Rethinking the role of transport and photochemistry in regional ozone pollution: Insights from ozone concentration and mass budgets

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Abstract. Understanding the role of transport and photochemistry is essential to alleviate ambient ozone pollution. However, ozone budget and source apportionment studies often report conflicting conclusions — Local photochemistry is the main cause of ozone pollution based on the analyses of the former, while contrary, non-local ozone transported to the region accounts for the majority in the latter results. In order to explore its potential causes, we calculated the contributions of both processes to the variations of mean ozone concentration and total ozone mass (the corresponding budgets are noted as ozone concentration and mass budget, respectively) within the atmospheric boundary layer (ABL) of the Pearl River Delta (PRD), China, based on the modelling results of WRF-CMAQ. Quantified results show that photochemistry drives the rapid increase of ozone concentrations in the daytime, whereas transport, especially the vertical exchange near the ABL top, controls the ozone mass budget. The changes in transport contributions in ozone budgets indicate the influences of the ABL diurnal cycle and regional wind fields, including prevailing winds and local circulations (sea breezes), on regional ozone pollution. Though transport in our simulations had a relatively limited effect on ozone concentration, its high contribution to ozone mass increase in the morning determined that most ozone in the PRD emanated from the outer regions. Consequently, the role of transport and photochemistry in ozone pollution may differ, depending on which of the two budgets is concerned. For future studies targeting ozone and other pollutants with moderately long atmospheric lifetimes, we suggest that attention should be paid to budget-type selections.

1 Introduction

Since first recognized in the Los Angeles smog, ambient ozone (O_3) pollution has been a problem for many highly populated urban regions around the globe (Fishman et al., 2003; Schultz et al., 2017; Fleming et al., 2018; Fowler et al., 2020). Exposure to O_3 threatens human health, crop yields and ecosystems, and results in increased mortality and economic losses (Mills et al., 2013; Ainsworth, 2017; Zhang et al., 2019). In addition, O_3 contributes to global warming not only directly as a greenhouse gas, but also indirectly by damaging plants and suppressing land carbon sinks (Sitch et al., 2007; Naik et al., 2021). Considering the above detrimental effects, efforts to reduce ambient O_3 pollution in polluted urban regions are keenly required.

Understanding O_3 processes in the atmosphere is an essential prerequisite to finding effective regional O_3 control strategies. Generally, high O_3 concentrations within a region are attributed to daytime photochemical production from O_3 precursors, i.e. NO_x (= NO + NO_2) and volatile organic compounds (VOCs), under the sunlight. However, since O_3 has a moderately long atmospheric lifetime (20-30 days; Stevenson et al., 2006; Bates and Jacob, 2019), the influence of dynamic processes on regional-level O_3 pollution is likely to be important as well (Vilà-Guerau de Arellano et al., 2015). This can be shown by the following two aspects. Firstly, O_3 is well mixed in the daytime convective atmospheric boundary layer (ABL), especially during severe O_3 pollution (Zhao et al., 2019; Tang et al., 2021). Due to ABL mixing, O_3 precursors emitted by near-ground sources are brought upwards to the upper ABL, where O_3 is more rapidly produced; afterwards, O_3 is transported downwards to the ground (Tang et al., 2017). Therefore, to alleviate near-ground O_3 pollution, the goal should be to reduce the overall O_3 level within the ABL — rather than only near the ground — based on the quantified influence of various O_3 processes throughout the ABL. Secondly, transport, including horizontal transport (mainly advection) and vertical exchange near the ABL top, may considerably contribute to regional O_3 pollution. More specially, through the vertical exchange in the morning, O_3 in the residual layer and/or free atmosphere is entrained into the ABL, leading to the rapid increase of O_3 concentration after sunrise (Kaser et al., 2017; Hu et al., 2018; Zhao et al., 2019). Transported O_3 may be derived from local sources, or transported from other regions, continents and even stratosphere under the combined effect of meso-, synoptic-, large- and global-scale atmospheric movements (Massagué et al., 2019). In addition, O_3 precursors may also be transported into the region and involved in O_3 production. These dynamic processes make the causes of regional O_3 pollution more complicated than normally realized.

In previous studies, the O_3 budget was often conducted to quantify the contributions of various chemical and transport processes to the variations of O_3 concentrations. For the mean O_3 concentration within the ABL ($\langle c_{O_3} \rangle$), its budget can be represented as in Lenschow et al. (1981), Janssen and Pozzer (2015) and Vilà-Guerau de Arellano et al. (2015):

$$\frac{\partial \langle c_{O_3} \rangle}{\partial t} = -\left(\bar{u} \frac{\partial \langle c_{O_3} \rangle}{\partial x} + \bar{v} \frac{\partial \langle c_{O_3} \rangle}{\partial y} \right) - \frac{\partial \overline{c_{O_3}' w'}}{\partial z} + S(O_3) \quad (1)$$

where u, v and w indicate wind speeds in the x-, y- and z-direction, respectively. Three items on the right side of Eq. (1) separately describe the contributions of 1) horizontal transport (advection), 2) vertical exchange near the ABL top, 3) gas-phase chemistry, dry deposition and other processes (the term $S(O_3)$ indicates their net contributions). Reported O_3 budget based on ground-based measurements (Su et al., 2018; Tan et al., 2018; Tan et al., 2019; Yu et al., 2020), aircraft-based mobile observations (Lenschow et al., 1981; Trousdell et al., 2016; Trousdell et al., 2019) and Process Analysis (PA) or alike modules in chemical transport models (CTMs) (Hou et al., 2014; Li et al., 2021a; Yan et al., 2021) often suggest that O_3 production through local photochemistry drives the noon-time increase of O_3 concentration, whereas transport reduces O_3 concentration over the same period. O_3 precursors are likely to be mainly derived from local emissions due to their relatively short lifetimes. Thus, according to these photochemistry-dominated O_3 budget results, local emission reduction seems more efficient in alleviating ambient O_3 pollution.

As an important characteristic of O_3, O_3 source indicates from which regions and/or emission sectors O_3 originates, of which the results can support effective air pollution control (Clappier et al., 2017; Thunis et al., 2019). The source apportionment of ambient O_3 often suggested that most O_3 emanated from non-local sources, including the global background and emissions outside the targeted regions (Guo et al., 2018; Pay et al., 2019; Liu et al., 2020). The mixing ratios of background O_3 in various regions of the world are mostly within the range of 30-50 ppb (Reid et al., 2008), high enough to ensure the dominance of non-local sources for O_3 pollution in less polluted regions. Since this part of O_3 is less likely to be controlled, the influence of O_3 and/or precursors transport from the upwind metropolitan regions has received much attention (Lelieveld et al., 2009; Boian and Andrade, 2012; Massagué et al., 2019). For regions where upwind sources notably contribute to O_3, focusing more on emission reductions on a larger scale rather than only reducing local emissions is needed to effectively control O_3 pollution. One successful example is the establishment of the "Ozone Transport Region" in the north-eastern US by the US Environmental Protection Agency, which promoted collaborative emission reductions among states to address inter-state O_3 transport (Novel, 1992). In China, O_3 pollution was overall more severe than in other countries recently (Lu et al., 2018). Since high pollutant emissions are widely distributed in East China, the so-called "gigacity" (Kulmala et al., 2021), upwind emissions often contribute more to O_3 pollution in the major city clusters compared to local emissions, as suggested by O_3 source studies in China (Liu et al., 2020). Therefore, transport seems to play a more important role in ambient O_3 pollution here as well, and the efforts of joint prevention and control among regions to reduce O_3 levels are necessary (Li et al., 2021b). Apparently, insights from O_3 source apportionment differ from the conclusions based on the O_3 budgets.

Simulations by Eulerian CTMs are capable of reproducing O_3 processes within the ABL. However, since the contribution of vertical exchange near the ABL top is not specifically quantified in normally used ABL parameterizations, it cannot be directly provided by the PA module but requires additional calculations (Kaser et al., 2017). Thus O_3 budget within the ABL on the hourly scale is seldom reported based on CTMs results. In this study, we constructed the post-processing tool

flux_4d_cal to quantify the contributions of O_3 processes, including gas-phase chemistry, horizontal transport and vertical exchange near the ABL top, in the O_3 budget within the ABL of the targeted region. The calculations were conducted based on the simulation results from the Weather Research and Forecasting (WRF) and Community Multiscale Air Quality (CMAQ) models, of which the details are briefly introduced in Sect. 2. To explore the reasons behind the contradictory views on the role of transport and photochemistry in regional ozone pollution between the O_3 budget in Eq. (1) and O_3 source apportionment, the other type of O_3 budget, the O_3 mass budget, was introduced by this tool. It aims to identify the contributions of O_3 processes to the variation of total O_3 mass within the ABL (m_{O_3}) and is written as:

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

where s_x, s_y, s_z are the areas of the interfaces in the x-, y- and z-direction, respectively, and V is the volume of the ABL column. Regional-level O_3 mass budget can be applied to illustrate better the changes in regional O_3 sources and their influencing factors (more in-detail discussions are given in Sect. 2.4). The O_3 budget shown in Eq. (1) is hereinafter re-defined as the O_3 concentration budget, which focuses on the contributions of O_3 processes to the variation of ABL-mean O_3 concentration. Moreover, based on the O_3 mass budgets in the sensitivity scenarios that zeroes out emissions in specific regions, the regional source of O_3 mass change contributed by different processes can also be identified. 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 in this study. The quantified results of O_3 concentration and mass budgets in the PRD illustrated the complex effects of O_3 processes, especially transport, on regional O_3 pollution, and revealed that the distinct views on the role of photochemistry and transport are possibly linked to the differences between two O_3 budgets.

2 Methodology: O_3 budget calculations and model setup

2.1 Processes in O_3 budgets

Figure 1 displays all processes considered in the calculation of O_3 budgets as well as the distributions of the PRD grids (lower-left panel; defined as the grids within the PRD), which include the border grids (defined as the PRD grids adjacent to the outer regions) and non-border grids.

Horizontal transport through the borders of the PRD in four directions and vertical exchange near the ABL top are the transport processes concerned in this study. For the latter, its contribution in the O_3 concentration budget (the second item on the right side of Eq. (1)) is quantified by Sinclair et al. (2010) and Jin et al. (2021):

$$-\frac{\partial\overline{c_{O_3}'w'}}{\partial z} = -\frac{\Delta c_{O_3}}{H}\frac{\partial H}{\partial t} - \frac{\Delta c_{O_3}}{H}\left(u_h\frac{\partial H}{\partial x} + v_h\frac{\partial H}{\partial y} - w_h\right) \quad (3)$$

where H is the ABL height; Δc_{O_3} is the difference between O_3 concentrations above and within the ABL; u_h, v_h and w_h are the ABL-top wind speeds in the x, y and z-direction, respectively. Items on the right side of Eq. (3) suggested that the occurrence of vertical exchange is attributed to 1) the temporal changes of ABL heights and 2) large-scale air motion (advection) perpendicular to the ABL top and its slope. Their contributions can be identified in the O_3 mass budget as well, of which the details are introduced in Sect 2.2. Hereafter, vertical exchanges due to the above two processes are marked as ABLex-H and ABLex-M, respectively. The contributions of all transport processes were quantified using meteorological parameters and O_3 concentrations modelled by WRF-CMAQ. The basic calculations of the above contributions in the O_3 concentration and mass budgets are separately introduced in the following two sections, and details about the calculation process are presented in Text S1.

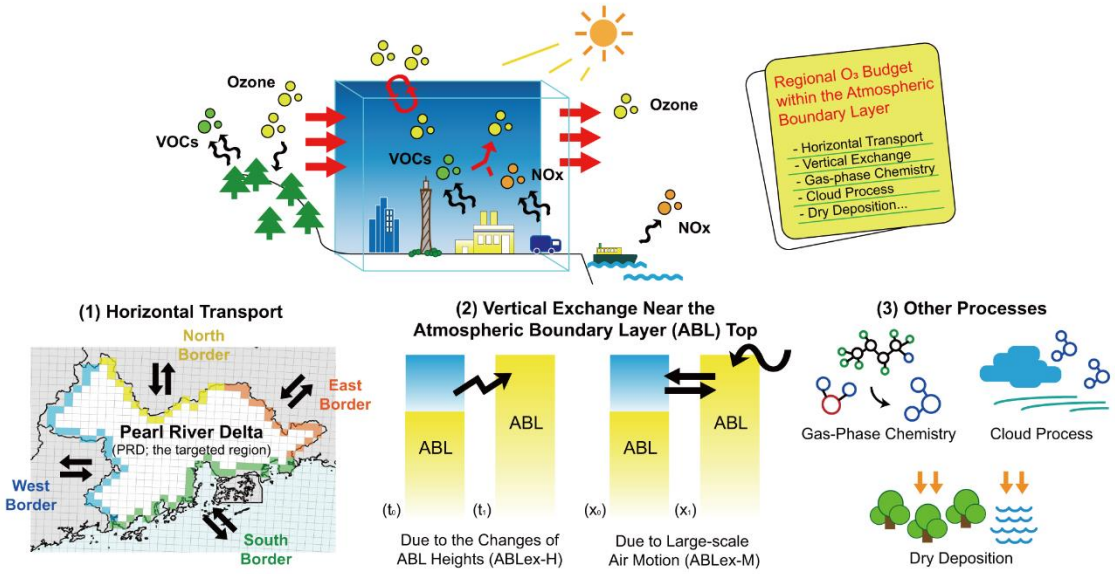

Figure 1. Schematic illustration of regional O_3 budgets (the upper panel) and processes considered (the lower panel): (1) Horizontal transport through the borders of the Pearl River Delta (PRD) in four directions (the distributions of the PRD grids are also shown: yellow, green, blue, orange for the north, south, west and east border grids, respectively, and white for the non-border grids); (2) Vertical exchange near the atmospheric boundary layer (ABL) top, including the process due to the changes of ABL heights (ABLex-H) and large-scale air motion (ABLex-M); (3) Other processes, including gas-phase chemistry, cloud process and dry deposition in this study.

Other processes in O_3 budgets include gas-phase chemistry (including daytime photochemical O_3 production and O_3 titration by NO), cloud process (including below and in-cloud mixing, aqueous-phase chemistry, wet deposition; Liu et al., 2011) and dry deposition. Their contributions are calculated based on the output of the PA module in CMAQ (for a more detailed description of calculations, see Text S1). Since diffusion near the boundaries and top of the region is expected to have a minor influence on the variation of O_3 concentration and mass, we did not involve this process in the quantifications.

2.2 Transport contributions in the O_3 mass budget

The method by Yang et al. (2012) and Chang et al. (2018) was applied to quantify the contributions of horizontal transport in the O_3 mass budget. For instance, the contribution of the advection through the west/east interface of a grid cell column within the ABL to total O_3 mass (F_{htrans}) in the column during the time interval dt is calculated as:

$$F_{htrans} = \int_0^H c_{O_3} uL \, dz \, dt \tag{4}$$

where L is the width of the grid cell (equal to the horizontal resolution of the model); dz is the height of vertical layers. For advection through the north/south interface, the calculation is similar to Eq. (4), except for using v instead of u. F_{htrans} values through every interface between one type of border and the outer region were summed up as the net contribution of horizontal transport through that border in the O_3 mass budget.

Following Sinclair et al. (2010) and Jin et al. (2021), the contribution of vertical exchange near the ABL top to O_3 mass (F_{ABLex}) during the time interval dt can be expressed as:

$$F_{ABLex} = F_{ABLex-H} + F_{ABLex-M} = c_{O_3\_h} \frac{\partial H}{\partial t} L^2 dt + c_{O_3\_h} \left(u_h \frac{\partial H}{\partial x} + v_h \frac{\partial H}{\partial y} - w_h \right) L^2 dt \tag{5}$$

where $c_{O_3\_h}$ is the O_3 concentration at the ABL top. Two terms on the right-most side of Eq. (5) separately describe the contributions of ABLex-H and ABLex-M (denoted separately as $F_{ABLex-H}$ and $F_{ABLex-M}$). F_{ABLex} values in all the PRD grids were summed up as the net contribution of vertical exchange near the ABL top in the O_3 mass budget.

2.3 Transport contributions in the O_3 concentration budget

For one or limited grid columns, it is possible to directly use Eq. (1) to quantify the O_3 concentration budget based on CTMs results. But for the ABL of the PRD, which comprises over 260 grid columns, such calculations could easily become over-complicated. Therefore, a different approach was applied to calculate the regional-level O_3 concentration budget.

Suppose that air parcels with a total volume of dV are transported into the ABL of the PRD (its original volume is V) during the time interval dt. For horizontal transport, the variation of $\langle c_{O_3} \rangle$ under its influence ($d\langle c_{O_3} \rangle_{htrans}$) can be written as:

$$d\langle c_{O_3} \rangle_{htrans} = \frac{F_{htrans} + \langle c_{O_3} \rangle (V - dV)}{V} - \langle c_{O_3} \rangle = \frac{F_{htrans} - \langle c_{O_3} \rangle \, dV}{V} \tag{6}$$

Since ABLex-M is also an advection process, its contribution in the O_3 concentration budget ($d\langle c_{O_3} \rangle_{ABLex-M}$) can be quantified using a similar formula, except for using $F_{ABLex-M}$ instead of F_{htrans}.

Through ABLex-H, air parcels in the residual layer and/or free atmosphere are merged into (or segmented out of) the ABL. Thus, the variation of $\langle c_{O_3} \rangle$ under its influence ($d\langle c_{O_3} \rangle_{ABLex-H}$) is expressed as:

$$d\langle c_{O_3} \rangle_{ABLex-H} = \frac{F_{ABLex-H} + \langle c_{O_3} \rangle V}{V + dV} - \langle c_{O_3} \rangle = \frac{F_{ABLex-H} - \langle c_{O_3} \rangle \, dV}{V + dV} \quad (7)$$

If the targeted region was small enough, Eqs. (6) and (7) would have the same forms as the corresponding items in Eq. (1), confirming the applicability of the above calculations (for details, see Text S2). All variables in Eqs. (6) and (7) can be quantified by the post-processing tool, making the method suitable for calculating the regional-scale O_3 concentration budget.

However, due to the prominent diurnal cycle of ABL, V in Eqs. (6) and (7) may change notably within an hour, leading to bias in the hourly estimations of $d\langle c_{O_3} \rangle_{htrans}$, $d\langle c_{O_3} \rangle_{ABLex-H}$ and $d\langle c_{O_3} \rangle_{ABLex-M}$ when using V at the start and end of the hour. In order to reduce this potential bias, we designed two calculation paths (Fig. S1):

- O_3 mass change → ABL volume change
- ABL volume change → O_3 mass change

where only O_3 mass or ABL volume changes in each calculation step. The contribution of ABLex-H can be decomposed into two parts: ABL volume change due to ABL development (collapse) leads to lower (higher) O_3 concentration, and O_3 transported into (out of) the ABL through ABLex-H leads to O_3 increase (decrease). These contributions are quantified separately in the ABL volume and O_3 mass change step. The contributions of other processes are quantified only in the O_3 mass change step. For one process, its contribution to the variation of O_3 concentration is calculated through both paths, and the mean value of two results serves as an estimation close to its real contribution in the O_3 concentration budget.

2.4 Difference between two O_3 budgets

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:

$$F_{htrans} = \langle c_{O_3} \rangle_{trans} \, dV \quad (8)$$

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

Apparently, F_{htrans} is related to the O_3 concentrations in the transported air parcels, but not to those in the targeted 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 levels. As shown in Eq. (9), it is linked to the difference between O_3 concentrations in the transported air parcels and the targeted region. 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 ($d\langle c_{O_3}\rangle_{htrans} < 0$). These effects are the same for ABLex-H and ABLex-M, also showing the above difference between the two O_3 budgets.

To understand the influence of various processes on O_3 sources, it is required to identify the sources of "new O_3" into the region and "disappeared O_3" out of the region contributed by processes, rather than how these processes lead to the variations of O_3 concentration. According to the above discussions, the O_3 mass budget is suitable to explain how transport and photochemistry determine the regional sources of O_3 in this study.

2.5 Model setup and validation

The O_3 concentration and mass budgets within the ABL of the PRD were calculated based on the WRF-CMAQ modelling results by Qu et al. (2021). In the models, two nested domains with the resolution of 36 and 12 km were set (denoted as d01 and d02 hereafter), and results in the finer d02 were used in the calculations of O_3 budgets. October 2015 (October 11–November 10, 2015) and July 2016 (July 1–31, 2016) were selected as the representative months in autumn and summer, respectively, for the PRD. Here, O_3 polluted days are defined when the maximum hourly O_3 concentrations exceed 200 μg/m^3, or the maximum 8-hour average O_3 concentrations 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). Further discussions focus on O_3 budgets during these days. The detailed setup of WRF-CMAQ, the validation of modelled meteorological parameters, O_3, NO_2 concentrations and hydrocarbons mixing ratios have been introduced by Qu et al. (2021). In this study, we also compared modelled ABL height, the vertical profiles of wind speed, direction and O_3 mixing ratio in Hong Kong (located in the south PRD) with corresponding observations from the IAGOS (In-service Aircraft for a Global Observing System; Petzold et al., 2015) dataset. As presented in Text S3, the acceptable modelling performance of these parameters indicates that the model provides reasonable initial data for the O_3 budget calculations.

If the calculation methods and assumptions were reasonable, the budget closure, or

$$\frac{\partial\langle c_{O_3}\rangle (or\ m_{O_3})}{\partial t} - \left(S_{htrans} + S_{ABLex} + S_{chem} + S_{cloud} + S_{ddep}\right) = 0 \quad (10)$$

would be achieved (S_{htrans}, S_{ABLex}, S_{chem}, S_{cloud} and S_{ddep} indicate the contributions of horizontal transport, vertical exchange near the ABL top, gas-phase chemistry, cloud process and dry deposition, respectively, in O_3 budgets). Therefore, we used Eq. (10) to examine the validity of the calculations. Total O_3 masses at the start and end of each hour were directly used to calculate the hourly variations of O_3 mass ($\frac{\partial m_{O_3}}{\partial t}$). Besides these, volumes at these two moments (calculated using ABL heights in all the PRD grids) were also needed to calculate the hourly variations of O_3 concentration ($\frac{\partial\langle c_{O_3}\rangle}{\partial t}$). The

contributions of various processes in the O_3 concentration and mass budgets were provided by the post-processing tool. As displayed in Fig. 2, hourly variations of O_3 concentration/mass and the corresponding net contributions from all processes show good correlations ($R^2 > 0.9$), with all fitted lines being close to the 1:1 line. Thus, the closure is met for the two O_3 budgets in both months, allowing for further analyses based on the quantified budgets.

2.6 Identifying regional sources of O_3 mass changes contributed by various processes

It is generally believed that transport (gas-phase chemistry) is closely linked to the contributions of non-local (local) emissions for O_3, but quantitative evaluation of the connections between O_3 processes and sources is still understudied. By combining O_3 budget calculations with the source apportionment method, the Brute Force Method (BFM; Clappier et al., 2017), we identified the regional sources of O_3 mass changes contributed by transport and gas-phase chemistry. Of interest were the contributions of emissions in the PRD, other regions within d02 (mainly East and Central China, short for EC-China), and regions outside d02 (the boundary conditions (BCON) of d02 modelling). The distributions of these regions are shown in Fig. S2. Besides the base scenario, three sensitivity scenarios were simulated:

- The PRD_zero scenario: Emissions in the PRD were zeroed out;
- The EC-China_zero scenario: Emissions in the EC-China were zeroed out;
- The All_zero scenario: All emissions within d02 were shut down.

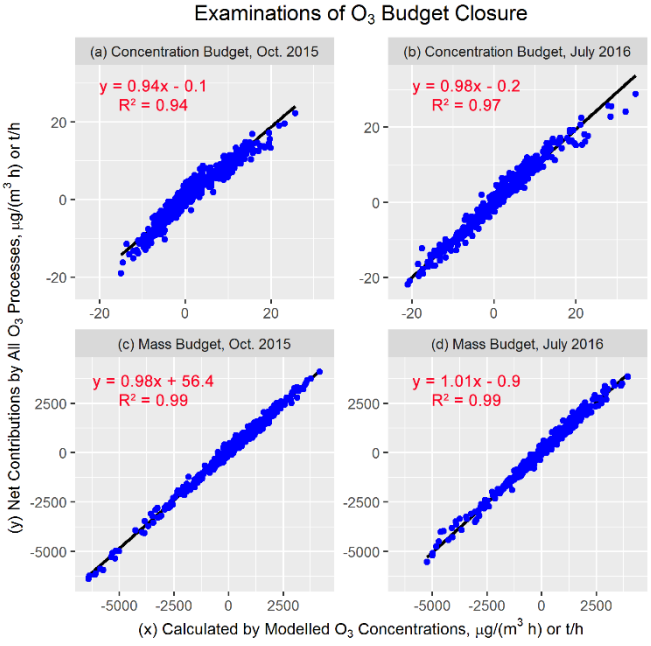

Figure 2. The examinations of O_3 budget closure in Oct. 2015 (a,c) and July 2016 (b,d) for the hourly O_3 concentration budget (a-b) and mass budget (c-d). The units for the O_3 concentration and mass budgets are µg/(m^3 h) and t/h, respectively. The solid black lines in the plots are the fitted lines.

For the process i, its hourly contributions in the O_3 mass budget in the base scenario and three sensitivity scenarios were quantified using the same method introduced in Sect. 2.2, which are marked as $f_{i,base}$, f_{i,PRD_zero}, $f_{i,EC-China\_zero}$, and f_{i,all_zero}, respectively. Then, the contributions of PRD, EC-China and BCON in O_3 mass changes attributed to the process i (separately denoted as $F_{i,PRD}$, $F_{i,EC-China}$, and $F_{i,BCON}$) were calculated as follows:

$$F_{i,PRD} = \frac{1}{2}[(f_{i,base} - f_{i,PRD\_zero}) + (f_{i,EC-China\_zero} - f_{i,all\_zero})] \quad (11)$$

$$F_{i,EC-China} = \frac{1}{2}[(f_{i,base} - f_{i,EC-China\_zero}) + (f_{i,PRD\_zero} - f_{i,all\_zero})] \quad (12)$$

$$F_{i,BCON} = f_{i,all\_zero} \quad (13)$$

In Eqs. (11) and (12), the contributions of emissions are calculated as the average results of these using top-down BFM ($(f_{i,base} - f_{i,PRD\_zero})$, $(f_{i,base} - f_{i,EC-China\_zero})$) for the PRD and EC-China emissions, respectively) and bottom-up BFM ($(f_{i,EC-China\_zero} - f_{i,all\_zero})$, $(f_{i,PRD\_zero} - f_{i,all\_zero})$) for the PRD and EC-China emissions, respectively). By doing so, the non-additivity (the sum of all contributions is not equal to the concerned metric) caused by the non-linearity between O_3 and precursors can be avoided (Qu et al., 2021).

3 Results

3.1 O_3 concentration budget

The upper panels of Fig. 3 show the diurnal changes of the O_3 concentration budget within the ABL of the PRD. According to the net contributions, O_3 concentration increased during most hours in the daytime, and its reduction at night was also considerable. We also compared the diurnal changes of ABL-mean O_3 concentration with those of observed and modelled mean near-ground O_3 concentrations in 18 sites of the Guangdong-Hong Kong-Macao PRD Regional Air Quality Monitoring Network (distributions are shown in Fig. S3). As presented in Fig. S4, three types of O_3 diurnal changes display similar characteristics. However, the budget of ABL-mean O_3 concentration can better reveal the influences of transport and photochemistry on the overall O_3 levels as well as the general causes of O_3 pollution in the targeted region. Such results in the PRD are discussed in the following.

Apparently, gas-phase chemistry controlled almost exclusively the O_3 concentration budget. During the morning hours, which are defined as the period from sunrise (~6:00 local time (LT) in autumn, ~5:00 LT in summer) to the O_3-peak hour (~14:00 LT), it (photochemistry) contributed to, on average, 74% and 95% of the O_3 concentration increase in autumn and summer, respectively. These contributions are notably higher than transport contributions (25% in autumn, 5% in summer). Gas-phase chemistry also led to the decrease of O_3 concentration at night, suggesting the impact of O_3 titration by emitted NO. It does not mean that the influence of transport on O_3 concentration can be neglected every hour. Considerable contributions of transport (mainly by ABLex-H) to O_3 increase are found 2-3 hours after sunrise, with the highest hourly

mean contributions reaching ~40% and ~25% in autumn and summer, respectively. It indicates the notable influences of air masses containing high-level O_3 entrained from residual layers. ABLex-M and horizontal transport may contribute to the increase or decrease of ABL-mean O_3 concentration, depending on the O_3 levels in air parcels transported into and out of the region (more analyses are given in Sect. 3.4). But overall, these two processes had only limited contributions to the variations of O_3 concentration. Dry deposition contributed to a considerable decrease in O_3 concentration, especially in the daytime, and served as the major sink process for O_3. To summarize, the results of the O_3 concentration budget indicate that gas-phase chemistry played a major role in the variations of O_3 concentrations in the PRD. In particular, photochemistry led to the rapid formation of O_3 pollution in the daytime, rather than transport. Our conclusions agree well with those in previous publications on the O_3 concentration budget (Lenschow et al., 1981; Hou et al., 2014; Trousdell et al., 2016; Su et al., 2018; Tan et al., 2018; Tan et al., 2019; Trousdell et al., 2019; Yu et al., 2020; Li et al., 2021a; Yan et al., 2021).

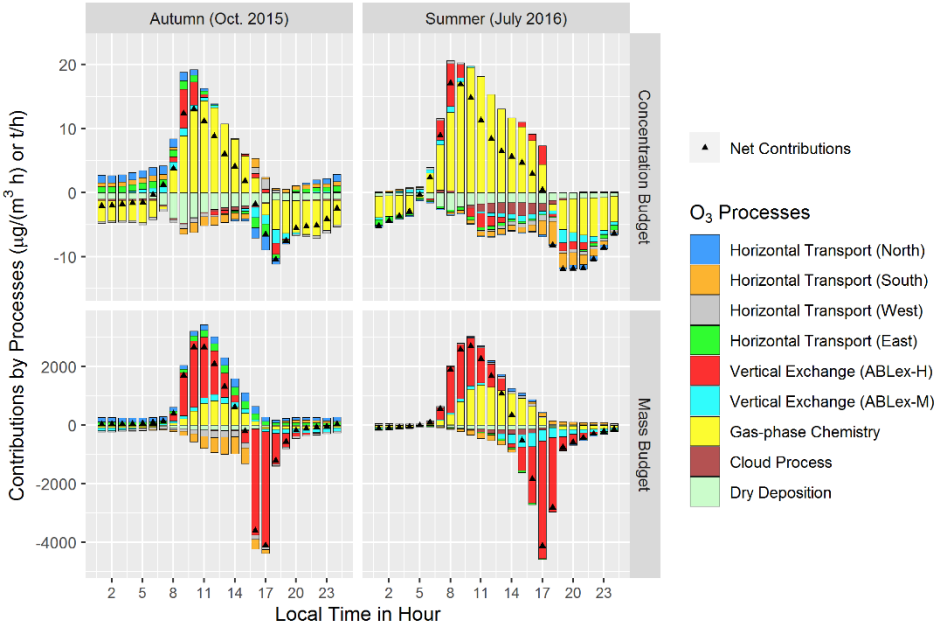

Figure 3. Mean diurnal changes of the O_3 concentration budget (the upper panels) and mass budget (the lower panels) on the polluted days of representative months in autumn (Oct. 2015; left panels) and summer (July 2016; right panels) within the atmospheric boundary layer of the Pearl River Delta. The units for the O_3 concentration and mass budgets are µg/(m^3 h) and t/h, respectively.

3.2 O_3 mass budget

The total O_3 mass within the ABL of the PRD increased during the morning hours, then decreased rapidly in the afternoon and remained stable at night in both autumn and summer (Fig. 3, the lower panels). The change of total O_3 mass agrees well with the ABL diurnal cycle (Lee, 2018) — daytime ABL development (collapse) and notable O_3 mass increase (decrease) almost occurred simultaneously, and the negligible changes in O_3 mass at night may be linked to the small variations of stable ABL.

The contribution of processes in the O_3 mass budget highlights the prominent role of transport. On average, it contributed to 78% and 53% of O_3 mass increase during the morning hours in autumn and summer, respectively, and over 90% of O_3 mass decrease during the afternoon hours of both seasons (defined as 14:00-19:00 LT in autumn and 14:00-20:00 LT in summer). Most O_3 was transported into or out of the PRD through the vertical exchange near the ABL top, especially ABLex-H, which explains the consistency between the changes of O_3 mass and ABL. The influences of ABLex-M and horizontal transport on O_3 mass were relatively limited. However, they indicated well the characteristics and variations of regional wind fields (more details are given in the next section). Gas-phase chemistry (photochemistry) also contributed to the increasing O_3 mass during the daytime, especially in summer. However, its mean contributions during the morning hours (22% in autumn, 47% in summer) were lower than those of transport. In addition, cloud process and dry deposition acted as O_3 sinks with negligible contributions to O_3 mass. Based on the above discussions, transport tends to be more important than photochemistry in the O_3 mass budget, which differs from the conclusions of the O_3 concentration budget.

The O_3 mass budget in this study overall agrees well with our common understanding of O_3 processes. The main role of transport (the vertical exchange near the ABL top) in the O_3 mass budget reflects the influence of the ABL diurnal cycle on regional O_3 pollution. Specifically, despite of relatively lower influence on O_3 concentration increase in comparison to that of photochemistry, massive O_3 being transported into the ABL during the morning hours nearly determines the regional sources of O_3 pollution. Quantified results combining O_3 mass budget and source apportionment are further discussed in Sect. 3.4.

3.3 Influences of regional wind fields on transport contributions in O_3 budgets

Through the contributions of horizontal transport and ABLex-M in O_3 budgets, the characteristics and variations of regional wind fields, including the prevailing winds and local circulations (sea breezes), can also be identified. Two main findings in this study are presented as follows:

(1) The contributions of horizontal transport and ABLex-M in autumn suggest the characteristics of prevailing winds in the PRD.

Northerly and easterly winds prevail in autumn (as indicated by the wind roses in Fig. S5). Thus, correspondingly, O_3 was transported into the PRD through its north and east borders, out of the PRD through the south and west borders, as shown in the O_3 mass budget (Fig. 3). O_3 masses transported out of the region were generally higher than those transported into the region in the daytime, which is attributed to higher downwind O_3 levels due to O_3 production from local emissions. "Low O_3 in, high O_3 out" also explains why horizontal transport led to the net decrease of O_3 concentration in the daytime. At night, O_3 was still transported into the region through the north and east borders of the PRD, but these processes became important

O_3 sources based on the O_3 concentration budget. This is to say, with relatively high O_3 levels compared to the NO_x-titrated urban atmosphere, air parcels transported from the upwind outskirts helped maintain night-time O_3 levels in the PRD to some extent.

The daytime contributions of ABLex-M in the O_3 mass budget also indicate the effects of prevailing northerly winds. The PRD has mountainous regions in the northern, western and eastern outskirts, as well as urban regions with lower altitudes in the central plain. Thus, the positive contributions of ABLex-M through the ABL top (in the z-direction) can be found in mountainous regions (Fig. S6a-b), suggesting north winds resulted in the downward transport of O_3 along the terrain. Daytime ABL heights in urban regions were, in general, higher than those in mountainous regions, which is the other reason why O_3 can be transported through the ABL slope (in the x-/y-direction) near the urban-rural interfaces when north wind prevailed (Fig. S6c-d). For the O_3 concentration budget, ABLex-M contributed to the increase of O_3 concentration during several hours after sunrise but the decrease of O_3 concentration in the afternoon. This different effect is attributed to different comparison results between ABL and above-ABL mean O_3 concentrations in the two periods (ABL < above-ABL in the morning, ABL > above-ABL in the afternoon; Fig. S7).

(2) The contributions of horizontal transport and ABLex-M in summer indicate the influence of sea breezes in the PRD.

Although southerly winds normally prevail in summer in the PRD (Fig. S5), on O_3 polluted days, air parcels from other directions could potentially influence the region as well (Qu et al., 2021). Thus the mean contribution of horizontal transport to O_3 mass in summer was lower than those in autumn. What interests us more is the different contributions of horizontal transport through the south border before and after ~14:00 LT, as indicated by the results of the O_3 mass budget. Two O_3 budgets also suggest high O_3 mass and concentration decreases contributed by ABLex-M in the afternoon. These phenomena are both related to the influence of sea breezes.

Figure 4 shows the near-ground wind roses at 14:00, 16:00 and 18:00 LT of O_3 polluted days in July 2016 based on the observational and modelling results in national meteorological sites within the PRD. At 14:00 LT, the main wind directions were W, SW and NW in both datasets. More S and SE winds occurred in later hours, and they became the prevailing winds at 18:00 LT — suggesting the gradual development of sea breezes in the PRD. Thus, O_3 was originally transported out of the PRD through the south border with negative contributions to O_3 mass; in the late afternoon, sea breezes reversed the directions of O_3 transport, resulting in positive contributions to O_3 mass by horizontal transport through the south border (Fig. 3). Moreover, sea breezes are connected to the changes of not only horizontal wind fields, but also vertical wind fields. Take the O_3 polluted day July 24th, 2016 for example, and the cross-section of O_3 concentrations and wind fields in the PRD at 16:00 LT is shown in Fig. 5 (the cross-section is made along the 113.2° E longitude, ranging from 26.0 to 20.0° N in latitude). Strong southerly wind and lower O_3 concentrations are found in the southern PRD, indicating the influence of sea

breezes on the region during that time. Near the interfaces where sea breezes encountered local air parcels (indicated by the drastic increase in O_3 levels from less than 100 μg/m^3 to about 100-150 μg/m^3), updrafts occurred, suggesting the formation of sea breeze front (Ding et al., 2004; You and Fung, 2019). It promoted the upward transport of O_3 from the ABL, or considerable O_3 mass decrease attributed to ABLex-M. The above influences of sea breezes can also be found in autumn but were weaker and occurred later.

Through the calculations and analyses of O_3 budgets, the contributions of complex transport processes in multiple scales to O_3 concentration and mass were quantified. These results can help us gain a deeper understanding of how transport influences regional O_3 pollution in the PRD.

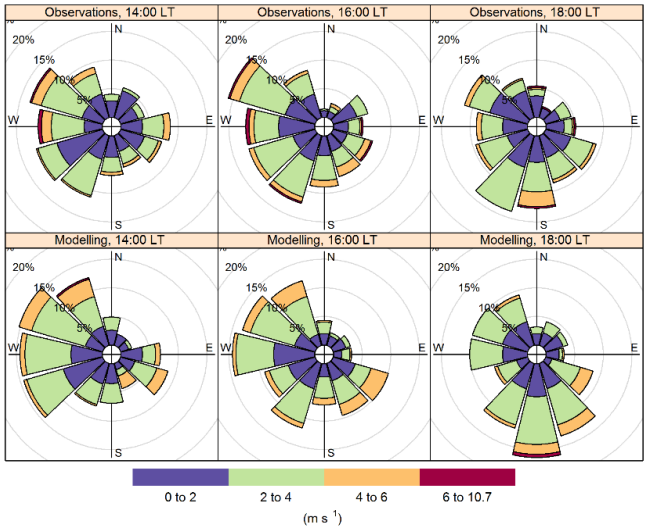

Figure 4. Wind roses at 14:00, 16:00, and 18:00 local time (LT) of the O_3 polluted days in July 2016 in the Pearl River Delta (PRD). Observational and modelling wind speeds and directions in 29 national meteorological sites within the PRD were used for this figure.

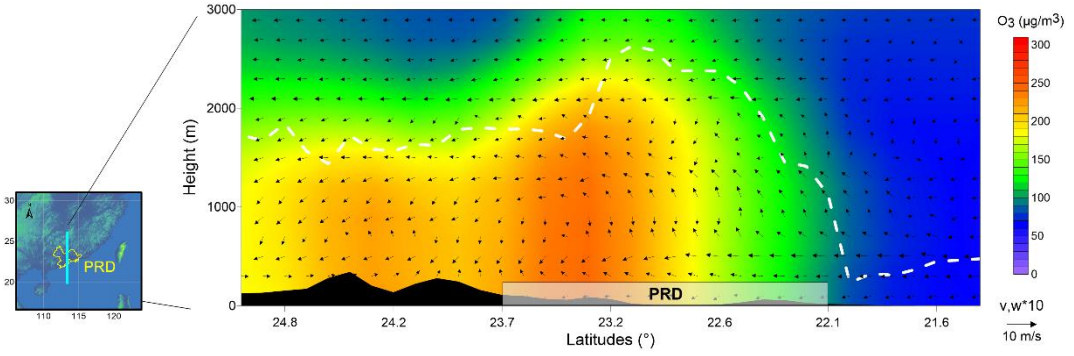

Figure 5. Cross-section of O_3 concentrations (μg/m^3) and wind fields at 16:00 local time on July 24th, 2016. The dashed white line indicates the top of the atmospheric boundary layer. PRD, Pearl River Delta.

3.4 Regional sources of O_3 mass changes contributed by transport and photochemistry

Based on previous publications (Li et al., 2012; Li et al., 2013; Yang et al., 2019; Gao et al., 2020), non-local sources often contributed to most O_3 in the PRD. This outcome is also true for the O_3 polluted days in the representative months of autumn and summer in this study, when non-local sources contributed on average to 89% and 65% of the O_3 in the PRD, respectively, in 9:00-17:00 LT (55% and 32% contributed by BCON, 34% and 33% contributed by EC-China in two months; Qu et al., 2021). To explain why non-local O_3 sources are dominant in the PRD, we identified the regional sources of O_3 mass changes contributed by the vertical exchange near the ABL top, horizontal transport and gas-phase chemistry (Fig. 6; the results in 5:00-20:00 LT are shown). Since the O_3 mass decrease overall showed similar regional sources as O_3 within the region, further analyses focus on the regional sources of O_3 mass increase, that is, O_3 transported into and produced within the PRD.

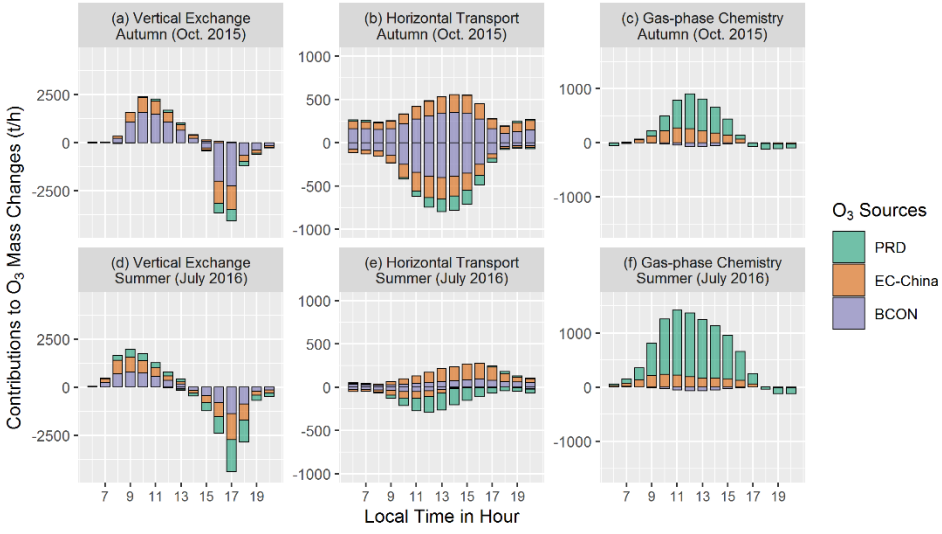

Figure 6. The regional sources of hourly O_3 mass changes contributed by (a,d) vertical exchange near the ABL top, (b,e) horizontal transport, and (c,f) gas-phase chemistry on the polluted days of representative months in autumn (Oct. 2015; a-c) and summer (July 2016; d-f). The results within 5:00-20:00 LT are shown here. PRD, Pearl River Delta; EC-China, East and Central China; BCON, the boundary conditions of d02 modelling, or the contribution of sources outside d02.

Through the vertical exchange near the ABL top, the process with the most notable contributions in the O_3 mass budget, massive non-local O_3 entered into the ABL of the PRD. In the morning-hour O_3 mass increase attributed to the process, BCON and EC-China accounted for 65% and 31%, respectively, in autumn. By contrast, local emissions only contributed to 4% in this transported O_3 during the same period, suggesting that local O_3 recirculation had only a limited influence on O_3 pollution. The results in summer were similar to those in autumn, except that the contributions of PRD (local) and EC-China emissions were higher in O_3 transported into the region through vertical exchange. In particular, local contribution accounted

for 20% in the transported O_3 during the morning hours, but was still lower than non-local contribution (38% and 42% for EC-China and BCON, respectively).

O_3 mass increase attributed to horizontal transport was connected to the contribution of non-local sources as well. In both seasons, O_3 transported into the PRD originated almost all from non-local sources.

It is not surprising that most O_3 produced through gas-phase chemistry (photochemistry) was related to local contributions, accounting for 66% and 82% during the daytime of autumn (6:00-19:00 LT) and summer (5:00-20:00 LT), respectively. However, the contributions of EC-China emissions in daytime O_3 mass increase reached 34% and 18% in two seasons, respectively, indicating the considerable influence of precursor transport on local O_3 photochemistry.

How do transport and photochemistry determine regional O_3 sources in the PRD? Based on the above results, the accumulated morning-hour O_3 mass increase exceeded 10000 t in the PRD for both seasons, which is 6-9 times larger than the original O_3 mass before sunrise (< 1500 t). Thus, daytime O_3 sources within the region were nearly determined by the sources of these newly transported and produced O_3. High contributions of transport, especially the vertical exchange near the ABL top, in O_3 mass changes as well as the dominance of non-local sources in this part of new O_3 ensured that non-local sources contributed to most O_3 in the PRD. Moreover, lower non-local contributions to O_3 in summer than in autumn can be attributed to the combined effects of higher photochemistry contributions in O_3 mass increase, lower non-local contributions in produced O_3 and higher local contributions in transported O_3. Although transport brings massive new O_3 — mostly non-local — into the region in the morning hours, it hardly leads to a drastic increase in O_3 concentration. Thus, transport seems to be less important than photochemistry in the O_3 concentration budget. Therefore, the difference between two O_3 budgets, or the different effects of transport on O_3 concentration and mass, may result in distinct understandings about the role of transport and photochemistry in regional O_3 pollution.

4 Conclusion and outlook

Reported O_3 budgets and source apportionments often concluded with a conflicting role of transport and photochemistry in ambient O_3 pollution. To explore its causes, we used the modelling results of WRF-CMAQ to quantify the contributions of various processes in the O_3 concentration and mass budgets. Results in the PRD revealed that gas-phase chemistry, including daytime photochemistry and night-time O_3 titration, drives the variations of O_3 concentration. Particularly, the former separately contributed to 74% and 95% of O_3 concentration increase in the morning of autumn and summer months. In contrast, transport, especially the vertical exchange near the ABL top, is the main process contributing to the O_3 mass increase in the morning (78% and 53% in autumn and summer, respectively) and its decrease in the afternoon (> 90%). The diurnal changes of transport contributions in two O_3 budgets are closely connected to the variations of ABL and regional

wind fields, including the prevailing winds and local circulations (sea breezes), in the PRD. Although massive O_3 transported into the ABL in the morning has a relatively limited influence on O_3 concentration increase (25% and 5% in autumn and summer, respectively) compared to photochemistry, it nearly determines the dominance of non-local sources for daytime O_3 in the PRD. The difference between two O_3 budgets, or the different effects of transport on O_3 concentration and mass, may explain why the roles of transport and photochemistry in regional O_3 pollution are inconsistent between different studies.

It should be noted that the conclusions in this study apply not only to tropospheric O_3 but also to other pollutants with moderately long atmospheric lifetimes, such as some of the secondary components in fine particulate matter. Transport and chemical transformation are both important processes for these pollutants, but for the former, it has different influences on the concentration and mass of pollutants on an hourly scale. Besides regional sources, in theory, the difference between the two budgets may also contribute to the inconsistency of other pollutant characteristics identified using different methods, such as the reaction pathways and sensitivities to precursor emissions. When pollutants with different characteristics are massively transported into the region, the variation of their concentrations is often not notable and thus neglected in the concentration budgets. However, according to the discussions in this study, the transport process is likely to change or even determine the characteristics of pollutants within the region. It also makes the considerable impacts of relatively slow chemistry along the transport on local pollution possible. Therefore, we suggested that attention should be paid to selecting a proper budget type and using correct budget calculation methods in related research.

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 in the model validation of key parameters in budget calculations, but also in the comparisons between observation- and modelling-based contributions by various processes in O_3 budgets. By doing so, more accurate regional-level O_3 budgets will be obtained.

This study concluded that transport and gas-phase chemistry play the main role in the O_3 concentration and mass budgets, respectively. Based on the two O_3 budgets, we suggest that emission reduction in the upwind regions can effectively lower daily-mean O_3 levels due to its high contributions to regional O_3, but a longer time is needed due to the slow response of O_3 concentration to transport. By contrast, reducing local emissions hinders rapid daytime O_3 concentration increase and lowers O_3 peak levels efficiently in the short term. The choice of which strategy to apply should depend on the specific goals of O_3 control (mean levels vs. peak levels; long-term vs. short-term), which are set based on a more in-depth understanding of O_3 effects on human health, crop yields and ecosystems. More efforts are required to systematically evaluate the effects of different emission reduction strategies on alleviating the detrimental effects of ambient O_3.

Data availability. The source codes of WRF and CMAQ are available at the site https://www2.mmm.ucar.edu/wrf/users/download/get_sources.html and https://www.cmascenter.org/cmaq/, respectively. FNL meteorological input files were downloaded from the site https://rda.ucar.edu/datasets/ds083.2/. MEIC v1.3 anthropogenic emission inventory is available at http://meicmodel.org/?page_id=560. The source codes of MEGAN can be found at https://bai.ess.uci.edu/megan/data-and-code. IAGOS dataset used in model validation was searched and downloaded from http://iagos-data.fr, which includes all profiles measured in flights taking off from and landing in Hong Kong during two representative months. We also provided the initial Fortran code used in ozone budget calculations and hourly O_3 concentration and mass budget results in two representative months (the initial data of Fig. 3) at https://doi.org/10.5281/zenodo.6259253.

Author contributions. KQ, XW and YZ designed the study. KQ, XW, TX did the simulations using the WRF-CMAQ model. JS, LZ and YZ provided observational results for model validation. KQ, XW, XC, YY, XJ and YZ developed the post-processing tool, conducted and analysed O_3 budget results. KQ, XW, MV and YZ wrote and revised this paper, with critical feedbacks from all other authors.

Competing interests. The authors declare no conflict of interest.

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