Responses to the Referee #1's Comments

Thank you very much for your providing valuable comments on this work. We have improved the original manuscript following your comments.

General comments

This is a very nice modeling and analysis study that highlights the role of urban breeze circulation on ozone. The manuscript provides clear, important interpretations for complicated nature of ozone transport and chemistry over the region of complex terrain, heterogeneous land-use and emissions of ozone precursors. Separate calculation of advection and chemical process is very helpful in understanding the ozone budget. This manuscript would be a good guide for air quality modelers to interpret the model results over urban areas surrounded by complex terrain and sea. I suggest this manuscript to be accepted for ACP with minor corrections.

Specific comments

1. The authors used the term of "Low NO_x" or "High NO_x" or "NO_x rich". The meaning of this definition can be understood in the context. However, "Low NO_x" is commonly referred to state of NO_x < ~0.1 ppbv. It might be better if overall NO_x level in Seoul can be defined in the regime of "NO_x-limited" or "VOC-limited" at first using the model values, then use "Low NO_x" or "High NO_x" within that regime. Depending on the regime where it is, reduction of NO_x can produce more ozone or less ozone. The authors can refer to the reference below and references therein.

Duncan, B. N., et al. (2010), Application of OMI observations to a space-based indicator of NO_x and VOC controls on surface ozone formation, Atmos. Environ., 44, 2213-2223.

Following your comment, we examined the sensitivities of O_3 to anthropogenic NO_x and anthropogenic VOC emissions using the brute force approach. Under ±20% changes in NO_x and VOC emissions, four simulations are performed. The simulation results show that the urban area in the present study is in a NO_x-saturated (or VOC-limited) regime. Please, see Table B1 in the responses to the Referee #2's comments. It is found that O_3 concentration decreases with decreasing VOC emissions but increases with decreasing NO_x emissions. So, in this study area, a reduction of NO_x can cause an enhanced O_3 production. The O_3 sensitivity result is briefly introduced in Sect. 4.3 in the revised manuscript. Note that we adopted the brute force approach to examine the direct sensitivities of O_3 to O_3 precursor emissions. The result of analysis following Duncan et al.'s (2010) method that uses the ratio of the tropospheric columns of formaldehyde to nitrogen dioxide ($HCHO/NO_2$ ratio) as an indicator of O_3 chemistry reaches the same conclusion that the O_3 formation in this urban area is NO_x-saturated (or VOC-limited) with the $HCHO/NO_2$ ratio of 0.1–0.4 (not shown). The reference, Duncan et al. (2010), is added in the revised manuscript.

2. Abstract line 11 Through the less O_3 destruction by NO in the NO_x-rich environment → Any comments on O_3 chemical production due to diluted nature in URBAN case? The same argument for line 14-15 in page 25812 in section 5.

In the deeper urban boundary layer, pollutants such as NO_x, O_3, and VOCs are more diluted in the urban area. Because O_3 precursor concentrations are reduced in the URBAN simulation, the chemical production of O_3 is actually reduced as compared with that in the NO-URBAN simulation. However, in the urban boundary layer, the reduced chemical loss of O_3 due to reduced NO is more significant than the reduced chemical production of O_3 due to reduced NO_2 and VOCs. So, the net chemical production (production + loss) of O_3 is enhanced in the URBAN simulation.

3. Page 25795 line 8-9 Did the model results reproduce the observations of wind and temperature?

The WRF-SNUUCM coupled model showed satisfactory performances in reproducing the diurnal variations of observed wind and temperature. The results of the model validation are given in Ryu and Baik (2012).

4. Page 25796 line 3-4 Was data assimilation or nudging of large scale meteorological field (NCEP final analysis data) applied? 72 hour is long for plume simulations without any of these adjustments of large-scale forcing.

In the present study, we did not apply data assimilation or nudging for the 72 h simulations. Nonetheless, both the meteorological variables and pollutant concentrations simulated by the models showed good agreements with the observations.

5. Page 25797 line 5-9 This part needs more clarification. Is base year of emission inventory 2007 and does it need to be adjusted (projected) to 2008 level? I thought the episode in 2010 was simulated in this study.

We chose an ozone episode occurred in 2010, but an emission inventory in 2010 is not available at present. Under the present circumstances, the gridded and speciated hourly anthropogenic emission data are derived from the emission inventory in 2007. The emission data based on the emission inventory in 2008 are not yet established, but the total annual emissions of pollutants in 2008 are available. To update the emission data with the up-to-date information, the amounts of NO_x (VOC) emitted are adjusted according to the ratio of the total annual emissions of NO_x (VOC) in 2008 to those in 2007. We conclude that this is the best way we can do at present. Following your comment, this part is clarified in the revised manuscript.

6. Page 25797 line 18 Could you provide specifics on observed temperature or insolation?

The maximum air temperature and the maximum hourly-averaged global solar radiation observed at Seoul Meteorological Observatory were 30.8℃ and 839 W m^{-2}, respectively. This sentence is added in the revised manuscript.

7. Page 25800 line 1-8 & Figure 3a and b The modeled ozone is lower where NO_x is higher in Figures 3a and b, which are not supported by the observations. And recirculating ozone over the ocean intruding into inland in the model seems to be too high. Any speculations for this in terms of NO_x and VOC emission inventory such as too high NO_x emission or too low VOC emission? It is notable that ozone over the ocean in NO-URBAN case is higher than that in URBAN case (Figures 3b, 3b, 9e, 9f). Any discussion on this? NO_2 measurements often include nitric acid, PAN, and other organic nitrates. In addition, the level of measurements is lower than the model first level, which made the comparison difficult for the species with large vertical gradient near the surface. It might be good to mention difficulties in comparing the model results with the measurements.

We agree with you. There could be uncertainties in the emission inventory, and the NO_x

(VOC) emissions could be estimated to be high (low) in some regions. Although it is hard to conclusively say that O_3 concentration over the ocean is overestimated because there is no monitoring site over the ocean, the overestimation of O_3 concentration and the underestimation of NO_2 concentration in the coastal region that belongs to the industrial/urban area where pollutant emissions are high could be due to the uncertainties in the emission inventory. Based on the results of the additional simulations, which are introduced in the response to the first specific comment, O_3 concentration is more sensitive to the NO_x emissions than to the VOC emissions in the study area. So, the uncertainties in the NO_x emissions could lead to relatively large errors for O_3.

The O_3 concentration over the ocean can be high because O_3 precursors are advected over the ocean in the nighttime/in the early morning. The advection of O_3 precursors over the ocean can lead to an enhanced O_3 production over the ocean in the daytime, so O_3 concentration can be high over the ocean. Please, see Fig. A1a that shows the advection of NO_x over the ocean at 05:00 LT in the URBAN simulation.

Figure A1a, b shows the horizontal distributions of NO_x concentration at 05:00 LT in the URBAN and NO-URBAN simulations. It is seen that more NO_x is advected over the ocean by the easterly flow in the NO-URBAN simulation than in the URBAN simulation. While the wind direction in the coastal region (in the region of ~126°30'E–126°45'E and 37°20'N–37°30'N) is south-easterly in the URBAN simulation, the wind direction in the coastal region is almost easterly in the NO-URBAN simulation. The change in wind direction in that region is likely due to the warmer air in the coastal urban area, i.e. urban heat island, (compare Fig. A1c with Fig. A1d). Therefore, it is speculated that the difference in amount of O_3 precursor transported in the nighttime/in the early morning toward the ocean primarily leads to the differences in O_3 production and O_3 concentration over the ocean in the daytime.

At the monitoring sites, unfortunately, nitric acid, PAN, and other organic nitrates are not measured. As you pointed out, the measurement heights are lower than the lowest model level. So, there could be relatively large discrepancies between observed and simulated pollutant concentrations, particularly for pollutants exhibiting large concentration variations in the vertical direction near the surface. Following your comment, this is mentioned in the revised manuscript.

8. Page 25802, line 26-28 The authors regard the entrainment as main cause for the increase

of ozone during 9-12 LT. It might be good to compare the contribution of entrainment (diffusion and/or advection) and chemistry to ozone budget in this time. A figure similar to Figure 6 for 9-12 LT helps to understand which process is more important.

In the morning, both the diffusion (and/or advection) and chemical processes are important in the ozone budget. Figure A2 shows the time series of ABL-averaged contributions of individual processes to O_3 concentration in the URBAN and NO-URBAN simulations and the vertical profiles of O_3 concentration and contributions of individual processes at 09:00 LT. While the diffusion and advection processes play important roles in the early morning, the chemical process plays an important role from the late morning (Fig. A2a, b). In the morning, O_3 concentration in the residual layer is higher than that in the boundary layer (Fig. A2c). It is seen that O_3 concentration above the boundary layer decreases by the diffusion process, indicating the entrainment process. In the lower boundary layer, O_3 concentration significantly increases by the diffusion process. The relatively lower contribution of diffusion process in the ABL-averaged contribution (Fig. A2a, b) is due to its opposite sign (contribution) between the upper and lower boundary layer. This discussion is briefly mentioned in the revised manuscript.

9. Figure 7 How does NO_2 profile look like? Since NO_2 is deposited at the surface, O_x is expected to decrease near the surface. Does the model emit NO_2 as well as NO? Can any comments on NO_2 profiles be added to understand O_x profiles?

The NO_2 profile is similar to the differential profile between O_x and O_3, i.e., O_x profile minus O_3 profile. The NO_2 profile is presented in Fig. A3. In the model, NO_2 is also emitted and the ratio of NO_2 emission to NO_x (NO + NO_2) emission is 0.05 in the SAPRC-99 mechanism. As you pointed out, NO_2 is deposited at the surface so its concentration decreases owing to the dry deposition process, but NO_2 concentration increases owing to other processes such as chemical process and emission process. So, the O_x concentration is the almost constant in the vertical direction near the surface.

10. Isoprene versus anthropogenic VOC (mobile and industrial sources) Throughout the manuscript, the importance of isoprene on ozone production over the mountain and urban area was addressed. It might be good to add the plot of model isoprene value to demonstrate

the role of isoprene. If isoprene is added in Figure 8 (like NO_2) or Figure 13, that would be very useful. In Figure 12, k[OH][VOC] is presented. Thus, isoprene can be plotted instead of k[OH][VOC] in Figure 13. Or NO_2, isoprene, and other VOCs at 1500 LT can be plotted following the cross section of Figure 10. It might be good to mention that dilution and transport of anthropogenic VOCs may follow NO_x.

The figures showing isoprene concentration and IPR/IRR analysis results related to isoprene are given in Figs. A4 and A5. First of all, we would like to stress that not only isoprene but also oxygenated VOCs (OVOCs) should be considered in this study area and that is why we consider k[OH][VOC] in Figs. 11, 12, and 13. Figure A4 shows the isoprene concentration, contributions of advection and chemical processes to isoprene concentration at 15:00 LT, which is plotted following the cross section of Fig. 10. The isoprene concentration is high over the mountain and the urban area where it is emitted. The advection of isoprene by the urban breeze is rather insignificant, so the isoprene concentration is relatively low in the regions where the urban breeze prevails. In addition, the difference in chemical loss of isoprene between the URBAN and NO-URBAN simulations is not so significant in the regions where the urban breeze prevails. So, the chemical loss of isoprene does not fully explain the difference in chemical production of O_3 in those regions. Figure A5 shows the integrated rates of reactions between OH and isoprene, OH and OVOCs, and OH and aldehydes (sum of formaldehyde, acetaldehyde, other aldehydes with higher order carbons, and aromatic aldehydes) at 15:00 LT. As seen in Fig. A4e showing the chemical loss of isoprene, the reaction between OH and isoprene does not show a significant increase in the regions where the urban breeze prevails (Fig. A5a). This is likely due to the high reactivity of isoprene. The lifetime of isoprene is a few minutes to a few hours (Atkinson and Arey, 2003; Liakakou et al., 2007). As can be seen in Fig. A5c, the rate of reactions between OH and OVOCs is high in the regions where the urban breeze prevails. Among a variety of OVOCs, aldehydes seem to play an important role in the enhanced O_3 production in the regions where the urban breeze prevails. Even though the isoprene that is emitted from the surroundings is certainly transported toward the urban area by the urban breeze, while the air mass is transported, a significant amount of isoprene is oxidized by OH and ozone, further producing OVOCs such as aldehydes and ketones. Therefore, not only isoprene but also OVOCs should be considered in this area.

As you pointed out, the transport of anthropogenic VOCs (AVOCs) tend to follow that of

NO_x. Figure A6 shows some examples of contributions of advection process to NO_x, alkanes that have reaction coefficient (k_{OH}) greater than 1×10^4 ppm^{-1} min^{-1} (ALK5), and aromatics that have k_{OH} greater than 2×10^4 ppm^{-1} min^{-1} (ARO2). It is clearly seen that both NO_x and AVOCs are transported upward in the urban area and that such upward transport of the ozone precursors does not occur in the NO-URBAN simulation. Following your comment, this point is included in the revised manuscript.

11. Wind vector and temperature If the authors have a nice plot comparing observed wind vector and/or temperature at 1500 LT with the model values as in Figure 3, I suggest to include it in the manuscript maybe just before Figure 3. That makes the arguments in the manuscript stronger.

Proving an urban breeze that develops in the study area using observation data would be necessary. However, we do not have enough stations located in proper positions in which we can detect an urban breeze well. In addition, because the study area is an urban area, there are many obstacles such as buildings near the observation stations. The near-surface winds can be substantially affected by local obstacles, particularly under weak synoptic wind conditions. Although a validation for near-surface wind vectors is difficult for these reasons, the diurnal variations of wind speed are generally well captured by the model as addressed in Ryu and Baik (2012).

I hope to see overall larger size of figures for the plots like Figure 3.

We expect larger size of figures in ACP because ACP adopts column-based figures.

References

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605–4638, 2003.

Liakakou, E., Vrekoussis, M., Bonsang, B., Donousis, Ch., Kanakidou, M., Mihalopoulos, N.: Isoprene above the Eastern Mediterranean: Seasonal variation and contribution to the oxidation capacity of the atmosphere, Atmos. Environ., 41, 1002–1010, 2007.

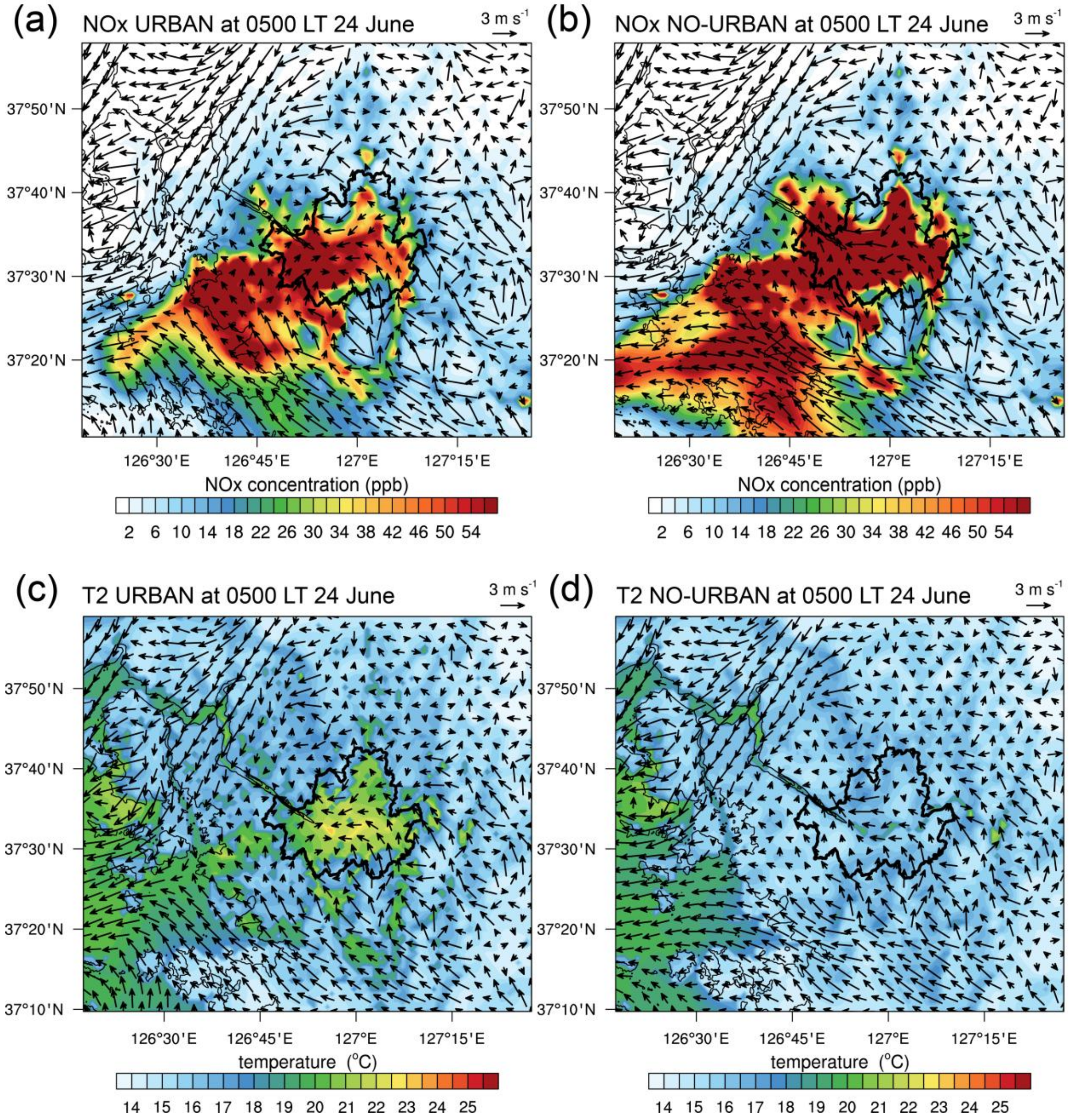

Fig. A1. Horizontal distributions of NO_x concentration and wind at the lowest model level at 05:00 LT (a) in the URBAN simulation and (b) in the NO-URBAN simulation. Horizontal distributions of near-surface temperature and wind at 05:00 LT (c) in the URBAN simulation and (d) in the NO-URBAN simulation.

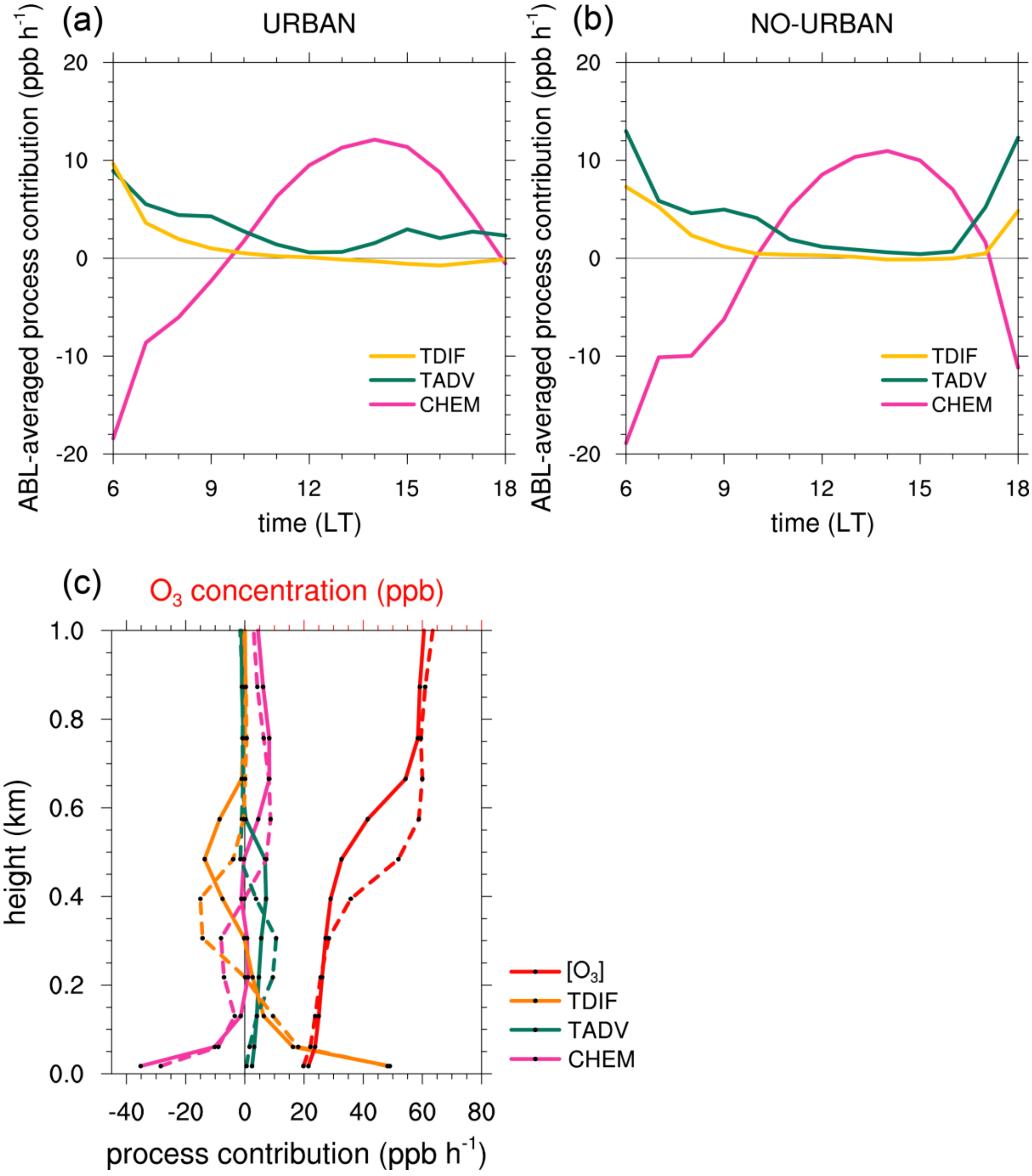

Fig. A2. Time series of ABL-averaged contributions of individual processes to O_3 concentration averaged over the urban analysis area (a) in the URBAN simulation and (b) in the NO-URBAN simulation. (c) Vertical profiles of O_3 concentration and contributions of individual processes to O_3 concentration averaged over the urban analysis area at 09:00 LT. The solid and dashed lines indicate the results of the URBAN simulation and of the NO-URBAN simulation, respectively.

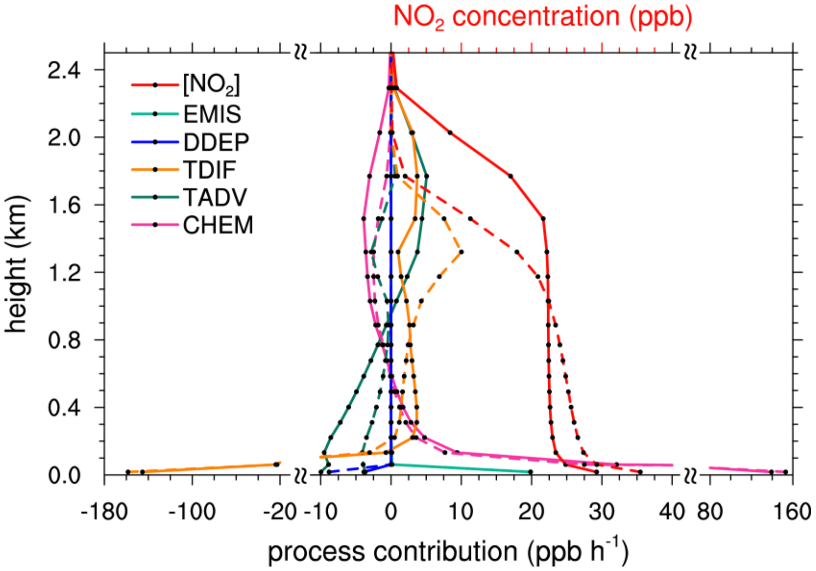

Fig. A3. 4 h-average vertical profiles of NO_2 concentration and contributions of individual processes to NO_2 concentration averaged over the urban analysis area for the period from 12:00 to 16:00 LT. The solid and dashed lines indicate the results of the URBAN simulation and of the NO-URBAN simulation, respectively.

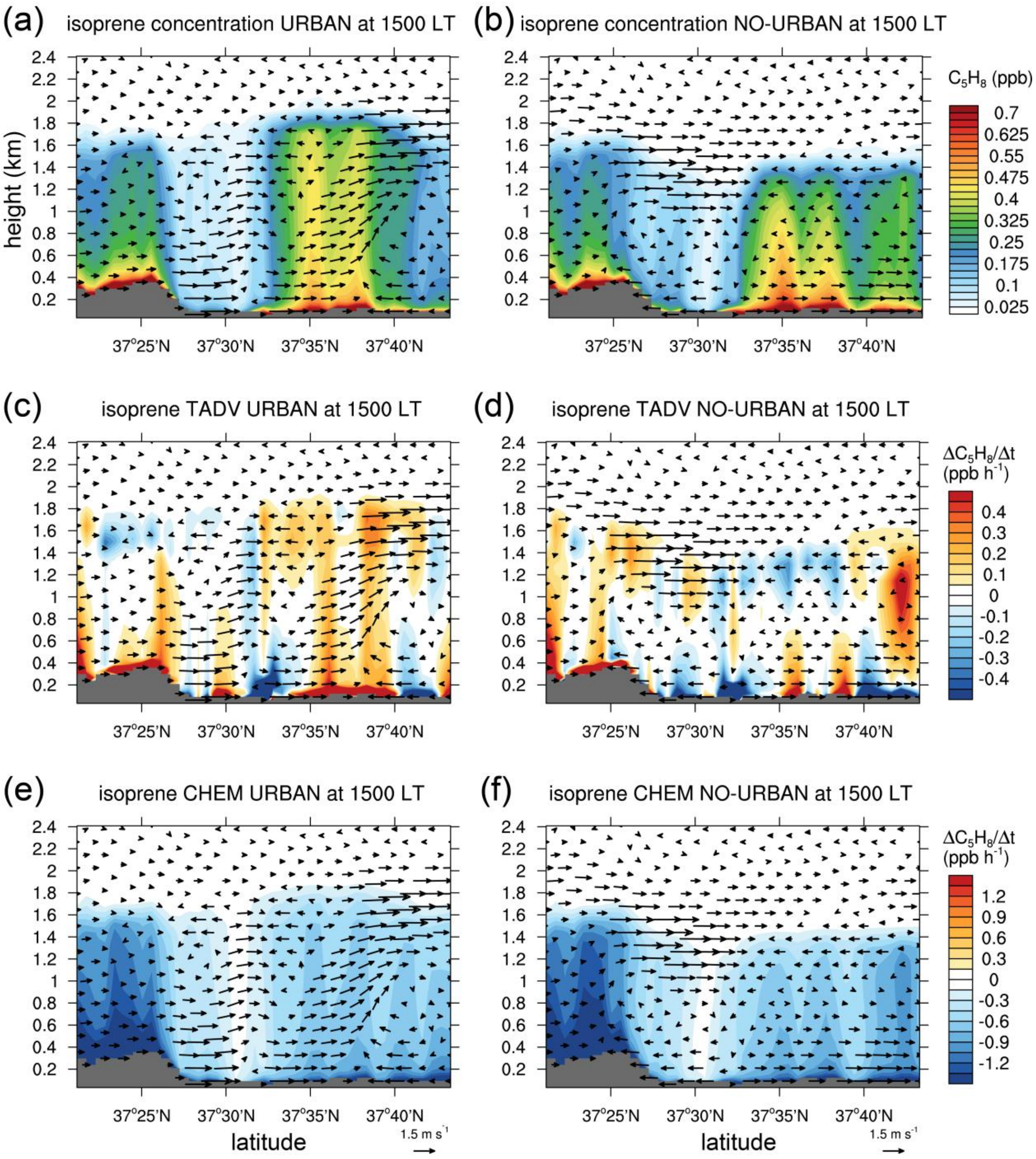

Fig. A4. Vertical cross sections of (a) isoprene concentration, (c) contribution of the advection process to isoprene concentration, (e) contribution of the chemical process to isoprene concentration, and wind along the line M-N in Fig. 1d at 15:00 LT in the URBAN simulation. (b), (d), and (f) are the same as (a), (c), and (e), respectively, but for the NO-URBAN simulation.

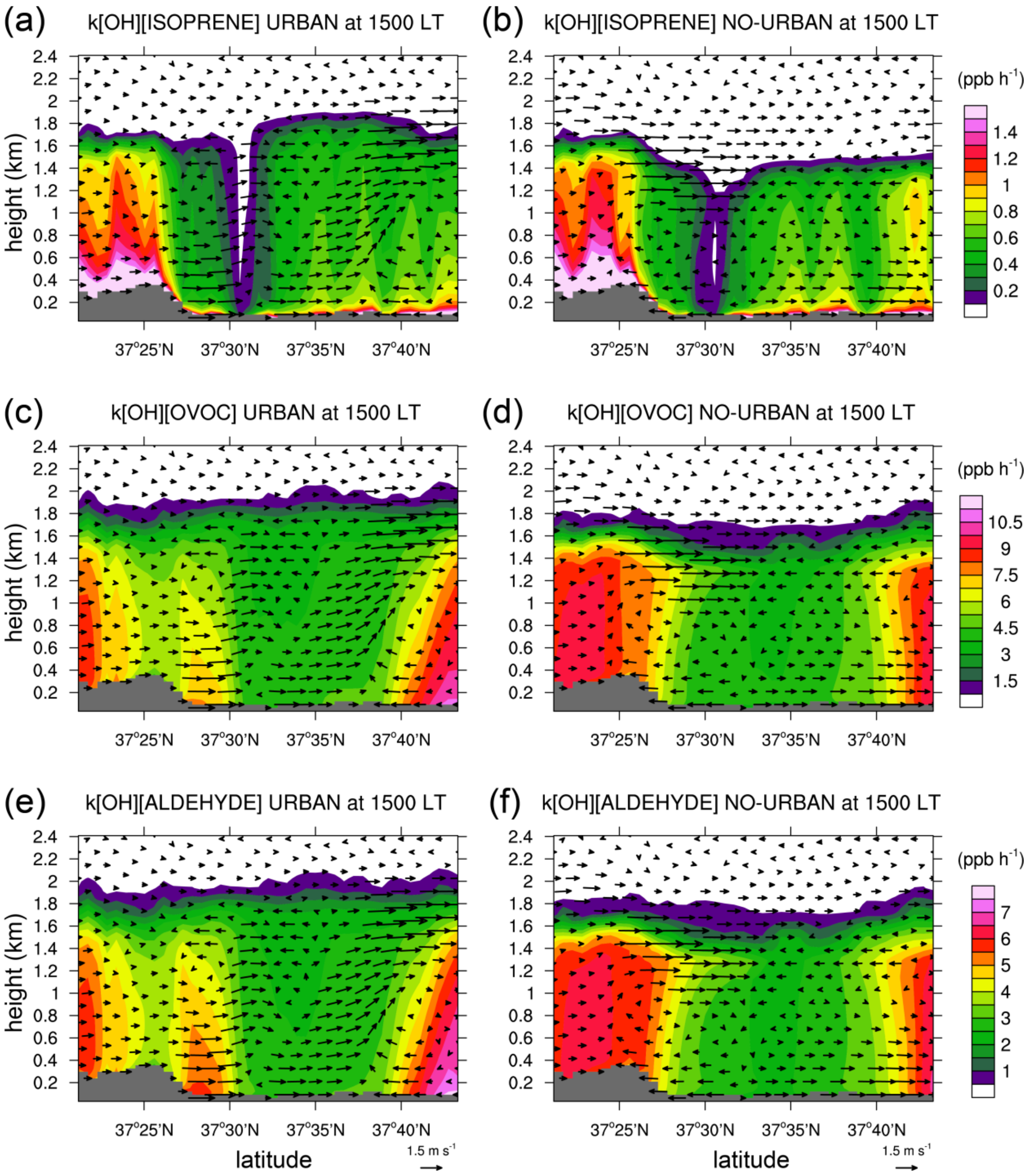

Fig. A5. Vertical cross sections of (a) rate of reaction between OH and isoprene, (c) rate of reactions between OH and oxygenated VOCs, (e) rate of reactions between OH and aldehydes, and wind along the line M-N in Fig. 1d at 15:00 LT in the URBAN simulation. (b), (d), and (f) are the same as (a), (c), and (e), respectively, but for the NO-URBAN simulation.

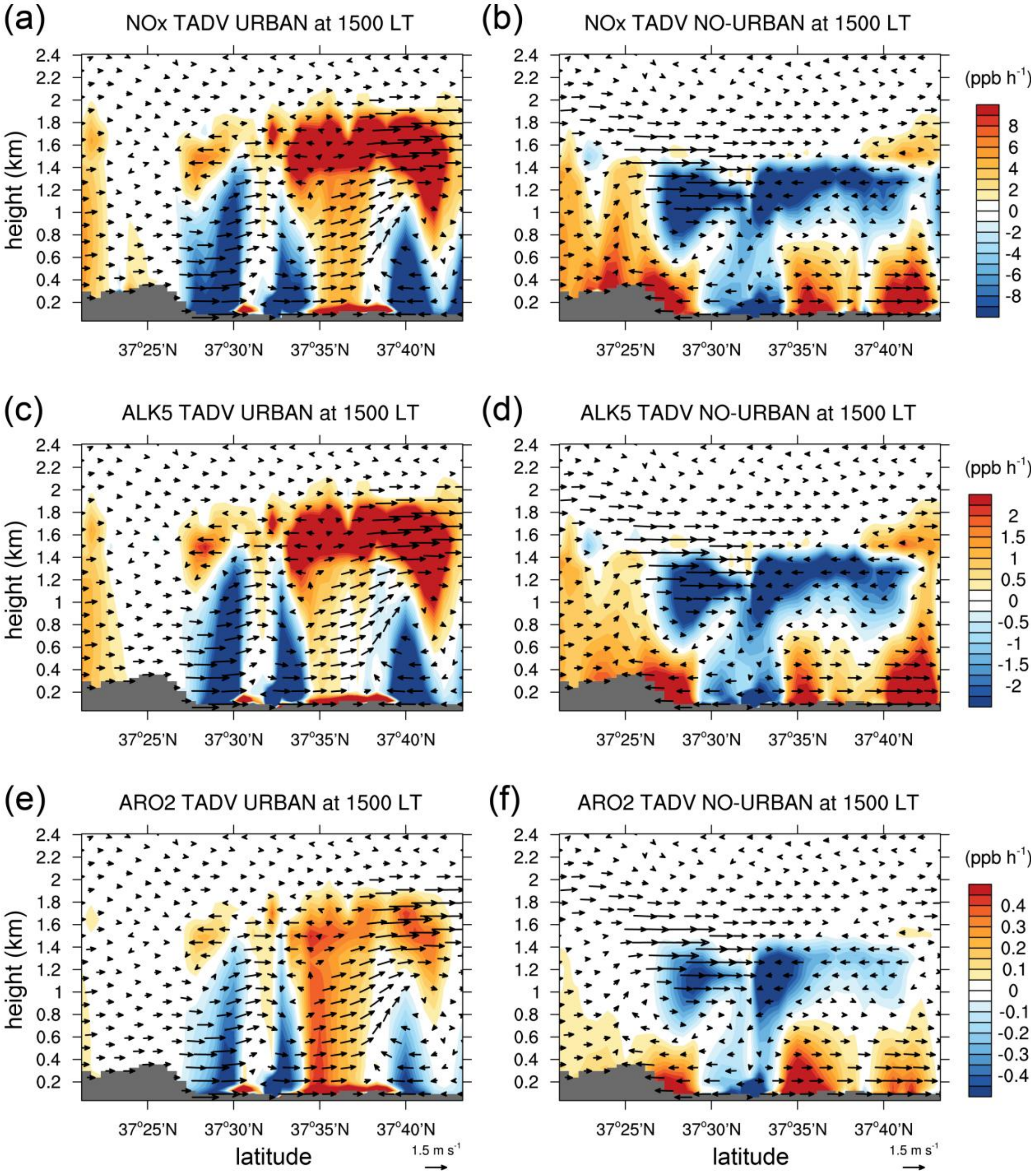

Fig. A6. Vertical cross sections of contributions of the advection process to (a) NO_x concentration, (c) ALK5 concentration, (e) ARO2 concentration, and wind along the line M-N in Fig. 1d at 15:00 LT in the URBAN simulation. (b), (d), and (f) are the same as (a), (c), and (e), respectively, but for the NO-URBAN simulation.