Abstract: Transport of passive and inert pollutant has been well explored in the past decades but its chemically reactive counterpart is rare. This paper examines the dispersion of chemically reactive pollutants over hypothetical urban areas using large-eddy simulation (LES). Under isothermal conditions, the flows in the urban canopy layer (UCL) over twelve idealized two-dimensional (2D) street canyons of unity aspect ratio are calculated. As a pilot study, the simple NOx-O3 chemistry, consisting of three chemical reactions, is considered. The ground-level area source of NO in the first street canyon and the background O3 from the prevailing wind initiate the NO2 production. NO and O3 react reversibly generating NO2 until chemical equilibrium which is measured by the photostationary state (PSS) of the system. Its spatial instability is a result of the difference in time scales in turbulent mixing and chemical reactions. Using various combinations of ground-level NO and background O3 concentrations, the sensitivity of photostationary state to turbulent mixing and chemical reactions is investigated. The PSS of the first street canyon increases with increasing ground-source NO. It is most stable at the recirculation centre due to the prolonged retention for a complete mixing of NO and O3. In the scenario of small ground-level NO and small background O3 (e.g. O3 = 1 ppb and NO = 1 ppb), the average PSS in the second to the twelfth street canyons increases gently as the NO concentration is low such that all the NO is used up in the first street canyon, leading to the negligible chemistry in the rest of the downstream canyons. While the NO-to-O3 ratio is increased to 1000/30, as an example, the average PSS from the second to twelfth canyons increases faster since the higher NO level promotes the downstream chemical reactions. Further increase the NO-to-O3 ratio, say 10000/1, the trend of the average PSS is non-linear in which a trough is observed in the fifth street canyon. This non-linear behaviour is likely governed by the turbulence and chemistry time scales.

Key words: Chemical reaction, large-eddy simulation, nitric oxide, nitrogen dioxides, physical diffusion, and time scale.

INTRODUCTION

The physical dispersion of passive and inert pollutants has been studied for many years, however, most pollutants are chemically reactive in fact. The secondary pollutants generated from chemical reactions are usually more harmful than the primary ones. For instance, long-time exposure to nitrogen dioxide (NO2) may impair lung function and increase the risk of respiratory symptoms, which, however, is more pernicious than its primary counterparts, nitric oxide NO and ozone O3 in the NOx – O3 chemistry mechanism (WHO, 2011). Thus, studies for the dispersion of chemically reactive pollutants should be performed in addition to the previous researches. Arellano et al. (1990) and Buitjers and Talmon (1987) developed a chemically reactive plume model (CRPM) to demonstrate the conversion of NO and NO2 using four chemical reactions of the NOx–O3 cycle. They considered macro-mixing and micro-mixing separately. Macro-mixing corresponds to the classical dispersion of pollutant in a turbulent atmosphere, while micro-mixing corresponds to the concentration fluctuations of chemically reactive species in a homogeneous mixture. The photostationary state (PSS) defect was found to be small by Baik et al. (2007) in the street canyon except near the roof level or the upper windward side of the street canyon. Garmory et al. (2009) used the Damköhler number to examine segregation effect. Baker et al. (2004) adopted the large-eddy simulation (LES) model to study the turbulent transport of chemically reactive pollutants, including NO, NO2, and O3, in a street canyon. The lower PSS defect value at the centre of the primary recirculation signifies the longer retention for a thorough pollutant mixing. The simple NOx–O3 chemistry mechanism is used in this study and the LES is employed to calculate the turbulent mixing. Only the total (mean and turbulent) PSS is analysed in attempt to elucidate the non-linearly coupled processes.

METHODOLOGY

LES with the one-equation subgrid-scale (SGS) model is adopted to simulate the flows and pollutant transport over idealized two-dimensional (2D) street canyons of unity aspect ratio (AR).

Chemistry Model

The simple, reversible NOx–O3 chemistry mechanism includes the following three equations of chemical reactions

\[ NO_j \xrightarrow{k_1} NO + O \]  
\[ O + O_2 + M \xrightarrow{k_2} O_3 + M \]  
\[ NO + O_3 \xrightarrow{k_3} NO_2 + O_3 \]  

Here, nitric oxide NO, nitrogen dioxide NO2, and ozone O3 are the three main air pollutants involved in the chemistry. The equations also consists of the ground-state oxygen atom O and the third molecule M (usually nitrogen N2 or oxygen O2 rich in the atmosphere) to absorb the excess vibration energy after generating O3. The rate constants of the chemical reactions (1) - (3) \( j_1 = 8.9 \times 10^{12} \text{ sec}^{-1} \), \( k_2 = 3.6398 \times 10^{-13} \text{ ppb}^{-1} \text{ sec}^{-1} \), and \( k_3 = 4.4334 \times 10^{-7} \text{ ppb}^{-1} \text{ sec}^{-1} \) are functions of temperature. Here we assume isothermal conditions (298 K) so the rate constants are constants. Ground-state oxygen atom O is highly reactive, thus its formation rate is fast that is equal to its depletion rate. The pseudo-steady state \( \partial [O] / \partial t = 0 \) is assumed. It is then calculated by \( [O] = (j_1/k_2) \times ([NO_2]/[O_3][M]) \).

Computational Domain

Figure 1a shows the three-dimensional (3D) computational domain developed for this study. The domain, whose total height is 8h, consists of twelve identical street canyons of building height h and a shear layer of 7h aloft, that extends 5h...
homogeneously in the spanwise direction. The street width of all the twelve canyons is the same as $h$, leading to the unity AR. The (background) pressure gradient drives the prevailing wind in the shear layer perpendicular to the street axis in order to represent the worst scenario of pollutant removal. The spanwise direction in the 3D computational domain is then averaged out to the 2D street canyons (Figure 1b) for data analyses.

![Figure 1. a) The 3D computational domain, b) the 2D computational domain of the chemistry model.](image)

**Boundary Conditions**
The infinitely long and infinitely repeating street canyons are implemented by the periodic boundary condition in the horizontal extents. The no-slip condition is used for all the solid boundaries and the domain top is in shear-free condition.

The prevailing wind enters into the domain from the inlet with background $O_3$, while the area source of NO is emitted from the ground of the first street canyon as a road of traffic. All the other solid boundaries are free of pollutants. The flows and pollutants are both assumed to be periodic in the spanwise direction so as to represent infinitely long street canyons.

**Grid Resolution**
Each street canyon comprises of $16 \times 80 \times 16$ grid cells in $x$-, $y$-, and $z$- directions, respectively. $384 \times 80 \times 140$ grid cells are used in the UCL above the street canyons. The whole domain is thus discretized by over 4.6 million grid cells in total. The grid size is uniform in the spanwise direction due to the homogeneity. While in the $x$- and $z$- directions, the grid cells are refined towards the wall for improved accuracy. Above the roof level, the grid size increases up to a factor of 3 for the grid in the vertical direction at the domain top.

**Damkohler Number**
The diffusion time scale $\tau_d$ is the time required for well-mixed condition. It is defined by the characteristic length scale $L$ and the friction velocity $u_f$ ($= \sqrt{r/\rho}$ with the shear stress $r$ and the fluid density $\rho$) as follow:

$$\tau_d = \frac{L}{u_f} \quad (4)$$

The reaction time scale $\tau_r$ is the time required for chemical reaction. Here, for the simple NO$_x$-O$_3$ chemistry mechanism in Equations (1)-(3), the reaction time scale of NO is

$$\tau_{NO} = \frac{1}{k_3[O_3]_0} \quad (5)$$

and the reaction time scale of O$_3$ is

$$\tau_{O3} = \frac{1}{k_3[NO]_0} \quad (6)$$

The Damkohler number $Da$ is to compare the physical diffusion and chemical reaction by taking the ratio of diffusion-to-reaction time scales, i.e. $\tau_d/\tau_r$. In other words, when $Da$ is larger than 1 (i.e. $\tau_d > \tau_r$), the chemical reaction is faster than the physical diffusion. Although the reaction is fast, the pollutants are not mixed uniformly for complete reaction. On the other hand, when $Da$ is smaller than 1 (i.e. $\tau_d < \tau_r$), the physical diffusion is faster than the chemical reaction such that the slow chemical reaction is in the well-mixed condition. The Damkohler number of NO is

$$Da_{NO} = \frac{\tau_d}{\tau_{NO}} = \frac{L}{u_f} \frac{1}{k_3[O_3]_0} \quad (7)$$

and the Damkohler number of O$_3$ is

$$Da_{O3} = \frac{\tau_d}{\tau_{O3}} = \frac{L}{u_f} \frac{1}{k_3[NO]_0} \quad (8)$$

**Photostationary State**
The following photostationary state (PSS) is employed to measure the degree of chemical equilibrium:

$$PSS = \frac{k_3[NO][O_3]}{f_r[NO_3]} \quad (9)$$

The value of 1 indicates the chemical equilibrium; otherwise it indicates a deviation from chemical equilibrium.

**RESULTS AND DISCUSSIONS**
Table 1 lists the corresponding $Da_{NO}$ and $Da_{O3}$ for different amount of ground area source NO and incoming O$_3$. The first highlighted is the average PSS inside the first street canyon due to the NO ground source there. Keeping the $Da_{NO}$ constant,
the average PSS increases monotonically with increasing $Da_{O_3}$ (Figure 2). As stated before, the value of $Da_{O_3}$ relies largely on the ground-source NO. The higher concentration of ground-level NO, corresponding to the higher $Da_{O_3}$, promotes the interaction of NO and $O_3$ for chemical reaction; and hence the elevated PSS (close to 1) is obtained (Figure 2). In low $Da_{O_3}$, the average PSS increases sharply but the trend is flattened in high $Da_{O_3}$. This finding is mainly due to the saturation of $O_3$ so the ground-source NO is in excess for complete chemical reactions.

Figure 3 shows the PSS of the first street canyon in the 10 sets of combinations. The local maximum PSS (more approximate to 1) appear at the centre of the primary recirculation in all the 10 cases. In Figure 3a, the PSS is peaked at the centre of the street canyon only, while in Figures 3b-3e, the maximum extends to the ground-level leeward corner due to the secondary recirculation. The chemical equilibrium is reached there as the recirculating speed is relatively slower and thus a longer retention time is available for the NO and $O_3$ to mix with each other for chemical reaction. The local minimum occurs at the roof level and windward façade. This is due to the entrainment of the prevailing wind rich background $O_3$ into the street canyon. The $O_3$ entrainment and the de-entrainment of the reacted or unreacted air pollutants over the roof and windward façade induce the chemical instability.

Table 1. Time scales and Damkohler numbers for 10 sets of data.

<table>
<thead>
<tr>
<th>NO</th>
<th>O$_3$</th>
<th>$\tau_d$</th>
<th>$\tau_{NO}$</th>
<th>$\tau_{O3}$</th>
<th>$\tau_{NO}/\tau_{O3}$</th>
<th>$Da_{NO}$</th>
<th>$Da_{O3}$</th>
<th>$Da_{NO}/Da_{O3}$</th>
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<td>1</td>
<td>16.9031</td>
<td>2.26E+3</td>
<td>1E+0</td>
<td>0.007494</td>
<td>0.007494</td>
<td>1</td>
<td></td>
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<td>2.26E+3</td>
<td>2.26E+0</td>
<td>1E+3</td>
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<td>7.52E-1</td>
<td>3E+3</td>
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<tr>
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<td>2.26E+3</td>
<td>3.22E-1</td>
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<td>2.82E-1</td>
<td>8E+3</td>
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In Figure 4, the average PSS of the twelve street canyons in the 10 cases are illustrated. At $Da_{NO}/Da_{O3} = 1$ (Figure 4a), the NO and $O_3$ sources are too small in concentrations so the chemistry mainly occurs inside the first street canyon. The little amount of NO is nearly used up in the first street canyon and is unable to pass to the downstream street canyons. Therefore the average PSS is low in the first street canyon and increases gradually from 0.789 in the second street canyon to 0.926 in the last one.
Lowering down the ratio $\frac{Da_{NO}}{Da_{O_3}}$ to 0.03 (Figure 4b), 0.02 (Figure 4c), and 0.001 (Figure 4d), the average PSS increases more rapidly from the second to tenth street canyons then slows down the increment in the last two street canyons. The lower background $O_3$ relative to ground-source NO facilitates the removal of NO from the first street canyon. Thus, the chemical reaction takes place inside the first few street canyons, leading to the sharp increase in the average PSS.

Further decrease the ratio $\frac{Da_{NO}}{Da_{O_3}}$ to 0.000333 (Figure 4e), the average PSS is flattened and increases much slowly in a rate of 0.66 in the second street canyon to 0.801 in the last street canyon canyon. The smaller background $O_3$ concentration leads to the slow chemical reaction that delays the reaction in the downstream street canyons, resulting in the slowly increasing average PSS.

In the ratio $\frac{Da_{NO}}{Da_{O_3}}$ of 0.000143 (Figure 4f), 0.000125 (Figure 4g), 0.000118 (Figure 4h), 0.000111 (Figure 4i) and 0.0001 (Figure 4j), non-linear trends of the average PSS are demonstrated. The troughs are located at the fourth or fifth street canyon among the five cases. The average PSS from the second to twelfth street canyons does not change significantly and the differences between the trough and the maximum average PSS do not exceed 0.8. The situations are thus similar to that of the ratio $Da_{NO}/Da_{O_3}$ of 0.000333, the high ratio of NO/O$_3$ facilitates the downstream chemical reaction. The non-linear average PSS may be caused by the reversible chemical reactions of Equations (1) and (3).

The trends of the average PSS are studied in different combinations of ground-source NO and background $O_3$. Although the value of average PSS (close to 1) only represents the more stable condition of the chemicals but not the lower concentration levels, it means that the situation is easier to be handled. When the average PSS is away from 1, the condition is more unstable. In other words, the air pollutant concentrations fluctuate more rapidly because of chemical reactions. Special strategies, say particularly lowering down a certain pollutant to reach the stable condition, are therefore needed to implement.

![Figure 4. The average PSS of the twelve street canyons of the $Da_{NO}/Da_{O_3}$: a) 1; b) 0.03; c) 0.02; d) 0.001; e) 0.00033; f) 0.000143; g) 0.000125; h) 0.000118; i) 0.000111; and j) 0.0001.](image)
CONCLUSIONS

The large-eddy simulation (LES) is adopted to consider the simple NO$_x$-O$_3$ chemistry mechanism with a two-dimensional (2D) computational domain consisting of twelve street canyons of unity aspect ratio (AR). In the simple NO$_x$-O$_3$ chemistry mechanism, three chemical reactions are involved with the ground-source NO in the first street canyon and the background O$_3$ from the incoming flow to initiate the NO$_2$ production. The term photostationary state (PSS) is introduced to quantify the stability of the reversible chemical reactions between NO, NO$_2$, and O$_3$. When looking into the first street canyon alone, the PSS is found to be maximised (closer to 1) at the centre of the primary recirculation and minimised (away from 1) at the roof level and windward façade. It is because the slow recirculating speed at the centre of the vortex promotes a longer retention time favourable for homogeneous mixing and the subsequent chemical reactions. On the other hand, the unstable condition at the roof level and windward façade is due to the abrupt entrainment of background O$_3$ into the street canyon and the de-entrainment of the unreacted and reacted flows. The average PSS in the first street canyon increases with increasing ground-source NO concentration as NO initiates the reaction until the saturation of entrained O$_3$. With the low-level ground-source NO and background O$_3$ (1 ppb of NO and 1 ppb of O$_3$), the gentle increment of average PSS from the second to last street canyons is clearly illustrated. It is caused by the small amount of NO which is used up in the first canyon, depressing the chemistry in the rest of the downstream street canyons. Increasing the NO-to-O$_3$ ratio (1000 ppb of NO and 30 ppb of O$_3$) promotes the downstream chemical reaction as the ground-source NO is abundant in the first street canyon that is able to pass downstream. Hence, the average PSS in the second to last street canyons increases more quickly. Unexpectedly a non-linear trend is observed when further increase the NO-to-O$_3$ ratio, say 10000/1. A trough of average PSS is developed in the fifth street canyon that is likely due to the reversible chemical reaction in the simple NO$_x$-O$_3$ chemistry mechanism.

REFERENCES


