Response to Interactive comment from Referee #2

We thank the referee#2 for taking the time to read the manuscript and offer helpful comments and suggestions. We have modified the manuscript according to the referee's comments. The detailed changes can be found in the word-tracking in the manuscript. Additionally, we added one more section (section 3.4 in the new manuscript) to analyse the impact of segregation on the ozone formation, which gives some insight on the coarse models. The point-to-point responses to the referee's comments are listed below. The referee's comment is repeated with our response in bold.

1) The paper addresses the topic to study segregation "in order to investigate the degree to which the rates of chemical reactions between two reactive species" are modified compared to the well mixed case. This is done for 5 reactions to study a) the influence of a non-homogeneous distribution of surface sources and b) the influence of topography for a concrete case, the Hong Kong island. They apply an LES embedded in WRF for the regional flow field.
The complete topic is a next step forward if the very systematic study of Ouwersloot et al. (2011) is considered, which is cited. Therefore, the paper represents a substantial contribution to science within the scope of ACP.

2) The application of LES to study segregation is for a concrete landscape in this way is new.

3) The conclusions reached are new with respect to comparable LES studies but will be improved if some additional figures and data (in tables) are added (Remarks).

Response: We have added more figures (Figure 5., 8., 12., 15.) as suggested.

4) The methods and assumptions seem to be valid but more quantitative information should be given for any reader for better understanding of the results.

Response: We have added more information according to the reviews' comments (see the responses to the remarks below and the word-tracking in the manuscript).

5) The interpretations and conclusions need some support by the quantitative presentation of some additional results (Remarks).

Response: More detailed interpretations of the results were added in the text (see the responses to the remarks below and the word-tracking in the manuscript).

6) The authors give credit to related work and indicate their own new contribution. They may also consider: Patton, E.G. et al. (2011): Boundary Layer Meteorol. 100, 91-129. Kramm, G., Meixner, F.X. (2000): Tellus 52A and some literature noted in the remarks.

Response: We have added more details of the methods, assumptions and results analysis to help the readers for better understanding. We have referred to the conceptual studies of Patton et al. (2001) and Kramm and Meixner (2000). For the changes in the manuscript, see the word-tracking.

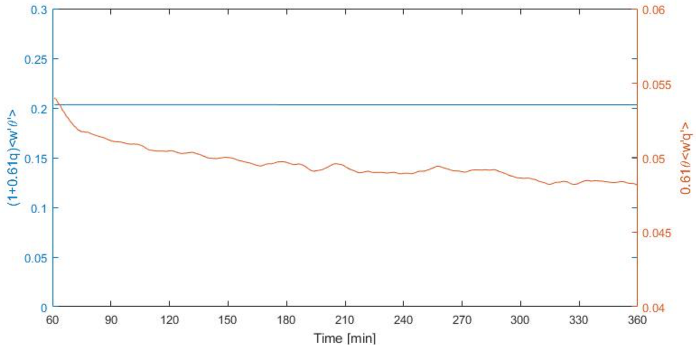
Remarks:
a) General Remarks: The presentation of segregation intensities IS is based on the time averaging concept. This is helpful to compare also to results obtained e.g. by:
Verver, G.H.L. et al. (2000), J. Geophys. Res. 105, 3983 - 4002;
Kaser, L. et al. (2015): Geophys. Res. Letter 42, 10.894 - 10.903;
Dlugi, R. et al. (2019): ACPD, as cited; and references in 7)
for the reaction OH + RH-B, which seem to be comparable to OH + isoprene by the rate constant, and for the reacion O3 + NO.

Response: We have added more comparisons with these studies in the section on results (Section 3.1 for homogeneous case and Section 3.2 for inhomogeneous case) with references to the suggested authors.

An LES without PBL-scheme is used, with prescribed sensible heat flux HS , and simplified moisture flux (section 2.2).
The "inner area" has urban area, forest area and "none" (Fig.2). But "none" is sea and sea has HS << 220Wm2! Please give specific information. The mechanism to produce turbulence should be, therefore, described in detail (A table may help). Please give also roughness properties for the sea, the urban area and the forest to explain the production of the TKE. Which term of the TKE - balance is dominant? Which processes produce TKE? Please also show wind profiles above sea, urban area, forest (hill). Are there rotating flow elements behind the hill?
What is the influence of bouyancy? You mention "convective conditions" in line 129, but does this really contribute to the TKE in your model setup? Did you specify PBL-height by Θ - or Θv - profile like in Ouwersloot et el. (2011)?
Please formulate a subsection on these details to inform any reader on the physics of the calculations for a better understanding.

Response: In order to focus on the terrain effect, the land-sea differences are not considered in this study. The surface of the entire domain is set as the land (there is no sea) with a fixed sensible heat flux of 230 W/m^2. This explanation has been added in the manuscript to avoid misunderstanding. The roughness of the different underlying surfaces for urban area and the forest is indeed important for the momentum flux and shear production of TKE, but in our case only a small area around the Island is urban region and to better distinct the effects of heterogeneous emission sources, a constant roughness length for land is used. In our case, the TKE is mainly produced by the buoyancy and shear. We didn't analyse the TKE balance or which term is dominant for our case because it's not the focus of this study. But we added the relationship between the TKE and segregation intensity in the section 3.3, see figure 11 in the manuscript. We have added the wind speed cross-section plots in Figure 8 to show the wind at different locations.
In our LES case, the buoyancy flux ($w'\theta_v'$) is from the surface sensible heat flux and moisture fluxes (similar as Ouwersloot et al., 2011). We set a fixed sensible heat flux of 230 W/m2 at the surface; while the latent heat flux was calculated in the model from a prescribed surface water vapor (see section 2.2). In our case, the buoyancy flux is also dominated by the kinematic sensible heat flux $w'\theta'$, which is almost 4 times of the kinematic moisture heat

flux (see figure below; the kinematic sensible heat buoyancy flux is 0.203, the kinematic latent heat buoyancy flux in the range of 0.048~0.054).



Domain-averaged surface buoyancy flux: $\langle w'\theta_v' \rangle \approx (1+0.61q)\langle w'\theta' \rangle + 0.61\theta\langle w'q' \rangle$ (see the formula from Ouwersloot et al., 2011)

Our case is a convective boundary layer, the vertical profiles of the virtual potential temperature θ_v do not present clear gradients, so we can't detect the PBL height well with the common method of θ_v gradient. This feature also can be seen in Ouwersloot et al. (2011). We tried several methods, e.g., maximum gradient of θ_v or total water mixing ratio, bulk Richardson number, the location of 90% of the maximum wind speed, and the maximum coverture of θ_v. The PBL heights from different methods are inconsistent, but they all can reflect the influence of terrain on the PBL height. By comparing with the results of mesoscale model WRF (PBLH variable in wrfout files), we found that modified θ_v gradient method (the first level with $\frac{\partial \theta_v}{\partial z} = \frac{\theta_v(z)-\theta_{v_s}}{z-z_s} > 0$, where θ_{v_s} is surface virtual potential temperature & z_s is the surface altitude) and bulk Richardson number method (the first level with $R_{ib} = \frac{g}{\theta_{v_s}} \frac{[\theta_v(z)-\theta_{v_s}][z-z_s]}{[u(z)-u_s]^2+[v(z)-v_s]^2} = 0.25$, the subscript "s" represents surface) are consistent with WRF output PBLH. We have chosen the modified θ_v gradient method for the PBLH calculation and added the description in Section 3.1. We have also added the PBL height in Figure 8 to show the influence of the terrain. Due to the complex influences of the terrain on the PBL height, we mainly focus on analysing the results below 800 m (which accounts for about 80% of the entire PBL).

b) In line 143-152 you give the emission rates. They are constant for all grid elements of the urban area and the forest. No heterogeneity within the areas is considered. So the scales of heterogeneity are above several hundred meters or more! In line 143 you mention "constant emissions" were used in the outer domain". But here you have sea, a harbour and emission of ships.
Please add maps like Fig.2 for emissions of NO, CO, RH-A and RH-B at the surface for a better understanding by any reader.

Response: The purpose is not to perform a fully realistic simulation taking into account the detailed emissions from harbours and individual ships, but to simulate a simple case at medium resolution (100 m) to assess how anthropogenic and biogenic emissions localized in different areas of the island contribute to the formation of ozone and other secondary species. Thus, we designed numerical experiments as follows: the inner domain (Hong Kong Island) that includes topography and inhomogeneous emissions is surrounded

by a flat outer domain area with homogeneous emissions that serves as a broad "boundary condition". In the inner domain, the emission rates for the anthropogenic species (NO, CO and RH-A) are uniform all over the "urban region" (mostly the edges of the island) and zero over other areas; and the emissions of biogenic RH-B are uniform over the forested hills (inside areas of the island) and zero elsewhere. This is shown in Figure 2. Separate emission maps for NO, CO, RH-A, and RH-B will not give more information in our case.

c) Line 234: You mention results on water vapour in Fig.1. If water vapour varies it is of direct influence on OH-production (Eq. R6).

Response: The reaction R6 uses the water vapor content from the model to calculate the OH concentration, so the water vapor should have direct influence on OH production, but the detail of the influence is not considered in this study.

d) Line 236: This is not "chemical equilibrium". These are stationary conditions. The ozone production is still visible for 2h and 4h! Note also you have "polluted conditions" while Ouwersloot et al.(2011) has low NOx (or even no NOx) conditions.

Response: We changed "chemical equilibrium" to "stationary condition" in the context. We agree that we made our calculations under polluted conditions for urban area, which is also a main difference from previous studies focusing on isoprene chemistry.

e) You mention several times that high TKE leads to higher (or high) segregation. Please present figures for each reaction to show IS versus TKE. Also Dlugi et al.(2014), ACP14, 10333-10362 presented their findings for IS (OH + isoprene) as function of TKE (their Fig.19).

Response: We have added the plots of TKE versus segregation for the simulation TERW in Figure 12. From this graph, we see that the segregation intensities increase with TKE for most reactions except for RH-B + OH. The lack of clear relationship between TKE and the segregation of RH-B + OH, might be due to the fact that RB-B is emitted on the top of the mountain where the TKE is small. Dlugi et al. (2014) showed that the segregation of isoprene + OH increases with TKE for campaigns in the forest. Our results are more complicated in exist of the terrain.

f) For comparison with literature you may also present (for negative and positive IS) IS as function of the covariance in Eq. 6 to test the hypothesis that "IS is proportional to the covariance" as mentioned by Kaser et al (2015). Dlugi et al.(2019) also presented a figure with r (your Eq. 8) as function of IS (their Fig.9). Such results may also be added to your presentation to compare with data from literature.

Response: We plotted the relationship between segregation intensity and r in Figure 5, and have added some comparison with the previous studies in the manuscript.

g) Table 1: Dimensions are missing for all quantities.

Response: We have added the unit in the table.

h) Table 3: Dimensions should be shifted to the right (numbers).

Response: It has been changed.

i) Please give the complete notation for "VMR".

Response: Corrected.

j) Fig.6: OH and RH-B: Segregation is given outside the area of emission! (also in Fig 9). How to explain positive IS ?

Response: From the vertical cross-section, we can see that the segregation intensity of RH-B and OH is small at the surface layer over the forest, so the segregation seems to be outside the area of emission. The positive segregation happens when the RH-B and OH are correlated. From Fig 5. RH-B and OH are both high at the edge between forest and urban area, leading to the positive correlation and thus positive segregation.

h) Please replace the notion "tracer" by "chemical compounds" or "reactants" or an- other specific word.

Response: Corrected.