding, we have further clarified this issue in the manuscript (page 16, line 6-8, page 17, line 1-2).

We understand that similar backward propagate methods have been used in some other study, we have implemented an age weighting scheme for the spatial distribution inversion, so that it fit better for the application on MAX-DOAS measurements. In order to avoid the confusion, we rephrased the sentences and added references to previous studies which use similar approach (page 15, line 16).

3) In section 3.5, the author compared the pollutants during the Youth Olympic Games with those before and after the event in order to characterize the effect of pollution control measures. Since pollution transports can impact Nanjing as the author demonstrates in section 3.4, the difference of transport conditions in the three periods should also be discussed. Meanwhile the author simply elaborates "As the meteorological conditions are very similar during the three periods". I think the author has to show wind fields, trajectories, precipitations, and temperatures in the three periods in order to convince the readers. Near-surface concentrations of the pollutants should be also derived from the MAX-DOAS profile inversion. Since near-surface concentrations

should be mainly dominated by the local emission, but VCDs (AODs) contain contributions of pollutant transports. Therefore it is also meaningful to include the comparisons of the surface concentrations as VCDs shown in Fig.9.

Response: We have added the meteorological measurements such as temperature, wind speed and wind direction to support the discussion. The meteorological data are shown in Figure 10. A brief description of the meteorological data is added to section 2.3.

In addition, surface mixing ratios of NO2 and HCHO are now supplemented in Figure 9c. A more detailed discussion regarding the reduction of surface NO2 and HCHO concentration is included in section 3.5 (page 20, line 9, page 21, line 1-5).

Specific Comments:

1) P4 L3: A reference should be given for QDOAS. Please clarify which of the two wavelength ranges is used for NO2 and HCHO?

Response: We have supplemented the fitting range in the text (page 5, line 1-2) and cited reference for the use of QDOAS software (page 4, line 2).

2) P4 L4: Please clarify the reference spectrum is the zenith measurement in individual elevation scan or around noon time?

Response: We use the zenith spectrum taken in the same measurement cycle as reference in the analysis. This information is now supplied in the manuscript (page 5, line 2).

3) Table 1: Do you determine the DOAS fit settings based on sensitivity studies (which are not shown) or previous studies? If you determined them based on previous studies, some references should be given. In addition, do you apply the wavelength dependent Ring suggested by Wagner et al., 2009? If not, please discuss why the additional Ring is not needed in your analysis. Wagner, T., Beirle, S., and Deutschmann, T.: Three-dimensional simulation of the Ring effect in observations of scattered sun light using

Monte Carlo radiative transfer models, Atmos. Meas. Tech., 2, 113-124, 2009.

Response: The DOAS fit settings are taken from QA4ECV project and have been adopted for the CINDI-2 campaign. We have referred these DOAS fit settings to the previous study (page 5, line 7-10).

4) Section 2.1.2: examples of DOAS fits should be shown, especially for HCHO, in order to convince the quality of HCHO analysis.

Response: We have added an example of the DOAS fit as Figure 1. A brief description is also supplemented in the manuscript (page 5, line 10-12).

5) P4 L17-19: How do you filter the data under continuous clouds when the variability of O4 dSCDs are not large?

Response: Our cloud filtering approach is based on the analysis of the time series of O4 DSCD measured at each elevation. As O4 DSCDs are expected varying smoothly with time under clear sky condition, rapid change of O4 DSCDs are likely related to the present of cloud in the atmosphere. Therefore, we applied a high pass filter to the O4 DSCD time series to screen out cloud contaminated observations. The only limitation of this cloud screening algorithm is that the algorithm cannot distinguish continuous and homogeneous cloud condition. However, it is rare that the cloud does not change for a long time (within an hour) and the cloud layer is homogeneous for all viewing directions. We have also tried the color index method for cloud screening. However, the color index method tends to filter data will high aerosol load as the sky is whiter under high aerosol load condition. In addition, the aerosol load are usually high in Nanjing, the color index method identifies most of these high aerosol data as cloud contaminated. Therefore, we use the former high pass filter method for cloud screening in this study. We have supplemented the limitation of the cloud screening algorithm in section 2.1.1 (page 6, line 2-5).

6) P5 L15: Since O4 VCD can systematically vary during a year due to variations

of temperature and pressure, as Wagner et al. (2018 AMT) demonstrated, the phenomenon can explain the scaling factor in many places. How do you consider the variation of temperatures in the retrievals of aerosols? If you don't consider it, a discussion on the uncertainties due to the effect has to be given.

Response: We use the U.S. standard mid-latitude atmosphere profiles for winter (January) and summer (July) and temporally interpolated to each month of the year for the radiative transfer simulation. This information is now supplemented in the manuscript (page 6, line 30-31)

7) P6 L11: How do you determine the single scattering albedo and asymmetry parameters, and also Ångström coefficient? The parameters can significantly change in the long-term measurements, uncertainty estimations of aerosol results due to the parameters should be given in the paper.

Response: These values are inherited from previous study. In order to investigate the uncertainty caused by the fixed set of aerosol optical properties, we performed sensitivity analysis using aerosol optical properties from the sun-photometer measurements in Nanjing and AERONET station $\sim$150km southeast of the measurement site. The result shows that the uncertainty caused by Ångström coefficient, single scattering albedo and asymmetric parameter is $\sim$2%, 1.5% and 4% respectively. This information is supplemented in the manuscript (page 7, line 27-30, page, line 29-31, page 11, line 1-5).

8) P6 L16-18: How do you determine the wavelengths of the AMF simulations of O4, NO2, and HCHO?

Response: We choose 360nm for the simulation of O4 DSCDs simply due the strong absorption at this wavelength. This wavelength is also commonly used in many studies for O4 simulations. As the NO2 DSCDs are also retrieved in the same fitting window, therefore, we adapted the same wavelength of 360nm for NO2 AMF simulation. For HCHO retrieval, our choice of AMF simulation wavelength of 340nm is close to the

center wavelength of the DOAS fitting window of 342nm. This wavelength is also commonly used in HCHO retrieval, e.g., De Smedt et al., 2018.

9) P6 L20: How do you deal with the NO2 above 3km? The considerable amount of NO2 at high altitudes might also impact retrievals of NO2 below 3km.

Response: The MAX-DOAS measurements are not sensitive to higher altitudes. Therefore, we assume that the NO2 profile follows the US standard atmosphere. We have supplied this information in the manuscript (page 7, line 32).

10) Section 2.1.3: Figures of comparisons of measured dSCDs and modeled dSCDs for profile retrievals should be shown in the manuscript or supplement to show the convergence of the profile retrievals.

Response: We have added an example of aerosol, NO2 and HCHO profile retrieval in Figure 2.

11) Section 2.3: The overpass time of OMI should be given.

Response: We have now added the overpass time of OMI (page 9, line 22-23).

12) P8 L13-14: Can the constraint of a-priori profile contribute to the underestimations? In order to show this, comparisons of measured dSCDs and modeled dSCDs are needed.

Response: We have added an example of aerosol, NO2 and HCHO profile retrieval in Figure 2 which included measured and modeled DSCDs.

13) P8 L28: As I know, there are not domestic heating systems in Nanjing since it is in the south of Huai River.

Response: The reviewer is partly correct. There is no centralized heating system in Nanjing, but some of the new buildings are equipped with individual heating system with typically run on natural gas or electricity. Although the domestic heating emissions from southern part of China are smaller than that of the northern China, their contri-

bution can still be significant. In order to avoid any confusion, we have rephrased the sentence in the manuscript (page 13, line 5-6).

14) P10, L1: The underestimation of OMI NO2 compared to MAX-DOAS is not consistent with Wang et al., 2017. The underestimation here is much stronger.

Response: See response to general comment 1.

15) P13, L6: Oxidation rate of VOCs to HCHO is also stronger in summer than in winter. The variations of oxidation rate can also contribute to seasonal pattern of HCHO. And secondary sources of HCHO are significant. The seasonal pattern of HCHO might be due to contributions of biogenic emissions of precursor VOCs. The sentence should be modified.

Response: We have revised the expression of the sentence and included the cause of higher oxidation rate of VOCs in summer (page 14, line 14-15)

16) P13, Figure 5: The color scale of subfigure (a) should be changed to allow seeing the gradient more clearly. As I elaborated in General comment (2), the relative distribution is much more important than the absolute values.

Response: We have adjusted the color scale of Figure 6 and 7.

17) P13, L16: Since you calculate the trajectories in each altitude grids of MAX-DOAS profiles, how do you combine the trajectories with the profiles? Do you assign partial columns in each vertical grid to different grid points in the map along trajectories at individual altitudes? The procedure need to be clarified.

Response: We have supplemented a more detailed description of the spatial reconstruction procedure (page 16, line 2-4).

18) P14, L5-6 how do you determine the lifetime and backward time? The question is corresponding to the general comment (2).

Response: See response to general comment 2.

19) P14, L12: As I demonstrate in comment (2), the quantitative comparisons with OMI data are not reasonable.

Response: See response to general comment 1.

20) P14, L19: Since HCHO is dominated by the secondary formations from VOCs, which have a long lifetime, therefore VOCs might be transported to a far distance and contribute to local HCHO concentrations. Therefore transport effects on HCHO might be even larger if the transports are from far distance. The backward time of trajectories of 6 hour might be not long enough in the reconstruction of HCHO maps. Following my general comment (2), I suggest you to generate the maps with different backward time of trajectories and compare the relative distributions with OMI maps.

Response: As discussed in response to general comment 2, we are not trying to reconstruct source map but the spatial distribution of HCHO. In addition, the lifetime is just used for the calculation of weighting factor. This approach is useful when multiple trajectories overlapping with each other within a single grid point. Of course we have looked into map with different backward time. As expected maps created with shorter backward time correlates better with OMI observations, but then the spatial coverage are very limited. In order to get a balance between having better spatial coverage and the reliability of the reconstructed pollution maps, these numbers are used in this study. This information is now added in the manuscript (page 17, line 7-8, page 18, line 1).

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