Response to anonymous Referee #2

We sincerely thank the reviewers for their constructive and thoughtful suggestions, which improve the quality of this paper. We have made the revisions and responses following your comments point by point.

The referee comments are shown in black.
The responses to the comments are shown in blue. The line numbers refer to the clean version of our revised manuscript.
The changes included in the revised manuscript are shown in red.

General comments:

Wu et al. present the development of an open-source CFD code based on OpenFOAM for Atmospheric Photolysis calculation to study the dispersion of reactive pollutants at the microscale. Full O3-NOx-VOCs chemistry has been implemented in the CFD model and compared with data from a box model simulation. Additionally, the accuracy of the model to predict the flow field and pollutant dispersion is evaluated in a 2D street canyon against wind tunnel measurements. This coupled system is applied to perform a comprehensive sensitivity test and examine the influence of the background precursors of O3, traffic emissions, and wind speed on pollutant concentrations in the street.

I think this work provides valuable information on the field of urban air quality modeling at the microscale and I suggest carefully addressing the following comments before publication in GMD.

1. Although distinct photochemical mechanisms have been implemented in the model, this paper just present results from the full chemical mechanism “CS07A”. Has the implementation of the rest of the photochemical schemes been properly evaluated? It should be mentioned in the manuscript, at least.
2. One of the limitations is that despite the model is fully coupled, the evaluation is performed separately (chemistry, flow, and dispersion of pollutants). It is probably because of the lack of measurements to validate this system; however, it should also be mentioned in the manuscript.
3. Conclusions. I would recommend improving this section and being more precise in giving the outcomes.

Response:

We are very thankful to reviewer for his/her constructive criticisms and valuable comments, which were of great help in improving the quality of the manuscript.

1. The validation of the full chemical mechanism is only conducted with CS07A. The detailed description has been added in section 2.2 and 3.1.
2. Due to the rarely wind tunnel experiments with chemical reactions, the model is only validated separately. Details have been added in section 3.3 and section 3.4. We will continue to follow up the research on model accuracy in the future.

Specific comments:

Specific comment 1:

#Line 9. How can this development improve the resolution?

Response:

Thanks a lot for your suggestion. The "improve the resolution" here means that the model can obtain the flow and pollutant dispersion in smaller scale. To make the expression clearer, we revised the sentence in the manuscript line 9-11:

Urban air quality issue is closely related to the human health and economic development. In order to investigate the street-scale flow and air quality, this study developed the Atmospheric Photolysis calculation framework (APFoam-1.0), an open-source CFD code based on OpenFOAM, which can be used to examine the micro-scale reactive pollutant formation and dispersion in the urban area.

Specific comment 2:

#Line13. The implementation of the atmospheric photochemical mechanism in the CFD model is evaluated with box model results. It should also be mentioned in the abstract.

Response:

Thanks a lot for your mention. The revision was done in the Abstract line 13-15:

Additionally, the model including photochemical mechanism (CS07A), air flow and pollutant dispersion has been validated and shows the good agreement with SAPRC modeling and wind tunnel experimental data, indicating that the APFoam has sufficient ability to study urban turbulence and pollutant dispersion characteristics.

Specific comment 3:

#Line 130. Similar to the reaction rates depending on *T,* might the photolysis rates be modified according to an input of the intensity of the light?

Response:

Thanks a lot for pointing out this. In the current version of the APFoam, the photolysis rates are calculated offline. The variation of the intensity of the light is not including in the model so far. We will keep move on to update the model in the future. The revision was done in the manuscript in line 144-146:

the model does not consider the variation of light intensity, the photolysis rates are obtained from the literature (Carter, 2010) rather than online calculation in order to improve the calculation efficiency.

Specific comment 4:

#Line 151-156. It should be mentioned (here or in Section 3.1.) whether the implementation of these three photochemical mechanisms has been evaluated.

Response:

Thanks a lot for the hint. The revision was done in the manuscript line 164-165:

In the section 3.1, CS07A has been validated while the other two mechanisms are not verified in this study but are still the available option to the users.

Specific comment 5:

#Line 213. Why is the simulation time set at 24h if no diurnal variation is considered?

Response:

Thanks a lot for your attention. The main purpose of setting the simulation time to 24h is to allow the reactants to fully react and to verify the stability of the model during long-term operation.

The revision was done in the manuscript line 229-231:

For the chemical mechanism, CS07A is selected for validation in this study, and simulation time is set as 24h without diurnal variation (i.e., chemical reaction rate is constant during simulation), allowing the reactants to fully react and verifying the stability of the model.

Specific comment 6:

#Line 215. “Figure 2 shows the concentrations of 52 species. . .” Is that average concentration over 24h or concentration at a specific time?

Response:

Thanks a lot for pointing out this. The results are the concentrations at 24h which is the last time step of the simulation. The revision was done in the manuscript line 232:

Figure 2 shows the concentrations of 52 species from two models at 24h which is the last time step of the simulation.

Specific comment 7:

#Line 229. The concentrations are extremely low (10ˆ-40 ppmV). I would recommend focusing on the comparison of CFD outputs and box model results just under realistic conditions since the largest differences occur when concentrations are almost zero and are mainly related to the different processing of these two models.

Response:

Thanks a lot for the hint. In the realistic conditions, the species concentrations can reach ~10^{-20} ppmv (Figure 2 results). We have also compared those results and found that the *RE*s of those species are less that 1%, showing the good agreement of two models. The revision was done in the manuscript line 243-244:

Overall, most of the $RE_{i,t}$ are less than 1% in the concentrations range between 0 to 10-20 ppmv (i.e., the concentrations under realistic conditions), indicating that simulation error of APFoam is less than 1% during the whole simulation period.

Specific comment 8:

#Line 254. “. . ., the prediction accuracy is better in simulating the low-wind-speed region”. Please add a reference.

Response:

Thanks a lot for your attention. The revision was done in the manuscript line 269-273:

Among the RANS turbulence models, in contrast to the modified k-ε models (e.g., realizable and RNG k-ε models), although the standard k-ε model performs worse in predicting turbulence in the strong wind region of urban districts (e.g. separate flows near building corner), the prediction accuracy is better in simulating the low-wind-speed region (e.g. weak wind in 2D street canyon sheltered by buildings at both sides) (Tominaga and Stathopoulos, 2013; Yoshie et al., 2007).

Specific comment 9:

#Line 296. The model acceptance criteria were previously defined in Chang and Hanna (2004) and Hanna and Chang (2012). Chang, J., Hanna, S., 2004. Air quality model performance evaluation. Meteorology and Atmospheric Physics 87 (1), 167-196. Hanna, S., Chang, J., 2012. Acceptance criteria for urban dispersion model evaluation. Meteorology and Atmospheric Physics 116 (3-4), 133-146. #Line 298. ". . .the respective NMSE, FB and R are 0.06, -0.13 and 0.95 (Table 1). . .". These values do not correspond to the values presented in Table 1.

Response:

Thanks a lot for pointing out this. The revision was done in the manuscript line 313-314:

In this simulation case, the respective NMSE, FB and R are 0.01, -0.04 and 0.99 (Table 2), which shows the good performance of the APFoam in flow field simulation.

Specific comment 10:

#Line 302. Is any photochemical mechanism used in this simulation? If not, it should be clarified that this evaluation is performed with no chemical reactions included.

Response:

Thanks a lot for your mention. The photochemical mechanism is not used in this simulation in order to be consistent with the wind tunnel experiments setting. The revision was done in the manuscript line 329-330:

In order to be consistent with the wind tunnel experiments setting, photochemical mechanism is not used in the simulation.

Specific comment 11:

#Line325. Please use the same nomenclature for the aspect ratio (H/W). It is also referred to as H/W=1 in the abstract.

Response:

Thanks a lot for the hint. The revision was done in the manuscript.

Specific comment 12:

#Line 331. Since the pollutant concentrations are presented in ppbv, could you also provide the emissions of NOx, VOCs and CO in ppbv s-1?

Response:

Thanks a lot for pointing out this. The revision was done in the manuscript line 373-374:

In this study, the emissions of NO_x, VOCs and CO are 4.37×10^{-8}, 2.34×10^{-8} and 2.03×10^{-7} kg m^{-3} s^{-1} (i.e., ~35, ~200 and ~170 ppbv s^{-1}), respectively.

Specific comment 13:

#Line 351. Could you explain why that time step is selected for the chemistry?

Response:

Thanks a lot for your attention. The timestep of the simulation follows the CFL condition from the previous studies (Bright et al., 2013; Garmory et al., 2009; Kim et al., 2012; Kwak et al., 2013; Sanchez et al., 2016; Zhong et al., 2017). We choose to use 0.1 s in this simulation. The chemistry is solved by the ordinary deferential equation (ODE) solvers in OpenFOAM library, in which the chemical reactions can be integrated by dividing the flow time step into serval sub-time steps, automatically. The revision was done in the manuscript line 199-202 and line 206-208:

Even so, the time step (Δt) generally follows the Courant–Friedrichs–Lewy (CFL) condition to maintain numerical stability, which is:

$$Co = \frac{U\Delta t}{\Delta x} \leq 1 \tag{13}$$

where Δx is the grid size.

The chemistry is solved by the ordinary deferential equation (ODE) solvers in OpenFOAM library, in which the chemical reactions can be integrated by dividing the flow time step into serval sub-time steps, automatically.

Specific comment 14:

#Line 368. Please also provide the percentage of VOC reduction over the total VOC emissions (as shown in Table 3).

Response:

Thanks a lot for pointing out this. The revision was done in the manuscript line 408-411:

Case_EMIS_Ctrl_VOC20%, Case_EMIS_Ctrl_VOC30% and Case_EMIS_Ctrl_VOC40% are the scenarios which apply the stricter VOCs control measures (corresponding to 20%, 30% and 40% more VOCs emission reduction which are 60%, 65% and 70% reduction of total VOCs emission, respectively) on the vehicles with traffic control policies.

Specific comment 15:

#Line 385. I do not agree with the sentence “While on the windward side, NOx concentrations are more affected by the background conditions rather than emissions”. NOx concentration on the windward side is more affected by the background conditions than that on the leeward side. However, the influence of the NOx emission on NOx concentration on the windward side is still larger than the background concentrations. Based on the results in Section 4.3., the influence of background concentrations on NOx concentration on the windward side is just around 10-20%.

Response:

Thanks a lot for the hint. The revision was done in the manuscript line 453-455:

While on the windward side, NO_x concentrations are less than that on the leeward side. This is because that the NO_x from emission source first affects the leeward side which leads to the high concentrations in this area. As the wind flows, the concentrations of NO_x gradually decrease due to the wind diffusion and dilution effect.

Specific comment 16:

#Line 396. “...NO could be up to 90%” higher in the simple chemistry case.

Response:

Thanks a lot for pointing out this. The revision was done in the manuscript.

Specific comment 17:

#Line 409-412. "...from the oxidation of background VOCs with OH will consume". Why is that oxidation only occur with background VOCs? Not sure how to distinguish the background VOCs from the emitted VOCs on the concentration in the street since pollutants are already well mixed and chemical reactions are non-linear.

Response:

Thanks a lot for your attention. The NO not only reacts with background VOCs but also emitted VOCs. The main reason why this sentence only concerning the background VOCs here is that this section analyzes the influence of background condition. The method to distinguish the VOCs source is by comparing the results from different zero out cases in this study. The method is presented in the manuscript line 394-398:

To investigate the effect of chemical mechanism, background condition of the precursors (BC), emission (EMIS) and wind condition (Uref) on the reactive pollutant concentrations in the street canyon, the cases of BC_zero_out, EMIS_zero_out and Uref0.5 are set up in numerical simulations. In the Case_BC_zero and Case_Emis_zero, the precursors of O_3 (i.e. NOx and VOCs) are removed from domain inlet (background boundary conditions) and pollutant source emissions, respectively, and then we compare the results with Base.

Specific comment 18:

#Line 420-423. I think it occurs in the Base case as well.

Response:

Thanks a lot for your mention. This also occurs in the Base case. As mentioned in the above question, this section analyzes the influence of background condition. Therefore, the expression only focuses on the impact of background conditions.

Specific comment 19:

#Line 446. "In summary...". Please explain this better.

Response:

Thanks a lot for the hint. Some details of the explanation are add. The revision was done in the manuscript line 514-518:

As mentioned above, RO_2 (the production of VOCs and OH) will cosume the NO and weaken the O_3 titration effect with NO. In Base case (Figure 17g), the reaction rate of RO_2 is negative, which means that RO_2 consumes the NO. However, in Case_Emis_zero, reaction rate of RO_2 is positive during the whole simulation period which means that there is not enough NO to react with RO_2 or even O_3 without the vehicular source. Therefore, the source emissions provide a large amount of NO which enhances the O_3 depletion in the street canyon.

Specific comment 20:

#Line 468. Is average or total concentration in the street? Please modify the caption in Fig. 15 as well.

Response:

Thanks a lot for your attention. The results are concentrations at 90 minutes. The revision was done in the manuscript line 539 (Figure 19 is Figure 15 in the original manuscript):

Figure 19 shows the concentrations of O_3, NO and NO_2 in different NO_x and VOCs emission control scenarios at 90 minutes.

Figure 19. The (a) O_3, (b) NO and (c) NO_2 concentrations at 90 minutes in different emission control scenarios

Specific comment 21:

#Line 490. This paper presents results from the coupling of the chemical mechanism CS07A and CFD model. It should also be clarified in this section.

Response:

Thanks a lot for the hint. The revision was done in the manuscript line 568-569:

By applying the APFoam with CS07A mechanism in the simulation of reactive pollutants in typical street canyon ($H/W = 1$), key factors of chemical processes are investigated.

Specific comment 22:

#Line 494. “. . ., 2D and 3D pollutant dispersion. . .”. The simulations are only performed in a 2D street canyon.

Response:

Thanks a lot for the mention. The 3D simulation is added in section 3.4. The revision was done in the manuscript line 340-364:

3.4 Pollutant dispersion in 3D street canyon

As mentioned in section 3.3, 3D pollutant dispersion validation with tracer gas is conducted in this study, following the pervious study (Zhang et al., 2019b). Simulation results also compares with the wind tunnel experimental data (Chang and Meroney, 2001). CFD domain configuration is presented in Figure 9a. In this case, six buildings are set in the domain. Building height (H) and street canyon width (W) is 0.08 m with the $H/W = 1$. Building length (Lx) and building width (Ly) is 0.276 m and 0.184 m, respectively. The distance between buildings and domain inlet, side boundary, top boundary and domain outlet are respective $5H$, $5H$, $10H$ and $15H$, for simulating a realistic results (Tominaga et al., 2008). Within the target street canyon, there are also 8 measurement points (4 of which on the leeward side and 4 on the windward side) for measuring the concentrations (Figure 9b). Besides, 6 more measurement points are also set on the top of the downstream building. Pollutant concentrations at each measurement point in this simulation case are normalized with respect to the P5 (C_i/C_5) within the street canyon. The source of the C_2H_6 is set as an inlet at the bottom of the target street canyon. The size of the source is 0.005 m in width and 0.092 m in length setting in the middle of canyon. The release velocity is 0.01 m s^{-1} toward top boundary and the mass fraction of the C_2H_6 is 1 (pure gas of C_2H_6). For 3D pollutant dispersion simulation, APreactingFoam solver with Standard k-ε model is applied to solver compressible unsteady-state turbulent flow and pollutant dispersion as well. Photochemical mechanism is not used in the simulation. The minimum grid size in this case is 0.0005 m with expansion ratio of 1.1 from the wall surface toward surrounding. Time step of simulation is set as 1×10^{-4} s and ODE solvers for chemistry is used in this validation case as well. Meanwhile, the inlet velocity and TKE profile are also retrieved from and fitted by the experimental data (Figure 10).

Figure 11 shows the comparison results between CFD simulation and experimental data. Overall, CFD simulation in 3D dispersion case slightly overestimates the concentrations in the street canyon. As for P23 and P24, the simulated results also overestimate, effected by the higher concentrations predicted within street canyon. Similarly, Statistical variables such as NMSE, FB and R are calculated to evaluate the performance of the model. As shown in Table 3, the value of NMSE, FB and R are 0.16, -0.21 and 0.93 in the 3D dispersion case, respectively, which agrees with acceptance criteria. In general, APFoam also shows the good performance in the 3D pollutant dispersion simulation.

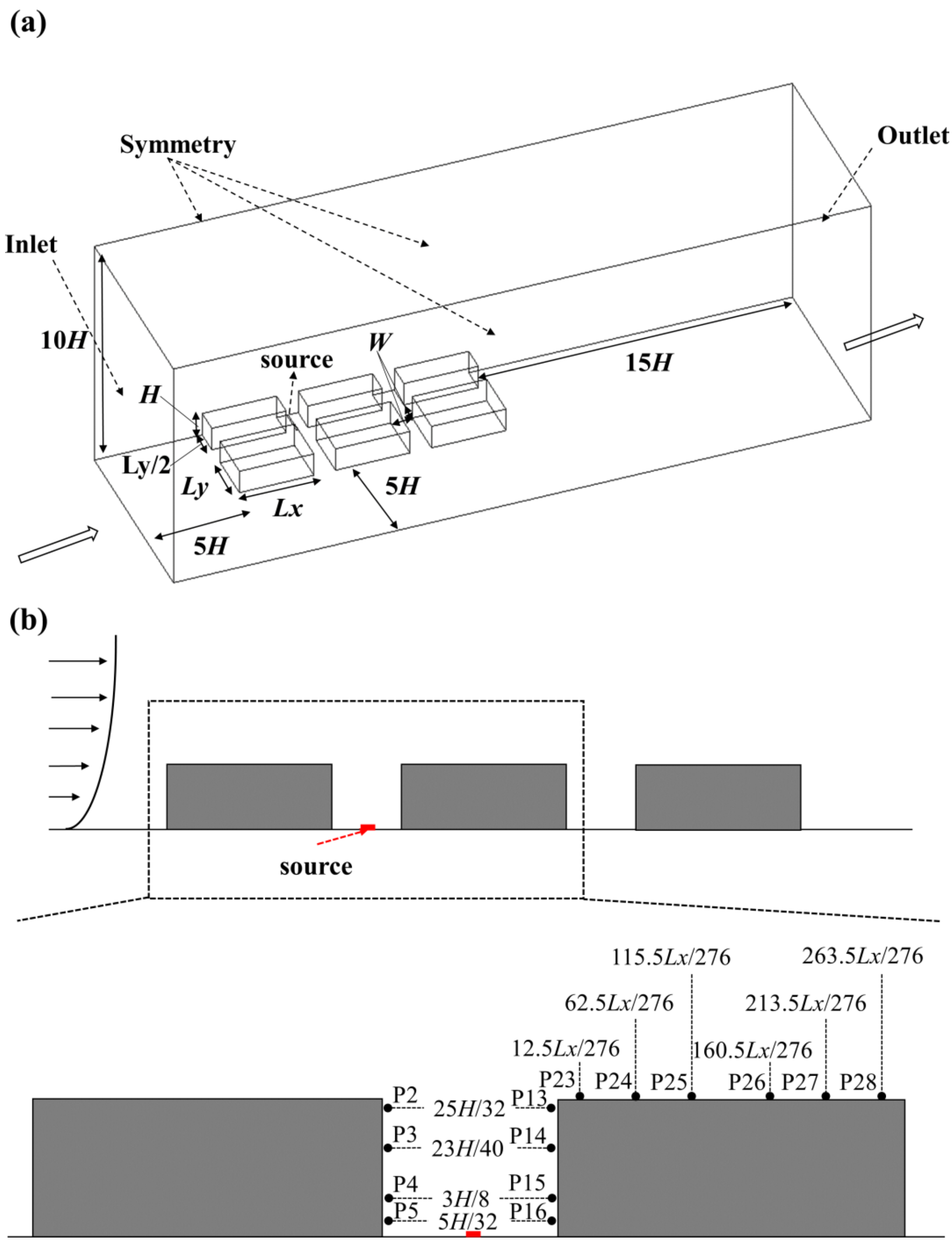


Figure 9. (a) The simulation domain of 3D pollutant dispersion and (b) the measurement points setting in the street canyon

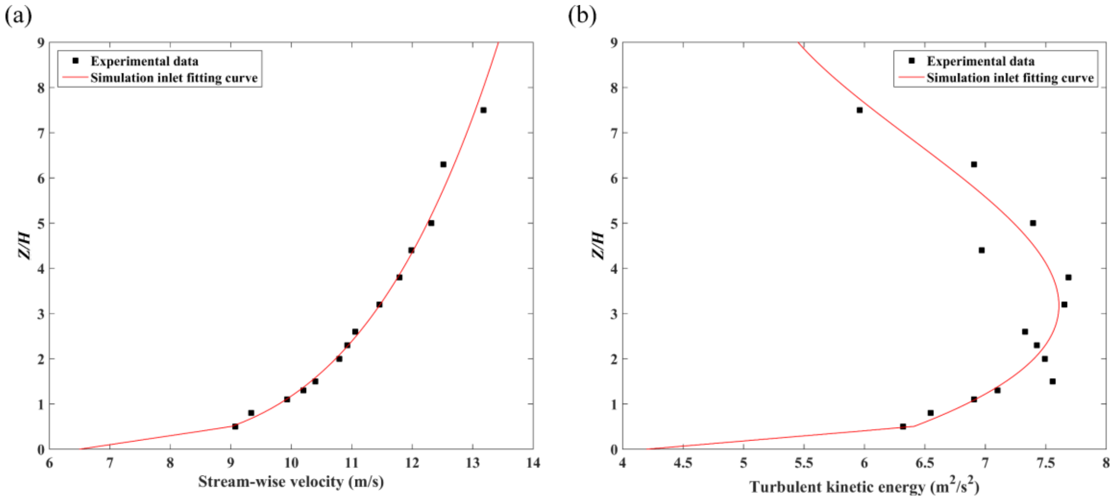


Figure 10. The inlet profile of (a) stream-wise velocity and (b) turbulent kinetic energy in 3D dispersion case

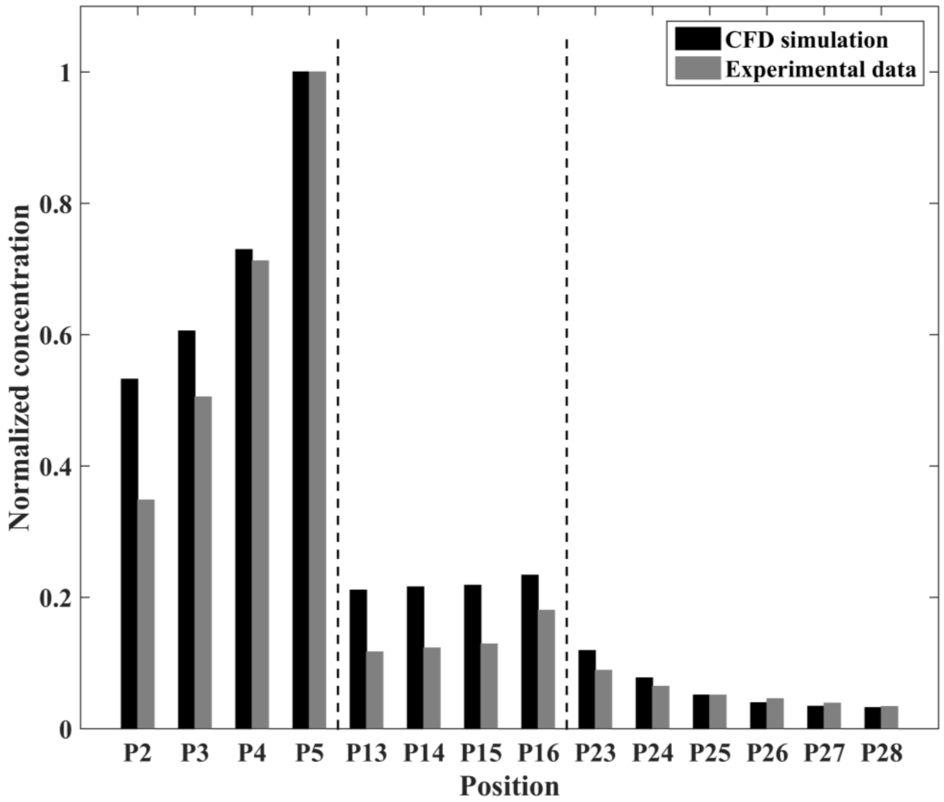


Figure 11. Normalized concentrations of CFD and experimental data at each measurement point in 3D dispersion case

Specific comment 23:

#Line 497. Add aspect ratio. #Line 498. Please provide the VOC-to-NOx emission ratio used in these simulations.

Response:

Thanks a lot for pointing out this. The revision was done in the manuscript line 568-569:

By applying the APFoam with CS07A mechanism in the simulation of reactive pollutants in typical street canyon (*H/W* = 1) with the VOCs to NO_x emission ratio ~ 5.7 in ppbv s^{-1}, key factors of chemical processes are investigated.

Specific comment 24:

#Line 499. “Other numerical sensitivity cases,. . .”. Please clarify what cases.

Response:

Thanks a lot for the mention. The revision was done in the manuscript line 571-573:

Other numerical sensitivity cases (Case_BC_zero, Case_Emis_zero and Case_Uref50%) reveal that vehicle emission is the main source of the NO and NO2, with the contribution of 82%–98% and 75%–90%, respectively.

Specific comment 25:

#Line 503. Due to the non-linearity of chemical reactions, how is the contribution from the boundary conditions to O3 concentration computed?

Response:

Thanks a lot for pointing out this. The method to computed the contribution from boundary condition to O_3 is by comarping the results from BC_zeros_out and Base case. The method is presented in the manuscript line 394-398:

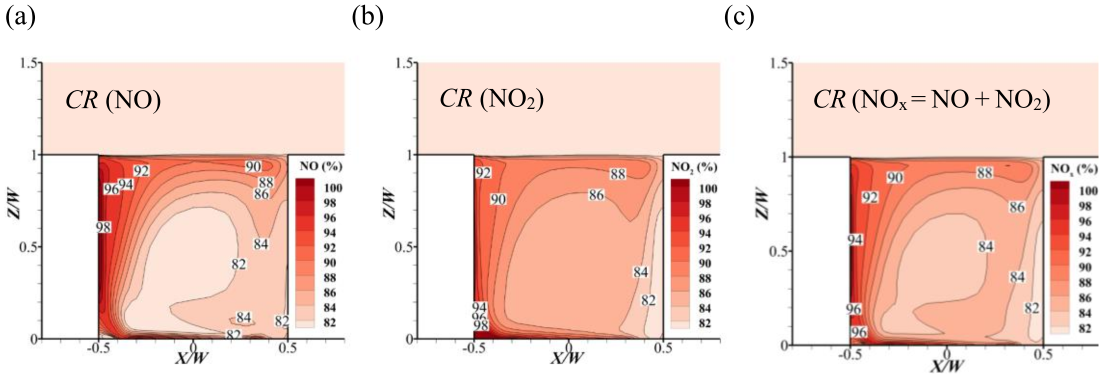
To investigate the effect of chemical mechanism, background condition of the precursors (BC), emission (EMIS) and wind condition (U_{ref}) on the reactive pollutant concentrations in the street canyon, the cases of BC_zero_out, EMIS_zero_out and Uref0.5 are set up in numerical simulations. In the Case_BC_zero and Case_Emis_zero, the precursors of O_3 (i.e. NOx and VOCs) are removed from domain inlet (background boundary conditions) and pollutant source emissions, respectively, and then we compare the results with Base.

Specific comment 26:

#Line 504. “Ventilation condition is another reason for the NOx concentrations increment, and the increase of NOx can be up to 98%”. I think that is to be expected. In steady state (or quasi-steady state) conditions, the concentration of a non-reactive pollutant is double when wind speed is divided by 2 (if emissions do not change). Despite NOx is not truly a non-reactive pollutant, due to the influence of the VOC reactions with NO and NO2, it might be almost considered as non-reactive as the sum of NO and NO2.

Response:

Thanks a lot for your attention. You provide us an interesting topic to discuss and analyze. It is true that if no chemical reactions exist, the change rate of pollutant concentration is 100% (i.e., the concentrations double) when the wind speed is 50% smaller. However, due to the chemical reaction, the concentration change rate of NO, NO$_2$ or NO$_x$ (sum of No and NO$_2$) are different between leeward and windward side. This is because that the windward side is nearer to and locates downwind regions of pollutant source in the flow trace. Thus, it takes shorter time for wind transport pollutants from the source to windward side. The effect of the chemical reaction has not yet been reflected and the concentration change rate is nearer to 100% (~90-98%) in the windward side. Moreover, the windward side is in the downwind regions and farther to the pollutant source in the flow trace. It takes longer time for pollutant to reach the windward side and more reactions occur in this longer period. Therefore, the change rates in this region are smaller (~80-90%).



The change rate of NO, NO$_2$ and NO$_x$ between different ventilation conditions

Technical comments:

#Line 44. “material” instead of “materiel”

#Line 297. Change “pervious” to “previous”.

#Line 371. Add “...change rate (CR_p). . .”

#Line 485. “polies” to “policies”

#Line 392. Change “Figure 11 shows the changes rates of pollutant concentrations and NO to NO$_2$

ratio. . .”

Response:

Thanks a lot for pointing out these problems. The revision was done in the manuscript.

Table 3. Add the name of the “full chemical mechanism” used in the simulations and mentioned in the manuscript (CS07A photochemical mechanism).

Figure 11-14. Please use the defined *CRp* (Eq. 28) to show the change rate of each pollutant in %.

Response:

Thanks a lot for pointing out these problems. The revision was done in the manuscript.

References:

Bright, V. B., Bloss, W. J. and Cai, X.: Urban street canyons: Coupling dynamics, chemistry and within-canyon chemical processing of emissions, Atmos. Environ., 68, 127–142, doi:10.1016/j.atmosenv.2012.10.056, 2013.

Garmory, A., Kim, I. S., Britter, R. E. and Mastorakos, E.: Simulations of the dispersion of reactive pollutants in a street canyon, considering different chemical mechanisms and micromixing, Atmos. Environ., 43(31), 4670–4680, doi:10.1016/j.atmosenv.2008.07.033, 2009.

Kim, M. J., Park, R. J. and Kim, J. J.: Urban air quality modeling with full O3-NOx-VOC chemistry: Implications for O3and PM air quality in a street canyon, Atmos. Environ., 47(2), 330–340, doi:10.1016/j.atmosenv.2011.10.059, 2012.

Kwak, K. H., Baik, J. J. and Lee, K. Y.: Dispersion and photochemical evolution of reactive pollutants in street canyons, Atmos. Environ., 70, 98–107, doi:10.1016/j.atmosenv.2013.01.010, 2013.

Sanchez, B., Santiago, J. L., Martilli, A., Palacios, M. and Kirchner, F.: CFD modeling of reactive pollutant dispersion in simplified urban configurations with different chemical mechanisms, Atmos. Chem. Phys., 16(18), 12143–12157, doi:10.5194/acp-16-12143-2016, 2016.

Zhong, J., Cai, X. M. and Bloss, W. J.: Large eddy simulation of reactive pollutants in a deep urban street canyon: Coupling dynamics with O3-NOx-VOC chemistry, Environ. Pollut., 224, 171–184, doi:10.1016/j.envpol.2017.01.076, 2017.