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Coupling dynamics and chemistry in the air pollution modelling of street canyons: a review

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Abstract:

Air pollutants emitted from vehicles in street canyons may be reactive, undergoing mixing and chemical processing before escaping into the overlying atmosphere. The deterioration of air quality in street canyons occurs due to combined effects of proximate emission sources, dynamical processes (reduced dispersion) and chemical processes (evolution of reactive primary and formation of secondary pollutants). The coupling between dynamics and chemistry plays a major role in determining street canyon air quality, and numerical model approaches to represent this coupling are reviewed in this article. Dynamical processes can be represented by Computational Fluid Dynamics (CFD) techniques. The choice of CFD approach (mainly the Reynolds-Averaged Navier-Stokes (RANS) and Large-eddy Simulation (LES) models) depends on the computational cost, the accuracy required and hence the application. Simplified parameterisations of the overall integrated effect of dynamics in street canyons provide capability to handle relatively complex chemistry in practical applications. Chemical processes are represented by a chemical mechanism, which describes mathematically the chemical removal and formation of primary and secondary species. Coupling between these aspects needs to accommodate transport, dispersion and chemical reactions for reactive pollutants, especially fast chemical reactions with time scales comparable to or shorter than that of typical turbulent eddies inside the street canyon. Different approaches to dynamical and chemical coupling have varying strengths, costs and levels of accuracy, which must be considered

in their use for provision of reference information concerning urban canopy air pollution to stakeholders considering traffic and urban planning policies.

Capsule:

Coupling between dynamics and chemistry plays a major role in determining street canyon air quality. Different coupling approaches have varying strengths, costs and levels of accuracy.

Keywords: Air pollution; Street canyon; Computational Fluid Dynamics (CFD); Large-eddy simulation; Box model; Chemical mechanism.

1 Introduction

The terminology "street canyon" typically describes a restricted space in an urban area with surrounding buildings, usually along both sides of a street (Jeong and Andrews, 2002). In such an atmospheric compartment, natural air ventilation through dynamical processes is drastically constrained compared with open space (Cheng et al., 2008). Emissions from vehicles, such as nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs) and particulate matter (PM), are predominant among various anthropogenic pollutant sources inside street canyons in urbanised areas. Many such emitted species are reactive (Park et al., 2015), undergoing chemical processing within the street canyon to generate secondary pollutants such as ozone (O_3) and secondary aerosol. The deterioration of air quality in street canyons therefore occurs due to combined effects of the emissions source, dynamical processes (reduced dispersion) and chemical processes (evolution of reactive primary and secondary pollutants) (Li et al., 2008b). The urban canopy is the location in which the majority of outdoor activities of the urban population occurs, and hence where substantial human exposure results for pedestrians, road-users and occupants of adjacent buildings which may gain their ventilation from the outdoor (canyon) environment. Exposure to such environments causes adverse health effects (Solazzo et al., 2011). Since both the primary and secondary pollutants exhibit inhomogeneous distributions in urban street canyons and vary substantially in abundance with time, it is not an easy task to assess individual or population exposure to such air pollutants. The pedestrian level (breathing height) in street canyons is expected to experience particularly high levels of pollutants due to the proximity to vehicle emissions. Pollutant abundance within street canyons frequently far exceeds that in the wider urban background; in 2005, for example, measured data at the London Marylebone Road 'super-site' showed that NO_2 hourly concentrations exceeded the hourly objective for 853 times compared with 0 times at the nearby London Westminster urban background site (Bady et al.). Both short term exposure to high levels of pollutants and long term exposure to lower levels may cause adverse health impacts (WHO, 2000). Air quality objectives, specified for long term averages (hours, days or annual) may be inadequate to account for the exposure associated with the real nonlinear fluctuations in pollutant abundance in urban street canyons, with repeated aperiodic peaks present for short periods. Understanding both dynamic and chemical processes governing the abundance of reactive pollutants in street canyons is of vital importance to accurately quantify personal exposure, and to help urban planners develop policies (e.g. street canyon design and utility of green infrastructure) to mitigate such health impacts.

Various approaches have been undertaken to investigate air pollution in street canyons, such as field measurements, physical modelling, numerical modelling and parametric (operational) modelling. Field measurements can provide first-hand information on pollutant abundance (subject to the limitations of measurement technologies), air flow and pollutant dispersion, and can ground-truth models, but with some limitations (e.g. challenges to data interpretation, uncontrollable meteorological conditions, low spatial coverage, and typically high expense). Physical modelling (e.g. wind tunnels and water channels) only provides insight into dynamics; such approaches are able to fully control testing parameters and sampling points, and to provide well-documented datasets for the evaluation of numerical models. Due to scale limitations, it is a challenge for such models to replicate fully the large-scale atmospheric turbulence of the real world and hence to scale the nonlinear photochemical reactions with a wide range of time scales. Numerical modelling can provide high spatial and temporal distributions of flow and pollutant fields in street canyons, with increasing accuracy and precision compared with the available observations for validation. Such models can be repeated with controllable test parameters at relatively low economic expense. However, they normally require a high level of computational resource and may require substantial input information (computational domain, flow characteristics, chemical schemes). Parametric modelling can provide useful time-series information regarding pollutant abundance for regulatory applications, based on semi-empirical parameterisation of street canyons (and emissions). This approach is relatively simple to use and demands far less computational cost than numerical modelling. However, due to the inherent semi-empirical assumptions, parametric models are unable to reproduce the detailed distribution of the flow or pollutant fields in street canyons.

Recent reviews have provided an overview of specific individual aspects of urban street canyon dynamics or pollution or chemistry. Ahmad et al. (2005) reviewed wind tunnel experiments on wind flow and pollutant dispersion patterns in street canyons. Vardoulakis et al. (2003) examined a range of approaches (from measurements to modelling) for the study of air quality in street canyons, focussing upon measurements and parametric modelling approaches, with little discussion of computational fluid dynamics (CFD) modelling. Subsequently, Li et al. (2006) conducted a separate review on the CFD modelling of wind flow and pollutant transport in street canyons, focussing upon dynamical processes of pollutant dispersion within street canyons, rather than on the chemical processes. Yazid et al. (2014) reviewed a variety of studies (from measurements to modelling) addressing flow structure and pollutant dispersion to provide guidelines for urban planning strategies. While this study briefly considered chemical reactions, there is limited discussion on the coupling of dynamics and chemistry. With ongoing improvements of advanced computer technology, it has become feasible to apply detailed numerical modelling approaches to explore the coupling between dynamical and chemical processes involving pollutant dispersion and transformation in street canyons. The dynamics-chemistry coupling approach has increasingly been applied to the street-canyon scale (e.g. Kwak and Baik (2014) and Zhong et al. (2015)) , with a range of related, but distinct approaches, and associated advances in our understanding of urban street canyon pollutant abundance. It is in this new context that the present paper reviews progress in the development of coupling between dynamics and chemistry, as applied to street-canyon air pollution modelling, with a focus upon gas-phase processes.

2 Modelling dynamics in street canyons

Street canyon geometry is normally characterised by the aspect ratio, i.e. H/W (building-height-to-street-width, herein referred as to AR) and L/W (building-length-to-street-width). According to

Vardoulakis et al. (2003), street canyons might be classified into avenue $(AR \leq 0.5)$, regular $(0.5 < AR < 2)$ and deep $(AR \geq 2)$ street canyons or into short $(L/W \leq 3)$, medium $(3 < L/W < 7)$ and long street canyons $(L/W \geq 7)$. This classification is based on the geometrical detail of a street canyon, which may be empirically derived and widely used. When L is infinitely large, this corresponds to a two-dimensional (2D) street canyon; otherwise, a three-dimensional (3D) street canyon architecture must be considered and the value of L describes the distance between two street intersections. Flow patterns in street canyons under neutral meteorological conditions with perpendicular approaching wind can be classified into three main regimes (Oke, 1987): isolated roughness flow (IRF), wake interference flow (WIF) and skimming flow (SF). The IRF regime is related to widely spaced buildings ($AR < 0.3$). The WIF regime is associated with the closer spaced buildings ($0.3 < AR < 0.7$). The SF regime occurs in more tightly spaced buildings ($AR > 0.7$), representing the worst-case scenario for pollutant dispersion.

2.1 Numerical modelling

As a numerical modelling technique, CFD is a powerful tool to explore experimental flow problems, to characterise air pollutant transport and dispersion processes, and to provide a detailed distribution of canyon flow and pollutant dispersion with high spatial-temporal resolution (Chang, 2006). A CFD package may include a series of numerical governing equations for turbulent flow and pollutant dispersion, potentially involving the coupling of both dynamics and chemistry. The turbulence closure schemes for the CFD packages are classified into two categories: Reynolds-averaged Navier–Stokes (RANS) and Large-Eddy Simulation (LES). RANS resolves only the mean time-averaged properties with all the turbulence motions to be modelled. In place of the time-averaging used in RANS, LES adopts a spatial filtering operation and consequently resolves large-scale eddies directly and parameterises small-scale eddies using sub-grid scale (SGS) turbulence models. In this aspect, the RANS approach is easier to be established and computationally faster than LES. The atmospheric turbulent flow in and above street canyons involves turbulent eddies on a variety of scales (McNabola et al., 2009). The sizes of large-scale eddies are usually comparable to the characteristic length of atmospheric turbulent flow, and are dependent on the street canyon geometry and turbulent flow boundary conditions. Small-scale eddies typically have a universal behaviour throughout the computational domain and are more dependent on the local energy dissipation. Applications of RANS and LES in street-canyon dynamics are discussed below.

2.1.1 Reynolds-averaged Navier–Stokes (RANS)

RANS can determine the mean turbulent flow in a domain quickly and has been widely used in engineering applications. The most commonly used RANS turbulence models for the investigation of the urban canopy flow include the standard $k-\varepsilon$ (k is the turbulence kinetic energy and ε is the dissipation rate) model, the renormalised-group (RNG) $k-\varepsilon$ model, the realizable $k-\varepsilon$ model and the Reynolds Stress model (RSM). The $k-\varepsilon$ models are generally eddy-viscosity models and they solve k and ε from their respective transport equations. The turbulence viscosity (μ_t) is calculated from $\mu_t = \rho C_\mu \frac{k^2}{\varepsilon}$ (where C_μ is a modelling constant, ρ is the density), which are then used to parameterise the Reynolds stresses in the $k-\varepsilon$ models. However, in the RSM, it calculates Reynolds stresses explicitly based on their respective transport equations.

The standard $k-\varepsilon$ model is well documented and can perform well in reproducing general structure for fully turbulent flow (Tsai and Chen, 2004). However, for street-canyon flow, it does not predict turbulence kinetic energy with good accuracy in regions close to the walls or to the shear layer at the canyon roof level (Sini et al. (1996); Hassan and Crowther (1998); Baik and Kim (1999)). Smagorinsky (1963) evaluated the standard $k-\varepsilon$ model using a water channel experiment (Baik et al., 2000) and investigated the effect of inflow turbulence intensities (Kim and Baik, 2003) on the flow dispersion in the street canyon. The turbulence kinetic energy and diffusivity were found to increase with an increase in the inflow turbulence intensity. Solazzo et al. (2008) employed the standard $k-\varepsilon$ model to investigate the effect of traffic-induced turbulence. Compared to a wind tunnel experiment (Kastner-Klein et al., 2001), the model performed well in terms of predicting the turbulence kinetic energy and mean horizontal velocity, but showed limitations in reproducing the mean vertical velocity.

The RNG $k-\varepsilon$ model applies a rigorous statistical technique (i.e. the renormalisation group mathematical theory (Yakhot and Orszag, 1986)) to determine the effective turbulent viscosity and includes an additional source term in the ε equation to capture the interaction between turbulence dissipation and mean shear. This model has been successfully implemented in simulating the street canyon transitional flow. Memon et al. (2010) applied the RNG $k-\varepsilon$ model to 2D isolated street canyons considering heating situations. Compared with a wind tunnel experiment (Uehara et al., 2000), there was a good agreement for the normalised potential temperature. The model underestimated the normalised horizontal velocity at the canyon roof level (by 10%) because the effect of 3D city blocks and roughness elements in the experiment not being fully represented by the 2D model. Kim and Baik (2004) carried out a 3D CFD model simulation coupled with the RNG $k-\varepsilon$ model to examine the wind flow in street canyons. Although their model reproduced the flow separation by buildings and reversed flow, it underestimated the turbulence kinetic energy and wind velocity compared with a wind tunnel experiment (Brown et al., 2000). Chan et al. (2002) conducted a series of $k-\varepsilon$ model simulations to study the flow dispersion in a 2D isolated street canyon. Compared to wind tunnel experiments, the RNG $k-\varepsilon$ approach was found to be optimal. They attributed this to the analytically derived formula of turbulent viscosity in the RNG $k-\varepsilon$ model.

The realizable $k-\varepsilon$ model has an improved equation for ε considering vorticity fluctuation and uses a variable of C_μ (while a constant value is adopted in both the standard $k-\varepsilon$ model and the RNG $k-\varepsilon$ model) to derive the turbulence viscosity. This model provides better performance for flows involving separation, rotation, and recirculation. Tian et al. (2009) developed an idealised 3D model based on the realizable $k-\varepsilon$ model to investigate the flow dispersion around arrays of buildings. Their model reproduced the secondary oval vortices around the buildings and the air exchange between the inside and outside street canyons. Gromke and Blocken (2015) adopted the realizable $k-\varepsilon$ model to simulate the flow and dispersion in and above 3D street canyons with avenue-trees. Their study demonstrated the capability of the realizable $k-\varepsilon$ model to simulate the flow and turbulence involving trees.

The RSM explicitly calculates the individual Reynolds stresses (poorly represented by the $k-\varepsilon$ models). Thus in theory the RSM can perform better for complex flows (e.g. street canyon flow) than the $k-\varepsilon$ models. However, the RSM is more complex involving more terms with more uncertainties to be modelled and greater computational cost. Nazridoust and Ahmadi (2006) applied the RSM, the standard and RNG $k-\varepsilon$ models to study the airflow and pollutant dispersion in 2D street canyons. The RSM generally agreed better with wind tunnel experimental data for pollutant concentrations among the turbulence models used in their study. The standard $k-\varepsilon$ model and the RNG $k-\varepsilon$ model predicted similar results for pollutant concentrations, in alignment with the findings of Chang and Meroney (2001). Koutsourakis et al. (2012) evaluated the performance of the RSM, standard $k-\varepsilon$ model and RNG $k-\varepsilon$ model in simulating the street canyon flows using six experimental datasets (i.e. Baik et al. (2000), Hoydysh and Dabberdt (1988), Depaul and Sheih (1986), Kovar-Panskus et al. (2002), Sahm et al. (2002) and Li et al. (2008a). The model with the best performance could be any of the three turbulence models depending on the experimental dataset used (e.g. vertical and horizontal velocities, and pollutant concentrations). The RNG $k-\varepsilon$ model generally possesses the best performance and has an improvement compared with the standard $k-\varepsilon$ model. Although the RSM can reproduce better near-wall phenomena than $k-\varepsilon$ models, the RSM needs much more computational time and has more difficulty to achieve convergence. Due to high uncertainties in street canyon geometry and wind conditions for both models and experiments, consideration of only one experimental dataset was found to be insufficient when assessing the performance of a particular turbulent model.

2.1.2 Large-Eddy Simulation (LES)

Although RANS is computationally fast and extensively adopted, it suffers some limitations such as handling complex geometries involving separation (such as building blocks), near-wall treatment and the empirical model parameters. The LES approach performs better than RANS in terms of modelling accuracy for flow turbulence, but has greater computational cost. With recent advances in computer technology, LES is increasingly affordable as a promising tool to investigate turbulent mixing processes for research purposes. Salim et al. (2011a) claimed that LES could potentially serve as an alternative to experiment for prediction of street-canyon flow characteristics in urban planning. The most commonly used SGS turbulence models in the LES approach to investigate the urban canopy flow include the Smagorinsky SGS model, the dynamic Smagorinsky SGS model and the one-equation SGS model.

The Smagorinsky SGS model (Smagorinsky, 1963) is widely used because of its simplicity and numerical stability in the parameterisation of the SGS stresses assuming that the small scale energy production and dissipation are in equilibrium. This SGS model can simulate many flows with reasonable accuracy. Cui et al. (2004) developed an LES model (the Smagorinsky SGS model), based on the Regional Atmospheric Modelling System (RAMS) meteorological code, to investigate turbulent flow in and above a street canyon (AR=1). Their study provided a detailed analysis of the turbulent canyon flow structure as well as the contributions of ejection or sweep events near the roof level to the momentum flux between the canyon and the boundary layer aloft. In comparison with wind-tunnel experimental data, their results showed that the LES model underestimated the momentum flux, indicated by a weaker mean primary vortex inside the canyon than that measured. They attributed this to (i) the limited domain size (which may underestimate the turbulent intensity above the canyon) and (ii) the relatively coarse mesh size near roof level where a strong wind shear and associated instability were present. Cai et al. (2008) further adopted this LES model (the Smagorinsky SGS model) based on RAMS meteorological code (Cui et al., 2004) to simulate the transfer characteristics of passive scalars corresponding to area sources over the road surface, the upstream wall and the downstream wall, respectively, in a 2D street canyon. By comparing with wind-tunnel experimental data (i.e. Meroney et al. (1996) and Kastner-Klein and Plate (1999)), they demonstrated the LES model captured the main characteristics of canyon flow and scalar dispersion.

The dynamic Smagorinsky SGS model (Germano et al., 1991) adopts the dynamical procedure to diagnose a local value for the Smagorinsky constant (which is used as a constant value in the Smagorinsky SGS model) based on the information from resolved scales. This dynamic model performs better in terms of the flow in the vicinity of boundaries compared with the traditional and simple Smagorinsky SGS model. However, the dynamic procedure requires much more computational cost and may lead to numerical instability. Michioka et al. (2011) adopted an LES model (the dynamic Smagorinsky SGS model) to examine the flow and pollutant dispersion mechanism in a 2D street canyon (AR=1). Compared with wind-tunnel experiments, the LES model provided qualitatively correct predictions of the velocity statistics, with small discrepancies when the computational domain size was smaller. They also found that the accuracy of the LES model would be improved with an increase of the streamwise domain size, i.e. to more than 10 times the canyon height, as suggested by Kanda et al. (2004). Michioka and Sato (2012) investigated the effect of incoming turbulent structure on the pollutant removal from 2D idealised street canyons using the same LES model as that adopted by Michioka et al. (2011). Their study showed that the turbulence structure of external flow influenced significantly on the turbulence kinetic energy within the canyon and the momentum exchange at the canyon roof level, but less on the mean velocity within the canyon. Liu et al. (2005) employed an LES model (the dynamic Smagorinsky SGS model) to investigate air exchange rate (ACH) and pollutant exchange rate (PCH) in street canyons with different aspect ratios of 0.5, 1.0 and 2.0 based on the detailed LES database by Liu and Barth (2002) and Liu et al. (2004). The ACH (PCH) was the integration of the product of instantaneous fluctuating vertical velocity (and the instantaneous pollutant concentration) over the air exchange area at the canyon roof level. The transient turbulence properties at the roof level were well represented by the ACH and PCH. It was found that more pollutants were trapped inside the street canyon near the ground with an increase in canyon aspect ratio.

The one-equation SGS model (Schumann, 1975) solves an additional transport equation for the SGS turbulence kinetic energy conservation to account for the SGS motion. This model keeps track of the total energy in the SGS, which are not included by the Smagorinsky models. Cheng and Liu (2011) developed an LES model (the one-equation SGS model) to investigate the turbulent flow and pollutant removal in and above 2D street canyons (AR=1). In comparison with the model configuration of Cui et al. (2004) , their grid resolution was slightly coarser (by 30 %) in the streamwise direction, but their domain sizes were larger by factors of 3, 1.5 and 2.7 in the streamwise, spanwise and vertical directions, respectively. However, the simulated intensity of the mean primary vortex in the canyon was weaker than that of Cui et al. (2004), and they therefore concluded that increasing LES domain size cannot fully rectify the under-predicted intensity of mean primary vortex. This comparison indicated that well-resolved shear layers at the canyon roof level with high gradients of velocities may be required and worth thorough investigation, e.g. a stochastic backscatter model to increase the momentum transfer across the canyon roof level (O'Neill et al., 2015). Li et al. (2008b) and Li et al. (2009) adopted LES models (based on the one-equation SGS model) to handle the flow and pollutant dispersion for deep street canyons with high ARs up to 10. The multiple primary vortices inside those deep street canyons were well reproduced by their model.

2.1.3 Comparison of RANS and LES

Walton et al. (2002) and Walton and Cheng (2002) compared LES (the dynamic Smagorinsky SGS model) and RANS (the standard $k-\varepsilon$ model) with field measurements and found that the LES model provided the better agreement with measurements, possibly due to the more accurate prediction of the turbulent intensities of the flow. Cheng et al. (2003) showed that both LES (the dynamic Smagorinsky SGS model) and RANS (the standard $k-\varepsilon$ model) could predict the main features of the *mean* air flow over an array of urban buildings with reasonable accuracy although

LES performed better than RANS in terms of capturing the details of the flow within the urban canopy. They reported that the computational cost of LES was about 100 times that of RANS. Xie and Castro (2006) also found that although LES (the Smagorinsky SGS model) better captured turbulent flow around buildings than RANS (the $k-\varepsilon$ models and RSM), its computational cost was at least an order of magnitude greater than that of RANS. Santiago et al. (2010) and Dejoan et al. (2010) reported that the local mean flow quantities predicted by LES (the Smagorinsky SGS model) were closer to the Mock Urban Setting Test (MUST) data than that predicted by RANS (the standard $k-\varepsilon$ model). Tominaga and Stathopoulos (2011) applied both LES (the Smagorinsky SGS model) and RANS (the RNG $k-\varepsilon$ model) to simulation of flow dispersion in a street canyon (AR=1). LES was found to give better results than RANS compared with a wind tunnel experiment. The turbulence diffusion was well reproduced by LES, but underestimated by RANS. The performance in modelling turbulence diffusion by LES or RANS played an important role in the accuracy of pollutant dispersion predictions (Tominaga and Stathopoulos, 2010). Salim et al. (2011a) and Salim et al. (2011b) evaluated the performance of LES (the dynamic Smagorinsky SGS model) and RANS (the standard $k-\varepsilon$ model and RSM) for the prediction of flow dispersion in a street canyon (AR=1) with avenue-like trees. It was found that LES predicted significantly more accurate better flow dispersion than RANS. Compared to RANS, LES provided better representation of scenarios with trees since LES can capture intermittent and unsteady flow fluctuations. Chung and Liu (2013) compared LES (the one-equation SGS model) and RANS (the RNG $k-\varepsilon$ model adopted in Liu et al. (2011)) in the calculation of ACH and PCH. They found that the contributions of the turbulent components to ACH and PCH are much more in the LES than those in the RANS, highlighting the importance of turbulence in the transport and dispersion of flow and pollutants.

2.2 Simplified parameterisation

Although numerical modelling is able to capture temporally and spatically detailed information about dynamics in street canyons, it is still very complex and computationally expensive for many practical applications. Parametric modelling based on simple operational relationships between the street-canyon flow and dispersion conditions is an alternative tool, which is relatively simple and demands much less computational cost (Murena et al., 2009). Numerical modelling, in turn, can serve to better evaluate and provide algorithms for implementation within parametric modelling. Detailed applications of the parametric modelling are given in the review papers of Vardoulakis et al. (2007) and Kakosimos et al. (2010). Here, we focus on simplified parameterizations of dynamics in street canyons.

Turbulent exchange (transfer) between the street canyon and the overlying atmospheric boundary layer controls pollutant abundance in the street canyon (Barlow et al., 2004) and plays a uniquely important role in parametric modelling (Murena, 2012). This turbulent exchange can be represented by a simplified parameter called the ‘transfer velocity’ (Salizzoni et al., 2009) or ‘air ventilation rate’ (Liu and Leung, 2008), herein referred to as ‘exchange velocity’ (Bright et al., 2013), which may be defined in a bulk format through Fick’s law of diffusion: $F_c = w_e(C_{can} - C_B)$, where F_c is the pollutant flux per unit area at the roof level, w_e is the exchange velocity, and C_{can} and C_B are the pollutant concentrations inside the canyon and at the background boundary layer, respectively. A parameterisation of the exchange velocity can be derived from a more comprehensive model (e.g. RANS or LES) of a specific street-canyon flow (if considering the street canyon as a box), e.g. Liu et al. (2005); Bright et al. (2013). More practically in the STREET model (Johnson et al., 1973) and the Operational Street Pollution Model (OSPM) (Buckland, 1998), it is assumed that the exchange velocity is proportional to the characteristic velocity in the overlying boundary layer. However, the dependence of exchange velocity on the street-canyon flow can be very complex and influenced by many parameters. Murena et al. (2011) investigated the effects of the external wind speed on the exchange velocity and a nearly linear relationship between them was found. Salizzoni et al. (2011) found that the turbulent exchange was dependent on the coupling between the turbulence in the shear layer and turbulent eddies in the external atmospheric flow. Caton et al. (2003) showed that under lower external turbulence, the shear layer turbulence governed the exchange processes and a linear assumption between the exchange velocity and the external wind speed could be derived, but under higher external turbulence, the exchange processes were dominated by the external turbulence and depended upon both the turbulent structure of the incoming flow and that of the shear layer. Liu et al. (2011) and Solazzo and Britter (2007) investigated the effect of aspect ratio on the exchange velocity and also found a linear relationship for a given AR, but also a varying relationship between the exchange velocity and the external wind speed depending on the flow regimes involved.

Such simplified parameterisations of turbulent exchange between the street canyon and the overlying atmospheric boundary layer represents the overall integrated effect of the dynamics in street canyons, but necessarily fails to reproduce the flow field within street canyons. The introduction of ‘exchange velocity’ enables the application of parametric models (such as the box model approach) into street canyon modelling. A street canyon is considered as a single well-mixed (homogeneous) box, assuming that emissions into the box are mixed instantaneously and uniformly distributed. This simplified dynamical framework permits relatively complex chemistry to be afforded within street canyon modelling.

3 Chemistry for air pollution modelling

Modelling dynamics in street canyons, which determines the evolution and physical removal of atmospheric pollutants, is only one component of the coupling approach of dynamics and chemistry. The representation of atmospheric chemistry for air pollution modelling also plays an important role for reactive species. Considering the street-canyon scale (short distance from emissions sources to receptors), the time scale of pollutant transport is of the order of minutes and therefore chemical transformation processes of significance in street canyons are those which display comparable (or shorter) timescales. Thus, some pollutants (such as CO and many hydrocarbons), which are not significantly influenced by chemical transformation on the second-to-minute timescales, can be regarded as passive scalars (non-reactive species) in a street canyon context. However, this is not the case for short-lived pollutants (such as NO_2 and O_3) and highly reactive chemical species (such as hydroxyl radical (OH), hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2)). For such species, chemical reactions must be taken into account for the prediction of pollutant abundance in street canyons. A chemical mechanism describes mathematically the chemical processes in the atmosphere for the removal and formation of primary and secondary chemical species (Jimenez et al., 2003), as discussed below, with a focus upon gas-phase processes.

3.1 Simple NO_x-O_3 chemistry

The simple NO_x-O_3 chemistry (Smagorinsky, 1963) describes the photochemical reactions between NO, NO_2 and O_3. In the presence of sun light, NO_2 is rapidly photolysed leading to NO and O_3 formation ($NO_2 + hv \rightarrow NO + O$; $O + O_2 + M \rightarrow O_3 + M$; hv represents a solar photon; M denotes a third body molecule which absorbs excess energy so that O and O_2 may recombine to form O_3) and NO can also react quickly with O_3 to re-form NO_2 ($O_3 + NO \rightarrow NO_2 + O_2$). NO_x emitted from vehicles into the street canyon is predominantly in form of NO with a small (but in many environments increasing) fraction of NO_2. Within the urban environments, the NO_x-O_3 titration interaction with freshly emitted NO can result in a significant local sink for O_3 in street canyons, providing a reduction of O_3 level compared with the surrounding rural areas (or overlying canopy layer). On a city-wide basis, this effect is also called the "urban decrement" (Munir et al., 2013). Due to its simplicity, the simple daytime NO_x-O_3 system has been previously adopted in parametric modelling, e.g. OSPM (Berkowicz, 2000) and ADMS (McHugh et al., 1997). The incorporation of such simple chemistry into street canyon dynamics model can also be affordable especially for otherwise expensive LES approaches (e.g. Baker et al. (2004)).

3.2 Complex chemistry

The simple NO_x-O_3 chemistry only accounts for daytime NO_x-O_3 interactions, without consideration of other NO_y (reactive nitrogen oxides) species, nighttime processing, and the oxidation of VOCs. Therefore, more realistic chemistry involving detailed inorganic and VOCs reactions should be also considered for a comprehensive description of the urban atmosphere. Such representations may include the reactions of radical species (e.g. OH, HO_2 and RO_2) which may result in additional (non-O_3) conversion of NO to NO_2, and hence to net ozone / oxidant production, that cannot be captured by the simple NO_x-O_3 chemistry. There are a wide range of mechanisms (from near-explicit to substantially reduced mechanisms) with varying complexity considering both NO_x and VOCs chemistry which have been applied in street canyon studies, and which are briefly discussed below.

3.2.1 MCM

The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism, representing in detail the gas-phase tropospheric degradation of primary VOCs and formation of (gaseous) secondary pollutants (Jenkin et al., 1997). The MCM v1.0 consists of over 2,400 species and 7,100 reactions describing the degradation of 120 VOCs (Derwent et al., 1998). The MCM v2.0 updates the chemistry of aromatic hydrocarbons and includes 3,487 species and 10,763 reactions (Whitehouse et al., 2004). To improve the chemical degradation of aromatics (Jenkin et al., 2003), the MCM v3.0 was developed, containing 12,691 organic reactions for 4,351 organic species, and 46 inorganic reactions (Saunders et al., 2003). To promote the understanding of aromatic photo-oxidation (Bloss et al., 2005), MCM v3.0 was updated to MCM v3.1 (about 13,500 chemical reactions and 5,900 species (Pinho et al., 2007)) and MCM v3.2 (about 17,000 chemical reactions and 6,700 species (Jenkin et al., 2012)). The MCM has been evaluated against an extensive experimental database from photochemical reaction chambers and field campaigns. Due to its near-explicit nature, the MCM is principally employed within box models, and is usually considered too expensive for 3D grid-based air pollution models. For such applications, it is necessary to develop reduced chemical mechanisms which of an appropriate size, and yet which retain a quantitative description of the atmospheric chemistry. The MCM may also be considered as a reference or benchmark mechanism for developing and evaluating such reduced chemical mechanisms. Reduced techniques include lumping, sensitivity analysis and timescale analysis approaches (Neophytou et al., 2004). The lumping technique condenses several unique species into single ones (Makar and Polavarapu, 1997) and has been the most frequently employed approach to the reduction of chemical mechanisms. Three approaches are commonly used (Zaveri and Peters, 1999), i.e. surrogate species, lumped molecule (lumping VOCs into a series of categories according to similarity of oxidation reactivity) and lumped structure (lumping VOCs according to their chemical nature as reflected in their molecular structures). The sensitivity analysis technique, also called "iterative screening and structure analysis", uses chemical reaction and sensitivity analysis to identify sensitive or key species by calculating concentrations of some species as a function of others (Mauersberger, 2005). Timescale analysis removes fast-reacting "steady-state" species, replacing these with calculated values, by distinguishing between "fast" and "slow" chemical time scales using the quasi-steady-state approximation (Lovas et al., 2006).

3.2.2 CRI Mechanism

The Common Representative Intermediates (CRI) Mechanism is a reduced chemical mechanism with intermediate complexity. The CRI is derived from the reference benchmark mechanism (MCM v3.1) using a lumped structure technique (Jenkin et al., 2008) based on the assumption that the number of reactive bonds (i.e. C-C and C-H) represent the index of the photochemical ozone production potential of each VOC (Jenkin et al., 2002). Base on this simple index, a set of generic intermediates (each of which is a "common representative") can be derived. Significantly reduced from MCM v3.1, the resultant mechanism CRI v2 consists of 1,183 chemical reactions and 434 species, but is still too detailed to incorporate into most chemistry-dispersion models. To further simplify CRI v2, a set of reduced derivative mechanisms (CRI v2-R1, CRI v2-R2,CRI v2-R3,CRI v2-R4 and CRI v2-R5) have been developed (Watson et al., 2008). The final reduced mechanism (CRI v2-R5) contains 555 chemical reactions of 196 species (including 22 VOCs) and is a useful reference mechanism for air quality modelling, focusing upon ozone production. Bright et al. (2013) further reduced the CRI v2-R5 and developed a Reduced Chemcial Scheme (RCS) evaluated against the MCM, which includes 136 reactions of 51 species, for the application into an LES model at the street canyon scale.

3.2.3 CBM

The Carbon Bond Mechanism (CBM-IV) was developed based on the lumped-structure condensation approach for chemical reactions of VOCs with similar carbon bonds (C-CHO,C-C, C=C, etc.) (Gery et al., 1989). The CBM-IV contains 81 reactions of 33 species. These species are classified into four groups: explicit organic species, organic species (carbon surrogates), organic species (molecular surrogates), and inorganic species (no lumping). Several other versions were also developed. Heard et al. (1998) compared the CBM-IV with CBM-EX (including 204 reactions and 90 species) and the reduced CBM-LEEDS (including 59 reactions of 29 species). Based on CBM-IV, Zaveri and Peters (1999) developed an extended mechanism called CBM-Z (including 132 reactions and 52 species). CBM-IV is a popular lumped-structure mechanism but does not contain some of the long-lived species and peroxy radical interactions, and has a relatively crude isoprene mechanism. Due to its compactness, CBM-IV is an attractive chemical mechanism for air quality modelling at the street canyon scale (e.g. Garmory et al. (2009); Kwak and Baik (2012); Kwak et al. (2013); Kwak and Baik (2014)).

3.2.4 GEOS-Chem

GEOS-Chem (Eller et al., 2009) is a chemistry-transport model for simulating atmospheric composition in the troposphere at the global scale, using the Goddard Earth Observing System (GEOS) meteorological information (Abad et al., 2011). The chemical mechanism in the GEOS-Chem model contains over 300 reactions of 80 species with explicit chemical schemes for main anthropogenic hydrocarbons and isoprene (Bey et al., 2001). Ito et al. (2007) developed a GEOS-Chem Mechanism extension (GEOSito), which includes a 490 reaction scheme of 179 species accounting for a detailed representation of hydroxyl alkyl nitrates. The GEOS-Chem photochemical scheme has been successfully extended to the street canyon application in terms of representing key photochemical species (Kim et al., 2012). The transport time scale at the global scale is much longer than that at the street canyon scale. When the global chemical scheme is adopted in a street canyon, the chemical effect of those species with chemical time scales bigger than the canyon dynamical residence time scale becomes less significant.

3.2.5 Generalized VOCs and NO_x Mechanism

The Generalized VOCs and NO_x Mechanism (Seinfeld and Pandis, 1998) contains 20 chemical reactions of 23 species. Although this mechanism is far from comprehensive, it maintains the key features of the VOC-NO_x chemistry thereby providing the capablity to qualitatively analyze the formation of O_3 through the conversion of VOCs and NO_x. The simple nature of this VOC-NO_x mechanism allows it to be incorporated into most air pollution models. An early attempt to implement the VOCs and NO_x Mechanism into the street-canyon box modelling on the investigation of O_3 formation can be seen from Liu and Leung (2008). The chemical processing in a street canyon mainly involves the photochemistry of gas-phase species. The Generalized VOCs and NO_x Mechanism includes most of the key chemical processing and can be considered as a promising tool to investigate the chemistry focusing on the formation of O_3.

3.2.6 Other chemical mechanisms

There are a number of other chemical mechanisms which have been applied to air pollution modelling; although not widely used in the street canyon simulations to date, they have the potential for future development in such applications. A chemical mechanism is often developed and evaluated based on laboratory, smog chamber and field measurement data and involves a large amount of chemical species and reactions to represent chemical processes in the atmosphere (Dodge, 2000). There has been an enormous growth in the understanding and application of chemistry in air pollution modelling. The limitation of computational resources should be considered in the application of a chemical mechanism for modelling the atmospheric chemistry. For grid-based air quality models, there may be millions of grid cells and therefore millions of calculations for discretised differential equations are needed for each species, which requires much computational time and memory storage (Stockwell et al., 2012). Several other chemical mechanisms are briefly discussed below.

The MIM (Mainz Isoprene Mechanism) developed by Pöschl et al. (2000) is a reduced isoprene degradation scheme, using a lumped molecule technique based on the Master Chemical Mechanism. It includes 44 chemical reactions of 16 species, originally constructed for atmospheric modelling at the global scale. Taraborrelli et al. (2009) updated the MIM into the MIM2 to represent more intermediates. MIM2 includes 199 chemical reactions of 68 species and is suitable for air quality modelling at both regional and global scales. The SAPRC Mechanism (SAPRC-90) was developed by a research group at the (then) Statewide Air Pollution Research Center (Carter, 1990). SAPRC-90 (158 chemical reactions of 54 species) is a lumped molecule mechanism, in which lumped species and reactions are used to describe the degradation of organic compounds. An updated version (SAPRC-99), which includes 198 reactions and 72 species, was developed by Carter (2000b). The latest version of the SAPRC Mechanism (SAPRC-07) has a total of 339 reactions of 119 species (Carter, 2010), giving separate representation for 748 types of VOCs. The SAPRC mechanisms can be used to calculate ozone reactivity scales for VOCs and predict impacts of emissions on formation of secondary pollutants. The CACM (Caltech Atmospheric Chemistry Mechanism) is a lumped-structure mechanism including a total of 361 reactions of 191 species (Griffin et al., 2002). The inorganic chemical scheme in the CACM is based on the SAPRC99, while the primary VOCs are reduced by a lumped-structure technique. CACM contains a detailed chemical scheme to characterise ozone formation and formation of semi-volatile products. The RACM (Regional Atmospheric Chemistry Mechanism) (Stockwell et al., 1997) consists of 237 reactions of 77 species revised from the Regional Acid Deposition Model (RADM2) Mechanism (Stockwell et al., 1990). RACM is a lumped-molecule chemistry mechanism to describe atmospheric chemistry on a regional scale. RACM has been coupled online with the RAMS model (Arteta et al., 2006). RACM is capable of simulating both the lower and upper troposphere from rural to urban areas. The EMEP (European Monitoring and Evaluation Programme) mechanism is related to policy studies in Europe including 148 reactions of 79 species (Gross and Stockwell, 2003). The EMEP mechanism applies a lumped molecule technique to give representations of organic compounds with a series of species of similar structure and reactivity. The EMEP mechanism is highly aggregated, and is usually only applied within the atmospheric boundary layer.

3.3 Comparison of chemical mechanisms

Table 1 shows a comparison of chemical mechanisms varying in complexity from nearly-explicit to highly-simplified. Each of the complex mechanisms contains an "inorganic mechanism" considering O_x-HO_x-NO_x-CO chemistry (Emmerson and Evans, 2009), and an "organic mechanism" mainly considering the degradation of VOCs. In terms of the "inorganic mechanisms", there is not too much variability among different chemical mechanisms as these processes are (comparatively) well understood. The NO_x-O_3 chemistry is simply extracted from the "inorganic mechanism". For more complex chemical mechanisms, the main difference depends upon the condensation scheme that reduces the number of VOCs and reactions involved. In principle, any chemical mechanisms originally developed at different scales, from global to urban, could be applied to the study of atmospheric chemistry / air pollution in street canyons (such as RCS, GEOS-Chem, CBM-IV). However, the chemical processes represented by such mechanisms are inherently non-linear since the chemical timescales of some species are very short and others are rather long and may be variably appropriate for the typically very high NO_x levels of street canyon environment. The chemical processing varies rapidly for these species with different timescales. For species with chemical timescales comparable to the street canyon dynamical scale, the associated chemical processes are particularly important (Bright et al., 2013). Due to the limitation of computational resources, the chemical mechanism adopted in a street canyon air pollution modelling should be as simple as possible to be affordable, but represents the key features of fast photochemical reactions in the real atmosphere at the street canyon scale. The chemical non-linearity leads to a number of difficulties for efficient coupling of chemistry with dynamic models (particularly in the street canyon context whose concentrations close to the emission region may be very high), which is the focus of the next section of this review.

4 Coupling dynamics and chemistry

The coupling between dynamics and chemistry plays a major role in air pollution modelling within street canyons. Several attempts have been made to deal with both the dynamical and the chemical complexity. Most long lived traffic-related pollutants (e.g. CO and VOCs) are dependent almost exclusively on canyon dynamical processing, rather than chemical processing, due to their much longer chemical oxidation time scales compared with the canyon dynamical residence time scale. Therefore, many previous studies (e.g. Cai et al. (2008); Solazzo et al. (2011); Madalozzo et al. (2014)) have only taken passive scalars into consideration, a well-established approach avoiding complex chemical processing. More recently, studies have considered increasing chemical reactivity and complexity; those associated with the simple NO_x-O_3 chemistry and then complex chemistry involving the VOCs (shown as Table 2) will be discussed below.

4.1 Coupling with simple NO_x-O_3 chemistry

For relatively short-lived traffic-related pollutants (e.g. NO_2 and O_3), the assumption of non-reactivity is not appropriate because their chemical time scales are comparable to, or shorter than, the canyon dynamical time scale. The chemical processing of NO_x and O_3 can play a key role in determining the spatial variation of these species in street canyons. Therefore, simple NO_x-O_3 chemistry was incorporated into street canyon dynamics models.

The first implementation of this approach can be found in Baker et al. (2004). They introduced the NO_x-O_3 chemistry into an LES model (the Smagorinsky SGS model) based on the RAMS numerical code under neutral meteorological conditions and examined the dispersion and transport of chemically reactive pollutants (NO, NO_2 and O_3) inside a regular street canyon (AR=1). The distributions of pollutants exhibited significant spatial variations dominated by a primary vortex in the street canyon, also found by a previous field observation (Xie et al., 2003). The concept of the photostationary state (PSS) defect (defined as $d_{ps}(\%) = (k_1[O_3][NO]/J_{NO_2}[NO_2]-1)\times 100$, where J_{NO_2}, k_1 are rate constants and $[C_i]$ represents the concentration of i^{th} species) was introduced. The PSS defect calculations showed that the chemistry was close to equilibrium within the primary canyon vortex, but far from equilibrium at the canyon roof level and near traffic emissions where two air parcels with distinctively different chemical composition meet. The PSS defect was shown to be a useful measure of reactive mixing in and above a street canyon. Their study highlighted the impact of chemical processing in the street canyon context, providing a basis for the coupling of reactive species. However, only very limited chemistry was considered.

Grawe et al. (2007) extended the overall framework of Baker et al. (2004) to the investigation of the local shading effects of windward and leeward walls on the NO_2 and O_3 concentrations. This study found that kerbside NO_2 and O_3 levels exhibited over 6 ppb differences due to the presence of local shading and that the magnitude of concentration differences exhibited a near-linear relationship with the reduction of the NO_2 photolysis frequency in shaded regions. The shading geometry was found to influence the spatial pollutant distribution within the canyon, rather than the overall abundance. Their study indicated that such shading effects can be extremely significant in deep street canyons. Only the effect of solar radiation on the chemical reaction rate (i.e. the NO_2 photolysis frequency) rather than, for example, solar heating was investigated in this study.

Baik et al. (2007) carried out a RANS model simulation (the RNG $k-\varepsilon$ model) coupled with simple NO_x-O_3 chemistry to examine reactive pollutant dispersion within a street canyon (AR=1) with bottom heating. The reaction rate constant and photolysis frequency were temperature-dependent in this study (while constant values were used in Baker et al. (2004)). An oscillation of the primary vortex was found in the street canyon when bottom heating was introduced and this caused a significant variation in chemical species abundance. This study found that the averaged temperature, NO and NO_2 concentrations had the same trend of oscillation, but opposite in sign to that of the O_3 concentration. The main features of the PSS defect were found to be consistent with the results of Baker et al. (2004). A budget analysis showed that advection and diffusion terms were much larger than the chemical reaction term in determining the abundance of NO and NO_2, but comparable to each for O_3. This budget analysis provided useful insight into the impact of chemical vs. dynamical processing of each species on the overall distribution and the findings indicated that the distribution of O_3 was affected by the inhomogeneous temperature in street canyons through chemistry. Although this study considered the effect of heating on both the dynamical process (changing the flow pattern) and chemical process (temperature-dependent chemical reaction rates), it was restricted to a single street bottom heating scenario.

Kang et al. (2008) further investigated the effect of street bottom heating (varying the intensities of heating) on flow and reactive pollutant dispersion using the same framework as Baik et al. (2007). They found that the centre of the primary vortex varied with the street-bottom heating intensity and thereby led to a significant variation of chemical species abundance. The evolution of the canyon-averaged NO concentration under different heating intensities was found to have three types of patterns (i.e. quasi-steady, oscillatory and fluctuating). The canyon-averaged concentrations tend to decrease with an increase of the heating intensity. The effect of street bottom heating on the concentration of O_3 through the temperature-dependent chemical reaction rates increases with heating intensity, but overall this chemical processing influence was small. These findings demonstrated that canyon-averaged patterns were mainly due to the dynamics influence of street-bottom heating rather than the chemical influence. However, experimental data were not available for the evaluation of the pollutant concentrations in the heating scenario.

Tong and Leung (2012) developed a RANS model (the RNG $k-\varepsilon$ turbulence model) coupled with simple NO_x-O_3 photochemistry to examine the spatial characteristics of reactive pollutants and the level of chemical equilibrium in idealised street canyons with aspect ratios varying from 0.5 to 8 under different ambient wind speeds and diurnal heating scenarios. The performance of this street canyon model under bottom heating on flow and temperature fields was evaluated both experimentally (Uehara et al., 2000) and numerically (i.e. Kim and Baik (2001); Xie et al. (2006)

and Memon et al. (2010)), and a satisfactory agreement (for normalised potential temperature and horizontal velocity) was found. The entrainment of O_3 from the overlying background into the canyon was found to be highly dependent upon the wind speed and canyon aspect ratio. The PSS defects approached zero (reaching chemical equilibrium) more easily for the deeper street canyons. They also found that the diurnal heating scenario significantly affected the pollutant exchange between the canyon and overlying background through influences on vortex circulation and chemical reaction rates from thermal effects.

Kikumoto and Ooka (2012) investigated the characteristics of reactive pollutant dispersion within a regular street canyon (AR=1) by performing an LES model (the Smagorinsky SGS model) coupled with a single bimolecular chemical reaction ($O_3 + NO \rightarrow product$). Their study indicated that the canyon-integrated chemical reaction rate was dependent on both the product of the reactants' mean concentrations, and on the correlation of their concentration fluctuations, which could be derived from the LES model. RANS usually considers only the mean term and omits the correlation term (which could be up to 20 % of the mean term in their study). In this aspect, LES can perform better than RANS by including additional turbulent fluctuations. NO_x and O_3 had contrasting mechanisms of transport and the correlation between each reactant's concentration fluctuations strongly influenced the overall rate of chemical reaction between them, especially at the canyon roof level.

Zhong et al. (2015) adopted an LES model (the one-equation SGS model) coupled with simple NO_x-O_3 photochemistry to examine the dispersion and transport of atmospheric pollutants in a deep urban street canyon (AR=2). The ozone production rate inferred from NO_x-O_3 non-equilibrium was found to be negative within the canyon, pointing to a systematic negative offset to ozone production rates inferred by analogous field measurement approaches in environments with incomplete mixing. This metric could serve to investigate the interplay of dynamics and chemistry in street canyons. Reactive pollutants exhibited significant spatial variation caused by the two unsteady vortices present, agreeing reasonably well with a water channel experiment (Li et al., 2008c). The deviation of species abundance from chemical equilibrium for the upper vortex was found to be greater than that for the lower vortex. An alternative, simplified two-box model was developed based on the existence of two vortices, assuming that the deep street canyon can be described by two individual well-mixed boxes with exchange between them. This two-box model can capture the significant contrasts in the concentration of species inside both the lower and upper canyon vortices as predicted by the LES simulation. However, this model only considered simple chemistry under neutral meteorological conditions with constant (no temperature or radiation dependence) reaction rates.

4.2 Coupling with complex chemistry

Very fast-reacting chemical species (e.g. OH, HO_2) play an important role in driving the chemical cycle of VOC degradation (O_3 precursors) leading to the additional peroxy-radical mediated conversion of NO to NO_2 (which is not represented by the simple NO_x-O_3 chemistry) and hence O_3 formation. These species, with chemical lifetimes of seconds, are primarily governed by local chemical processing and their abundance varies substantially within street canyons. Complex chemical mechanisms considering both NO_x and VOCs chemistry were therefore incorporated into canyon dynamical models.

Liu and Leung (2008) implemented a one-box chemistry model using the generalized VOCs and NO_x mechanism (Seinfeld and Pandis, 1998) to couple the dynamics and chemistry in street canyons (AR=0.5, 1, 2). Air ventilation rates were derived from LES models for different ARs (Liu et al., 2005). They found that the O_3 concentration within street canyons was dependent upon both the VOCs and NO_x emission rates. When the ratio of VOCs to NO_x emission rates was higher than 10, the O_3 concentration could reach up to the order of 100 ppb. The emission ratio of VOCs and NO_x could therefore be a useful indicator for the increase in O_3 levels in street canyons. Because their study treated the whole canyon as one well-mixed box for all ARs, the model was unable to reproduce the significant contrasts of pollutant concentration between the lower and upper canyon which are observed experimentally.

Garmory et al. (2009) employed the Stochastic Field method to characterise turbulent reacting flow for an investigation of the transport and dispersion of reactive scalars within a street canyon (AR=1.2) adopting both simple NO_x-O_3 chemistry and the CBM-IV mechanism. The flow field was based on the standard $k-\varepsilon$ model. The Stochastic Field method can be incorporated into the RANS model and captures both the means and variances of pollutant abundance together with consideration of segregation effects on overall reaction rates. This statistical information could not be obtained from traditional RANS models. The variance of reactive pollutants was found to be very high - of the order of the mean values at the canyon roof level (with strong mixing). They found that for both mechanisms, there were similar predictions and no significant segregation effect (the fluctuation from the mean in their study) for most major species (e.g. NO, NO_2 and O_3). However, for some fast reacting chemical species (e.g. OH, HO_2 etc.), there were significant segregation effects.

Kim et al. (2012) adopted the RNG $k-\varepsilon$ turbulence (RANS) model coupled with both simple NO_x-O_3 chemistry and the GEOS-Chem photochemical scheme to investigate transport and dispersion of reactive pollutants within a street canyon (AR=1). An online photolysis rate calculation module was applied to account for the surface heating effect of diurnal solar radiation on the photolysis rate coefficients. The NO concentrations predicted from simple NO_x-O_3 chemistry had a difference up to 100 ppb (i.e. the relative error was about 20%~30%) compared to those of Baker et al. (2004). They attributed this discrepancy to the different turbulence models, RANS in this study and LES in Baker et al. (2004). Compared with field measurements, the model over-predicted the NO concentration by a factor of 3. This big relative error in NO concentration was expected to decrease as NO_x emissions became lower. There was an evidence of a significant difference in predicted O_3 concentration between complex photochemistry and the simple NO_x-O_3 chemistry, indicating the importance of additional formation of O_3 through VOC oxidation processes. This study highlighted the importance of photochemistry in controlling the concentration of oxidation products (e.g. NO_2 and O_3) within street canyons.

Kwak and Baik (2012) employed the RNG $k-\varepsilon$ turbulence (RANS) model coupled with the CBM-IV mechanism to explore reactive pollutant dispersion within idealised street canyons (AR=1) and to investigate O_3 sensitivity to NO_x and VOCs emissions. According to the dispersion characteristics of NO, NO_2 and O_3 in the simple NO_x-O_3 chemistry model, the dispersion of species in this simulation were identified and classified into three types, denoted by NO-type, NO_2-type and O_3-type, with maximum concentrations near the bottom of the street canyon, close to the centre of the street canyon, and above the street canyon, respectively. The dispersion type of a reactive species was found to be dependent upon the ratio of VOCs to NO_x emission rates. Their study showed that the OH concentration increased with an increase in the VOCs to NO_x emission ratio, indicating an important role for OH in determining the dispersion type. The O_3 concentration was found to be negatively correlated with NO_x emissions but weakly correlated with VOCs emissions. This was possibly due to the high NO-to-NO_2 ratio in the street canyon, where the NO titration of O_3 was more pronounced compared to NO_2 photolysis. Their study provided a good understanding of the dispersion characteristics of reactive species and the O_3 sensitivity to a range of NO_x and VOCs emission scenarios for the street canyon.

Kwak et al. (2013) implemented the same RANS model and chemical mechanism as those adopted by Kwak and Baik (2012), but focusing on the photochemical evolution of reactive species within street canyons (AR=1,2). The concept of photochemical ages (defined as the time-integrated exposures of an air parcel to O_3 and OH respectively) was introduced to represent the O_3 and OH oxidation processes, and normalised by their respective background ages. The normalised photochemical ages, ranging from 0 (emission characteristics) to 1 (background characteristics), had the advantage of avoiding the uncertainty of calculating the averaged O_3 and OH concentrations individually. They found that both O_3 and OH oxidation processes were of importance for the photochemistry at the canyon-scale. Overall, O_3 was chemically reduced in the lower part, but chemically produced in the upper part of the deep street canyon (AR=2). This interesting finding indicated that O_3 was not always chemically reduced in a street canyon. From a sensitivity analysis, the concentration of O_3 was found to be weakly sensitive to the wind speed. An increase of O_3 concentration was found with an increase in the ratio of VOCs to NO_x emissions, consistent with Liu and Leung (2008). This finding implied that the O_3 concentration was more sensitive to changes of emissions than to changes in dynamics. In terms of characterizing O_3 and OH chemical processing, the photochemical age concept was applicable to characterise the photochemistry at the street-canyon scale, and could potentially be extended to the neighbourhood scale.

Bright et al. (2013) employed an LES model (the Smagorinsky SGS model) coupled with a Reduced Chemcial Scheme (RCS) and the simple NO_x-O_3 photochemistry to investigate the effects of mixing and chemcial processing on the atmospheric composition in a urban street canyon (AR=1). A one-box chemistry model was also adopted for the comparison with the LES coupled chemistry model to assese the effect of dynamic and chemical processing. The LES coupled chemistry model was found to underestimate the concentration of NO_x, OH and HO_2, but overestimate the concentration of O_3 averaged over the whole canyon compared to the one-box chemistry model. The segregation effect caused by the incomplete mixing was found to reduce the overall canyon-averaged reaction rate and be responsible for the spatial inhomogeneity of reactive species. It was shown that the RCS scheme predicted higher levels of NO_2 and O_3, but a lower level of NO compared with the simple NO_x-O_3 photochemistry. This can be explained by the additional NO to NO_2 conversion through VOCs oxidation chemistry present in the RCS. Their study provided a better understanding of the atmospheric “pre-processing” of emissions from the street canyon prior to release to the wider overlying background.

Kwak and Baik (2014) adopted the RNG $k-\varepsilon$ turbulence (RANS) model coupled with the CBM-IV mechanism to examine the removal and entrainment of reactive pollutants at the canyon roof level via the diurnal variation in NO_x and O_3 exchange between the 2D street canyon (AR=1) and the overlying background air. In the morning, two conter-rotating vortices were found in the street canyon because the heating of downwind wall was stronger than that of upwind wall. Therefore, the NO_x and O_3 exchange was found to be dominated by turbulent flow. However, in the afternoon, only one intensified primary vortex was found because heating of the downwind wall was lower than that of the upwind wall. The turbulent flow became comparable to the mean flow in terms of the NO_x and O_3 exchange. Their findings indicated that the exchange veloctities were strongly dependent on both the flow pattern induced by surface heating and the photochemistry in the street canyons (Bright et al., 2013).

Zhong et al. (2014) implemented photochemical box models to investigate the segregation effects of heterogeneous emissions on O_3 levels in idealised urban street canyons and evaluate the associated uncertainty when grid-averaged emissions were adopted. The chemical mechanism applied was the RCS developed by Bright et al. (2013). Chemical effects arising from the heterogeneity of emissions and dynamic effects represented by the exchange velocity (derived from CFD models) between the canyon and the overlying background on the O_3 levels were extensively investigated. The O_3 levels within street canyons were found to be strongly linked to the segregation of spatially varying emissions and to be balanced by both chemistry and dynamics. Their study indentified a straightforward approach to consider the effects of both chemistry and dynamics using box models with a wide range of emission scenarios. However, this study was restricted to two boxes representing two idealised street canyons (totally segregated) with emission heterogeneity.

Park et al. (2015) implemented the RNG $k-\varepsilon$ turbulence (RANS) model coupled with the GEOS-Chem photochemical scheme (also used in the study by Kim et al. (2012)) to investigate the effect of canyon aspect ratio on pollutant dispersion in street canyons. One vortex was observed for canyons with $1 \le AR \le 1.6$, while two vortices were found for canyons where $1.6 < AR \le 2$. At the street bottom, there was a significant contrast in the flow pattern between those two types of canyons. For cases with a low ratio of VOCs to NO_x emission, the O_3 concentrations in street canyons were much lower than those in the overlying background. This was attributed to the titration of O_3 by high levels of NO. For cases with higher ratio of VOCs to NO_x emission, O_3 in the lower canyon was slightly titrated by NO, but in the upper canyon O_3 was formed by NO_2

photolysis following VOCs oxidation processes. The ratio of VOCs to NO_x emission was an important indicator in determining the street-level O_3 concentration.

Simple NO_x-O_3 chemistry plays an important role in the street canyon chemistry. The NO_x-O_3 photostationary state defect is a useful measure of reacting mixing in the street canyon environment (Baker et al., 2004). Due to its simple nature, simple NO_x-O_3 chemistry can easily be coupled with either LES or RANS models. Complex chemical mechanisms involve detailed VOCs oxidation reactions driven by fast radicals (e.g. OH and HO_2), leading to additional NO to NO_2 conversion (non-O_3). In this sense, complex chemical mechanisms are more realistic than simple NO_x-O_3 chemistry. However, due to large amounts of chemical reactions and species, more efforts need to be spent when incorporating a complex chemical mechanism into numerical models. LES models perform better in terms of the turbulent mixing of pollutants within street canyons, but require much more computational cost than RANS. LES can be used to investigate the detailed mechanism of pollutant dispersion and transport (e.g. Baker et al. (2004); Kikumoto and Ooka (2012); Bright et al. (2013); Zhong et al. (2015)), with higher (e.g. for NO_x) or lower (e.g. for O_3, OH and HO_2) concentrations in the canyon than those at the overlying background. RANS provides the capability to run quickly for a few scenarios, such as varying intensities of street heating ambient wind speeds, canyon aspect ratios and emissions (e.g. Kang et al. (2008); Tong and Leung (2012); Kwak and Baik (2012); Kwak et al. (2013); Park et al. (2015)). With simplified parameterisation of street canyon air ventilation, box models can be run very quickly for a series of wind conditions and emission scenarios (e.g. Liu and Leung (2008); Zhong et al. (2014)) so that complex chemical mechanisms are affordable for street canyon chemistry modelling.

5 Modelling concerns

5.1 Street canyon geometry

Street canyon geometry plays an important role in determining the flow patterns and pollutant dispersion within street canyons. The AR (aspect ratio) influences the number of primary re-circulations formed inside a street canyon and the higher the AR is, the larger the number of primary re-circulations will be. A single primary vortex is formed within regular street canyons (e.g. Baker et al. (2004)) and multiply primary vortices are formed within deep street canyons (e.g. Li et al. (2009); Murena (2012); Zhong et al. (2015)). The vortices formed in street canyons influence pollutant dispersion behaviour and air ventilation. There is evidence that higher concentrations of pollutants are found in street canyons with higher aspect ratios. Liu et al. (2004) showed that the percentages of pollutants residing inside street canyons (compared to the total pollutants in the computational domain) with aspect ratios of 0.5, 1.0 and 2.0 were about 95%, 97% and 99%, respectively. Li et al. (2009) found that there was a higher pollutant accumulation at the ground level in the street canyon with AR=5 compared with that with AR=3. This could be driven by the very low wind speed at ground level, which slowed the dispersion of ground-level pollutant. This finding was consistent with field measurements in a deep street canyon with AR=5.7 (Murena and Favale (2007); Murena et al. (2008)), which showed that the concentration at pedestrian level in the deep street canyon could be up to three times that in a regular street canyon with AR=1. The shape of the roofs also influences the turbulence at the canyon roof level and hence the dispersion of pollutants. Pitched roofs are expected to induce more energetic eddies and have more turbulent exchange of pollutants at the canyon roof level than flat roofs (Louka et al., 2000).

5.2 Meteorological conditions

Meteorological conditions (e.g. ambient wind and solar radiation) significantly affect the flow and dispersion of reactive pollutants in street canyons. The ambient wind speed plays an important role in the formation and intensity of primary vortices thereby determining pollutant retention time in the canyon, while its direction influences the number and shape of such vortices (Baik et al., 2003). Nazridoust and Ahmadi (2006) showed that turbulence intensity within street canyon increased with the ambient wind speed. As pollutant dispersion is strongly dependent on the turbulence in the street canyon, higher wind speeds lead to stronger street-canyon turbulent flow and thereby making it more effective for pollutants to be removed from the street canyon. This behaviour was also found by Huang et al. (2000). Small secondary vortices were formed at the corner of the street canyon under low wind speed conditions, but would disappear under higher wind speed conditions. Michioka and Sato (2012) examined the effect of incoming turbulent structure on the canyon flow and pollutant dispersion. The pollutant concentration in the street canyon decreased with an increase in the incoming turbulent intensity. Changes in ambient wind direction significantly affected the recirculation pattern in the canyon (Soulhac et al. (2008); Soulhac and Salizzoni (2010); Blackman et al. (2015)) and thereby influenced pollutant dispersion. Pollutant dispersion was more effective for an oblique flow than a perpendicular flow, as found in field measurements by Kumar et al. (2008). In the presence of solar radiation, surfaces of the ground and buildings are heated, which will influence the atmospheric stability and (to an extent) the chemical reaction rate constants (e.g. Baik et al. (2007)). The flow field and pollutant dispersion in street canyons can be significantly affected by additional thermally induced vortices. The combination of mechanically induced vortices (from wind) and the thermally induced vortices (from heating) adds further complexity (Xie et al., 2005). Cai (2012a) and Cai (2012b) identified two characteristic heating scenarios in a street canyon: the assisting case (both roof and upwind wall heating) and the opposing case (both roof and downwind wall heating) depending on the direction of the thermal-driven flow in relation to the wind-driven circulation. Li et al. (2012) investigated the effect of ground heating on flow and pollutant dispersion in street canyons with AR=0.5,1, and 2, and found that the flow and pollutant patterns underwent significant changes. In general, ground heating enhanced the mixing of pollutants in street canyons.

5.3 Emissions

Traffic is considered to be the major source of emissions in urban street canyons. Vehicle emissions can be derived based on traffic information and the emission factors of each class of vehicle. Typically, traffic information contains vehicle fleet composition, average speeds and traffic volumes. For roads equipped with automatic traffic counts, this traffic information can be easily obtained. The emission rates for each emitted pollutant (e.g. CO, VOCs, NO_x) can serve as the input for air pollution modelling (Boddy et al., 2005). Xie et al. (2009) compared a series of measured data for the CO concentration and the traffic volumes under the same wind direction and a linear relationship between them was found, as CO is a relatively inert chemical species (on the canyon timescale). The NO_2/NO_x emission ratio by volume from vehicles has typically been applied as 1/11 (e.g. Baker et al. (2004)) or 1/10 (e.g. Bright et al. (2013)), reflecting that the fraction of directly emitted NO_2 was much lower than that of NO from vehicles, making the production of NO_2 through the NO titration reaction more important. However, there is evidence of recent increases in NO_2/NO_x emission ratios, up to about 25 % (Carslaw and Rhys-Tyler, 2013). The O_3 concentration within street canyons is dependent upon both VOCs and NO_x emission rates. O_3 was found to be more sensitive to changes in emissions rather than to changes in dynamics. The anticipated trend over 2005-2020 in VOCs to NO_x emission rates, based upon scenarios of UK fleet composition projections (NAEI, 2003) and UK Road Vehicle Emission Factors (Boulter et al., 2009) suggested that although both VOCs to NO_x emissions have (and are expected to) generally decrease with time, the O_3 concentration in street canyons will have slightly increased due to these effects - although other changes (e.g. in background ozone) may dominate the absolute observed levels / trends. Finally, it is important to note that real-world emissions may vary substantially from both vehicle type-approval data, and from inventory values - e.g. Grimmond et al. (1998).

5.4 Chemical transformation of pollutants

Emissions from vehicles may be reactive, changing dramatically the chemical composition of the atmosphere in street canyon environments. Such emissions undergo chemical transformation to varying extents within the recirculation driven by the canyon flow before their escape into the overlying atmosphere. Such chemical transformations can occur on a wide range of timescales, posing difficulty for computationally efficiently handling of chemical processes when these must be coupled with dynamics at the street canyon scale. The choice of chemical mechanism employed must be considered depending on the complexity of chemistry involved, and the application. For street canyon modelling, numerical issues arise because the governing equation systems are highly nonlinear, and extremely stiff (Verwer and Simpson, 1995) especially when highly reactive species (such as OH and HO_2) are considered alongside longer-lived VOCs. If diurnal heat (temperature) effects on the chemistry are included, extra complexity arises since most reaction rates and (to a lesser extent) photolysis frequencies are influenced by changes in temperature (Kim et al., 2012). Particular attention should be paid to the handling of fast-reacting species, e.g. applying a sufficiently short integration time interval (Bright et al., 2013). Also, in the regions close to the emisison source and to the shear layer (which must be well-resolved), negative values of concentrations may occur in numerical simulations, due to the presence of high concentration gradients, which in addition to being implausible affect the stability of the stiff chemical system (Alexandrov et al., 1997). Such negative concentrations indicate unsatisfactory convergence or insufficiently short integration timescales.

6 Conclusions

This article presents a review of air pollution modelling within street canyons, focusing on the coupling of dynamics and chemistry. For dynamics, the CFD technique has become a powerful numerical tool, mainly including the RANS and LES models. RANS models are, by their nature, a steady-state methodology while LES models can handle the unsteadiness and intermittency of the canyon flow and retrieve transient structures of turbulence in street canyons. The choice between approaches depends on the computational cost, the accuracy required and hence the application. A parameter (i.e. 'exchange velocity') representing the overall integrated effect of dynamics in street canyons provides capablity to handle relatively complex chemistry in practical applications. The representation of the chemistry (i.e. the chemical mechanism) for air pollution modelling is also an important component for this coupling approach. For short-lived traffic-related pollutants (e.g. NO_2 and O_3), chemical time scales are comparable to the canyon dynamic time scale. The chemical processing of NO_x and O_3 can play a key role in determining the spatial variation of these species in street canyons. Simple NO_x-O_3 chemistry only accounts for the O_3 chemistry changes driven by

NO_x, without consideration of VOCs processing. More complex chemistry involving VOCs (resulting in the additional conversion of NO to NO_2 that cannot be represented by simple NO_x-O_3 chemistry) should be considered for application to the real urban atmosphere. A wide range of chemical mechanisms with varying complexity considering both NO_x and VOCs chemistry can potentially be adopted in street canyon simulations. A variety of factors should be considered such as street canyon geometry, meteorological conditions, emissions and chemical transformation of pollutants. Modelling air pollution within a street canyon requires state-of-the-art dynamic models coupled with high-quality chemical mechanisms to simulate the concentrations and spatial patterns of key atmospheric chemical species, providing reference information regarding air quality inside street canyons for policy-makers in support of decision making for traffic policy and urban planning.

Future directions in this area could be: 1) Development of a widely accepted procedure for representation of street-canyon dynamics; 2) Clear guidance as to the level of detail of photochemistry required for different street canyon applications, and the consequences for systematic over/under-prediction of reactive species abundance arising from this; 3) Application of RANS models coupled with complex chemical mechanisms focusing on a variety of factors for practical application; 4) Application of Large Eddy Simulations (LES) coupled with complex chemical mechanisms focusing on the detailed interaction of dynamic and chemical processing in street canyons; 5) Box models with more comprehensive / complex chemical mechanisms focusing on the testing of simplified dynamic parameters (e.g. exchange velocities), in particular to allow efficient exploration of chemical emission scenarios; 6) Thermal effects (e.g. caused by solar radiation) on both dynamics and chemical processing; 7) Effects of more complex urban configurations (e.g. intersections, irregular buildings, parking spaces and trees) on both the dynamics and the associated chemical processing; 8) Near-field evolution of traffic-derived particulate matter, including both chemical and physical (e.g. evaporation, condensation) effects; 9) CFD-chemistry modelling coupled with mesoscale meteorological and chemistry-transport models for the investigation of reactive pollutant dispersion in urban areas (Kwak et al., 2015).

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Table 1 Comparison of chemical mechanisms for air quality modelling

Full name of chemical mechanisms	Reduction type	Reference	Versions	Reaction NO.	Species NO.	Applied scale
Master Chemical Mechanisms	Near-explicit	Derwent et al. (1998)	MCM v1.0	>7,100	>2,400	Troposphere
		Whitehouse et al. (2004)	MCM v2.0	10,763	3,487	
		Saunders et al. (2003)	MCM v3.0	12,737	>4351	
		Pinho et al. (2007)	MCM v3.1	~13,500	~5,900	
		Jenkin et al. (2012)	MCM v3.2	~17,000	~6,700	
Common Representative	LM	Jenkin et al. (2008)	CRI v2	1183	434	Troposphere
Intermediates Mechanism		Watson et al. (2008)	CRI v2-R1	1012	373	
			CRI v2-R2	988	352	
			CRI v2-R3	882	296	
			CRI v2-R4	643	219	
			CRI v2-R5	555	196	
		Bright et al. (2013)	RCS	136	51	Urban
Carbon Bond Mechanism	LS	Gery et al. (1989)	CBM-IV	81	33	Urban/Regional
		Heard et al. (1998)	CBM-EX	204	90	
		Heard et al. (1998)	CBM-LEEDS	59	29	
		Zaveri and Peters (1999)	CBM-Z	132	52	
Goddard Earth	/	Eller et al. (2009)	GEOS-Chem	300	80	Global

Observing System-Chemistry		Ito et al. (2007)	GEOSito	490	179	
Generalized VOCs and NO_x Mechanism	/	(Seinfeld and Pandis, 1998)	/	20	23	Urban
Mainz Isoprene Mechanism	LM	Pöschl et al. (2000)	MIM	44	16	Regional/Global
		Taraborrelli et al. (2009)	MIM2	199	68	
Statewide Air Pollution Research Center	LM	Carter (1990)	SAPRC-90	158	54	Urban
		Carter (2000b)	SAPRC-99	198	72	
		Carter (2010)	SAPRC-07	339	119	
Caltech Atmospheric Chemistry Mechanism	LS	Griffin et al. (2002)	CACM	361	191	Urban
Regional Atmospheric Chemistry Mechanism	LM	Stockwell et al. (1997)	RACM	237	77	Regional
	LM	Stockwell et al. (1990)	RADM2	158	63	
European Monitoring and Evaluation Programme	LM	Gross and Stockwell (2003)	EMEP	148	79	Regional
NO_x-O_3 chemistry	/	Smagorinsky (1963)	/	3	5	Urban

Note: LS denotes the lumped structure reduction technique. LM denotes the lumped molecule reduction technique.

Table 2 Comparison of selected studies coupling dynamics and chemistry in street canyons

Reference	Research model	AR (H/W)	Vortex No.	Chemical mechanism	Remarks
Baker et al. (2004)	LES	1	1	NO_x-O_3 chemistry	*Significant spatial variations of NOx and O_3 *Introduction of the photostationary state defect
Grawe et al. (2007)	LES	1	1	NO_x-O_3 chemistry	*Shading effect *A near-linear relationship between concentration differences and the reduction of the NO_2 photolysis rate
Baik et al. (2007)	RANS	1	1	NO_x-O_3 chemistry	*Street bottom heating scenario *Budget analysis of the advection, diffusion and chemical reaction term
Kang et al. (2008)	RANS	1	1	NO_x-O_3 chemistry	* Varying the intensities of street bottom heating *Significant change in pattern of the flow and pollutant dispersion
Tong and Leung (2012)	RANS	0.5-8	Varying	NO_x-O_3 chemistry	* Different diurnal heating scenarios * Varying canyon aspect ratios
Kikumoto and Ooka (2012)	LES	1	1	NO_x-O_3 chemistry	* Contrasting transport mechanism for NO_x and O_3 * Correlation of concentration fluctuations
Zhong et al. (2015)	LES	2	2	NO_x-O_3 chemistry	*Two-box model *Inferred O_3 production rates
Liu and Leung (2008)	Box model	0.5,1, 2	Box	Generalized VOCs-NO_x mechanism	* O_3 sensitivity to the NO_x and VOCs emissions * One-box chemsitry model * Parameteriaed air ventilation rate
Garmory et al. (2009)	RANS	1.2	1	NO_x-O_3 chemistry and CBM-IV	* Field Monte Carlo method for turbulent reacting flow simulation * Segregation effect and micro-mixing
Kim et al. (2012)	RANS	1	1	NO_x-O_3 chemistry	* An online photolysis rate calculation module

				and GEOS-Chem	* Consideration of dry deposition
Kwak and Baik (2012)	RANS	1	1	CBM-IV	* Dispersion type of reactive species * O_3 sensitivity to the NO_x and VOCs emissions
Kwak et al. (2013)	RANS	1 , 2	1 -,2	CBM-IV	* Photochemical evolution * O_3 and OH oxidation processes
Bright et al. (2013)	LES, Box model	1	1	NO_x-O_3 chemistry and RCS	* Segregation effect * Comparion with box model * Atmospheric “pre-processing”
Kwak and Baik (2014)	RANS	1	1 or 2	CBM-IV	* Surface heating *Diurnal variation of NO_x and O_3 exchange
Zhong et al. (2014)	Box model	1	Box	RCS	* Segregation effect * Simple box models * Considering both chemical and dynamical effects
Park et al. (2015)	RANS	1-2	1-2	GEOS-Chem	* Varying canyon aspect ratios *Varying ratios of VOCs emission to NO_x emission

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