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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_x), 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 (O₃) 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 NO₂ 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 ε 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 ε from their respective transport equations. The turbulence viscosity (μ_t) is calculated
159 from $\mu_t = \rho C_\mu \frac{k^2}{\varepsilon}$ (where C_μ is a modelling constant, ρ is the density), which are then used to
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 ε 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 ε considering vorticity fluctuation and
192 uses a variable of C_μ (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 NO_2 and O_3) and highly reactive chemical species (such
376 as hydroxyl radical (OH), hydroperoxy radical (HO_2) and organic peroxy radicals (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 NO_x - O_3 chemistry**

382 The simple NO_x - O_3 chemistry (Smagorinsky, 1963) describes the photochemical reactions between
383 NO, NO_2 and O_3 . In the presence of sun light, NO_2 is rapidly photolysed leading to NO and 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 O_2 may recombine to form O_3)
386 and NO can also react quickly with O_3 to re-form NO_2 ($\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$). 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 NO_2 . Within the urban environments, the NO_x - O_3 titration
389 interaction with freshly emitted NO can result in a significant local sink for O_3 in street canyons,
390 providing a reduction of 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 NO_x - 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 NO_x - O_3 chemistry only accounts for daytime NO_x - O_3 interactions, without
398 consideration of other 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, HO₂ and RO₂) which may
402 result in additional (non-O₃) conversion of NO to NO₂, and hence to net ozone / oxidant production,
403 that cannot be captured by the simple NO_x-O₃ chemistry. There are a wide range of mechanisms
404 (from near-explicit to substantially reduced mechanisms) with varying complexity considering both
405 NO_x 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_x Mechanism**

481 The Generalized VOCs and NO_x 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_x chemistry thereby providing the capability to qualitatively analyze the
484 formation of O₃ through the conversion of VOCs and NO_x. The simple nature of this VOC-NO_x
485 mechanism allows it to be incorporated into most air pollution models. An early attempt to
486 implement the VOCs and NO_x Mechanism into the street-canyon box modelling on the
487 investigation of O₃ 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_x 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 O₃.

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. NO_2 and 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 NO_x and 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 (NO , NO_2 and 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 NO₂, but
605 comparable to each for O₃. 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 O₃ 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 O₃ 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_x-O₃ 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 O₃ 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 O₃ 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-O₃ 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-O₃ 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, HO₂) play an important role in driving the chemical
664 cycle of VOC degradation (O₃ precursors) leading to the additional peroxy-radical mediated
665 conversion of NO to NO₂ (which is not represented by the simple NO_x-O₃ chemistry) and hence O₃
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_x 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_x 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 O₃ concentration within street canyons was dependent upon both
674 the VOCs and NO_x emission rates. When the ratio of VOCs to NO_x emission rates was higher than
675 10, the O₃ concentration could reach up to the order of 100 ppb. The emission ratio of VOCs and
676 NO_x could therefore be a useful indicator for the increase in O₃ 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_x-O₃ 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, NO₂ and O₃).
690 However, for some fast reacting chemical species (e.g. OH, HO₂ 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_x-
693 O₃ 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_x-O₃ 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_x emissions became lower. There was an evidence of a significant difference in predicted O₃
702 concentration between complex photochemistry and the simple NO_x-O₃ chemistry, indicating the
703 importance of additional formation of O₃ through VOC oxidation processes. This study highlighted
704 the importance of photochemistry in controlling the concentration of oxidation products (e.g. NO₂
705 and O₃) 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 O₃ sensitivity to NO_x and VOCs emissions. According to the dispersion
709 characteristics of NO, NO₂ and O₃ in the simple NO_x-O₃ chemistry model, the dispersion of species
710 in this simulation were identified and classified into three types, denoted by NO-type, NO₂-type and
711 O₃-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_x emission rates. Their study
714 showed that the OH concentration increased with an increase in the VOCs to NO_x emission ratio,
715 indicating an important role for OH in determining the dispersion type. The O₃ concentration was
716 found to be negatively correlated with NO_x emissions but weakly correlated with VOCs emissions.
717 This was possibly due to the high NO-to-NO₂ ratio in the street canyon, where the NO titration of
718 O₃ was more pronounced compared to NO₂ photolysis. Their study provided a good understanding
719 of the dispersion characteristics of reactive species and the O₃ sensitivity to a range of NO_x 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 O₃ and OH respectively) was introduced to represent the O₃ 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 O₃ and OH concentrations
728 individually. They found that both O₃ and OH oxidation processes were of importance for the
729 photochemistry at the canyon-scale. Overall, O₃ 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 O₃ was not always chemically reduced in a street canyon. From a sensitivity analysis,

732 the concentration of O_3 was found to be weakly sensitive to the wind speed. An increase of O_3
733 concentration was found with an increase in the ratio of VOCs to NO_x emissions, consistent with
734 Liu and Leung (2008). This finding implied that the O_3 concentration was more sensitive to changes
735 of emissions than to changes in dynamics. In terms of characterizing O_3 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_x - O_3 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_x , OH and HO_2 , but
744 overestimate the concentration of O_3 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_2 and O_3 , but a lower level
748 of NO compared with the simple NO_x - O_3 photochemistry. This can be explained by the additional
749 NO to NO_2 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_x and O_3 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_x and O_3 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 NO_x and 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 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 O_3 levels were extensively investigated.
769 The 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 NO_x emission, the O_3 concentrations in street
780 canyons were much lower than those in the overlying background. This was attributed to the
781 titration of O_3 by high levels of NO. For cases with higher ratio of VOCs to NO_x emission, O_3 in the
782 lower canyon was slightly titrated by NO, but in the upper canyon O_3 was formed by NO_2

783 photolysis following VOCs oxidation processes. The ratio of VOCs to NO_x emission was an
784 important indicator in determining the street-level 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 HO_2), leading to additional NO to NO_2 conversion
790 (non- 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 NO_x) or lower (e.g. for O_3 , OH and 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_x) 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 NO₂/NO_x 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 NO₂ was much lower than that of NO from vehicles, making the production of NO₂ through
866 the NO titration reaction more important. However, there is evidence of recent increases in
867 NO₂/NO_x emission ratios, up to about 25 % (Carslaw and Rhys-Tyler, 2013). The O₃ concentration
868 within street canyons is dependent upon both VOCs and NO_x emission rates. O₃ 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_x 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_x emissions have (and are expected to) generally decrease with time,
873 the O₃ 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 HO₂) 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. NO₂
908 and O₃), chemical time scales are comparable to the canyon dynamic time scale. The chemical
909 processing of NO_x and O₃ can play a key role in determining the spatial variation of these species in
910 street canyons. Simple NO_x-O₃ chemistry only accounts for the O₃ chemistry changes driven by

911 NO_x, without consideration of VOCs processing. More complex chemistry involving VOCs
912 (resulting in the additional conversion of NO to NO₂ that cannot be represented by simple NO_x-O₃
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_x 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 _x Mechanism	/	(Seinfeld and Pandis, 1998)	/	20	23	Urban
Mainz Isoprene Mechanism	LM	Pöschl et al. (2000)	MIM	44	16	Regional/Global
		Taraborrelli et al. (2009)	MIM2	199	68	
Statewide Air Pollution Research Center	LM	Carter (1990)	SAPRC-90	158	54	Urban
		Carter (2000b)	SAPRC-99	198	72	
		Carter (2010)	SAPRC-07	339	119	
Caltech Atmospheric Chemistry Mechanism	LS	Griffin et al. (2002)	CACM	361	191	Urban
Regional Atmospheric Chemistry Mechanism	LM	Stockwell et al. (1997)	RACM	237	77	Regional
	LM	Stockwell et al. (1990)	RADM2	158	63	
European Monitoring and Evaluation Programme	LM	Gross and Stockwell (2003)	EMEP	148	79	Regional
NO _x -O ₃ chemistry	/	Smagorinsky (1963)	/	3	5	Urban

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

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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 _x -O ₃ chemistry	*Significant spatial variations of NO _x and O ₃ *Introduction of the photostationary state defect
Grawe et al. (2007)	LES	1	1	NO _x -O ₃ chemistry	*Shading effect *A near-linear relationship between concentration differences and the reduction of the NO ₂ photolysis rate
Baik et al. (2007)	RANS	1	1	NO _x -O ₃ chemistry	*Street bottom heating scenario *Budget analysis of the advection, diffusion and chemical reaction term
Kang et al. (2008)	RANS	1	1	NO _x -O ₃ chemistry	* Varying the intensities of street bottom heating *Significant change in pattern of the flow and pollutant dispersion
Tong and Leung (2012)	RANS	0.5-8	Varying	NO _x -O ₃ chemistry	* Different diurnal heating scenarios * Varying canyon aspect ratios
Kikumoto and Ooka (2012)	LES	1	1	NO _x -O ₃ chemistry	* Contrasting transport mechanism for NO _x and O ₃ * Correlation of concentration fluctuations
Zhong et al. (2015)	LES	2	2	NO _x -O ₃ chemistry	*Two-box model *Inferred O ₃ production rates
Liu and Leung (2008)	Box model	0.5,1,2	Box	Generalized VOCs-NO _x mechanism	* O ₃ sensitivity to the NO _x and VOCs emissions * One-box chemistry model * Parameterised air ventilation rate
Garmory et al. (2009)	RANS	1.2	1	NO _x -O ₃ chemistry and CBM-IV	* Field Monte Carlo method for turbulent reacting flow simulation * Segregation effect and micro-mixing
Kim et al. (2012)	RANS	1	1	NO _x -O ₃ chemistry	* An online photolysis rate calculation module

				and GEOS-Chem	* Consideration of dry deposition
Kwak and Baik (2012)	RANS	1	1	CBM-IV	* Dispersion type of reactive species * O ₃ sensitivity to the NO _x and VOCs emissions
Kwak et al. (2013)	RANS	1, 2	1-,2	CBM-IV	* Photochemical evolution * O ₃ and OH oxidation processes
Bright et al. (2013)	LES, Box model	1	1	NO _x -O ₃ chemistry and RCS	* Segregation effect * Comparison with box model * Atmospheric "pre-processing"
Kwak and Baik (2014)	RANS	1	1 or 2	CBM-IV	* Surface heating * Diurnal variation of NO _x and O ₃ exchange
Zhong et al. (2014)	Box model	1	Box	RCS	* Segregation effect * Simple box models * Considering both chemical and dynamical effects
Park et al. (2015)	RANS	1-2	1-2	GEOS-Chem	* Varying canyon aspect ratios * Varying ratios of VOCs emission to NO _x emission

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