Response to Reviewer I

General Comments:

- Understanding the processes controlling the O_3 concentration in a specific area is important to design emission reduction strategies to reduce the harmful effects of tropospheric O_3. This paper focuses on two processes that take place in the O_3 cycle: transport and photochemistry.
- The paper discusses two methodological approaches to understand two O_3 processes (transport and photochemistry) which are the O_3 budget and the O_3 source apportionment. Authors claims that there is a contradictory view on the role of transport and photochemistry in O_3 pollution between the budget calculation studies and O_3 source apportionment studies, because both studies provide different information. In my point of view, they are two different approaches difficult to compare, so it is normal they provide different results. However, as the authors show in the paper it is possible to learn from the both of them.
- I think the paper is organized in a way that it does not help to understand its objective and methodology, even it shows a hard work behind. So, in my opinion, this manuscript was hard to follow and understand, and consequently to review. Furthermore, it could help if authors improve the readability of the text. Overall, there are too many pronouns and missing nouns that make difficult to follow the main idea of some sentences. Authors should review the text carefully and provide a more accurate reference to key concepts, also being consistent in the way they do it along the manuscript.

Response:

We appreciate the valuable comments and suggestions. We've tried to adjust the structure of the paper and make a lot of revisions to improve its readability.

Before in-detail responses, we want to clarify the "contradictory" in this paper. Reported O_3 concentration budgets often show that photochemistry is the main process leading to the rapid increase of O_3 concentrations, but fail to explain why most O_3 in the region is transported from the outside regions, as suggested by O_3 source apportionment. It indicates that the O_3 concentration budget cannot completely illustrate the effects of transport and photochemistry on regional O_3 pollution. By calculating, analysing and comparing the O_3 concentration and mass budget, this study aims to comprehensively understand the role of transport and photochemistry in regional O_3 pollution.

The contents of this paper includes:

1) Development of the method to quantify the two O_3 budgets (Sect. 2.1-2.3);

2) Analysis and comparison of the results from the two O_3 budgets (methodology described in Sect. 2.5, results discussed in Sect. 3);

3) Assessment of the role of transport and photochemistry in determining the regional origins of O_3 (methodology described in Sect. 2.6, result presented in Sect. 4).

Results show that photochemistry dominates the changes of O_3 concentrations, or plays a major role in the O_3 concentration budget. Although transport only leads to limited changes of O_3 concentrations, its large contributions in the O_3 mass budget ensure that it determines the characteristics of O_3 pollution, e.g., the regional origins of O_3 in this study. Based on the conclusions, we suggest the insights from both concentration and mass budgets are necessary to comprehensively understand the role of transport and chemistry in regional O_3 pollution. Suggestions based on the two O_3 budgets are also provided for policy-makers when making strategies to alleviate O_3 pollution.

Our responses to specific comments and corresponding revisions are as follows (in blue and red, respectively). Note that line numbers are these in the revised manuscript with author's changes.

Specific comments:

1) Abstract: difficult to get the important of the problem from the four first lines.

Response:

We revised the first four lines in the Abstract as (in lines 20-24):

Understanding the role of transport and photochemistry is essential to mitigate tropospheric ozone (O_3) pollution within a region. In previous studies, the O_3 concentration budget has been widely used to determine the contributions of two processes to the variations of O_3 concentrations. These studies often conclude that local photochemistry is the main cause of regional O_3 pollution; however, they fail to explain why O_3 in a targeted region is primarily derived from O_3 and/or its precursors transported from the outside regions as reported by many studies of O_3 source apportionment.

2) The abstract does not help to understands the objective and the methodology approach. Ozone budget calculation and O_3 source apportionment studies seems two different type of approaches difficult to compare, so it is normal they provide different results.

Response:

We agree that different methods can give different results, but it is also important to know why they are different. For this study, the O_3 concentration budget fails to explain why most O_3 is transported from the outside regions, suggesting that this method cannot completely illustrate the effects of transport and photochemistry on regional O_3 pollution. By calculating, analysing and comparing the O_3 concentration and mass budgets, this study not only more comprehensively reveals the role of transport and photochemistry in regional O_3 pollution, but also clarifies the connections between O_3-related processes and the characteristics of O_3, i.e. the regional origins of O_3 in this study.

To make a clearer introduction, we revised the objective and the methodology in the abstract, shown in lines 27-32:

Here, we present a method to calculate the hourly contributions of O_3-related processes to the variations of not only the mean O_3 concentration, but also the total O_3 mass (the corresponding budgets are noted as the O_3 concentration and mass budget, respectively) within the atmospheric boundary layer (ABL) of the concerned region. Based on the modelling results of WRF-CMAQ, the two O_3 budgets were applied to comprehensively understand the effects of transport and photochemistry on the O_3 pollution over the Pearl River Delta (PRD) region in China.

3) Line 29: you mention two budgets, but you have not introduced them in the abstract. Is that related with the two type of studies?

Response:

Two budgets are introduced in lines 27-31:

Here, we present a method to calculate the hourly contributions of O_3-related processes to the variations of not only the mean O_3 concentration, but also the total O_3 mass (the corresponding budgets are noted as the O_3 concentration and mass budget, respectively) within the atmospheric boundary layer (ABL) of the concerned region.

The O_3 mass budget is used to explain the results of O_3 source apportionment. According to the discussions in Sect. 4 of this paper, transport and photochemistry determine the regional origins of O_3 by influencing their contributions in the O_3 mass budget as well as the regional origins of O_3 mass attributed to these O_3-related processes.

4) Line 74: the subject of that sentence "O_3 source" does not make sense. Could your elaborate more the idea in that sentence.

Response:

We agree that "O_3 source" might be a confusing item for the readers. Here, "O_3 source" was used to indicate the regional origins of O_3, or how much the concerned regions contribute to O_3 pollution. We revised the sentence into (in lines 107-111):

O_3 source apportionment is performed to identify the regional and/or sectoral origins of O_3, of which the results are also used to support air pollution control (Clappier et al., 2017; Thunis et al., 2019). Here, we only discuss the regional origins of O_3, because the contributions of sources outside the region (or emissions within the region, defined as local emissions hereafter) provide information on the influence of transport (or photochemistry) on O_3 pollution.

We also revised other "O_3 sources" in the manuscript into "the results of O_3 source apportionment", "regional origins of O_3" or alike items.

5) Line 88: "O_3 source studies". Use the same set of words to mention these studies. I guess in this case you want to say "O_3 source apportionment studies". The same comment in lines 90-91, "source apportionment studies" and "O_3 budget studies".

Response:

We accept your suggestion. However, the two sentences mentioned in the comment were deleted in the revised version. For the similar expressions afterwards, we revised them into "O_3 source apportionment studies", "O_3 concentration budget studies" or alike items.

6) Line 93: "CTM are capable of reproducing O_3 processes". In this sentence, you are attributing too much credibility to CTM, but models are not perfect and not always reproduce all the processes. I would be more realistic with what CTM can do, so I would suggest to rewrite this sentence.

Response:

Thanks for your suggestion. The expression here is inaccurate. In the revised manuscript, this sentence was deleted.

7) Lines 93-103 is specifically to CMAQ, it does not apply to any Eulerian CTMS (i.e. not CTM has a PA module).

Response:

Accepted. In the revised manuscript, we pointed out that the method is applied to budget calculations based on WRF-CMAQ results, as shown in lines 173-174:

WRF-CMAQ employs the Process Analysis (PA) module to assess the contributions of O_3-related processes to the variations of O_3 concentrations within each grid cell.

8) Line 121: "Horizontal transport through the borders of the PRD in four directions". Is that correct? I guess you have two horizontal directions (x and y).

Response:

We did not state it clearly. The borders of the PRD were classified as the north, south, west, east border. Horizontal transport through four types of the PRD borders were separately quantified in O_3 budgets. Thus, we added more explanations about the classification of border (grid) in lines 199-201:

The PRD grids with one or several interfaces with the outer regions are defined as the border grids, and they can be further classified as the grids in the north, south, west and east borders based on their locations.

and also revised the expressions about the horizontal transport processes in lines 204-205:

The transport processes include horizontal transport through the four types of borders and vertical exchange through the ABL top.

9) Section 2.5 Model setup and validation. Even the model setup is described in the Qu et al. (2021) some basic details should be provided in the text, for example CMAQ and WRF version. Furthermore, the section is named "validation". You mainly referenced Qu et al. (2021) but readers would appreciate a paragraph describing "why" we can trust on your modeling system's results. The evaluation of ABL height with IAGOS measurements is very interesting. Could you elaborate more on the problems with CMAQ during the night?

Response:

We agreed that it is necessary to provide more details on model setup, thus relative contents were added in lines 334-352:

The WRF (version 3.2) and CMAQ (version 5.0.2) models were used to simulate the meteorological and pollutant fields, respectively. Two domains with the resolution of 36 and 12 km (denoted as d01 and d02 hereafter) were set up for the one-way nested simulations, and results in the finer d02 were used in the calculations of O_3 budgets. To represent the contributions of global background to O_3, the initial and boundary conditions for the coarse d01 domain were provided from the global model, the Model for Ozone and Related Chemical Tracers, version 4 (MOZART-4). The PRD inventory provided by the Guangdong Environmental Monitoring Centre, the Multi-resolution Emission Inventory for China (MEIC) inventory for the mainland China (He, 2012), the MIX inventory for the Asian regions outside of mainland China (Li et al., 2017) and biogenic emissions simulated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN; version 2.10) model were used in the simulations. SAPRC07 (Carter, 2010) and AERO6 were applied as the gas-phase chemistry mechanism and the aerosol scheme, respectively. The simulations of O_3 pollution in the PRD were performed for October 2015 (October 11–November 10, 2015) and July 2016 (July 1–31, 2016), which were selected as the representative months in autumn and summer, respectively. Here, O_3 polluted days are defined when the maximum hourly O_3 concentrations of the day exceed 200 μg/m^3, or the maximum 8-hour average O_3 concentrations of the day exceed 160 μg/m^3 (both are the Grade-II O_3 thresholds in the Chinese National Ambient Air Quality Standard) in any municipality of the PRD. According to this definition, there were 16 and 12 O_3 polluted days in the two months, respectively (more information is given in Table S1). The mean O_3 budgets during these days were calculated and discussed in the present study.

As for the validation, we agreed that the relative discussions were limited in this part. Thus, we gave more information on:

1) the validation of meteorological parameters, O_3, NO_2 concentrations and the mixing ratios of hydrocarbons by Qu et al. (2021);

2) the validation of atmospheric boundary layer height, wind speed, direction and ozone mixing ratio at different heights described in detail in Text S3

in a new paragraph, as shown in lines 354-369:

We evaluated the performance of WRF-CMAQ modelling based on multiple observational datasets. The modelling results of meteorological parameters (including temperature, relative humidity and wind speed), O_3, NO_2 concentrations and the mixing ratios of hydrocarbons were validated with corresponding observations in the PRD by Qu et al. (2021a). The performance of the model to simulate the above variables was overall satisfying with low biases and high correlations (for details, see Qu et al., 2021a). In this study, we further compared the modelled ABL height, the vertical profiles of wind speed, direction and O_3 mixing ratio in Hong Kong (located in the south PRD) with the corresponding observations from the IAGOS (In-service Aircraft for a Global Observing System; Petzold et al., 2015) dataset. The modelled ABL heights showed similar hourly variations during the day as the observational results ($R = 0.76$), with mean bias of -1.1 m (Fig. S2). The mean biases of mean wind speeds are within the range of ± 1 m/s in all height ranges (0-1 km, 1-2 km, 2-5 km), and the results of IAGOS and WRF model indicate similar variations of prevailing wind directions in different seasons and height ranges (Fig. S3). Moreover, modelled O_3 mixing ratios in Oct. 2015 are overestimated by 6% and 26% in the height range of 0-1 km and 1-2 km, respectively, and sufficiently illustrate the development, maintenance and dissipation of O_3 pollution during the month (Fig. S4). More detailed evaluations on the model performance of these parameters are presented in Text S3 of the Supplement. Overall, the model performance is acceptable, indicating that the model can provide reasonable data for the calculations of O_3 budgets.

In this study, we evaluated the modelling performance of atmospheric boundary layer (ABL) height based on the IAGOS potential temperature profiles during daytime, but not at night. One reason is that in Oct.

2015, night-time records are less (30/105 = 28.6%) due to reduced flights at night. Besides, by using potential temperature profiles to determine night-time stable ABL height, large errors may occur (Dai et al., 2014). In order to have more precise O_3 budgets, more concerns on night-time ABL height are surely needed in further observations and model validation.

10) Line 220: "acceptable" from which point of view?

Response:

In this part, we evaluated the modelling performance of atmospheric boundary layer height, wind speeds, directions and O_3 mixing ratios at different heights. The results are summarized as follows:

- The modelled ABL heights showed similar hourly variations during the day as the observational results (R = 0.76), with mean bias of -1.1 m.
- The mean biases of mean wind speeds are within the range of ± 1 m/s in all height ranges (0-1 km, 1-2 km, 2-5 km), and the results of IAGOS and WRF model indicate similar variations of prevailing wind directions in different seasons and height ranges.
- Modelled O_3 mixing ratios in Oct. 2015 are overestimated by 6% and 26% in the height range of 0-1 km and 1-2 km, respectively, and sufficiently illustrate the development, maintenance and dissipation of O_3 pollution during the month.

High correlations and low biases of these parameters ensures that the modelling results can be used for further analyses, thus they are "acceptable".

According the comment No. 9, relative results are described in the revised manuscript, in lines 354-369.

11) Line 221: "reasonable" from which point of view?

Response:

This question is similar as the last one. The good performance of key parameters indicates that the modelling results are close to these in reality, thus they are "reasonable" for further usage in O_3 budget calculations.

12) Line 236-237: Is that sentence well written?

Response:

We revised the sentence into (in lines 387-391):

The question to be addressed is how O_3-related processes determine the regional origins of O_3. By combining the O_3 mass budget calculations with the BFM source apportionment method, we identified the regional origins of O_3 mass changes due to transport and photochemistry (gas-phase chemistry).

13) Source apportion method: Could you comment on the brute force disadvantages for O_3 source apportionment calculation? Could CMAQ-ISAM source apportionment method improve your results?

Response:

For this part of the study, the goal is to identify the regional origins in the O_3 mass changes attributed to transport and gas-phase chemistry (photochemistry). Besides the base scenario, three sensitivity scenarios need to be simulated in the Brute Force Method (BFM), which means increased simulation cost. But the regional source contributions in the O_3 mass changes attributed by non-transport processes, including gas-phase chemistry (photochemistry), can be identified. As a tagging method, the ISAM module in CMAQ can be used to identify the regional origins in the O_3 mass changes attributed to transport by using O_3 concentrations contributed by various regions in calculations. The simulation costs can be reduced, since it is not needed to simulate three sensitivity scenarios. However, as far as we acknowledge, the results for gas-phase chemistry (photochemistry) cannot be provided by the ISAM.

14) Conclusions: "This study concluded that transport and gas-phase chemistry play the main role in the O_3 concentration and mass budgets". Is it not new, right? Could you elaborate more this sentence as the main conclusion of this work.

Response:

Main conclusions of this study are given in the first paragraph of Sect. 5. This paragraph aims to discuss the application of O_3 budgets in the practice of O_3 pollution control. As the first sentence, this sentence fails to start the afterward discussions, thus was revised as (in lines 726-728):

The present study concluded that transport and gas-phase chemistry play the main role in the O_3 mass and concentration budgets, respectively. As a consequence of our assessment, what should policy-makers do to effectively alleviate regional O_3 pollution?

15) Conclusions: Could you elaborate more in the biases in your modelling results? For example, discussing the uncertainties in your emission data, meteorological fields, chemical and meteorological boundary conditions, chemistry in the models.

Response:

Emissions, meteorological fields, chemical and meteorological boundary conditions, chemistry and many other factors in models could all influence the results of two O_3 budgets. However, this study focuses on the comparison between two O_3 budgets to provide a complete view on the role of transport and photochemistry in regional O_3 pollution. To have more precise O_3 budgets, we suggest to conduct more supporting observations and have more comparisons between observational and modelling results. Specifically, the observational and modelling contributions by various O_3-related processes in the O_3 budgets can be directly compared. Such results are important for further model development because it indicates which process contribute to high uncertainties in O_3 modelling. Relative contents are discussed in the Sect. 5, in lines 717-724.

Uncertainty remains in the calculated O_3 budgets, which is partly related to the biases in the modelling results. Therefore, supporting observations are essential for future research. Recent progress in observational techniques (Zhao et al., 2021; Zhou et al., 2021) has enabled three-dimensional measurements of meteorological parameters and O_3 concentrations with high spatiotemporal resolution and coverage. These data can be used not only for the model validation of key parameters in budget calculations, but also for the comparisons between observation- and modelling-based contributions by various O_3-related processes in O_3 budgets (Kaser et al., 2017). The comparison of contributions by O_3-related processes is indicative of the main uncertainties in O_3 pollution modelling, and is therefore also important for further model developments.

Technical corrections:

1) Line 93: CTM not defined

Response:

This sentence containing "CTM" was deleted in the revised manuscript.

2) Line 95: PA module not defined.

Response:

Revised accordingly in line 173:

WRF-CMAQ employs the Process Analysis (PA) module to assess the contributions of O_3-related processes…

3) I would suggest used "tropospheric ozone" instead of "ambient O_3" when possible.

Response:

We agreed that to avoid confusion with ozone in stratosphere, "tropospheric ozone" is a better term to be used. It was revised accordingly in line 47-49:

Since first recognized as a key contributor to the Los Angeles smog, tropospheric ozone (O_3) pollution has received considerable attentions in many highly populated areas in the world...

Afterwards, "O_3" is directly used for relative discussions.

Additional statement:

Due to their strong professionalism in the areas of atmospheric pollution and modelling as well as high involvement in revising this paper, we are honoured to add Maria Kanakidou and Guy Brasseur as co-authors of this paper.

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