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# 1 **Coupling dynamics and chemistry in the air pollution** 2 **modelling of street canyons: a review**

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## 8 **Abstract:**

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

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

28 **Capsule:**

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

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

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## 46 **1 Introduction**

47 The terminology “street canyon” typically describes a restricted space in an urban area with  
48 surrounding buildings, usually along both sides of a street (Jeong and Andrews, 2002). In such an  
49 atmospheric compartment, natural air ventilation through dynamical processes is drastically  
50 constrained compared with open space (Cheng et al., 2008). Emissions from vehicles, such as  
51 nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), volatile organic compounds (VOCs) and particulate  
52 matter (PM), are predominant among various anthropogenic pollutant sources inside street canyons  
53 in urbanised areas. Many such emitted species are reactive (Park et al., 2015), undergoing chemical  
54 processing within the street canyon to generate secondary pollutants such as ozone (O<sub>3</sub>) and  
55 secondary aerosol. The deterioration of air quality in street canyons therefore occurs due to  
56 combined effects of the emissions source, dynamical processes (reduced dispersion) and chemical  
57 processes (evolution of reactive primary and secondary pollutants) (Li et al., 2008b). The urban  
58 canopy is the location in which the majority of outdoor activities of the urban population occurs,  
59 and hence where substantial human exposure results for pedestrians, road-users and occupants of  
60 adjacent buildings which may gain their ventilation from the outdoor (canyon) environment.  
61 Exposure to such environments causes adverse health effects (Solazzo et al., 2011). Since both the  
62 primary and secondary pollutants exhibit inhomogeneous distributions in urban street canyons and  
63 vary substantially in abundance with time, it is not an easy task to assess individual or population  
64 exposure to such air pollutants. The pedestrian level (breathing height) in street canyons is expected  
65 to experience particularly high levels of pollutants due to the proximity to vehicle emissions.  
66 Pollutant abundance within street canyons frequently far exceeds that in the wider urban  
67 background; in 2005, for example, measured data at the London Marylebone Road ‘super-site’  
68 showed that NO<sub>2</sub> hourly concentrations exceeded the hourly objective for 853 times compared with  
69 0 times at the nearby London Westminster urban background site (Bady et al.). Both short term  
70 exposure to high levels of pollutants and long term exposure to lower levels may cause adverse  
71 health impacts (WHO, 2000). Air quality objectives, specified for long term averages (hours, days

72 or annual) may be inadequate to account for the exposure associated with the real nonlinear  
73 fluctuations in pollutant abundance in urban street canyons, with repeated aperiodic peaks present  
74 for short periods. Understanding both dynamic and chemical processes governing the abundance of  
75 reactive pollutants in street canyons is of vital importance to accurately quantify personal exposure,  
76 and to help urban planners develop policies (e.g. street canyon design and utility of green  
77 infrastructure) to mitigate such health impacts.

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

97 modelling. However, due to the inherent semi-empirical assumptions, parametric models are unable  
98 to reproduce the detailed distribution of the flow or pollutant fields in street canyons.

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

## 119 **2 Modelling dynamics in street canyons**

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

122 Vardoulakis et al. (2003), street canyons might be classified into avenue ( $AR \leq 0.5$ ), regular  
123 ( $0.5 < AR < 2$ ) and deep ( $AR \geq 2$ ) street canyons or into short ( $L/W \leq 3$ ), medium  
124 ( $3 < L/W < 7$ ) and long street canyons ( $L/W \geq 7$ ). This classification is based on the geometrical  
125 detail of a street canyon, which may be empirically derived and widely used. When  $L$  is infinitely  
126 large, this corresponds to a two-dimensional (2D) street canyon; otherwise, a three-dimensional (3D)  
127 street canyon architecture must be considered and the value of  $L$  describes the distance between two  
128 street intersections. Flow patterns in street canyons under neutral meteorological conditions with  
129 perpendicular approaching wind can be classified into three main regimes (Oke, 1987): isolated  
130 roughness flow (IRF), wake interference flow (WIF) and skimming flow (SF). The IRF regime is  
131 related to widely spaced buildings ( $AR < 0.3$ ). The WIF regime is associated with the closer spaced  
132 buildings ( $0.3 < AR < 0.7$ ). The SF regime occurs in more tightly spaced buildings ( $AR > 0.7$ ),  
133 representing the worst-case scenario for pollutant dispersion.

## 134 **2.1 Numerical modelling**

135 As a numerical modelling technique, CFD is a powerful tool to explore experimental flow problems,  
136 to characterise air pollutant transport and dispersion processes, and to provide a detailed distribution  
137 of canyon flow and pollutant dispersion with high spatial-temporal resolution (Chang, 2006). A  
138 CFD package may include a series of numerical governing equations for turbulent flow and  
139 pollutant dispersion, potentially involving the coupling of both dynamics and chemistry. The  
140 turbulence closure schemes for the CFD packages are classified into two categories: Reynolds-  
141 averaged Navier–Stokes (RANS) and Large-Eddy Simulation (LES). RANS resolves only the mean  
142 time-averaged properties with all the turbulence motions to be modelled. In place of the time-  
143 averaging used in RANS, LES adopts a spatial filtering operation and consequently resolves large-  
144 scale eddies directly and parameterises small-scale eddies using sub-grid scale (SGS) turbulence  
145 models. In this aspect, the RANS approach is easier to be established and computationally faster  
146 than LES. The atmospheric turbulent flow in and above street canyons involves turbulent eddies on  
147 a variety of scales (McNabola et al., 2009). The sizes of large-scale eddies are usually comparable

148 to the characteristic length of atmospheric turbulent flow, and are dependent on the street canyon  
149 geometry and turbulent flow boundary conditions. Small-scale eddies typically have a universal  
150 behaviour throughout the computational domain and are more dependent on the local energy  
151 dissipation. Applications of RANS and LES in street-canyon dynamics are discussed below.

### 152 2.1.1 Reynolds-averaged Navier–Stokes (RANS)

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

162 The standard  $k - \varepsilon$  model is well documented and can perform well in reproducing general  
163 structure for fully turbulent flow (Tsai and Chen, 2004). However, for street-canyon flow, it does  
164 not predict turbulence kinetic energy with good accuracy in regions close to the walls or to the shear  
165 layer at the canyon roof level (Sini et al. (1996); Hassan and Crowther (1998); Baik and Kim  
166 (1999)). Smagorinsky (1963) evaluated the standard  $k - \varepsilon$  model using a water channel experiment  
167 (Baik et al., 2000) and investigated the effect of inflow turbulence intensities (Kim and Baik, 2003)  
168 on the flow dispersion in the street canyon. The turbulence kinetic energy and diffusivity were  
169 found to increase with an increase in the inflow turbulence intensity. Solazzo et al. (2008) employed  
170 the standard  $k - \varepsilon$  model to investigate the effect of traffic-induced turbulence. Compared to a wind  
171 tunnel experiment (Kastner-Klein et al., 2001), the model performed well in terms of predicting the



172 turbulence kinetic energy and mean horizontal velocity, but showed limitations in reproducing the  
173 mean vertical velocity.

174 The RNG  $k-\varepsilon$  model applies a rigorous statistical technique (i.e. the renormalisation group  
175 mathematical theory (Yakhot and Orszag, 1986)) to determine the effective turbulent viscosity and  
176 includes an additional source term in the  $\varepsilon$  equation to capture the interaction between turbulence  
177 dissipation and mean shear. This model has been successfully implemented in simulating the street  
178 canyon transitional flow. Memon et al. (2010) applied the RNG  $k-\varepsilon$  model to 2D isolated street  
179 canyons considering heating situations. Compared with a wind tunnel experiment (Uehara et al.,  
180 2000), there was a good agreement for the normalised potential temperature. The model  
181 underestimated the normalised horizontal velocity at the canyon roof level (by 10%) because the  
182 effect of 3D city blocks and roughness elements in the experiment not being fully represented by  
183 the 2D model. Kim and Baik (2004) carried out a 3D CFD model simulation coupled with the RNG  
184  $k-\varepsilon$  model to examine the wind flow in street canyons. Although their model reproduced the flow  
185 separation by buildings and reversed flow, it underestimated the turbulence kinetic energy and wind  
186 velocity compared with a wind tunnel experiment (Brown et al., 2000). Chan et al. (2002)  
187 conducted a series of  $k-\varepsilon$  model simulations to study the flow dispersion in a 2D isolated street  
188 canyon. Compared to wind tunnel experiments, the RNG  $k-\varepsilon$  approach was found to be optimal.  
189 They attributed this to the analytically derived formula of turbulent viscosity in the RNG  
190  $k-\varepsilon$  model.

191 The realizable  $k-\varepsilon$  model has an improved equation for  $\varepsilon$  considering vorticity fluctuation and  
192 uses a variable of  $C_\mu$  (while a constant value is adopted in both the standard  $k-\varepsilon$  model and the  
193 RNG  $k-\varepsilon$  model) to derive the turbulence viscosity. This model provides better performance for  
194 flows involving separation, rotation, and recirculation. Tian et al. (2009) developed an idealised 3D  
195 model based on the realizable  $k-\varepsilon$  model to investigate the flow dispersion around arrays of  
196 buildings. Their model reproduced the secondary oval vortices around the buildings and the air

197 exchange between the inside and outside street canyons. Gromke and Blocken (2015) adopted the  
198 realizable  $k - \varepsilon$  model to simulate the flow and dispersion in and above 3D street canyons with  
199 avenue-trees. Their study demonstrated the capability of the realizable  $k - \varepsilon$  model to simulate the  
200 flow and turbulence involving trees.

201 The RSM explicitly calculates the individual Reynolds stresses (poorly represented by the  
202  $k - \varepsilon$  models). Thus in theory the RSM can perform better for complex flows (e.g. street canyon  
203 flow) than the  $k - \varepsilon$  models. However, the RSM is more complex involving more terms with more  
204 uncertainties to be modelled and greater computational cost. Nazridoust and Ahmadi (2006) applied  
205 the RSM, the standard and RNG  $k - \varepsilon$  models to study the airflow and pollutant dispersion in 2D  
206 street canyons. The RSM generally agreed better with wind tunnel experimental data for pollutant  
207 concentrations among the turbulence models used in their study. The standard  $k - \varepsilon$  model and the  
208 RNG  $k - \varepsilon$  model predicted similar results for pollutant concentrations, in alignment with the  
209 findings of Chang and Meroney (2001). Koutsourakis et al. (2012) evaluated the performance of the  
210 RSM, standard  $k - \varepsilon$  model and RNG  $k - \varepsilon$  model in simulating the street canyon flows using six  
211 experimental datasets (i.e. Baik et al. (2000), Hoydysh and Dabberdt (1988), Depaul and Sheih  
212 (1986), Kovar-Panskus et al. (2002), Sahm et al. (2002) and Li et al. (2008a). The model with the  
213 best performance could be any of the three turbulence models depending on the experimental  
214 dataset used (e.g. vertical and horizontal velocities, and pollutant concentrations). The RNG  $k - \varepsilon$   
215 model generally possesses the best performance and has an improvement compared with the  
216 standard  $k - \varepsilon$  model. Although the RSM can reproduce better near-wall phenomena than  $k - \varepsilon$   
217 models, the RSM needs much more computational time and has more difficulty to achieve  
218 convergence. Due to high uncertainties in street canyon geometry and wind conditions for both  
219 models and experiments, consideration of only one experimental dataset was found to be  
220 insufficient when assessing the performance of a particular turbulent model.

### 221 2.1.2 Large-Eddy Simulation (LES)

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

232 The Smagorinsky SGS model (Smagorinsky, 1963) is widely used because of its simplicity and  
233 numerical stability in the parameterisation of the SGS stresses assuming that the small scale energy  
234 production and dissipation are in equilibrium. This SGS model can simulate many flows with  
235 reasonable accuracy. Cui et al. (2004) developed an LES model (the Smagorinsky SGS model),  
236 based on the Regional Atmospheric Modelling System (RAMS) meteorological code, to investigate  
237 turbulent flow in and above a street canyon ( $AR=1$ ). Their study provided a detailed analysis of the  
238 turbulent canyon flow structure as well as the contributions of ejection or sweep events near the  
239 roof level to the momentum flux between the canyon and the boundary layer aloft. In comparison  
240 with wind-tunnel experimental data, their results showed that the LES model underestimated the  
241 momentum flux, indicated by a weaker mean primary vortex inside the canyon than that measured.  
242 They attributed this to (i) the limited domain size (which may underestimate the turbulent intensity  
243 above the canyon) and (ii) the relatively coarse mesh size near roof level where a strong wind shear  
244 and associated instability were present. Cai et al. (2008) further adopted this LES model (the  
245 Smagorinsky SGS model) based on RAMS meteorological code (Cui et al., 2004) to simulate the  
246 transfer characteristics of passive scalars corresponding to area sources over the road surface, the

247 upstream wall and the downstream wall, respectively, in a 2D street canyon. By comparing with  
248 wind-tunnel experimental data (i.e. Meroney et al. (1996) and Kastner-Klein and Plate (1999)), they  
249 demonstrated the LES model captured the main characteristics of canyon flow and scalar dispersion.

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

272 well represented by the ACH and PCH. It was found that more pollutants were trapped inside the  
273 street canyon near the ground with an increase in canyon aspect ratio.

274 The one-equation SGS model (Schumann, 1975) solves an additional transport equation for the  
275 SGS turbulence kinetic energy conservation to account for the SGS motion. This model keeps track  
276 of the total energy in the SGS, which are not included by the Smagorinsky models. Cheng and Liu  
277 (2011) developed an LES model (the one-equation SGS model) to investigate the turbulent flow and  
278 pollutant removal in and above 2D street canyons (AR=1). In comparison with the model  
279 configuration of Cui et al. (2004) , their grid resolution was slightly coarser (by 30 %) in the  
280 streamwise direction, but their domain sizes were larger by factors of 3, 1.5 and 2.7 in the  
281 streamwise, spanwise and vertical directions, respectively. However, the simulated intensity of the  
282 mean primary vortex in the canyon was weaker than that of Cui et al. (2004), and they therefore  
283 concluded that increasing LES domain size cannot fully rectify the under-predicted intensity of  
284 mean primary vortex. This comparison indicated that well-resolved shear layers at the canyon roof  
285 level with high gradients of velocities may be required and worth thorough investigation, e.g. a  
286 stochastic backscatter model to increase the momentum transfer across the canyon roof level  
287 (O'Neill et al., 2015). Li et al. (2008b) and Li et al. (2009) adopted LES models (based on the one-  
288 equation SGS model) to handle the flow and pollutant dispersion for deep street canyons with high  
289 ARs up to 10. The multiple primary vortices inside those deep street canyons were well reproduced  
290 by their model.

### 291 **2.1.3 Comparison of RANS and LES**

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

298 LES performed better than RANS in terms of capturing the details of the flow within the urban  
299 canopy. They reported that the computational cost of LES was about 100 times that of RANS. Xie  
300 and Castro (2006) also found that although LES (the Smagorinsky SGS model) better captured  
301 turbulent flow around buildings than RANS (the  $k-\varepsilon$  models and RSM), its computational cost  
302 was at least an order of magnitude greater than that of RANS. Santiago et al. (2010) and Dejoan et  
303 al. (2010) reported that the local mean flow quantities predicted by LES (the Smagorinsky SGS  
304 model) were closer to the Mock Urban Setting Test (MUST) data than that predicted by RANS (the  
305 standard  $k-\varepsilon$  model). Tominaga and Stathopoulos (2011) applied both LES (the Smagorinsky  
306 SGS model) and RANS (the RNG  $k-\varepsilon$  model) to simulation of flow dispersion in a street canyon  
307 (AR=1). LES was found to give better results than RANS compared with a wind tunnel experiment.  
308 The turbulence diffusion was well reproduced by LES, but underestimated by RANS. The  
309 performance in modelling turbulence diffusion by LES or RANS played an important role in the  
310 accuracy of pollutant dispersion predictions (Tominaga and Stathopoulos, 2010). Salim et al.  
311 (2011a) and Salim et al. (2011b) evaluated the performance of LES (the dynamic Smagorinsky SGS  
312 model) and RANS (the standard  $k-\varepsilon$  model and RSM) for the prediction of flow dispersion in a  
313 street canyon (AR=1) with avenue-like trees. It was found that LES predicted significantly more  
314 accurate better flow dispersion than RANS. Compared to RANS, LES provided better  
315 representation of scenarios with trees since LES can capture intermittent and unsteady flow  
316 fluctuations. Chung and Liu (2013) compared LES (the one-equation SGS model) and RANS (the  
317 RNG  $k-\varepsilon$  model adopted in Liu et al. (2011)) in the calculation of ACH and PCH. They found  
318 that the contributions of the turbulent components to ACH and PCH are much more in the LES than  
319 those in the RANS, highlighting the importance of turbulence in the transport and dispersion of  
320 flow and pollutants.

## 321 **2.2 Simplified parameterisation**

322 Although numerical modelling is able to capture temporally and spatially detailed information  
323 about dynamics in street canyons, it is still very complex and computationally expensive for many

324 practical applications. Parametric modelling based on simple operational relationships between the  
325 street-canyon flow and dispersion conditions is an alternative tool, which is relatively simple and  
326 demands much less computational cost (Murena et al., 2009). Numerical modelling, in turn, can  
327 serve to better evaluate and provide algorithms for implementation within parametric modelling.  
328 Detailed applications of the parametric modelling are given in the review papers of Vardoulakis et  
329 al. (2007) and Kakosimos et al. (2010). Here, we focus on simplified parameterizations of dynamics  
330 in street canyons.

331 Turbulent exchange (transfer) between the street canyon and the overlying atmospheric boundary  
332 layer controls pollutant abundance in the street canyon (Barlow et al., 2004) and plays a uniquely  
333 important role in parametric modelling (Murena, 2012). This turbulent exchange can be represented  
334 by a simplified parameter called the ‘transfer velocity’ (Salizzoni et al., 2009) or ‘air ventilation  
335 rate’ (Liu and Leung, 2008), herein referred to as ‘exchange velocity’ (Bright et al., 2013), which  
336 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  
337 the pollutant flux per unit area at the roof level,  $w_e$  is the exchange velocity, and  $C_{can}$  and  $C_B$  are  
338 the pollutant concentrations inside the canyon and at the background boundary layer, respectively.  
339 A parameterisation of the exchange velocity can be derived from a more comprehensive model (e.g.  
340 RANS or LES) of a specific street-canyon flow (if considering the street canyon as a box), e.g. Liu  
341 et al. (2005); Bright et al. (2013). More practically in the STREET model (Johnson et al., 1973) and  
342 the Operational Street Pollution Model (OSPM) (Buckland, 1998), it is assumed that the exchange  
343 velocity is proportional to the characteristic velocity in the overlying boundary layer. However, the  
344 dependence of exchange velocity on the street-canyon flow can be very complex and influenced by  
345 many parameters. Murena et al. (2011) investigated the effects of the external wind speed on the  
346 exchange velocity and a nearly linear relationship between them was found. Salizzoni et al. (2011)  
347 found that the turbulent exchange was dependent on the coupling between the turbulence in the  
348 shear layer and turbulent eddies in the external atmospheric flow. Caton et al. (2003) showed that  
349 under lower external turbulence, the shear layer turbulence governed the exchange processes and a

350 linear assumption between the exchange velocity and the external wind speed could be derived, but  
351 under higher external turbulence, the exchange processes were dominated by the external  
352 turbulence and depended upon both the turbulent structure of the incoming flow and that of the  
353 shear layer. Liu et al. (2011) and Solazzo and Britter (2007) investigated the effect of aspect ratio  
354 on the exchange velocity and also found a linear relationship for a given AR, but also a varying  
355 relationship between the exchange velocity and the external wind speed depending on the flow  
356 regimes involved.

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

### 365 **3 Chemistry for air pollution modelling**

366 Modelling dynamics in street canyons, which determines the evolution and physical removal of  
367 atmospheric pollutants, is only one component of the coupling approach of dynamics and chemistry.  
368 The representation of atmospheric chemistry for air pollution modelling also plays an important role  
369 for reactive species. Considering the street-canyon scale (short distance from emissions sources to  
370 receptors), the time scale of pollutant transport is of the order of minutes and therefore chemical  
371 transformation processes of significance in street canyons are those which display comparable (or  
372 shorter) timescales. Thus, some pollutants (such as CO and many hydrocarbons), which are not  
373 significantly influenced by chemical transformation on the second-to-minute timescales, can be  
374 regarded as passive scalars (non-reactive species) in a street canyon context. However, this is not



375 the case for short-lived pollutants (such as  $\text{NO}_2$  and  $\text{O}_3$ ) and highly reactive chemical species (such  
376 as hydroxyl radical (OH), hydroperoxy radical ( $\text{HO}_2$ ) and organic peroxy radicals ( $\text{RO}_2$ )). For such  
377 species, chemical reactions must be taken into account for the prediction of pollutant abundance in  
378 street canyons. A chemical mechanism describes mathematically the chemical processes in the  
379 atmosphere for the removal and formation of primary and secondary chemical species (Jimenez et  
380 al., 2003), as discussed below, with a focus upon gas-phase processes.

### 381 **3.1 Simple $\text{NO}_x$ - $\text{O}_3$ chemistry**

382 The simple  $\text{NO}_x$ - $\text{O}_3$  chemistry (Smagorinsky, 1963) describes the photochemical reactions between  
383 NO,  $\text{NO}_2$  and  $\text{O}_3$ . In the presence of sun light,  $\text{NO}_2$  is rapidly photolysed leading to NO and  $\text{O}_3$   
384 formation ( $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ ;  $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ ;  $h\nu$  represents a solar photon; M denotes  
385 a third body molecule which absorbs excess energy so that O and  $\text{O}_2$  may recombine to form  $\text{O}_3$ )  
386 and NO can also react quickly with  $\text{O}_3$  to re-form  $\text{NO}_2$  ( $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ ).  $\text{NO}_x$  emitted from  
387 vehicles into the street canyon is predominantly in form of NO with a small (but in many  
388 environments increasing) fraction of  $\text{NO}_2$ . Within the urban environments, the  $\text{NO}_x$ - $\text{O}_3$  titration  
389 interaction with freshly emitted NO can result in a significant local sink for  $\text{O}_3$  in street canyons,  
390 providing a reduction of  $\text{O}_3$  level compared with the surrounding rural areas (or overlying canopy  
391 layer). On a city-wide basis, this effect is also called the “urban decrement” (Munir et al., 2013).  
392 Due to its simplicity, the simple daytime  $\text{NO}_x$ - $\text{O}_3$  system has been previously adopted in parametric  
393 modelling, e.g. OSPM (Berkowicz, 2000) and ADMS (McHugh et al., 1997). The incorporation of  
394 such simple chemistry into street canyon dynamics model can also be affordable especially for  
395 otherwise expensive LES approaches (e.g. Baker et al. (2004)).

### 396 **3.2 Complex chemistry**

397 The simple  $\text{NO}_x$ - $\text{O}_3$  chemistry only accounts for daytime  $\text{NO}_x$ - $\text{O}_3$  interactions, without  
398 consideration of other  $\text{NO}_y$  (reactive nitrogen oxides) species, nighttime processing, and the  
399 oxidation of VOCs. Therefore, more realistic chemistry involving detailed inorganic and VOCs

400 reactions should be also considered for a comprehensive description of the urban atmosphere. Such  
401 representations may include the reactions of radical species (e.g. OH, HO<sub>2</sub> and RO<sub>2</sub>) which may  
402 result in additional (non-O<sub>3</sub>) conversion of NO to NO<sub>2</sub>, and hence to net ozone / oxidant production,  
403 that cannot be captured by the simple NO<sub>x</sub>-O<sub>3</sub> chemistry. There are a wide range of mechanisms  
404 (from near-explicit to substantially reduced mechanisms) with varying complexity considering both  
405 NO<sub>x</sub> and VOCs chemistry which have been applied in street canyon studies, and which are briefly  
406 discussed below.

### 407 **3.2.1 MCM**

408 The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism, representing in  
409 detail the gas-phase tropospheric degradation of primary VOCs and formation of (gaseous)  
410 secondary pollutants (Jenkin et al., 1997). The MCM v1.0 consists of over 2,400 species and 7,100  
411 reactions describing the degradation of 120 VOCs (Derwent et al., 1998). The MCM v2.0 updates  
412 the chemistry of aromatic hydrocarbons and includes 3,487 species and 10,763 reactions  
413 (Whitehouse et al., 2004). To improve the chemical degradation of aromatics (Jenkin et al., 2003),  
414 the MCM v3.0 was developed, containing 12,691 organic reactions for 4,351 organic species, and  
415 46 inorganic reactions (Saunders et al., 2003). To promote the understanding of aromatic photo-  
416 oxidation (Bloss et al., 2005), MCM v3.0 was updated to MCM v3.1 (about 13,500 chemical  
417 reactions and 5,900 species (Pinho et al., 2007)) and MCM v3.2 (about 17,000 chemical reactions  
418 and 6,700 species (Jenkin et al., 2012)). The MCM has been evaluated against an extensive  
419 experimental database from photochemical reaction chambers and field campaigns. Due to its near-  
420 explicit nature, the MCM is principally employed within box models, and is usually considered too  
421 expensive for 3D grid-based air pollution models. For such applications, it is necessary to develop  
422 reduced chemical mechanisms which of an appropriate size, and yet which retain a quantitative  
423 description of the atmospheric chemistry. The MCM may also be considered as a reference or  
424 benchmark mechanism for developing and evaluating such reduced chemical mechanisms. Reduced  
425 techniques include lumping, sensitivity analysis and timescale analysis approaches (Neophytou et

426 al., 2004). The lumping technique condenses several unique species into single ones (Makar and  
427 Polavarapu, 1997) and has been the most frequently employed approach to the reduction of  
428 chemical mechanisms. Three approaches are commonly used (Zaveri and Peters, 1999), i.e.  
429 surrogate species, lumped molecule (lumping VOCs into a series of categories according to  
430 similarity of oxidation reactivity) and lumped structure (lumping VOCs according to their chemical  
431 nature as reflected in their molecular structures). The sensitivity analysis technique, also called  
432 “iterative screening and structure analysis”, uses chemical reaction and sensitivity analysis to  
433 identify sensitive or key species by calculating concentrations of some species as a function of  
434 others (Mauersberger, 2005). Timescale analysis removes fast-reacting “steady-state” species,  
435 replacing these with calculated values, by distinguishing between “fast” and “slow” chemical time  
436 scales using the quasi-steady-state approximation (Lovas et al., 2006).

### 437 **3.2.2 CRI Mechanism**

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

451 against the MCM, which includes 136 reactions of 51 species, for the application into an LES  
452 model at the street canyon scale.

### 453 **3.2.3 CBM**

454 The Carbon Bond Mechanism (CBM-IV) was developed based on the lumped-structure  
455 condensation approach for chemical reactions of VOCs with similar carbon bonds (C-CHO, C-C,  
456 C=C, etc.) (Gery et al., 1989). The CBM-IV contains 81 reactions of 33 species. These species are  
457 classified into four groups: explicit organic species, organic species (carbon surrogates), organic  
458 species (molecular surrogates), and inorganic species (no lumping). Several other versions were  
459 also developed. Heard et al. (1998) compared the CBM-IV with CBM-EX (including 204 reactions  
460 and 90 species) and the reduced CBM-LEEDS (including 59 reactions of 29 species). Based on  
461 CBM-IV, Zaveri and Peters (1999) developed an extended mechanism called CBM-Z (including  
462 132 reactions and 52 species). CBM-IV is a popular lumped-structure mechanism but does not  
463 contain some of the long-lived species and peroxy radical interactions, and has a relatively crude  
464 isoprene mechanism. Due to its compactness, CBM-IV is an attractive chemical mechanism for air  
465 quality modelling at the street canyon scale (e.g. Garmory et al. (2009); Kwak and Baik (2012);  
466 Kwak et al. (2013); Kwak and Baik (2014) ).

### 467 **3.2.4 GEOS-Chem**

468 GEOS-Chem (Eller et al., 2009) is a chemistry-transport model for simulating atmospheric  
469 composition in the troposphere at the global scale, using the Goddard Earth Observing System  
470 (GEOS) meteorological information (Abad et al., 2011). The chemical mechanism in the GEOS-  
471 Chem model contains over 300 reactions of 80 species with explicit chemical schemes for main  
472 anthropogenic hydrocarbons and isoprene (Bey et al., 2001). Ito et al. (2007) developed a GEOS-  
473 Chem Mechanism extension (GEOSito), which includes a 490 reaction scheme of 179 species  
474 accounting for a detailed representation of hydroxyl alkyl nitrates. The GEOS-Chem photochemical  
475 scheme has been successfully extended to the street canyon application in terms of representing key

476 photochemical species (Kim et al., 2012). The transport time scale at the global scale is much  
477 longer than that at the street canyon scale. When the global chemical scheme is adopted in a street  
478 canyon, the chemical effect of those species with chemical time scales bigger than the canyon  
479 dynamical residence time scale becomes less significant.

### 480 **3.2.5 Generalized VOCs and NO<sub>x</sub> Mechanism**

481 The Generalized VOCs and NO<sub>x</sub> Mechanism (Seinfeld and Pandis, 1998) contains 20 chemical  
482 reactions of 23 species. Although this mechanism is far from comprehensive, it maintains the key  
483 features of the VOC-NO<sub>x</sub> chemistry thereby providing the capability to qualitatively analyze the  
484 formation of O<sub>3</sub> through the conversion of VOCs and NO<sub>x</sub>. The simple nature of this VOC-NO<sub>x</sub>  
485 mechanism allows it to be incorporated into most air pollution models. An early attempt to  
486 implement the VOCs and NO<sub>x</sub> Mechanism into the street-canyon box modelling on the  
487 investigation of O<sub>3</sub> formation can be seen from Liu and Leung (2008). The chemical processing in a  
488 street canyon mainly involves the photochemistry of gas-phase species. The Generalized VOCs and  
489 NO<sub>x</sub> Mechanism includes most of the key chemical processing and can be considered as a  
490 promising tool to investigate the chemistry focusing on the formation of O<sub>3</sub>.

### 491 **3.2.6 Other chemical mechanisms**

492 There are a number of other chemical mechanisms which have been applied to air pollution  
493 modelling; although not widely used in the street canyon simulations to date, they have the potential  
494 for future development in such applications. A chemical mechanism is often developed and  
495 evaluated based on laboratory, smog chamber and field measurement data and involves a large  
496 amount of chemical species and reactions to represent chemical processes in the atmosphere  
497 (Dodge, 2000). There has been an enormous growth in the understanding and application of  
498 chemistry in air pollution modelling. The limitation of computational resources should be  
499 considered in the application of a chemical mechanism for modelling the atmospheric chemistry.  
500 For grid-based air quality models, there may be millions of grid cells and therefore millions of

501 calculations for discretised differential equations are needed for each species, which requires much  
502 computational time and memory storage (Stockwell et al., 2012). Several other chemical  
503 mechanisms are briefly discussed below.

504 The MIM (Mainz Isoprene Mechanism) developed by Pöschl et al. (2000) is a reduced isoprene  
505 degradation scheme, using a lumped molecule technique based on the Master Chemical Mechanism.  
506 It includes 44 chemical reactions of 16 species, originally constructed for atmospheric modelling at  
507 the global scale. Taraborrelli et al. (2009) updated the MIM into the MIM2 to represent more  
508 intermediates. MIM2 includes 199 chemical reactions of 68 species and is suitable for air quality  
509 modelling at both regional and global scales. The SAPRC Mechanism (SAPRC-90) was developed  
510 by a research group at the (then) Statewide Air Pollution Research Center (Carter, 1990). SAPRC-  
511 90 (158 chemical reactions of 54 species) is a lumped molecule mechanism, in which lumped  
512 species and reactions are used to describe the degradation of organic compounds. An updated  
513 version (SAPRC-99), which includes 198 reactions and 72 species, was developed by Carter  
514 (2000b). The latest version of the SAPRC Mechanism (SAPRC-07) has a total of 339 reactions of  
515 119 species (Carter, 2010), giving separate representation for 748 types of VOCs. The SAPRC  
516 mechanisms can be used to calculate ozone reactivity scales for VOCs and predict impacts of  
517 emissions on formation of secondary pollutants. The CACM (Caltech Atmospheric Chemistry  
518 Mechanism) is a lumped-structure mechanism including a total of 361 reactions of 191 species  
519 (Griffin et al., 2002). The inorganic chemical scheme in the CACM is based on the SAPRC99,  
520 while the primary VOCs are reduced by a lumped-structure technique. CACM contains a detailed  
521 chemical scheme to characterise ozone formation and formation of semi-volatile products. The  
522 RACM (Regional Atmospheric Chemistry Mechanism) (Stockwell et al., 1997) consists of 237  
523 reactions of 77 species revised from the Regional Acid Deposition Model (RADM2) Mechanism  
524 (Stockwell et al., 1990). RACM is a lumped-molecule chemistry mechanism to describe  
525 atmospheric chemistry on a regional scale. RACM has been coupled online with the RAMS model  
526 (Arteta et al., 2006). RACM is capable of simulating both the lower and upper troposphere from

527 rural to urban areas. The EMEP (European Monitoring and Evaluation Programme) mechanism is  
528 related to policy studies in Europe including 148 reactions of 79 species (Gross and Stockwell,  
529 2003). The EMEP mechanism applies a lumped molecule technique to give representations of  
530 organic compounds with a series of species of similar structure and reactivity. The EMEP  
531 mechanism is highly aggregated, and is usually only applied within the atmospheric boundary layer.

### 532 **3.3 Comparison of chemical mechanisms**

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

553 canyon context whose concentrations close to the emission region may be very high), which is the  
554 focus of the next section of this review.

## 555 **4 Coupling dynamics and chemistry**

556 The coupling between dynamics and chemistry plays a major role in air pollution modelling within  
557 street canyons. Several attempts have been made to deal with both the dynamical and the chemical  
558 complexity. Most long lived traffic-related pollutants (e.g. CO and VOCs) are dependent almost  
559 exclusively on canyon dynamical processing, rather than chemical processing, due to their much  
560 longer chemical oxidation time scales compared with the canyon dynamical residence time scale.  
561 Therefore, many previous studies (e.g. Cai et al. (2008); Solazzo et al. (2011); Madalozzo et al.  
562 (2014)) have only taken passive scalars into consideration, a well-established approach avoiding  
563 complex chemical processing. More recently, studies have considered increasing chemical  
564 reactivity and complexity; those associated with the simple  $\text{NO}_x\text{-O}_3$  chemistry and then complex  
565 chemistry involving the VOCs (shown as Table 2) will be discussed below.

### 566 **4.1 Coupling with simple $\text{NO}_x\text{-O}_3$ chemistry**

567 For relatively short-lived traffic-related pollutants (e.g.  $\text{NO}_2$  and  $\text{O}_3$ ), the assumption of non-  
568 reactivity is not appropriate because their chemical time scales are comparable to, or shorter than,  
569 the canyon dynamical time scale. The chemical processing of  $\text{NO}_x$  and  $\text{O}_3$  can play a key role in  
570 determining the spatial variation of these species in street canyons. Therefore, simple  $\text{NO}_x\text{-O}_3$   
571 chemistry was incorporated into street canyon dynamics models.

572 The first implementation of this approach can be found in Baker et al. (2004). They introduced the  
573  $\text{NO}_x\text{-O}_3$  chemistry into an LES model (the Smagorinsky SGS model) based on the RAMS  
574 numerical code under neutral meteorological conditions and examined the dispersion and transport  
575 of chemically reactive pollutants ( $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$ ) inside a regular street canyon ( $\text{AR}=1$ ). The  
576 distributions of pollutants exhibited significant spatial variations dominated by a primary vortex in  
577 the street canyon, also found by a previous field observation (Xie et al., 2003). The concept of the



578 photostationary state (PSS) defect (defined as  $d_{ps}(\%) = (k_1[O_3][NO]/J_{NO_2}[NO_2]-1) \times 100$ , where  
579  $J_{NO_2}$ ,  $k_1$  are rate constants and  $[C_i]$  represents the concentration of  $i^{th}$  species) was introduced.  
580 The PSS defect calculations showed that the chemistry was close to equilibrium within the primary  
581 canyon vortex, but far from equilibrium at the canyon roof level and near traffic emissions where  
582 two air parcels with distinctively different chemical composition meet. The PSS defect was shown  
583 to be a useful measure of reactive mixing in and above a street canyon. Their study highlighted the  
584 impact of chemical processing in the street canyon context, providing a basis for the coupling of  
585 reactive species. However, only very limited chemistry was considered.

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

595 Baik et al. (2007) carried out a RANS model simulation (the RNG  $k-\epsilon$  model) coupled with  
596 simple  $NO_x-O_3$  chemistry to examine reactive pollutant dispersion within a street canyon (AR=1)  
597 with bottom heating. The reaction rate constant and photolysis frequency were temperature-  
598 dependent in this study (while constant values were used in Baker et al. (2004)). An oscillation of  
599 the primary vortex was found in the street canyon when bottom heating was introduced and this  
600 caused a significant variation in chemical species abundance. This study found that the averaged  
601 temperature,  $NO$  and  $NO_2$  concentrations had the same trend of oscillation, but opposite in sign to  
602 that of the  $O_3$  concentration. The main features of the PSS defect were found to be consistent with

603 the results of Baker et al. (2004). A budget analysis showed that advection and diffusion terms were  
604 much larger than the chemical reaction term in determining the abundance of NO and NO<sub>2</sub>, but  
605 comparable to each for O<sub>3</sub>. This budget analysis provided useful insight into the impact of chemical  
606 vs. dynamical processing of each species on the overall distribution and the findings indicated that  
607 the distribution of O<sub>3</sub> was affected by the inhomogeneous temperature in street canyons through  
608 chemistry. Although this study considered the effect of heating on both the dynamical process  
609 (changing the flow pattern) and chemical process (temperature-dependent chemical reaction rates),  
610 it was restricted to a single street bottom heating scenario.

611 Kang et al. (2008) further investigated the effect of street bottom heating (varying the intensities of  
612 heating) on flow and reactive pollutant dispersion using the same framework as Baik et al. (2007).  
613 They found that the centre of the primary vortex varied with the street-bottom heating intensity and  
614 thereby led to a significant variation of chemical species abundance. The evolution of the canyon-  
615 averaged NO concentration under different heating intensities was found to have three types of  
616 patterns (i.e. quasi-steady, oscillatory and fluctuating). The canyon-averaged concentrations tend to  
617 decrease with an increase of the heating intensity. The effect of street bottom heating on the  
618 concentration of O<sub>3</sub> through the temperature-dependent chemical reaction rates increases with  
619 heating intensity, but overall this chemical processing influence was small. These findings  
620 demonstrated that canyon-averaged patterns were mainly due to the dynamics influence of street-  
621 bottom heating rather than the chemical influence. However, experimental data were not available  
622 for the evaluation of the pollutant concentrations in the heating scenario.

623 Tong and Leung (2012) developed a RANS model (the RNG  $k - \varepsilon$  turbulence model) coupled with  
624 simple NO<sub>x</sub>-O<sub>3</sub> photochemistry to examine the spatial characteristics of reactive pollutants and the  
625 level of chemical equilibrium in idealised street canyons with aspect ratios varying from 0.5 to 8  
626 under different ambient wind speeds and diurnal heating scenarios. The performance of this street  
627 canyon model under bottom heating on flow and temperature fields was evaluated both  
628 experimentally (Uehara et al., 2000) and numerically (i.e. Kim and Baik (2001); Xie et al. (2006)

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

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

646 Zhong et al. (2015) adopted an LES model (the one-equation SGS model) coupled with simple  
647  $NO_x$ - $O_3$  photochemistry to examine the dispersion and transport of atmospheric pollutants in a deep  
648 urban street canyon ( $AR=2$ ). The ozone production rate inferred from  $NO_x$ - $O_3$  non-equilibrium was  
649 found to be negative within the canyon, pointing to a systematic negative offset to ozone production  
650 rates inferred by analogous field measurement approaches in environments with incomplete mixing.  
651 This metric could serve to investigate the interplay of dynamics and chemistry in street canyons.  
652 Reactive pollutants exhibited significant spatial variation caused by the two unsteady vortices  
653 present, agreeing reasonably well with a water channel experiment (Li et al., 2008c). The deviation  
654 of species abundance from chemical equilibrium for the upper vortex was found to be greater than

655 that for the lower vortex. An alternative, simplified two-box model was developed based on the  
656 existence of two vortices, assuming that the deep street canyon can be described by two individual  
657 well-mixed boxes with exchange between them. This two-box model can capture the significant  
658 contrasts in the concentration of species inside both the lower and upper canyon vortices as  
659 predicted by the LES simulation. However, this model only considered simple chemistry under  
660 neutral meteorological conditions with constant (no temperature or radiation dependence) reaction  
661 rates.

## 662 **4.2 Coupling with complex chemistry**

663 Very fast-reacting chemical species (e.g. OH, HO<sub>2</sub>) play an important role in driving the chemical  
664 cycle of VOC degradation (O<sub>3</sub> precursors) leading to the additional peroxy-radical mediated  
665 conversion of NO to NO<sub>2</sub> (which is not represented by the simple NO<sub>x</sub>-O<sub>3</sub> chemistry) and hence O<sub>3</sub>  
666 formation. These species, with chemical lifetimes of seconds, are primarily governed by local  
667 chemical processing and their abundance varies substantially within street canyons. Complex  
668 chemical mechanisms considering both NO<sub>x</sub> and VOCs chemistry were therefore incorporated into  
669 canyon dynamical models.

670 Liu and Leung (2008) implemented a one-box chemistry model using the generalized VOCs and  
671 NO<sub>x</sub> mechanism (Seinfeld and Pandis, 1998) to couple the dynamics and chemistry in street  
672 canyons (AR=0.5, 1, 2). Air ventilation rates were derived from LES models for different ARs (Liu  
673 et al., 2005). They found that the O<sub>3</sub> concentration within street canyons was dependent upon both  
674 the VOCs and NO<sub>x</sub> emission rates. When the ratio of VOCs to NO<sub>x</sub> emission rates was higher than  
675 10, the O<sub>3</sub> concentration could reach up to the order of 100 ppb. The emission ratio of VOCs and  
676 NO<sub>x</sub> could therefore be a useful indicator for the increase in O<sub>3</sub> levels in street canyons. Because  
677 their study treated the whole canyon as one well-mixed box for all ARs, the model was unable to  
678 reproduce the significant contrasts of pollutant concentration between the lower and upper canyon  
679 which are observed experimentally.

680 Garmory et al. (2009) employed the Stochastic Field method to characterise turbulent reacting flow  
681 for an investigation of the transport and dispersion of reactive scalars within a street canyon  
682 (AR=1.2) adopting both simple NO<sub>x</sub>-O<sub>3</sub> chemistry and the CBM-IV mechanism. The flow field was  
683 based on the standard  $k - \varepsilon$  model. The Stochastic Field method can be incorporated into the RANS  
684 model and captures both the means and variances of pollutant abundance together with  
685 consideration of segregation effects on overall reaction rates. This statistical information could not  
686 be obtained from traditional RANS models. The variance of reactive pollutants was found to be  
687 very high - of the order of the mean values at the canyon roof level (with strong mixing). They  
688 found that for both mechanisms, there were similar predictions and no significant segregation effect  
689 (the fluctuation from the mean in their study) for most major species (e.g. NO, NO<sub>2</sub> and O<sub>3</sub>).  
690 However, for some fast reacting chemical species (e.g. OH, HO<sub>2</sub> etc.), there were significant  
691 segregation effects.

692 Kim et al. (2012) adopted the RNG  $k - \varepsilon$  turbulence (RANS) model coupled with both simple NO<sub>x</sub>-  
693 O<sub>3</sub> chemistry and the GEOS-Chem photochemical scheme to investigate transport and dispersion of  
694 reactive pollutants within a street canyon (AR=1). An online photolysis rate calculation module was  
695 applied to account for the surface heating effect of diurnal solar radiation on the photolysis rate  
696 coefficients. The NO concentrations predicted from simple NO<sub>x</sub>-O<sub>3</sub> chemistry had a difference up to  
697 100 ppb (i.e. the relative error was about 20%~30% ) compared to those of Baker et al. (2004).  
698 They attributed this discrepancy to the different turbulence models, RANS in this study and LES in  
699 Baker et al. (2004). Compared with field measurements, the model over-predicted the NO  
700 concentration by a factor of 3. This big relative error in NO concentration was expected to decrease  
701 as NO<sub>x</sub> emissions became lower. There was an evidence of a significant difference in predicted O<sub>3</sub>  
702 concentration between complex photochemistry and the simple NO<sub>x</sub>-O<sub>3</sub> chemistry, indicating the  
703 importance of additional formation of O<sub>3</sub> through VOC oxidation processes. This study highlighted  
704 the importance of photochemistry in controlling the concentration of oxidation products (e.g. NO<sub>2</sub>  
705 and O<sub>3</sub>) within street canyons.

706 Kwak and Baik (2012) employed the RNG  $k - \varepsilon$  turbulence (RANS) model coupled with the CBM-  
707 IV mechanism to explore reactive pollutant dispersion within idealised street canyons (AR=1) and  
708 to investigate O<sub>3</sub> sensitivity to NO<sub>x</sub> and VOCs emissions. According to the dispersion  
709 characteristics of NO, NO<sub>2</sub> and O<sub>3</sub> in the simple NO<sub>x</sub>-O<sub>3</sub> chemistry model, the dispersion of species  
710 in this simulation were identified and classified into three types, denoted by NO-type, NO<sub>2</sub>-type and  
711 O<sub>3</sub>-type, with maximum concentrations near the bottom of the street canyon, close to the centre of  
712 the street canyon, and above the street canyon, respectively. The dispersion type of a reactive  
713 species was found to be dependent upon the ratio of VOCs to NO<sub>x</sub> emission rates. Their study  
714 showed that the OH concentration increased with an increase in the VOCs to NO<sub>x</sub> emission ratio,  
715 indicating an important role for OH in determining the dispersion type. The O<sub>3</sub> concentration was  
716 found to be negatively correlated with NO<sub>x</sub> emissions but weakly correlated with VOCs emissions.  
717 This was possibly due to the high NO-to-NO<sub>2</sub> ratio in the street canyon, where the NO titration of  
718 O<sub>3</sub> was more pronounced compared to NO<sub>2</sub> photolysis. Their study provided a good understanding  
719 of the dispersion characteristics of reactive species and the O<sub>3</sub> sensitivity to a range of NO<sub>x</sub> and  
720 VOCs emission scenarios for the street canyon.

721 Kwak et al. (2013) implemented the same RANS model and chemical mechanism as those adopted  
722 by Kwak and Baik (2012), but focusing on the photochemical evolution of reactive species within  
723 street canyons (AR=1,2). The concept of photochemical ages (defined as the time-integrated  
724 exposures of an air parcel to O<sub>3</sub> and OH respectively) was introduced to represent the O<sub>3</sub> and OH  
725 oxidation processes, and normalised by their respective background ages. The normalised  
726 photochemical ages, ranging from 0 (emission characteristics) to 1 (background characteristics),  
727 had the advantage of avoiding the uncertainty of calculating the averaged O<sub>3</sub> and OH concentrations  
728 individually. They found that both O<sub>3</sub> and OH oxidation processes were of importance for the  
729 photochemistry at the canyon-scale. Overall, O<sub>3</sub> was chemically reduced in the lower part, but  
730 chemically produced in the upper part of the deep street canyon (AR=2). This interesting finding  
731 indicated that O<sub>3</sub> was not always chemically reduced in a street canyon. From a sensitivity analysis,

732 the concentration of O<sub>3</sub> was found to be weakly sensitive to the wind speed. An increase of O<sub>3</sub>  
733 concentration was found with an increase in the ratio of VOCs to NO<sub>x</sub> emissions, consistent with  
734 Liu and Leung (2008). This finding implied that the O<sub>3</sub> concentration was more sensitive to changes  
735 of emissions than to changes in dynamics. In terms of characterizing O<sub>3</sub> and OH chemical  
736 processing, the photochemical age concept was applicable to characterise the photochemistry at the  
737 street-canyon scale, and could potentially be extended to the neighbourhood scale.

738 Bright et al. (2013) employed an LES model (the Smagorinsky SGS model) coupled with a  
739 Reduced Chemical Scheme (RCS) and the simple NO<sub>x</sub>-O<sub>3</sub> photochemistry to investigate the effects  
740 of mixing and chemical processing on the atmospheric composition in a urban street canyon  
741 (AR=1). A one-box chemistry model was also adopted for the comparison with the LES coupled  
742 chemistry model to assess the effect of dynamic and chemical processing. The LES coupled  
743 chemistry model was found to underestimate the concentration of NO<sub>x</sub>, OH and HO<sub>2</sub>, but  
744 overestimate the concentration of O<sub>3</sub> averaged over the whole canyon compared to the one-box  
745 chemistry model. The segregation effect caused by the incomplete mixing was found to reduce the  
746 overall canyon-averaged reaction rate and be responsible for the spatial inhomogeneity of reactive  
747 species. It was shown that the RCS scheme predicted higher levels of NO<sub>2</sub> and O<sub>3</sub>, but a lower level  
748 of NO compared with the simple NO<sub>x</sub>-O<sub>3</sub> photochemistry. This can be explained by the additional  
749 NO to NO<sub>2</sub> conversion through VOCs oxidation chemistry present in the RCS. Their study provided  
750 a better understanding of the atmospheric “pre-processing” of emissions from the street canyon  
751 prior to release to the wider overlying background.

752 Kwak and Baik (2014) adopted the RNG  $k-\varepsilon$  turbulence (RANS) model coupled with the CBM-  
753 IV mechanism to examine the removal and entrainment of reactive pollutants at the canyon roof  
754 level via the diurnal variation in NO<sub>x</sub> and O<sub>3</sub> exchange between the 2D street canyon (AR=1) and  
755 the overlying background air. In the morning, two counter-rotating vortices were found in the street  
756 canyon because the heating of downwind wall was stronger than that of upwind wall. Therefore, the  
757 NO<sub>x</sub> and O<sub>3</sub> exchange was found to be dominated by turbulent flow. However, in the afternoon,

758 only one intensified primary vortex was found because heating of the downwind wall was lower  
759 than that of the upwind wall. The turbulent flow became comparable to the mean flow in terms of  
760 the  $\text{NO}_x$  and  $\text{O}_3$  exchange. Their findings indicated that the exchange velocities were strongly  
761 dependent on both the flow pattern induced by surface heating and the photochemistry in the street  
762 canyons (Bright et al., 2013).

763 Zhong et al. (2014) implemented photochemical box models to investigate the segregation effects of  
764 heterogeneous emissions on  $\text{O}_3$  levels in idealised urban street canyons and evaluate the associated  
765 uncertainty when grid-averaged emissions were adopted. The chemical mechanism applied was the  
766 RCS developed by Bright et al. (2013). Chemical effects arising from the heterogeneity of  
767 emissions and dynamic effects represented by the exchange velocity (derived from CFD models)  
768 between the canyon and the overlying background on the  $\text{O}_3$  levels were extensively investigated.  
769 The  $\text{O}_3$  levels within street canyons were found to be strongly linked to the segregation of spatially  
770 varying emissions and to be balanced by both chemistry and dynamics. Their study indentified a  
771 straightforward approach to consider the effects of both chemistry and dynamics using box models  
772 with a wide range of emission scenarios. However, this study was restricted to two boxes  
773 representing two idealised street canyons (totally segregated) with emission heterogeneity.

774 Park et al. (2015) implemented the RNG  $k - \varepsilon$  turbulence (RANS) model coupled with the GEOS-  
775 Chem photochemical scheme (also used in the study by Kim et al. (2012)) to investigate the effect  
776 of canyon aspect ratio on pollutant dispersion in street canyons. One vortex was observed for  
777 canyons with  $1 \leq AR \leq 1.6$ , while two vortices were found for canyons where  $1.6 < AR \leq 2$ . At the  
778 street bottom, there was a significant contrast in the flow pattern between those two types of  
779 canyons. For cases with a low ratio of VOCs to  $\text{NO}_x$  emission, the  $\text{O}_3$  concentrations in street  
780 canyons were much lower than those in the overlying background. This was attributed to the  
781 titration of  $\text{O}_3$  by high levels of  $\text{NO}$ . For cases with higher ratio of VOCs to  $\text{NO}_x$  emission,  $\text{O}_3$  in the  
782 lower canyon was slightly titrated by  $\text{NO}$ , but in the upper canyon  $\text{O}_3$  was formed by  $\text{NO}_2$



783 photolysis following VOCs oxidation processes. The ratio of VOCs to  $\text{NO}_x$  emission was an  
784 important indicator in determining the street-level  $\text{O}_3$  concentration.

785 Simple  $\text{NO}_x\text{-O}_3$  chemistry plays an important role in the street canyon chemistry. The  $\text{NO}_x\text{-O}_3$   
786 photostationary state defect is a useful measure of reacting mixing in the street canyon environment  
787 (Baker et al., 2004). Due to its simple nature, simple  $\text{NO}_x\text{-O}_3$  chemistry can easily be coupled with  
788 either LES or RANS models. Complex chemical mechanisms involve detailed VOCs oxidation  
789 reactions driven by fast radicals (e.g. OH and  $\text{HO}_2$ ), leading to additional NO to  $\text{NO}_2$  conversion  
790 (non- $\text{O}_3$ ). In this sense, complex chemical mechanisms are more realistic than simple  $\text{NO}_x\text{-O}_3$   
791 chemistry. However, due to large amounts of chemical reactions and species, more efforts need to  
792 be spent when incorporating a complex chemical mechanism into numerical models. LES models  
793 perform better in terms of the turbulent mixing of pollutants within street canyons, but require much  
794 more computational cost than RANS. LES can be used to investigate the detailed mechanism of  
795 pollutant dispersion and transport (e.g. Baker et al. (2004); Kikumoto and Ooka (2012); Bright et al.  
796 (2013); Zhong et al. (2015)), with higher (e.g. for  $\text{NO}_x$ ) or lower (e.g. for  $\text{O}_3$ , OH and  $\text{HO}_2$ )  
797 concentrations in the canyon than those at the overlying background. RANS provides the capability  
798 to run quickly for a few scenarios, such as varying intensities of street heating ambient wind speeds,  
799 canyon aspect ratios and emissions (e.g. Kang et al. (2008); Tong and Leung (2012); Kwak and  
800 Baik (2012); Kwak et al. (2013); Park et al. (2015)). With simplified parameterisation of street  
801 canyon air ventilation, box models can be run very quickly for a series of wind conditions and  
802 emission scenarios (e.g. Liu and Leung (2008); Zhong et al. (2014)) so that complex chemical  
803 mechanisms are affordable for street canyon chemistry modelling.

## 804 **5 Modelling concerns**

### 805 **5.1 Street canyon geometry**

806 Street canyon geometry plays an important role in determining the flow patterns and pollutant  
807 dispersion within street canyons. The AR (aspect ratio) influences the number of primary re-

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

## 825 **5.2 Meteorological conditions**

826 Meteorological conditions (e.g. ambient wind and solar radiation) significantly affect the flow and  
827 dispersion of reactive pollutants in street canyons. The ambient wind speed plays an important role  
828 in the formation and intensity of primary vortices thereby determining pollutant retention time in  
829 the canyon, while its direction influences the number and shape of such vortices (Baik et al., 2003).  
830 Nazridoust and Ahmadi (2006) showed that turbulence intensity within street canyon increased with  
831 the ambient wind speed. As pollutant dispersion is strongly dependent on the turbulence in the street  
832 canyon, higher wind speeds lead to stronger street-canyon turbulent flow and thereby making it  
833 more effective for pollutants to be removed from the street canyon. This behaviour was also found

834 by Huang et al. (2000). Small secondary vortices were formed at the corner of the street canyon  
835 under low wind speed conditions, but would disappear under higher wind speed conditions.  
836 Michioka and Sato (2012) examined the effect of incoming turbulent structure on the canyon flow  
837 and pollutant dispersion. The pollutant concentration in the street canyon decreased with an increase  
838 in the incoming turbulent intensity. Changes in ambient wind direction significantly affected the  
839 recirculation pattern in the canyon (Soulhac et al. (2008); Soulhac and Salizzoni (2010); Blackman  
840 et al. (2015)) and thereby influenced pollutant dispersion. Pollutant dispersion was more effective  
841 for an oblique flow than a perpendicular flow, as found in field measurements by Kumar et al.  
842 (2008). In the presence of solar radiation, surfaces of the ground and buildings are heated, which  
843 will influence the atmospheric stability and (to an extent) the chemical reaction rate constants (e.g.  
844 Baik et al. (2007)). The flow field and pollutant dispersion in street canyons can be significantly  
845 affected by additional thermally induced vortices. The combination of mechanically induced  
846 vortices (from wind) and the thermally induced vortices (from heating) adds further complexity  
847 (Xie et al., 2005). Cai (2012a) and Cai (2012b) identified two characteristic heating scenarios in a  
848 street canyon: the assisting case (both roof and upwind wall heating) and the opposing case (both  
849 roof and downwind wall heating) depending on the direction of the thermal-driven flow in relation  
850 to the wind-driven circulation. Li et al. (2012) investigated the effect of ground heating on flow and  
851 pollutant dispersion in street canyons with AR=0.5,1, and 2, and found that the flow and pollutant  
852 patterns underwent significant changes. In general, ground heating enhanced the mixing of  
853 pollutants in street canyons.

### 854 **5.3 Emissions**

855 Traffic is considered to be the major source of emissions in urban street canyons. Vehicle emissions  
856 can be derived based on traffic information and the emission factors of each class of vehicle.  
857 Typically, traffic information contains vehicle fleet composition, average speeds and traffic  
858 volumes. For roads equipped with automatic traffic counts, this traffic information can be easily  
859 obtained. The emission rates for each emitted pollutant (e.g. CO, VOCs, NO<sub>x</sub>) can serve as the input

860 for air pollution modelling (Boddy et al., 2005). Xie et al. (2009) compared a series of measured  
861 data for the CO concentration and the traffic volumes under the same wind direction and a linear  
862 relationship between them was found, as CO is a relatively inert chemical species (on the canyon  
863 timescale). The NO<sub>2</sub>/NO<sub>x</sub> emission ratio by volume from vehicles has typically been applied as 1/11  
864 (e.g. Baker et al. (2004)) or 1/10 (e.g. Bright et al. (2013)), reflecting that the fraction of directly  
865 emitted NO<sub>2</sub> was much lower than that of NO from vehicles, making the production of NO<sub>2</sub> through  
866 the NO titration reaction more important. However, there is evidence of recent increases in  
867 NO<sub>2</sub>/NO<sub>x</sub> emission ratios, up to about 25 % (Carslaw and Rhys-Tyler, 2013). The O<sub>3</sub> concentration  
868 within street canyons is dependent upon both VOCs and NO<sub>x</sub> emission rates. O<sub>3</sub> was found to be  
869 more sensitive to changes in emissions rather than to changes in dynamics. The anticipated trend  
870 over 2005-2020 in VOCs to NO<sub>x</sub> emission rates, based upon scenarios of UK fleet composition  
871 projections (NAEI, 2003) and UK Road Vehicle Emission Factors (Boulter et al., 2009) suggested  
872 that although both VOCs to NO<sub>x</sub> emissions have (and are expected to) generally decrease with time,  
873 the O<sub>3</sub> concentration in street canyons will have slightly increased due to these effects - although  
874 other changes (e.g. in background ozone) may dominate the absolute observed levels / trends.  
875 Finally, it is important to note that real-world emissions may vary substantially from both vehicle  
876 type-approval data, and from inventory values - e.g. Grimmond et al. (1998).

## 877 **5.4 Chemical transformation of pollutants**

878 Emissions from vehicles may be reactive, changing dramatically the chemical composition of the  
879 atmosphere in street canyon environments. Such emissions undergo chemical transformation to  
880 varying extents within the recirculation driven by the canyon flow before their escape into the  
881 overlying atmosphere. Such chemical transformations can occur on a wide range of timescales,  
882 posing difficulty for computationally efficiently handling of chemical processes when these must be  
883 coupled with dynamics at the street canyon scale. The choice of chemical mechanism employed  
884 must be considered depending on the complexity of chemistry involved, and the application. For  
885 street canyon modelling, numerical issues arise because the governing equation systems are highly

886 nonlinear, and extremely stiff (Verwer and Simpson, 1995) especially when highly reactive species  
887 (such as OH and HO<sub>2</sub>) are considered alongside longer-lived VOCs. If diurnal heat (temperature)  
888 effects on the chemistry are included, extra complexity arises since most reaction rates and (to a  
889 lesser extent) photolysis frequencies are influenced by changes in temperature (Kim et al., 2012).  
890 Particular attention should be paid to the handling of fast-reacting species, e.g. applying a  
891 sufficiently short integration time interval (Bright et al., 2013). Also, in the regions close to the  
892 emission source and to the shear layer (which must be well-resolved), negative values of  
893 concentrations may occur in numerical simulations, due to the presence of high concentration  
894 gradients, which in addition to being implausible affect the stability of the stiff chemical system  
895 (Alexandrov et al., 1997). Such negative concentrations indicate unsatisfactory convergence or  
896 insufficiently short integration timescales.

## 897 **6 Conclusions**

898 This article presents a review of air pollution modelling within street canyons, focusing on the  
899 coupling of dynamics and chemistry. For dynamics, the CFD technique has become a powerful  
900 numerical tool, mainly including the RANS and LES models. RANS models are, by their nature, a  
901 steady-state methodology while LES models can handle the unsteadiness and intermittency of the  
902 canyon flow and retrieve transient structures of turbulence in street canyons. The choice between  
903 approaches depends on the computational cost, the accuracy required and hence the application. A  
904 parameter (i.e. 'exchange velocity') representing the overall integrated effect of dynamics in street  
905 canyons provides capability to handle relatively complex chemistry in practical applications. The  
906 representation of the chemistry (i.e. the chemical mechanism) for air pollution modelling is also an  
907 important component for this coupling approach. For short-lived traffic-related pollutants (e.g. NO<sub>2</sub>  
908 and O<sub>3</sub>), chemical time scales are comparable to the canyon dynamic time scale. The chemical  
909 processing of NO<sub>x</sub> and O<sub>3</sub> can play a key role in determining the spatial variation of these species in  
910 street canyons. Simple NO<sub>x</sub>-O<sub>3</sub> chemistry only accounts for the O<sub>3</sub> chemistry changes driven by

911 NO<sub>x</sub>, without consideration of VOCs processing. More complex chemistry involving VOCs  
912 (resulting in the additional conversion of NO to NO<sub>2</sub> that cannot be represented by simple NO<sub>x</sub>-O<sub>3</sub>  
913 chemistry) should be considered for application to the real urban atmosphere. A wide range of  
914 chemical mechanisms with varying complexity considering both NO<sub>x</sub> and VOCs chemistry can  
915 potentially be adopted in street canyon simulations. A variety of factors should be considered such  
916 as street canyon geometry, meteorological conditions, emissions and chemical transformation of  
917 pollutants. Modelling air pollution within a street canyon requires state-of-the-art dynamic models  
918 coupled with high-quality chemical mechanisms to simulate the concentrations and spatial patterns  
919 of key atmospheric chemical species, providing reference information regarding air quality inside  
920 street canyons for policy-makers in support of decision making for traffic policy and urban planning.

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

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 939 partnership with the China Scholarship Council (CSC).

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945 **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 <sub>x</sub> 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 <sub>x</sub> -O <sub>3</sub> chemistry	/	Smagorinsky (1963)	/	3	5	Urban

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

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947 **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 <sub>x</sub> -O <sub>3</sub> chemistry	*Significant spatial variations of NO <sub>x</sub> and O <sub>3</sub> *Introduction of the photostationary state defect
Grawe et al. (2007)	LES	1	1	NO <sub>x</sub> -O <sub>3</sub> chemistry	*Shading effect *A near-linear relationship between concentration differences and the reduction of the NO <sub>2</sub> photolysis rate
Baik et al. (2007)	RANS	1	1	NO <sub>x</sub> -O <sub>3</sub> chemistry	*Street bottom heating scenario *Budget analysis of the advection, diffusion and chemical reaction term
Kang et al. (2008)	RANS	1	1	NO <sub>x</sub> -O <sub>3</sub> 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 <sub>x</sub> -O <sub>3</sub> chemistry	* Different diurnal heating scenarios * Varying canyon aspect ratios
Kikumoto and Ooka (2012)	LES	1	1	NO <sub>x</sub> -O <sub>3</sub> chemistry	* Contrasting transport mechanism for NO <sub>x</sub> and O <sub>3</sub> * Correlation of concentration fluctuations
Zhong et al. (2015)	LES	2	2	NO <sub>x</sub> -O <sub>3</sub> chemistry	*Two-box model *Inferred O <sub>3</sub> production rates
Liu and Leung (2008)	Box model	0.5,1,2	Box	Generalized VOCs-NO <sub>x</sub> mechanism	* O <sub>3</sub> sensitivity to the NO <sub>x</sub> and VOCs emissions * One-box chemistry model * Parameterised air ventilation rate
Garmory et al. (2009)	RANS	1.2	1	NO <sub>x</sub> -O <sub>3</sub> 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 <sub>x</sub> -O <sub>3</sub> 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 <sub>3</sub> sensitivity to the NO <sub>x</sub> and VOCs emissions
Kwak et al. (2013)	RANS	1, 2	1-,2	CBM-IV	* Photochemical evolution * O <sub>3</sub> and OH oxidation processes
Bright et al. (2013)	LES, Box model	1	1	NO <sub>x</sub> -O <sub>3</sub> chemistry and RCS	* Segregation effect * Comparison with box model * Atmospheric "pre-processing"
Kwak and Baik (2014)	RANS	1	1 or 2	CBM-IV	* Surface heating * Diurnal variation of NO <sub>x</sub> and O <sub>3</sub> 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 <sub>x</sub> emission

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