



## Numerical study on the ozone formation inside street canyons using a chemistry box model

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### Abstract

Tropospheric ozone is a secondary air pollutant produced in the presence of nitrogen oxides ( $\text{NO}_x$ ), volatile organic compounds (VOCs), and solar radiation. In an urban environment, ground-level vehicular exhaust is the major anthropogenic source of ozone precursors. In the cases of street canyons, pollutant dilution is weakened by the surrounding buildings that creates localized high concentration of  $\text{NO}_x$  and VOCs, and thus leads to high potential of ozone formation. By considering the major physical and chemical processes, a chemistry box model is employed to investigate the characteristics of ozone formation due to vehicular exhaust inside street canyons under the worst case scenario, i.e. the calm wind condition. It is found that a high level of ozone concentration, of the order of 100 ppbv and higher, would occur inside the street canyons, in particular, when the emission rate (concentration) ratio of VOCs to  $\text{NO}_x$  is greater than 10. This elevated ozone concentration appears at the transition from VOCs to  $\text{NO}_x$  sensitivity and may extend to a few hundreds.

**Key words:** volatile organic compounds; VOCs-to- $\text{NO}_x$  ratio; air quality; vehicular emission; chemistry box model

### Introduction

It has been identified that tropospheric ozone ( $\text{O}_3$ ) poses adverse impacts on human respiratory systems and agricultural products, thus causes much concern to many metropolitan areas such as Los Angeles, London, and Hong Kong. Ozone is a secondary pollutant, formed through a series of chemical reactions in the presence of nitrogen oxides ( $\text{NO}_x$ ), volatile organic compounds (VOCs), and solar radiation. Vehicular exhaust is the major source of anthropogenic pollutants in urban areas, where often suffer from high concentration of ozone precursors, particularly inside street canyons. The pedestrian-level VOCs concentration in Hong Kong is high compared with other metropolises that is likely related to the heavy vehicular emissions in the dense built environment (Chan *et al.*, 2002). The subsequent ozone formation is normally treated as a regional-scale problem over the city but not as a local-scale problem inside street canyons. For example, the Environmental Protection Department of the Hong Kong Special Administrative Region measures the ambient air pollutant concentration (including ozone) at elevated ambient monitoring stations, and transforms it into an air pollution index (API). However, the ozone measurement is not included in any roadside pedestrian-level monitoring stations. Recently, Zhang *et al.* (2007) monitored the concentration of various air pollutants in

Hong Kong and the Pearl River Delta region. They found that the ozone precursors emitted from Hong Kong and Guangdong province are of comparable importance. In addition, most of the ozone is generated locally within the Hong Kong territory through photolysis and is characterized by the VOCs-sensitive conditions. The difficulty in defining the origins of ozone in field measurements, whether it is freshly formed due to its precursors emitted from the vehicles in the vicinity or is entrained from the troposphere, is the major technical barrier for isolating the regional influence of air pollutants. As a result, the local-scale photochemical behaviors of ozone and its precursors inside street canyons have been barely explored.

Indeed, our understanding of the chemical processes of air pollutants in street canyons and urban environment is rather limited. The mechanism of pollutant transport is complicated by numerous parameters such as the ambient wind speed and direction, geometry of the street canyon, and temperature stratification. Research efforts have mainly focused on the physical processes of pollutant transport inside street canyons (Li *et al.*, 2006). However, apart from the primary pollutants, formation of secondary pollutants should not be overlooked because of its high formation potential. Considering nitric oxide (NO), nitrogen dioxide ( $\text{NO}_2$ ), and ozone as the reactive chemical species in an idealized street canyon of aspect ratio 1, Baker *et al.* (2004) investigated the detailed turbulent transport of chemically reactive species by large-eddy simulation (LES). They found that the reactive mixing of chemical species is

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relatively stable at the centre core and the ground-level windward corner of the street canyons. However, it is relatively unstable along the windward wall and the wake of the emission source. Using the same chemical reactive species, Baik *et al.* (2007) found that the contributions to ozone budget from the chemical reaction, advection and turbulent diffusion terms are comparable with each other. Because of the unaffordable computational load, the chemical mechanisms used in these two studies were simple (VOCs are omitted). Nevertheless, their findings paved the foundation of including chemical reactive species and demonstrated the importance of chemical processes in street canyon air pollution research.

Recently, Liu and Barth (2002) and Liu *et al.* (2004) investigated the air ventilation and pollutant removal mechanisms (which are governed by the roof-level vertical turbulence) for idealized street canyons when the background wind direction is perpendicular to the street axis. Subsequently, they quantified the air exchange rates (ACH) for street canyons of aspect (building-height-to-street-width) ratios ranged from 0.5 to 2.0 using LES (Liu *et al.*, 2005). Using these ACH values, a generalized VOCs and NO<sub>x</sub> mechanism (Seinfeld and Pandis, 1998), a chemistry box model was then constructed to calculate the physical and chemical behaviors of chemically reactive species inside urban street canyons. The use of chemistry box model assuming spatial homogeneity lessens the computational hurdle of calculating the coupled physical and chemical processes simultaneously so that a more comprehensive chemical mechanism is adopted. The output from this model helps investigate the possibility of local-scale (pedestrian-level) ozone formation inside street canyons as well as the associated characteristic chemical behaviors.

## 1 Methodology

Mass conservation of individual chemical species in a box model yields the mathematical model in the form of an ordinary differential equation in the time domain

$$\frac{d}{dt}C_{\Phi}(t) = \frac{S_{\Phi}}{V} - \frac{Q}{V}C_{\Phi}(t) + \Delta_{\Phi} \quad (1)$$

where,  $t$  (s) is the time,  $V$  (m<sup>3</sup>) is the volume of street canyon,  $Q$  (m<sup>3</sup>/s) is the air ventilation rate,  $C_{\Phi}$  (ppbv) is the concentration of chemical species,  $S_{\Phi}$  (m<sup>3</sup>/s) is the chemical species emission rate, and  $\Delta_{\Phi}$  (ppbv/s) is the source or sink due to chemical reactions. The chemical species are assumed to be well-mixed in the box model (street canyon). The emission and removal of chemical species are the physical processes while the gas-phase chemical reactions are the chemical processes inside the street canyons.

The dominant mechanism of chemical species removal inside the street canyons is by the turbulence at roof level (Liu and Barth, 2002; Liu *et al.*, 2004). Detailed analysis of the roof-level turbulent transport shows that the ACH is a function of street-canyon aspect ratios (Table 1). Liu *et al.* (2005) employed the LES to calculate the pseudo-steady-state flow field inside the street canyons of aspect

**Table 1** Parameters for the street canyons used in the present study

Street canyon aspect ratios	$V = H \times W \times L$ (m <sup>3</sup> )	$T$ (s)	$Q$ (m <sup>3</sup> /s)	Dimensionless ACH (V/T)
0.5	20,000 = 10×20×100	100	12	0.06
1.0	10,000 = 10×10×100	100	5	0.05
2.0	20,000 = 20×10×100	100	5	0.025

$V$ : volume of street canyon;  $H$ : building height;  $W$ : street width;  $L$ : street length;  $T$ : characteristic time scale;  $Q$ : rate of air ventilation. The roof-level wind speed is 0.1 m/s perpendicular to street axis. The dimensionless air exchange rates (ACH) are obtained from Liu *et al.* (2005).

ratios ranged from 0.5 to 2.0. The air ventilation rate in the form of air removal or entry is then calculated by the transient vertical velocity fluctuation and the ventilation area at roof level. Upward wind flow removes polluted air out of a street canyon, while downward wind flow drives fresh air into it. The temporal average of the transient air ventilation rate yields the averaged value, which is then made dimensionless by the street canyon volume  $V$  and the reference time scale  $T$  to obtain the ACH. Generally, higher prevailing wind speed favors air ventilation while higher street canyon aspect ratio suppresses pollutant removal.

Three 100-meter-long hypothetical street canyons, of different aspect ratios varying from 0.5 to 2.0 (Table 1), are considered in this study with roof-level wind speed equal to 0.1 m/s. This low wind speed represents an almost calm wind condition, which is normally considered as the worst pollution scenario because of the weakened ventilation. The respective ventilation rates of the street canyons can be calculated based on the ACH values determined by Liu *et al.* (2005).

The chemical transformations of gas-phase chemical species are considered as the major chemical processes inside the street canyons; neither depositions nor phase changes are taken into account. The generalized VOCs and NO<sub>x</sub> mechanism (Seinfeld and Pandis, 1998) is employed to calculate the conversion of NO<sub>x</sub> and VOCs to ozone by photolysis. It consists of 23 chemically reactive species (Table 2) and 20 chemical reactions (Table 3). This mechanism contains most of the key features and is an appropriate tool for qualitative analysis of O<sub>3</sub> formation (Seinfeld and Pandis, 1998). In the current study, the vehicular exhaust is assumed to be the dominant air pollutant emission source in the street canyons. The relative amount of nitric oxide and nitrogen dioxide, which are emitted continuously from the vehicles inside the street canyons, is assumed to be in the ratio of 9 to 1. Similarly, the VOCs emissions from vehicles are assumed to be made up of equal amounts of hydrocarbons (RH, R representing the alkyl carbon chain), formaldehyde (HCHO), and aldehydes (RCHO), which are also continuously emitted in the street canyons. A wide range of emission rates for NO<sub>x</sub> and VOCs, ranged from 1×10<sup>-7</sup> to 1×10<sup>-5</sup> m<sup>3</sup>/s, was tested in the current sensitivity analysis. Tong *et al.* (2000) measured the composition of tailpipe exhaust from a passenger car, a petrol van, a diesel van, and a double-decker bus under idle conditions. The emission rates of NO<sub>x</sub> and VOCs were, respectively, in the ranges of 1.08×10<sup>-7</sup>–3.13×10<sup>-6</sup> m<sup>3</sup>/s and 1.79×10<sup>-7</sup>–1.53×10<sup>-6</sup> m<sup>3</sup>/s for a single idling vehicle at 298 K and 1 atmospheric pressure.

**Table 2** Gas-phase chemically reactive species considered in the present chemistry box model

Chemical species	Remark
Nitric oxide (NO)	Vehicular exhaust in the form of nitrogen oxides NO <sub>x</sub>
Nitrogen dioxide (NO <sub>2</sub> )	
Formaldehyde (HCHO)	Vehicular exhaust in the form of volatile organic compounds (VOCs)
Aldehydes (RCHO)	
Hydrocarbons (RH)	
Ozone (O <sub>3</sub> )	CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub>
Hydroxyl radical (OH•)	
Hydroproxyl radical (HO <sub>2</sub> •)	
Peroxyl radical (RO <sub>2</sub> •)	
Peroxyacetyl nitrate (PAN)	
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	ground state; pseudo steady-state approximation
Oxygen atom (O)	
Oxygen atom (O( <sup>1</sup> D))	singlet-D; pseudo steady-state approximation
Alkoxy radical (RO•)	pseudo steady-state approximation
Carbon monoxide (CO)	final products
Acylperoxy (RC(O)O <sub>2</sub> •)	
Nitric acid (HNO <sub>3</sub> )	
Hydroperoxide (ROOH)	
Oxygen (O <sub>2</sub> )	
Nitrogen (N <sub>2</sub> )	2.09×10 <sup>8</sup> ppbv (constant)
Moisture (H <sub>2</sub> O)	7.81×10 <sup>8</sup> ppbv (constant)
	1.55×10 <sup>7</sup> ppbv (constant; 50% relative humidity)
Carbon dioxide (CO <sub>2</sub> )	3.55×10 <sup>5</sup> ppbv (constant)
Hydrogen (H <sub>2</sub> )	5.80×10 <sup>2</sup> ppbv (constant)

R represents an alkyl carbon chain.

**Table 3** Generalized VOCs and NO<sub>x</sub> reaction mechanism (Seinfeld and Pandis, 1998) adopted in this study

Chemical reaction	Rate constants at 298 K and 1 atmospheric pressure
NO <sub>2</sub> +hν → NO + O	8.90×10 <sup>-3</sup> s <sup>-1</sup>
O + O <sub>2</sub> +M → O <sub>3</sub> +M	3.64×10 <sup>-13</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
O <sub>3</sub> +NO → NO <sub>2</sub> +O <sub>2</sub>	4.43×10 <sup>-4</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
RH + OH• → RO <sub>2</sub> •+H <sub>2</sub> O	6.48×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
HCHO+hν → 2HO <sub>2</sub> •+CO	2.96×10 <sup>-5</sup> s <sup>-1</sup>
HCHO+hν → H <sub>2</sub> +CO	4.25×10 <sup>-5</sup> s <sup>-1</sup>
HCHO + OH• → HO <sub>2</sub> • + CO + H <sub>2</sub> O	4.25×10 <sup>-5</sup> s <sup>-1</sup>
RCHO + OH• → RC(O)O <sub>2</sub> •+H <sub>2</sub> O	3.89×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
RO <sub>2</sub> •+NO → NO <sub>2</sub> +RO•	2.19×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
RC(O)O <sub>2</sub> •+NO → NO <sub>2</sub> +RO <sub>2</sub> •+CO <sub>2</sub>	5.91×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
RO•+O <sub>2</sub> → RCHO + HO <sub>2</sub> •	4.68×10 <sup>-5</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
HO <sub>2</sub> •+NO → NO <sub>2</sub> +OH•	2.12×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
O <sub>3</sub> +hν → O <sub>2</sub> +O( <sup>1</sup> D)	3.65×10 <sup>-5</sup> s <sup>-1</sup>
OH•+NO <sub>2</sub> → HNO <sub>3</sub>	2.81×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
HO <sub>2</sub> •+HO <sub>2</sub> • → H <sub>2</sub> O <sub>2</sub> +O <sub>2</sub>	1.24×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
RO <sub>2</sub> •+HO <sub>2</sub> • → ROOH + O <sub>2</sub>	1.38×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
RC(O)O <sub>2</sub> •+NO <sub>2</sub> +M → PAN + M	2.14×10 <sup>-1</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>
PAN → RC(O)O <sub>2</sub> •+NO <sub>2</sub>	5.20×10 <sup>-4</sup> s <sup>-1</sup>
HO <sub>2</sub> •+O <sub>3</sub> → OH + 2O <sub>2</sub>	4.93×10 <sup>-5</sup> ppbv <sup>-1</sup> .s <sup>-1</sup>

M represents the concentration of third molecule, usually nitrogen or oxygen molecules that absorb the excessive vibration energy.

In a heavy traffic metropolis, such as Hong Kong, tens of idling or slowly moving vehicles are often stuck in a 100-meter-long street section in which the order of magnitude of vehicular emission rates is about 1×10<sup>-6</sup> m<sup>3</sup>/s. As such, the current parametric test covers the possible ranges of vehicular emission rates in a realistic situation.

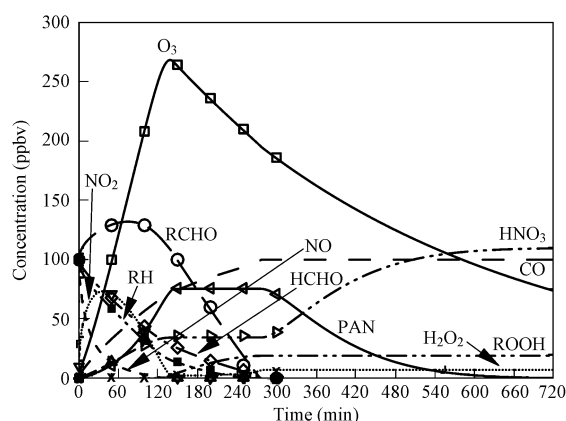
The chemical rate constants (Table 3) are calculated according to Seinfeld and Pandis (1998), where the

chemical reactions are assumed to take place in a sunny afternoon at 298 K, 1 atmospheric pressure, and 50% relative humidity. The mathematical model expressed by Eq.(1) is solved explicitly by the fourth-order Runge-Kutta scheme. Because of the broad range of concentrations of the chemical species, pseudo-steady-state approximation (PSSA) is employed to calculate the formation of ground-state (O) and singlet-D (O(<sup>1</sup>D)) oxygen atoms. With alkoxy radical (RO•), a small time-step increment (2 micro-seconds) is used in the current calculation, because of the fast chemical reactions. The street canyons are prescribed as free of chemical species initially (t = 0 s). Afterward, the physical and chemical processes are being developed after switching on the source, removal, and chemical mechanisms. The concentration of the chemical species gradually achieves steady-state values, which are presented in Table 3.

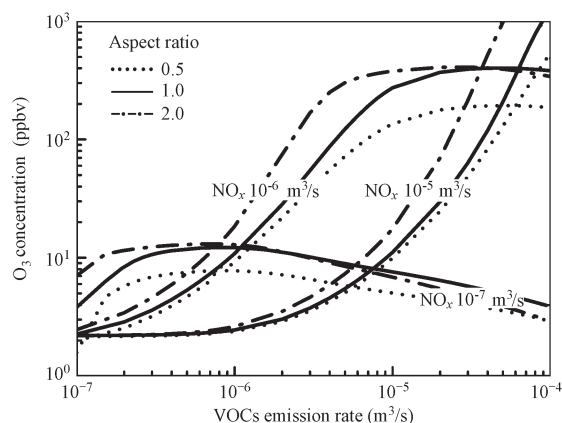
The performance of our chemistry box model has been compared with that of Seinfeld and Pandis (1998), where considered the temporal chemical behaviors of 100 ppbv of hydrocarbons, 100 ppbv of formaldehyde, 100 ppbv of aldehydes, 100 ppbv of nitric oxide, and 10 ppbv of nitrogen dioxide. These pollutants are initially well-mixed and then the source terms are switched off throughout the computation. As shown in Fig.1, the output from our chemistry box model calculation is comparable with that of Seinfeld and Pandis (1998). It is noteworthy that it takes about 120 min for maximum ozone formation, so ozone most probably will be formed after noon time as observed commonly in field measurements.

## 2 Results and discussion

Figure 2 depicts the steady-state ozone concentration (C<sub>O<sub>3</sub></sub>) in the street canyons of aspect ratios 0.5, 1.0, and 2.0, with a wide range of NO<sub>x</sub> and VOCs emission rates (from 1×10<sup>-7</sup> to 1×10<sup>-5</sup> m<sup>3</sup>/s). The concentration of ozone produced varied from a few to hundreds ppbv. The results indicate that it is possible for considerable ozone formation (ozone concentration greater than 100 ppbv) to take place inside the street canyons under calm



**Fig. 1** Temporal behavior of selected chemically reactive species calculated by the generalized VOCs and NO<sub>x</sub> mechanism employed in this paper. The symbols represent data points extracted from Seinfeld and Pandis (1998).



**Fig. 2** Steady-state ozone concentration ( $C_{O_3}$ ) plotted as functions of the emission rates of  $NO_x$  and volatile organic compounds (VOCs) inside street canyons of aspect ratios 0.5, 1.0, and 2.0.  $NO_x$  concentrations are  $10^{-5}$ ,  $10^{-6}$ ,  $10^{-7}$   $m^3/s$ , respectively.

wind conditions with certain ranges of  $NO_x$  and VOCs emission rates. The output from the chemistry box model shows that, even with small  $NO_x$  emission rates ( $1 \times 10^{-6}$   $m^3/s$ ), high ozone concentration (greater than 100 ppbv) could be formed inside the street canyons. Despite this high ozone formation potential, pedestrian-level ozone is generally less concerned. For example, in Hong Kong, roadside ozone levels are not monitored by the roadside air quality monitoring stations, probably due to a belief that a significant amount of these secondary pollutants cannot be formed in a local scale before being removed from the street canyons.

The results of the chemistry box model show that only an insignificant amount of ozone (concentration less than 10 ppbv) will be formed inside the street canyons if the VOCs emission rate is not large enough to activate the chemical mechanism for ozone formation (Fig.2), i.e., solely increasing the  $NO_x$  emission rate finally leads to VOCs-sensitive conditions that cannot increase the ozone concentration inside the street canyons (Sillman 1999; Sillman and He, 2002). This finding is in line with the ozone isopleth plot, expressing the  $C_{O_3}$  as a function of nitrogen oxides ( $C_{NO_x}$ ) and VOCs ( $C_{VOCs}$ ) concentration along the air trajectories in Atlanta (Jeffries and Crouse, 1990) and the theoretical ozone response diagram (Milford *et al.*, 1994). It is interesting to note from Fig.2 that in some occasions a small  $NO_x$  emission rate could lead to large ozone production. For example, the ozone concentration at a small  $NO_x$  emission rate,  $1 \times 10^{-7}$   $m^3/s$ , is greater than that of other higher  $NO_x$  emission rates by an order of magnitude, provided that the VOCs emission rate is higher and in the range of  $1 \times 10^{-7}$  to  $1 \times 10^{-5}$   $m^3/s$ . Hence, as shown in the model calculation, ozone formation inside street canyons is characterized by both the emission rates of  $NO_x$  and VOCs.

Further studying the ozone formation potential inside the street canyons (Fig.2), with different VOCs and  $NO_x$  emission rates, shows that, for a particular  $NO_x$  emission rate, the ozone concentration remains at low level (less than 10 ppbv) as long as it is greater than the VOCs emission rate. The ozone concentration is around 10 ppbv when

the emission rates of  $NO_x$  and VOCs are about the same. Further increase in the VOCs emission rate leads to a sharp increase in ozone concentration. The ozone concentration gradually reaches a broad local maximum when the VOCs emission rate is about 10 to 100 times greater than its  $NO_x$  counterpart. After passing through the peak of ozone concentration, further increase in the VOCs emission rate does not extend the increasing of ozone concentration anymore. Instead, it decreases gradually in which the chemistry system is moving from VOCs-sensitive into VOCs-saturated ( $NO_x$ -sensitivity) conditions. The highest ozone level calculated by the current chemistry box model appears at the transition from VOCs to  $NO_x$  sensitivity that is in line with the study of a larger spatial scale focusing at the Milan area (Martilli *et al.*, 2002). Analogously, at a small VOCs emission rate,  $1 \times 10^{-7}$   $m^3/s$ , increasing the  $NO_x$  emission rate does not lead to increasing ozone concentration. At the same time, with a higher VOCs emission rate of  $1 \times 10^{-6}$   $m^3/s$ , maximum ozone concentration occurs when the  $NO_x$  emission rate is  $1 \times 10^{-7}$   $m^3/s$ . Hence, the ozone concentration inside street canyons is not a monotonic function of  $NO_x$  or VOCs emission rates. In fact, solely increasing either the  $NO_x$  or VOCs emission rates does not always lead to increasing ozone concentration. Instead, the ozone concentration may decrease under certain combinations.

In calm wind conditions, the ozone formation behaviors inside the street canyons exhibit similar trends for different street canyon aspect ratios. The street canyon of the smallest aspect ratio (equals 0.5) has the largest ventilation rate, where ozone concentration is lower than that of the other two street canyons of larger aspect ratios for all the emission rates tested. On the other hand, the ozone concentration inside the street canyon of aspect ratio 2.0 is higher than that of the other two, except when the VOCs emission rate is higher than a certain value. This finding is mainly attributed to the resident time of the chemical species inside the street canyon that affects directly the formation of secondary chemical species. The results support that the longer resident time of chemical species inside a narrower street canyon favors the chemical reaction between nitrogen dioxide and hydroxyl radical. Hence, a smaller VOCs emission rate is sufficient to activate the chemical mechanism for ozone formation at the same level of nitrogen oxides. Further increase in VOCs emission rate suppresses the ozone formation (VOCs-saturated) in the street canyon of aspect ratio 2.0, compared with that of aspect ratio 1.0. Under this circumstance, the oxidation of nitrogen dioxide is suppressed and eventually leads to the reduced ozone concentration.

The perfectly well-mixed condition is assumed in this chemistry box model. As such, the spatial inhomogeneity of ozone cannot be calculated. It is widely accepted that the air pollutant concentration on the leeward side is higher than that on the windward side of a street canyon. Hence, it is deduced that the ozone concentration would be higher on the leeward side due to the higher levels of primary air pollutants.

Figure 3 depicts the ozone concentration as a function

of the VOCs concentration to  $\text{NO}_x$  concentration ratio ( $C_{\text{VOCs}}/C_{\text{NO}_x}$ ). It is noteworthy that all the data points collapse on a single curve for  $C_{\text{VOCs}}/C_{\text{NO}_x} \leq 1$ . The street-level ozone concentration increases sharply (by one to almost three order of magnitudes) when  $C_{\text{VOCs}}/C_{\text{NO}_x}$  is in the range of 1 to 10. A broad maximum of ozone concentration extends to  $C_{\text{VOCs}}/C_{\text{NO}_x} \approx 100$ . For rarely high-level of  $\text{NO}_x$  emission at  $10^{-5} \text{ m}^3/\text{s}$ , the ozone concentration could be boosted to hundreds ppbv when  $C_{\text{VOCs}}/C_{\text{NO}_x} \approx 10$ . The ozone level decreases slightly thereafter with further increase in  $C_{\text{VOCs}}/C_{\text{NO}_x}$  ratios that signifies the VOCs-saturated chemical system. It is worth mentioning that, compared with other experimental and modeling findings in which the chemistry system begins VOCs-saturated and the ozone concentration begins to drop for  $C_{\text{VOCs}}/C_{\text{NO}_x}$  ratios greater than 10, the broad maximum of ozone concentration calculated by the current chemistry box model covers  $10 \leq C_{\text{VOCs}}/C_{\text{NO}_x} \leq 100$ . This unique finding in street canyon air pollution chemistry is mainly due to the limited ventilation. As shown in Fig.2, the peak ozone concentration shifts toward the right-hand side with increasing street canyon aspect ratio, i.e. the reduced air ventilation widens the coverage of the ozone maximum and delayed the VOCs-saturated conditions until the  $C_{\text{VOCs}}/C_{\text{NO}_x}$  ratio is greater than 100.

The above results indicate that high ozone concentration may occur when VOCs emission (concentration) is several to hundreds folds higher than  $\text{NO}_x$  emission (concentration). Under normal circumstances of a modernized city, the  $\text{NO}_x$  emission is normally higher than that of VOCs. Under this situation, the ozone formation potential may not be significant. However, in some cities/areas, such as

Hong Kong and Vietnam, that may have higher VOCs emission due to, for example, proximity of industrial estates or an increased number of gasoline vehicles and motor bikes, the potential increase in ozone formation may not be overlooked. In fact, the nitrogen oxides and VOCs sensitivity is an essential factor for an effective ozone abatement strategy at street-canyon environment.

### 3 Conclusions

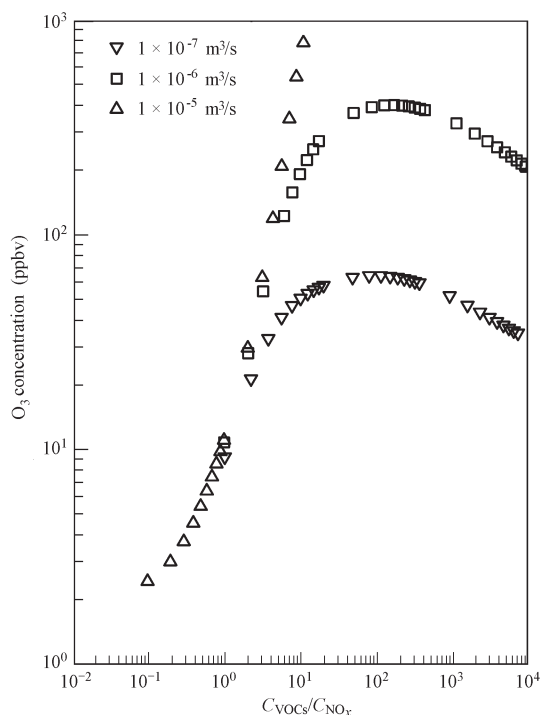
A chemistry box model is developed to account for the physical and chemical processes in hypothetical urban street canyons. It is shown that high pedestrian-level ozone concentration (greater than 100 ppbv) can be formed through photochemical reactions inside street canyons. The ozone concentration inside street canyons is a function of the VOCs emission rate (concentration) to the  $\text{NO}_x$  emission rate (concentration) ratio ( $C_{\text{VOCs}}/C_{\text{NO}_x}$ ). In the street-canyon configuration studied, the ozone level remains low (less than 10 ppbv) as long as the emission rate (concentration) of VOCs is less than that of  $\text{NO}_x$ . On the other hand, high ozone concentration inside street canyons would be experienced if the emission rate (concentration) of VOCs is about 10 to 100 times that of  $\text{NO}_x$ . This paper serves as a stepping stone for studying the ozone-formation characteristics inside street canyons, which are often neglected by researchers and control authorities. Further experimental testing is required to confirm the results, particularly in the range of  $0.1 \leq C_{\text{VOCs}}/C_{\text{NO}_x} \leq 10$ , where sharp increase in pedestrian-level ozone concentration occurs. Similar to controlling the ambient ozone concentration, the findings in this paper demonstrate that the VOCs emission rate (concentration) to the  $\text{NO}_x$  emission rate (concentration) ratio is a useful indicator for the development of ozone control strategy in pedestrian-level street canyon environment.

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**Fig. 3** Steady-state  $\text{O}_3$  concentration ( $C_{\text{O}_3}$ ) plotted as functions of the VOCs to  $\text{NO}_x$  concentration ratio ( $C_{\text{VOCs}}/C_{\text{NO}_x}$ ) inside a street canyon of aspect ratio 1.0 with roof-level wind speed at 0.1 m/s. Emission rates of  $\text{NO}_x$  are  $1 \times 10^{-7}$ ,  $1 \times 10^{-6}$ , and  $1 \times 10^{-5} \text{ m}^3/\text{s}$ .

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