Response to Reviewer II

General Comments:

Qu et al. present an analysis of the O_3 budget in the ABL in two different ways: a concentration budget and a mass budget. They apply the budget calculations to the O_3 budget over the Pearl River Delta based on simulations with WRF-CMAQ. The 2 different ways of calculating the O_3 budget lead to opposing views on the main contributions to the O_3 budget: while photochemistry dominates in the concentration budget, (vertical) transport dominates the mass budget. A tool is developed to calculate the budget contributions. A control simulation is performed, and in addition 3 brute force emission reduction scenarios are carried out. Budget calculation following the 2 methods are performed and the differences discussed.

Unfortunately, the way the paper is written makes it hard to judge its scientific merits, and I cannot recommend acceptation in its current form.

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.

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.

Major comments:

1) This is a dense paper without much guidance for the reader as to where you are going, which makes it hard to follow, and hard to judge the scientific merits of the work you describe. I had to reread it 3 times and still I am getting lost in the details. Please rewrite it in a more structured way, and indicate the purpose of each section in its first sentence. For instance, in section 2.6 a number of scenario runs seems to appear out of the blue. Where are the results of these runs used/discussed?

Response:

Thanks for the suggestions. We have revised the manuscript and made it more structured, clear and reader-friendly. Pointing out the purpose of each section is surely a good way to provide readers more clues in reading — we have applied this suggestion in the revisions.

The basic logic of this paper is as follows. The objective is to comprehensively illustrate the effects of transport and photochemistry on regional O_3 pollution from the perspectives of both O_3 concentration and mass budgets. Three tasks are included in this study:

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).

In the introduction part, we re-wrote the relevant paragraphs to overview the structure of this manuscript, as shown in lines 157-192:

In the ABL of the concerned region, the mean O_3 concentration and total O_3 mass are both conserved, which means that their variations are equal to the net contributions by various O_3-related processes including transport and photochemistry. These relationships can be represented by the O_3 concentration budget and mass budget, respectively. Unlike the aforementioned O_3 concentration budget in Eq. (1), the hourly O_3 mass budget, written as

$$\frac{\partial m_{O_3}}{\partial t} = -\left(\bar{u} s_x \langle c_{O_3} \rangle + \bar{v} s_y \langle c_{O_3} \rangle\right) - \overline{c_{O_3}' w'} s_z + S(O_3) V \quad (2)$$

is seldom reported (m_{O_3} is the total O_3 mass within the ABL of the region; s_x, s_y, s_z are the areas of the interfaces in the x-, y- and z-direction, respectively; V is the volume of the ABL column). Due to the varied effects of transport on O_3 concentration and mass, the O_3 mass budget differs from the O_3 concentration budget but is more suitable to explore the influence of transport and photochemistry on the results of O_3 source apportionment (more detailed explanations are given in Sect. 2.4). In order to comprehensively understand the role of transport and photochemistry in regional O_3 pollution, in the present study, we developed a method to calculate both the O_3 concentration and mass budget based on the simulation results from the Weather Research and Forecasting (WRF) and Community Multiscale Air Quality (CMAQ) models, and also analysed, compared the results of the two regional-level O_3 budgets. The Pearl River Delta (PRD) region, a city cluster located on the southeast coast of China and exposed to severe O_3 pollution in summer and autumn (Gao et al., 2018), was selected as the targeted region. The tasks for this study can be summarized as follows:

1) Development of the method to quantify the two O_3 budgets

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. However, to obtain the regional-level O_3 concentration and mass budgets, the results of PA module are not sufficient. One reason is that the contribution of vertical exchange through the ABL top is not specifically quantified in commonly used ABL parameterizations, thus requires additional calculations (Kaser et al., 2017). Additionally, calculations based on the PA results are needed to identify the contributions of other O_3-related processes to ABL-mean O_3 concentration as well as the results of the O_3 mass budget. To address this, we developed a method to quantify the two O_3 budgets, of which the details are given in Sect. 2.1-2.3.

2) Analysis and comparison of the results from the two O_3 budgets

Based on the simulations of O_3 pollution in the PRD with the model setup introduced in Sect. 2.5, the two O_3 budgets were calculated for further analyses and comparisons to reveal the role of transport and photochemistry in regional O_3 pollution from a more comprehensive perspective. Relative discussions are presented in Sect. 3.

3) Assessment of the role of transport and photochemistry in determining the regional origins of O_3

The Brute Force Method (BFM; Clappier et al., 2017), a widely used source apportionment method, was combined with the O_3 mass budget calculation to determine the contributions of emissions within and outside the PRD as well as background sources to the O_3 transported into or produced by photochemistry in the region (methodology described in Sect. 2.6). The results, as discussed in Sect. 4, reveal the impacts of transport and photochemistry in determining the regional origins of O_3 in the PRD, and explain why the different views on the role of two processes in regional O_3 pollution are suggested by the O_3 concentration budget and O_3 source apportionment studies.

We also separated the original Sect. 3 (named *Results*) as two parts,

Sect. 3 Analyses and comparisons of O_3 concentration and mass budget

and

Sect. 4 Effects of transport and photochemistry on the regional origins of O_3

which separately discuss the results of aforementioned task 2 and 3.

2) What is actually lacking is an explanation of why 2 different budget methods give such different results. Is it mainly a boundary conditions problem? A change in mass does not lead to a change in concentration when the background concentration is similar over larger regions? Maybe it is discussed in L445-448?

Response:

The two O_3 budgets describe the conservations of O_3 concentration and mass in the atmospheric boundary layer (ABL) of the region. As introduced in Sect. 2.4, the different results of two O_3 budgets are mainly attributed to the different effects of transport on O_3 concentration and mass. When O_3 is transported into (or out of) the ABL of the region through the advection process (horizontal transport and vertical exchange through the ABL top due to large-scale air motion (ABLex-M)), surely total O_3 mass increases (or decreases). However, whether O_3 concentration increases or decreases also depends on the difference between O_3 concentrations in the region and transported air parcels — that is why clean (polluted) air parcels being transported into the region dilutes (aggravates) O_3 pollution. The effect of transport can be understood as to replace a part of air mass with the transported air parcel. If O_3 concentration is higher (or lower) in the transported air parcel, by replacing, mean O_3 concentration within the region will increase (or decrease). This effect also applies to the exchange through the ABL top due to the temporal changes of ABL heights (ABLex-H). For example, after sunrise, O_3 mass in the ABL of the region increases rapidly along with the development of ABL. This process can be viewed as two air parcels combining into one, and whether O_3 concentration increases or decreases also depends on the difference of O_3 concentrations in two air parcels — but O_3 mass surely increases. More detailed contents are discussed in Sect. 2.4, in lines 301-321:

The difference between the two O_3 budgets is linked to the varied effects of transport on O_3 mass and concentration. Suppose that the mean O_3 concentration in the transported air parcels is $\langle c_{O_3}\rangle_{trans}$. For horizontal transport, its contributions in the O_3 mass and concentration budgets can be separately written as:

$$F_{htrans} = \langle c_{O_3}\rangle_{trans}\, dV \tag{8}$$

$$d\langle c_{O_3}\rangle_{htrans} = \frac{dV}{V}\left(\langle c_{O_3}\rangle_{trans} - \langle c_{O_3}\rangle\right) \tag{9}$$

Apparently, F_{htrans} is related to the O_3 concentrations in the transported air parcels, but not to those in the studied region. It indicates how much O_3 is transported into or out of the region. Whether it is positive or negative only depends on the direction of transport — O_3 being transported into (out of) the region leads to the increase (decrease) of O_3 mass, which corresponds to a positive (negative) contribution in the O_3 mass budget. In contrast, $d\langle c_{O_3}\rangle_{htrans}$ quantifies how much horizontal transport alters regional-mean O_3 concentrations, and is linked to the difference between O_3 concentrations in the transported air parcels and the studied region (Eq. (9)). O_3 being transported into (out of) the region does not necessarily result in a higher (lower) O_3 concentration. For instance, when clean air parcels with relatively low O_3 levels are transported into the region, they dilute O_3 pollution and reduce O_3 concentration ($d\langle c_{O_3}\rangle_{htrans} < 0$). Given that ABLex-M is also an advection process, the above difference applies to this process as well. For ABLex-H, its contributions in the O_3 mass and concentration budgets are expressed as:

$$F_{ABLex-H} = \langle c_{O_3}\rangle_{trans}\, dV \quad (10)$$

$$d\langle c_{O_3}\rangle_{ABLex-H} = \frac{dV}{V + dV}\left(\langle c_{O_3}\rangle_{trans} - \langle c_{O_3}\rangle\right) \quad (11)$$

Similarly, ABL development and collapse lead to the increase and decrease of O_3 mass, respectively, but whether they contribute to higher or lower O_3 concentration also depends on the difference between O_3 concentration in the transported air parcels and that in the region. Based on the above discussion, these transport processes all show different effects on O_3 mass and concentration — the effect of transport on the variations of O_3 mass is only related to the characteristics of the transported air parcels, namely their volumes and O_3 concentrations within (Eqs. (8) and (10)), while how transport contributes to the variations of O_3 concentration is linked to the difference between O_3 concentrations in the transported air parcels and the region (Eqs. (9) and (11)).

It is possible that change in mass does not lead to a change in concentration when the background concentration is similar over larger regions. For example, suppose that air parcels with the volume of dV and the O_3 concentration of $\langle c_{O_3}\rangle_{trans}$ are transported into the region through the ABLex-H process. The contributions of such a process to O_3 mass and concentration (denoted as $F_{ABLex-H}$ and $d\langle c_{O_3}\rangle_{ABLex-H}$, respectively) can be expressed as (Eqs. (10-11) of the manuscript):

$$F_{ABLex-H} = \langle c_{O_3}\rangle_{trans}\, dV$$

$$d\langle c_{O_3}\rangle_{ABLex-H} = \frac{dV}{V + dV}\left(\langle c_{O_3}\rangle_{trans} - \langle c_{O_3}\rangle\right)$$

where V is the original volume of the ABL of the region, $\langle c_{O_3}\rangle$ is the initial mean O_3 concentration. $F_{ABLex-H}$ is surely positive, since $\langle c_{O_3}\rangle_{trans}$ and dV are both above 0. As an extreme case, if $\langle c_{O_3}\rangle_{trans} = \langle c_{O_3}\rangle$, then $d\langle c_{O_3}\rangle_{ABLex-H} = 0$, which means that the transport, or "combination", of air parcels with the same O_3 concentration leads to increased O_3 mass and volume in the ABL of the region at the same time, but O_3 concentration does not change.

In L445-448 of the original manuscript, we discussed why the conclusions in this paper are important for further studies. Differences in the concentration and mass budgets apply to not only O_3, but also other pollutants with moderately long atmospheric lifetimes, such as fine particulate matter and some of its components. Transport may fail to notably alter pollutant concentration, but can significantly contribute to the changes of pollutant mass. Specifically, massive pollutant being transported into the ABL in the morning nearly determines the characteristics of pollutant within the region — besides the origins of pollutants, they also include the contributions of different reaction pathways and sensitivities to precursor emissions. But in the concentration budget, the effects of transport on these characteristics are often ignored. In order to fully understand the effects of transport, chemistry and other related processes, we suggest that the insights from both concentration and mass budgets are required for future studies.

Minor comments:

1) L50 (and throughout MS): O_3 processes --> O_3-related processes

Response:

Accepted and revised as suggested.

2) L74: pls rephrase sentence

Response:

This sentence is revised into (in lines 107-109):

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).

3) L416: "High contributions of …" Unclear sentence. Please rephrase.

Response:

This sentence is revised into (in lines 650-654):

By combining the O_3 mass budget and O_3 source apportionment, we identified the O_3 mass increase due to O_3-related processes as local (PRD) and non-local (EC-China and BCON) contributions. According to the results discussed before, high contributions of transport in the morning-hour O_3 mass increase and the dominance of non-local source contributions in this part of new O_3 ensure that non-local sources contributed to most O_3 in the PRD.

4) L461: what do you mean by 'a longer time'?

Response:

"A longer time" is vague, thus it is revised as in lines 732-733:

However, for short-term air pollution control, this strategy is not efficient because emission reduction in upwind regions may need to start days earlier before the polluted periods.

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.

References

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