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# Urban street canyons: coupling dynamics, chemistry and within-canyon chemical processing of emissions

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## Abstract

Street canyons, formed by rows of buildings in urban environments, are associated with high levels of atmospheric pollutants emitted primarily from vehicles, and substantial human exposure. The street canyon forms a semi-enclosed environment, within which emissions may be entrained in a recirculatory system; chemical processing of emitted compounds alters the composition of the air vented to the overlying boundary layer, compared with the primary emissions. As the prevailing atmospheric chemistry is highly non-linear, and the canyon mixing and predominant chemical reaction timescales are comparable, the combined impacts of dynamics and chemistry must be considered to quantify these effects. Here we report a model study of the coupled impacts of dynamical and chemical processing upon the atmospheric composition in a street canyon environment, to assess the impacts upon air pollutant levels within the canyon, and to quantify the extent to which within-canyon chemical processing alters the composition of canyon outflow, in comparison to the primary emissions within the canyon. A new model for the simulation of street canyon atmospheric chemical processing has been developed, by integrating an existing Large-Eddy Simulation (LES) dynamical model of canyon atmospheric motion with a detailed chemical reaction mechanism, a Reduced Chemical Scheme (RCS) comprising 51 chemical species and 136 reactions, based upon a subset of the Master Chemical Mechanism (MCM). The combined LES-RCS model is used to investigate the combined effects of mixing and chemical processing upon air quality within an idealised street canyon. The effect of the combination of dynamical (segregation) and chemical effects is determined by comparing the outputs of the full LES-RCS canyon model with those obtained when representing the canyon as a zero-dimensional box model (i.e. assuming mixing is complete and instantaneous). The LES-RCS approach predicts lower (canyon-averaged) levels of  $\text{NO}_x$ , OH and  $\text{HO}_2$ , but higher levels of  $\text{O}_3$ , compared with the box model run under identical chemical and emissions conditions. When considering the level of chemical detail implemented, segregation effects were found to reduce the error introduced by simplifying the reaction mechanism. Chemical processing of emissions within the canyon leads to a significant increase in the  $\text{O}_x$  flux from the canyon into the overlying boundary layer, relative to primary emissions, for the idealised case considered here. These results demonstrate that within-canyon atmospheric chemical processing can substantially alter the concentrations of pollutants injected into the urban canopy layer, compared with the raw emission rates within the street canyon. The extent to which these effects occur is likely to be

36 dependent upon the nature of the domain (canyon aspect ratio), prevailing meteorology and emission /  
37 pollution scenario considered.

38

39 *Keywords:* Street Canyons; Air Pollution; Large-eddy simulation; NO<sub>x</sub>; Ozone

40

## 41 **1. Introduction**

42 Urban street canyons, formed by parallel rows of buildings enclosing a vehicular roadway, represent a  
43 unique atmospheric environment. Street canyons are commonly the location of substantial primary  
44 pollutant emissions, usually dominated by traffic sources. They are also locations where substantial  
45 receptor exposure occurs, for pedestrians, road-users and occupants of adjacent buildings which may  
46 source their ventilation from the canyon environment. The semi-enclosed form of many urban street  
47 canyons can give rise to re-circulatory air flow, reducing the ventilation of the canyon to the overlying  
48 urban boundary layer, and further increasing air pollution levels, to potentially harmful levels with  
49 serious implications for public health, vegetation and the built environment (Vardoulakis et al., 2003).  
50 Atmospheric composition within street canyons is determined by a combination of the composition of  
51 background air mixed in from above the canyon, vehicle exhaust and other emissions from within the  
52 street, and the mixing and chemical processing of pollutants within the canyon. The interaction of  
53 these factors determines both the pollutant concentrations experienced within the canyon, their spatial  
54 and temporal variation, the extent to which emissions may undergo chemical processing within the  
55 canyon prior to their release into the overlying boundary layer. As the atmospheric chemical reaction  
56 system which describes the interaction between nitrogen oxides, ozone and organic compounds is  
57 highly non-linear, and the timescale of many of the chemical processes is comparable to the timescale  
58 of the large-scale canyon circulation and mixing (seconds to minutes), it is necessary to consider both  
59 dynamical and chemical effects to understand the abundance and distribution of reactive species  
60 within a street canyon. The aim of this work is to investigate this chemical - dynamical coupling on  
61 the street canyon scale, and to gain insight into the oxidative nature of such an environment to  
62 understand the potential effects upon within-canyon atmospheric composition (and hence pollutant  
63 exposure), and how the canyon outflow composition may differ from the primary emissions, as a  
64 result of within-canyon chemical processing.

65

66 The airflow characteristics of street canyon dynamics are dependent on the overlying wind direction  
67 and speed, and the canyon geometry. In the most simple case, when the direction of the prevailing  
68 wind is perpendicular to the canyon axis and the street canyon aspect ratio (defined as the ratio of  
69 canyon height ( $H$ ) to canyon width ( $W$ )) is unity ( $H/W = 1$ ), skimming flow is observed in which a  
70 large proportion of the flow does not enter the canyon and instead skims over the top of buildings  
71 (Oke, 1987). This flow regime results in the formation of a large primary canyon vortex (Fig. 1) in  
72 which recirculation effectively decouples the canyon atmosphere from the background air above,

73 resulting in reduced exchange and poor ventilation. As a result, skimming flow is relatively  
74 ineffective in removing pollutants from within the canyon (Hunter et al., 1992). Strong intermittency  
75 in the street canyon re-circulation was observed using roof level measurements by Louka et al. (2000)  
76 who concluded that the mean flow within the canyon was merely a residual of an unsteady turbulent  
77 re-circulation. It was proposed that the strong intermittency observed in the recirculation may be due  
78 to the intermittent nature of the mechanism that couples the flow within the canyon with that above  
79 i.e. the shear layer at roof level (Fig. 1). This provides an effective ventilation mechanism allowing air  
80 to escape and efficient mixing to occur when the shear layer moves to an upward position. Such  
81 events, known as sweeps and ejections, are the major turbulent processes that govern pollutant  
82 removal from street level to the background atmosphere above (Cheng and Liu, 2011).

83  
84 Primary pollutants such as nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and volatile organic compounds  
85 (VOCs) are frequently present in significantly higher concentrations within the street canyon when  
86 compared to the overlying background atmosphere, as expected considering proximity to (traffic)  
87 emission sources. The oxides of nitrogen (NO<sub>x</sub> = NO + NO<sub>2</sub>), released predominantly in vehicle  
88 exhaust, dominate gas phase chemistry in urban environments. In polluted urban air, levels of the  
89 hydroxyl radical (OH) are strongly dependent on chemical cycling, which in turn is dependent on  
90 levels of NO<sub>x</sub>. OH initiated VOC degradation in the presence of NO<sub>x</sub> can result in the formation of  
91 secondary pollutants such as ozone (O<sub>3</sub>). O<sub>3</sub> is of particular concern in terms of canyon atmospheric  
92 composition due to its detrimental effects on human health, vegetation, and the built environment.  
93 Within such canyons, O<sub>3</sub> levels are often reduced compared with the overlying air (and more  
94 generally, within urban regions compared with the surrounding areas) due to titration by primary NO,  
95 an effect known as the urban decrement (AQEG, 2009). Under sunlit conditions, NO<sub>x</sub> chemistry is  
96 governed by the photochemical steady state (PSS) chemistry in which NO, NO<sub>2</sub> and O<sub>3</sub> establish  
97 equilibrium. Interactions with peroxy radicals lead to additional NO-to-NO<sub>2</sub> conversion and result in  
98 the net production of O<sub>3</sub>. As such, it is valuable to assess the extent to which pollutants may be  
99 processed prior to their emission into the wider urban atmosphere, in order to gain an insight into the  
100 importance of the oxidative environment of the street canyon.

101  
102 Long lived pollutants such as carbon monoxide (CO) and volatile organic compounds (VOCs) are  
103 unlikely to show a substantial variation in concentration within a street canyon due to chemical  
104 processing alone, with their distributions governed near-exclusively by canyon dynamics. Chemical  
105 processing of NO<sub>x</sub> and O<sub>3</sub>, which have shorter chemical lifetimes, occurs on similar timescales to  
106 those of the key dynamical processes within the urban canopy layer, thereby causing these species to  
107 exhibit a marked variation within the canyon. Very short lived species, such as OH and HO<sub>2</sub>, with  
108 atmospheric lifetimes of seconds, are highly variable within the canyon and respond rapidly to  
109 changes in chemical composition on the canyon scale.

110  
111 Canyon dynamics and composition have been the subject of field measurement campaigns, wind  
112 tunnel experiments and numerical modelling investigations. As road traffic represents the dominant  
113 emission source within typical street canyons, in situations where a single primary vortex forms, a  
114 large gradient of pollutant concentration is observed across the street with the highest concentration of  
115 many pollutants evident toward the leeward wall. A number of field studies have shown that the  
116 concentration of pollutants on the leeward side of the street can be significantly greater than that on  
117 the windward side and that a vertical decrease in concentration on both sides of the street is observed  
118 (Baker et al., 2004; Berkowicz et al., 2002; DePaul and Sheih, 1985; Tomlin et al., 2009; Xie et al.,  
119 2003). Although important in terms of model validation, field studies are often relatively sparse in  
120 terms of their resolution / spatial coverage and can be influenced considerably by the prevailing  
121 meteorological conditions and complex geometry of the surrounding urban environment. Reduced  
122 scale physical models (wind tunnel experiments) have also been used to study pollutant dispersion  
123 and canyon dynamics and have provided evidence for significant horizontal and vertical gradients in  
124 the concentration of passive pollutants within and above the canyon (Gromke et al., 2008; Kastner-  
125 Klein and Plate, 1999; Pavageau and Schatzmann, 1999; Salizzoni et al., 2009; Tomlin et al., 2009);  
126 however scale effects, and the high spatial and temporal resolution of observations required for full  
127 understanding, provide substantial opportunity to use numerical models to investigate canyon  
128 dynamics and composition.

129  
130 Model studies focussing on high resolution representation of canyon fluid dynamics and pollutant  
131 transport/dispersion processes have utilised Reynolds-Averaged Navier-Stokes (RANS) models such  
132 as large-eddy simulation (LES) to simulate canyon turbulent flow and associated pollutant dispersion;  
133 a number of these have been reviewed by Li et al. (2006). Most research has involved the simulation  
134 of passive pollutant dispersal (Cai et al., 2008; Cheng and Liu, 2011; Li et al., 2008; Li et al., 2009;  
135 Liu and Barth, 2002; Liu et al., 2004; Salim et al., 2011; So et al., 2005). In contrast, relatively little  
136 attention has been given to modelling the dispersion of reactive pollutants with most practical  
137 applications tending to focus on the dispersion of a passive scalar, or including only a limited number  
138 of chemical reactions (Baik et al., 2007; Baker et al., 2004; Garmory et al., 2009; Wang and Mu,  
139 2010). Baker et al. (2004) investigated the turbulent dispersion and transport of reactive pollutants  
140 within a street canyon using a large-eddy simulation model with very simple  $\text{NO}_x\text{-O}_3$  titration  
141 chemistry (a two-reaction system) applied, to investigate the deviation from PSS arising from  
142 dynamical effects. Substantial deviations from the expected bulk photochemical steady state were  
143 found, which were quantified as the photostationary state defect (PSSD). The highest values of the  
144 PSSD and therefore greatest deviation from chemical equilibrium, were observed well above the  
145 canyon ( $z/H \approx 1.3$ ) corresponding the outer extent of the escaping canyon plume – i.e. where polluted  
146 canyon air meets less polluted background air flowing over the canyon. A significant variation in the

147 photostationary state defect within the canyon was also found to occur with the highest ‘within  
148 canyon’ values observed downwind of the emission source and toward ground level on the windward  
149 wall, due to entrainment of air by the canyon vortex. The lowest values of the passive scalar co-  
150 emitted with  $\text{NO}_x$  were observed in the centre of the canyon vortex. The same limited reaction scheme  
151 was subsequently used by Grawe et al. (2007) to investigate the effect of local shading on pollutant  
152 concentrations. Baik et al. (2007) used the same simple representation of the photochemistry to study  
153 the dispersion of reactive pollutants within the street canyon, using a RANS-based dynamical model.  
154 A similar variation in the photostationary state defect was found, with the largest deviation from  
155 chemical equilibrium found above roof level where canyon outflow meets background air, and the  
156 region closest to chemical equilibrium found to be the within the canyon vortex. The limited  
157 chemical mechanisms present in these studies however neglects the impact of more detailed  
158 atmospheric chemistry, for example, peroxy-radical mediated  $\text{NO}$  to  $\text{NO}_2$  conversion with associated  
159  $\text{O}_3$  (or total oxidant) production, or  $\text{NO}_x$  removal through formation of reservoir compounds.

160  
161 Few studies have investigated the dispersion of reactive pollutants by applying more comprehensive  
162 photochemical reaction schemes to dynamical models. Due to limitations in computing power it is  
163 not practical to include the full range of chemical species and reactions that occur in the urban  
164 atmosphere (even should all such emissions and reactions be known), particularly when combined  
165 with computationally expensive dynamical models such as LES. Explicit representation of the  
166 oxidation processes taking place within the canyon may contain several thousand chemical species  
167 and over 20,000 reactions (Dodge, 2000). Owing to the computational expense of such models it is  
168 still impractical to include *near*-explicit chemical schemes (such as the Master Chemical Mechanism  
169 – see below) as a true representation of the canyon chemistry. As a result a number of *reduced*  
170 chemical mechanisms, including those reviewed by Dodge (2000), have been developed that  
171 reasonably accurately represent the chemical environment of urban canyons, and may be effectively  
172 and affordably applied to photochemical / dynamical models.

173  
174 The work of Garmory et al. (2009) used the Stochastic Fields (SF) method to simulate turbulent  
175 reacting flows and the dispersion of reactive scalars within the street canyon. This research applied  
176 the same simple chemical scheme as used by Baker et al. (2004), Grawe et al. (2007) and Baik et al.  
177 (2007), and utilised a number of statistical methods to characterise atmospheric processing within the  
178 canyon. The results of this initial study were in close agreement with those of Baker et al. and Baik et  
179 al., with lowest values of the photostationary state defect located within the canyon, and greatest  
180 values observed just above roof level, within the mixing layer. In addition to the simple scheme the  
181 more detailed Carbon Bond Mechanism (CBM-IV; Gery et al., 1989) was used. Comparing both  
182 mechanisms, the effect of segregation was quantified by evaluating the Damköhler number,  $Da$ ,  
183 defined as the ratio of the mixing timescale to the chemical timescale. A value of  $Da \gg 1$  indicates

184 that the chemistry / dynamical interaction is important and that segregation effects must be accounted  
185 for (Garmory et al., 2006; Krol et al., 2000). If  $Da \ll 1$ , species become well mixed much more  
186 rapidly than their chemical processing timescale, and hence segregation effects are minimal. For  
187 intermediate- and long-lived species, including important species such as  $O_3$  and  $NO$ , Garmory et al.  
188 found the effect of segregation to be minimal; however for a number of the shorter lived radical  
189 species this work, using the CBM-IV mechanism, demonstrated significant differences in predicted  
190 concentration in the mixing region above the canyon when segregation effects were considered.

191

192 A six-species chemical reaction scheme was applied using both box and LES model frameworks by  
193 Krol et al. (2000), with a focus upon the larger atmospheric boundary layer scale (rather than the  
194 street canyon domain). Akin to Garmory et al. (2009), this research investigated the deviation from  
195 chemical equilibrium, as a result of the turbulent nature of the convective boundary layer, in terms of  
196 the intensity of segregation. It was found that turbulence inherent in the convective boundary layer  
197 results in large concentration fluctuations and that these give rise to a divergence from chemical  
198 equilibrium in contrast to that obtained using box model calculations. When species are emitted  
199 uniformly the volume averaged concentrations were found to deviate only slightly from the box  
200 model concentrations, however when reactive hydrocarbons were emitted non-uniformly (as is likely  
201 to occur in reality) segregation effects are increased, with volume averaged LES model results  
202 showing that the rate of destruction of reactive hydrocarbons (RH - representing all reactive  
203 hydrocarbons and intermediate species) may be reduced by up to 30 % when compared to that  
204 calculated using the box model – i.e. the box model dynamical framework substantially  
205 underestimates the chemical lifetime of emitted species within the canyon. It was also found that if  
206 both the turbulent timescale and the chemical timescale of a compound are comparable, the integrated  
207 flux of RH through the RH-OH reaction will be reduced due to the chemistry-turbulence interaction.  
208 Pugh et al. (2011) also investigated boundary layer segregation effects using field measurements  
209 taken above a tropical rainforest in South-East Asia. The effect of segregation on the reaction between  
210 OH and isoprene was determined using high temporal resolution isoprene concentration data. It was  
211 found that the reduction in the effective rate constant for the reaction of isoprene with OH due to  
212 segregation effects was typically less than 15 %; an intensity of segregation considerably lower than  
213 that needed to explain observed inconsistencies between measured and modelled OH concentrations  
214 produced by global and box models of atmospheric chemistry in isoprene rich environments (e.g.  
215 Lelieveld et al., 2008).

216

217 Most recently, Kwak & Baik (2012) reported CFD simulations of street canyon atmospheric  
218 composition incorporating the CBM-IV mechanism, and explored the sensitivity of within-canyon  
219 ozone levels to perturbations in  $NO_x$  and VOC emissions. Ozone was found to be negatively  
220 correlated with  $NO_x$ , reflecting the impact of  $NO$  titration dominating over  $NO_2$  photolysis as a source

221 of ozone; this was characterised as a negatively  $\text{NO}_x$ -sensitive regime. Kim et al. (2012) report  
222 comparison of CFD simulations using the chemical code from the GEOS-Chem model (Bey et al.,  
223 2001) with field observations in a street canyon in Guangzhou, China. The model successfully  
224 reproduced the observed levels of species which are essentially passive on the canyon timescale (e.g.  
225 CO), but substantially overestimated NO (factor of three). In contrast to the work of Garmory et al.,  
226 Kim et al. found that modelled canyon  $\text{O}_3$  levels varied substantially with the chemical mechanism  
227 applied – in comparison with the full reaction scheme, application of a reduced mechanism ( $\text{NO}_x$ - $\text{O}_3$   
228 photostationary steady state only) led to increases in within-canyon  $\text{O}_3$  levels of up to 150 %. The  
229 importance of within-canyon processing of emissions, the level of chemical detail necessary to  
230 satisfactorily account for such processing, and quantification of the resulting pollutant export to the  
231 urban atmosphere, remain open questions.

232  
233 In the present work, we describe the development of a new model combining a validated  
234 representation of street canyon dynamics, together with a sufficiently detailed chemical mechanism to  
235 fully assess the impacts of chemistry - dynamics coupling upon atmospheric composition and  
236 atmospheric oxidation rates within a street canyon regime. This model combines an LES dynamical  
237 treatment with a newly developed and computationally affordable chemical mechanism (termed the  
238 reduced chemical scheme, RCS). The RCS mechanism itself was developed from a near-explicit  
239 chemical mechanism (the Master Chemical Mechanism; Jenkin et al., 1997), and is validated against  
240 the MCM (which in turn has been validated against field and chamber observations), under conditions  
241 and timescales relevant to the street canyon regime. In contrast to our previous work, (Baker et al.,  
242 2004; Grawe et al., 2007) the level of chemical detail incorporated in the RCS allows the within-  
243 canyon VOC oxidation, associated net ozone (or oxidant) production, and  $\text{NO}_x$  removal through  
244 conversion to reservoir species, to be evaluated – all processes well known to be of importance in the  
245 real atmosphere, but which the more simple chemical mechanisms cannot address. We apply the  
246 combined LES-RCS model to evaluate impacts of the combined chemical and dynamical processes  
247 upon within-canyon atmospheric composition and its variability (and hence pollutant exposure), and  
248 to evaluate how the canyon outflow differs from the primary emissions within the canyon, as a  
249 consequence of within-canyon chemical processing. The effects of chemistry and dynamics are  
250 separated by comparing the canyon-average results from full LES-RCS simulations, with those  
251 performed under identical chemical conditions, using a box model alone (which corresponds to  
252 uniform and instantaneous mixing). A representative flux of processed pollutants out of the street  
253 canyon into the overlying boundary layer is determined.

254

## 255 **2. Development of the reduced chemical scheme (RCS)**

### 256 *2.1 Chemical Mechanism*



257 In order to develop a suitable model to study street canyon atmospheric composition a representation  
258 of the chemistry to be applied within the dynamical model is required. To achieve this, a zero-  
259 dimensional box model was used as an efficient tool to develop a chemical reaction mechanism which  
260 was sufficiently computationally affordable when implemented within the (computationally  
261 expensive) LES dynamical model. The most accurate representation of gas-phase tropospheric  
262 chemistry can be achieved through the use of near-explicit chemical mechanisms such as the Master  
263 Chemical Mechanism (MCM) (Jenkin et al., 1997) or the Generator for Explicit Chemistry and  
264 Kinetics of Organics in the Atmosphere (GECKO-A) (Aumont et al., 2005). The MCM v3.1  
265 describes the degradation of 135 volatile organic compounds (VOCs) including the major UK  
266 anthropogenic emissions and biogenic species including isoprene and the monoterpenes  $\alpha$ - and  $\beta$ -  
267 pinene, including over 5,900 chemical species and 13,500 chemical reactions (Bloss et al., 2005;  
268 Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003). The MCM has been evaluated using  
269 high quality datasets obtained from experiments carried out in large outdoor environmental reaction  
270 chambers and ambient field observations. As the MCM is too computationally expensive to  
271 incorporate directly into the LES framework, a subset of the MCM, the Common Representative  
272 Intermediates mechanism version CRI v2-R5 (Jenkin et al., 2008; Watson et al., 2008), which  
273 includes 19 emitted anthropogenic VOCs to represent full speciation, 196 chemical species and 555  
274 reactions, was used as a starting point for further scheme reduction. The reduced chemical scheme  
275 derived from this (hereafter referred to as the RCS) was then compared with the full MCM simulation,  
276 the latter providing the standard for RCS evaluation. The reduced form of the CRI has itself been  
277 evaluated in comparison to the MCM and other mechanisms, and found to replicate well both  
278 integrated ozone production on timescales of days, and (of more relevance here) OH levels on  
279 timescales of hours under polluted (industrial) conditions (Emmerson and Evans, 2009).

280

## 281 *2.2 Mechanism Development*

282 In order to reduce the CRI v2-R5, the scope of simulations was initially limited to daytime scenarios,  
283 allowing night time only chemistry to be removed (parent VOC degradation by  $\text{NO}_3$  and inorganic  
284  $\text{NO}_3/\text{NO}_y$  reactions were retained). Further reduction was achieved by eliminating parent compounds,  
285 and any unique daughter products, which had little effect on the key chemical intermediates under  
286 street canyon conditions, while scaling the abundance of other (parent) compounds to retain the same  
287 OH reactivity. The metrics used to assess each simplification were concentrations of OH, NO,  $\text{NO}_2$ ,  
288  $\text{O}_3$  and hydroperoxy radical ( $\text{HO}_2$ ), the key criterion being to maintain OH levels within 10 % of those  
289 predicted by the (full) MCM using the (full) parent VOC set. The explicit inorganic chemistry from  
290 the MCM was fully retained. The initial concentrations of pollutants used in developing the reduced  
291 chemical scheme were determined using observations taken during the Tropospheric ORganic  
292 CHemistry experiment (TORCH) field campaign carried out in suburban London (Lee et al., 2006),  
293 with the  $\text{NO}_x$  range extended to cover a range from 15 and 513 ppb, to better represent the conditions

294 that may occur within a street canyon. The number of parent VOCs considered was reduced, using  
 295 VOC reactivity (with respect to OH) as a proxy for ozone production potential on the short timescales  
 296 relevant to the street canyon residence time. Physically the OH reactivity of a VOC represents the  
 297 inverse of the lifetime of OH due to loss by reaction with that species; OH reactivity provides a  
 298 suitable measure of the overall potential for VOC oxidation and subsequent formation of organic  
 299 peroxy radicals and hence O<sub>3</sub> formation. The remaining parent VOC abundance was adjusted to  
 300 maintain the total OH reactivity (Equation 1), at the (observed) value of 3.4 s<sup>-1</sup> (Lee et al., 2006).

$$301 \quad k'_{OH} = \sum k_{1(OH+VOC_1)}[VOC]_1 + k_{2(OH+VOC_2)}[VOC]_2 + k_{3(OH+VOC_3)}[VOC]_3 \dots \quad (1)$$

302 The final RCS includes 51 chemical species and 136 reactions; with methane and 8 parent non-  
 303 methane hydrocarbons (NMHCs) included in the mechanism (Table 1: isoprene, ethene, propene,  
 304 formaldehyde, acetaldehyde, methanol, ethanol and peroxyacetyl nitrate).

305

### 306 *2.3 Evaluation of the RCS*

307 The accuracy of the RCS was assessed in comparison to the evolution of species concentrations  
 308 calculated using the full MCM for a single air parcel, initialised using the starting concentrations  
 309 listed in Table 1. Over a four hour period, the maximum percentage difference in OH between the  
 310 RCS and the MCM was approximately 6 %, which is within the bounds of the smallest errors  
 311 associated with the measurement of OH (7 – 16 %) (Heard and Pilling, 2003). For NO, NO<sub>2</sub>, O<sub>3</sub> and  
 312 HO<sub>2</sub> the largest differences between the RCS and the MCM, which occur toward the end of the four  
 313 hour time period, are 15 %, 7 %, 4 % and 14 % respectively. At the 30 minute time point, more  
 314 relevant to canyon residence times, smaller differences of 0.4 %, 0.1 %, 0.2 %, 1.1 % were observed  
 315 respectively, with 0.7 % for OH. The RCS and MCM were also compared under elevated NO<sub>x</sub>  
 316 conditions (NO = 1000 ppb and NO<sub>2</sub> = 120 ppb) which may be experienced within canyons due to  
 317 proximity to vehicle exhausts. The maximum differences observed over a four hour period were 3 %,  
 318 13 %, 16 %, and 4 % for NO, NO<sub>2</sub>, O<sub>3</sub> and HO<sub>2</sub> respectively with 12 % for OH. At  $t = 30$  minutes the  
 319 modelled differences were 0.3 %, 1.7 %, 2.1 %, 3.0 % and 2.4 % for NO, NO<sub>2</sub>, O<sub>3</sub>, HO<sub>2</sub> and OH  
 320 respectively. These values are significantly smaller than the uncertainty associated with emissions and  
 321 with the measurement of such pollutants (Boulter et al., 2009; Lee et al., 2006).

322

### 323 **3. Configuration of models used to simulate urban street canyon composition**

324 Two principal approaches are applied here to simulate atmospheric composition and pollutant  
 325 processing in street canyons. The primary tool is the full LES-RCS model, which represents the most  
 326 comprehensive treatment of the combined effects of dynamics, chemistry and emissions; the LES-  
 327 RCS domain included both the street canyon and the overlying boundary layer (described below,  
 328 section 3.1). The LES-RCS output was compared with simulations in which the street canyon was  
 329 approximated by a zero-dimensional box model (“Box-RCS”), corresponding to a scenario in which

330 concentrations are homogeneous (*i.e.* the volume of air is assumed to be instantaneously and  
 331 completely mixed). In this scenario, the box model corresponds to the within-canyon region ( $z/H \leq$   
 332 1), and exchange with the overlying boundary layer was parameterised using an exchange velocity  
 333 expression, as described below.

334

### 335 *3.1 Configuration of the LES-RCS model*

336 The LES dynamical model was used to simulate atmospheric motion and turbulent flow in and above  
 337 an idealised street canyon with an aspect (height/width) ratio of one. The model is based on the  
 338 Regional Atmospheric Modelling System (RAMS), described in more detail in Cui *et al.* (2004). The  
 339 prevailing wind direction in the model remains constant and perpendicular to the canyon axis, which  
 340 is representative of a worst case scenario from the perspective of pollutant accumulation, in which  
 341 canyon ventilation is minimal. The wind speed was initially set to zero below the roof level and  
 342 increased logarithmically to a maximum speed,  $U_{max}$ , of  $2.5 \text{ m s}^{-1}$  at the top of the domain. Mesh  
 343 resolution in the  $x$ ,  $y$  directions were  $\Delta x = 0.3 \text{ m}$ ,  $\Delta y = 1.0 \text{ m}$  respectively. In the  $z$  direction,  $\Delta z = 0.3$   
 344 m within the canyon and gradually stretched by a factor of 1.15 above roof level ( $z = 18.0 \text{ m}$ ) to a  
 345 maximum of  $5.0 \text{ m}$  at the top of the domain ( $z = 94 \text{ m}$ ). Cyclic boundary conditions were applied to  
 346 all three velocity components along  $x$ - and  $y$ -directions. The temperature was defined as  $293 \text{ K}$   
 347 throughout the whole model domain, representative of neutral conditions. Fig. 2a illustrates the street  
 348 canyon domain included in the LES model, while Fig. 2b shows the developed flow field within and  
 349 above the canyon. The dynamical part of the LES model for a canyon with an aspect ratio  $H/W$  of 1  
 350 has been validated by Cui *et al.* (2004), through comparisons of the mean wind and resolved-scale  
 351 turbulent kinetic energy (TKE) against wind-tunnel experiments, while the scalar part of the model  
 352 under various  $H/W$  ratios has been validated by Cai *et al.* (2008), in which the normalized fluxes were  
 353 compared with wind-tunnel measurements.

354

355 In each experiment, the model was run without chemistry for 30 minutes in order for the turbulent  
 356 dynamics to reach a quasi-equilibrium state (Cai *et al.*, 2008). At this time, concentrations of all 51  
 357 chemical species (initial concentration as listed in Table 1; intermediate and product concentrations as  
 358 calculated from a 30-minute model integration) were inserted in the whole model domain uniformly.  
 359 This set of values was also used as the inlet boundary conditions above the upwind building

360 throughout the simulation. At the outlet boundary, the advective condition,  $\frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial x} = 0$ , was

361 applied to all chemical species, where  $c_i$  represents the concentration of species,  $i$  and  $u$  is horizontal  
 362 velocity. For the intermediate- and longer-lived chemical species included in the chemical  
 363 mechanism, for example,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{CO}$ , a timestep of  $10^{-2} \text{ s}$  was used in the numerical  
 364 integration, while for shorter lived species such as  $\text{OH}$ ,  $\text{HO}_2$  and  $\text{RO}_2$  a timestep of  $10^{-3} \text{ s}$  was

365 employed. These timestep values were empirically chosen to balance the requirement for stable  
 366 output / convergence against integration time.

367

368 Emissions within the canyon were represented by two line sources centred at 2.5 m to the left and  
 369 right of the canyon centre, signifying two lanes of traffic. Each of the line sources was considered to  
 370 have a Gaussian distribution (where  $\sigma_x = 3$  m and  $\sigma_y = 1$  m), which were located at 1.0 m above the  
 371 road as illustrated in Figure 1, and were continuous in nature. The emission rates included in the  
 372 model were determined using the UK Road Vehicle Emission Factors (2009 - Boulter et al., 2009)  
 373 and are representative of moderate weekday traffic (1500 vehicles per hour) for an urban road with  
 374 cars travelling at an average speed of 30 mph. The total emissions for NO, NO<sub>2</sub>, CO, ethene (C<sub>2</sub>H<sub>4</sub>),  
 375 propene (C<sub>3</sub>H<sub>6</sub>), formaldehyde (HCHO) and acetaldehyde (CH<sub>3</sub>CHO) used were 101, 17, 377, 36, 24,  
 376 11 and 16  $\mu\text{g m}^{-1} \text{s}^{-1}$ , which equate to 900, 100, 3593, 347, 150, 96 and 98 ppb emitted into one LES  
 377 model cell (0.3 m  $\times$  0.3 m  $\times$  1 m) per second, respectively. Photolysis frequencies were calculated  
 378 offline using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model v4.1 (Madronich and  
 379 Flocke, 1998), using conditions representative of those for a street canyon in Birmingham, UK (52°  
 380 29' N; -1°54' W) at 12.00 UTC on 1<sup>st</sup> August, giving a calculated solar zenith angle of 34°. The  
 381 ground elevation was specified as 0.12 km and the atmosphere was assumed to be cloud free. A  
 382 surface albedo of 0.15 was defined i.e. typical of an urban street surface (DFT, 2009; Liu et al., 2011).  
 383 Photolysis rates were held constant over the modelling period in order to reduce the computational  
 384 expense once implemented in the LES, reflecting the short residence time (minutes) of a typical street  
 385 canyon air parcel (Baker et al., 2004; Vardoulakis et al., 2003). Following the initiation of the  
 386 emissions and chemistry, the combined effects of emission, mixing and chemical processing on  
 387 atmospheric composition could then be simulated by the LES-RCS model, and the results examined to  
 388 provide an insight into the processes affecting atmospheric composition over a 180 minute period.

389

390 Using the LES-RCS model, 3-D data was obtained over the period from 30 to 210 minutes at 5 s time  
 391 intervals. Results were averaged along the  $y$ -axis over the length of the canyon ( $L_y$  - along which the  
 392 resolved-scale turbulence is homogeneous), across the width of the canyon (the  $x$ -axis;  $W$ ) and over  
 393 the height of the canyon (the  $z$ -axis;  $H$ ) to give a volume averaged (0-D) within-canyon concentration  
 394 as a function of time, i.e.:

$$395 \quad \bar{c}_i(t) = \frac{1}{W \cdot H \cdot L_y} \int_{-0.5W}^{0.5W} \int_0^H \int_0^{L_y} c_i(x, y, z, t) dx dy dz. \quad (2)$$

396 The LES results were averaged along the length of the canyon in the  $y$  axis ( $L_y$ ), across the width of  
 397 the canyon in the  $x$  axis ( $W$ ), over the height of the canyon in the  $z$  axis ( $H$ ) and averaged over the  
 398 final hour of the simulation ( $150 \leq t \leq 210$  min, i.e. after 30 minutes of dynamical and 120 minutes of

399 chemical spin-up) to give a time and volume averaged within canyon concentration, for comparison  
 400 with the box-model scenario.

$$401 \quad \bar{c}_i = \frac{1}{W \cdot H \cdot L_y \cdot (t_2 - t_1)} \int_{t_1}^{t_2} \int_{-0.5W}^{0.5W} \int_0^H \int_0^{L_y} c_i(x, y, z, t) dx dy dz dt. \quad (3)$$

402 The LES results were also averaged along the length of the canyon in the y axis ( $L_y$ ) and over the final  
 403 60 minutes of the averaging period to give 2-D time averaged concentrations ( $150 \leq t \leq 210$  min) i.e.:

$$404 \quad \langle \varphi \rangle(x, z) = \frac{1}{L_y \cdot (t_2 - t_1)} \int_{t_1}^{t_2} \int_0^{L_y} \varphi(x, y, z, t) dy dt, \quad (4)$$

405 where  $\varphi$  can be  $w$  or  $c_i$ . Following Eq. (4),  $\tilde{\varphi} = \varphi - \langle \varphi \rangle$  represents the resolved fluctuations of  $\varphi$   
 406 about  $\langle \varphi \rangle$ . Thus the following quantities are defined: the resolved-scale vertical turbulent flux,  
 407  $F_{turb} = \langle \tilde{w} \tilde{c}_i \rangle$ , the vertical advective flux,  $F_{adv} = \langle w \rangle \langle c_i \rangle$ , and total resolved-scale vertical flux  
 408  $F_{total} = F_{turb} + F_{adv}$ . These are 2D quantities showing the spatial pattern of these variables in the  $x$   
 409 and  $z$  domain. For the purposes of analysis, vertical mixing ratio profiles were extracted from the 2-D  
 410 time averaged concentrations at five sites across the canyon. In addition, the horizontally-averaged  
 411 vertical profile of the passive scalar's flux inside and above the canyon was derived (Equation 5):

$$F(z) = \frac{1}{W} \int_{-0.5W}^{0.5W} F(x, z) dx. \quad (5)$$

412

### 413 3.2 Configuration of the zero-dimensional box-RCS model

414 As one aim of this work is to compare canyon-average concentrations predicted by the full LES-RCS  
 415 model using Equation 2, with their equivalents determined using a zero-dimensional box model, under  
 416 identical chemical and emission conditions, treatment for the exchange between the street canyon and  
 417 the overlying boundary layer was required. In the case of the LES-RCS model, the modelled domain  
 418 (Figure 2) includes both within-canyon and above-canyon regions, and so implicitly incorporates  
 419 exchange between the canyon and the overlying boundary layer. For the box model scenario, mixing  
 420 with an overlying boundary layer was achieved by implementing a suitable exchange velocity ( $\omega$ )  
 421 within the model, defined as:

$$422 \quad \omega_t = \frac{F_c}{\bar{c} - c_B} \quad (6)$$

423 where  $F_c$  is the pollutant flux  $F_i$  at roof level ( $z/H = 1$ ) and the denominator is the difference between  
 424 the mean concentration within the canyon ( $\bar{c}$ ) and the background concentration above the canyon  
 425 ( $c_B$ ). In the case of the box model simulations, the composition of the overlying boundary layer was  
 426 assumed to be constant, and set equal to the LES-RCS domain inlet composition.

427 The value of  $\omega_t$  was determined using LES simulations of a passive scalar (a non-reactive emitted  
428 species which is conserved within the model, and whose concentrations are therefore determined by  
429 dynamics alone) to evaluate mean rate of exchange between the canyon and boundary layer in the  
430 LES simulations. A mean value of  $\omega_t = 0.021 \text{ m s}^{-1}$  was determined, averaged over the final hour of  
431 the simulation ( $150 \leq t \leq 210 \text{ min}$ ). Use of a single mean value removes the variability in the LES  
432 simulations (arising from periodic sweep / ejection events) – apparent in the comparisons of mean  
433 concentrations discussed below. The chemical scheme, photolysis treatment and emissions were  
434 identical in the LES-RCS and Box-RCS model cases.

435

## 436 **4. Results and discussion**

### 437 *4.1 Spatial variation*

438 Fig. 3 illustrates the mean mixing ratios of the passive scalar (subject solely to dispersion / mixing)  
439 and of a number of chemical species, averaged over the final 60 minutes of the 210 minute simulation  
440 (logarithmic colour scales for  $\text{O}_3$ , OH and  $\text{HO}_2$ ). Major features apparent are the primary vortex that  
441 spans the canyon and the shear layer at roof level that increases in amplitude and becomes  
442 increasingly turbulent downwind, trapping pollutants toward the leeward wall and allowing greater  
443 exchange toward the windward wall. Increased levels of NO,  $\text{NO}_2$  and the passive scalar are observed  
444 within the street canyon compared to the background atmosphere above roof level, as expected. The  
445 highest concentrations of these species are found at low level toward the leeward wall, a result of the  
446 limited dispersion and chemical processing of emissions before they are transported downwind from  
447 their sources located towards the centre of the street. In the case of  $\text{NO}_2$ , increased levels observed  
448 toward the leeward wall at street level arise through secondary formation through reaction of NO with  
449 entrained  $\text{O}_3$ , i.e. through the oxidation of emitted NO, in addition to that emitted directly.  $\text{HO}_x$  levels  
450 are much lower within the canyon than in the background air, with a local maximum in the centre of  
451 the vortex, a semi-isolated region of entrained background air. Elevated OH within this region  
452 (relative to the periphery of the canyon) primarily reflects a reduced OH sink, in particular reaction  
453 with NO – see below.

454

455 Fig. 4 illustrates the vertical mixing ratio profiles of  $\text{O}_3$ , NO,  $\text{NO}_2$ , OH and  $\text{HO}_2$  shown using a  
456 logarithmic scale at five across street locations within the canyon ( $z/H \leq 2$ ). The concentrations of  $\text{O}_3$ ,  
457 OH and  $\text{HO}_2$  increase near roof level on the approach to the less polluted background atmosphere  
458 above. The smallest transition between within canyon and background concentrations of all chemical  
459 species occurs toward the windward wall due to the increase in exchange of air between the canyon  
460 and the background air above in this region associated with the turbulent nature of the shear layer at  
461 this point. Towards the leeward wall a sharp contrast exists between the canyon and the background  
462 atmosphere, marked by a large change in concentration with height at roof level as pollutants become

463 effectively trapped by the relatively impermeable shear layer that exists in this region. Fig. 4(a)  
 464 illustrates a significant change in the concentration of NO and NO<sub>2</sub> across the canyon with the  
 465 concentration of NO at street level toward the leeward wall more than double (2.3 x) that observed on  
 466 the windward side, whilst NO<sub>2</sub> levels are over a third higher (1.4 x). The highest mixing ratios of  
 467 ozone within the canyon are evident toward the windward wall and in particular toward roof level  
 468 where ozone rich air is brought into the canyon from aloft. Toward the leeward wall the mixing ratios  
 469 of both NO and NO<sub>2</sub> show a significant decrease with height above roof level where levels rapidly  
 470 approach those of the background atmosphere. Moving toward the windward wall of the canyon  
 471 again results in a much more gradual transition between within canyon and the background  
 472 atmosphere as the influence of the shear layer spans a greater distance in this region causing the air  
 473 well above the canyon to be mixed with that escaping from within.

474  
 475 The change in mixing ratio of OH and HO<sub>2</sub> is illustrated in Fig. 4(b). Within the canyon the greatest  
 476 concentrations of both OH and HO<sub>2</sub> are observed toward roof level at the windward wall where  
 477 concentrations are slightly higher for OH and over a third greater for HO<sub>2</sub> when compared to that at  
 478 street level toward the leeward wall. OH and HO<sub>2</sub> levels are higher in the centre of the primary  
 479 canyon vortex. Close to roof level ( $z/H \approx 1.1$ ) toward the leeward wall of the canyon OH and HO<sub>2</sub>  
 480 approach their background mixing ratios of 0.22 and 1.54 ppt respectively, while these levels are only  
 481 achieved well above at  $z/H \approx 1.5$  on the windward side of the canyon. The reductions in OH and HO<sub>2</sub>  
 482 within the canyon compared to the background atmosphere are 64 % and 85 % respectively  
 483 (averaged across the canyon). Mean within canyon levels of NO and NO<sub>2</sub> of 168 and 68 ppb  
 484 respectively (Table 3) are considerably greater than the overlying urban boundary layer, while within-  
 485 canyon O<sub>3</sub> levels are on average 11.2 ppb lower than those in the background atmosphere.

486 Figure 5(a) illustrates the mixing ratio of the sum of organic peroxy radicals (i.e.  $\Sigma RO_2$ , here  
 487 excluding HO<sub>2</sub>) determined by the LES-RCS, averaged over the final 60 minutes of the simulation  
 488 (logarithmic colour scale). The RO<sub>2</sub> abundance exhibits a similar pattern to that of OH, with a local  
 489 minimum toward the lower leeward wall and maxima observed within the primary vortex, close to the  
 490 mixing layer at roof level and toward the windward wall, and a tongue of elevated RO<sub>2</sub> accompanying  
 491 the entrained air into the vortex on the windward side. To further investigate the importance of HO<sub>x</sub>  
 492 sources and sinks within and above the canyon, the chemical rate of production / loss for OH was  
 493 evaluated, using time averaged ( $150 \leq t \leq 210$  min) reactant concentrations determined for three  
 494 locations (indicated in Fig. 5a): (V) within the vortex ( $z/H = 0.5$ ,  $x/W = 0$ ), (L) toward the leeward  
 495 wall ( $z/H \approx 0.08$ ,  $x/W \approx -0.3$ ) and (B) in the background atmosphere above the canyon ( $z/H \approx 1.2$ ,  $x/W$   
 496  $\approx -0.3$ ). The change in OH with respect to time is governed by the rate of production and loss, as  
 497 below (neglecting transport, negligible for OH):

$$498 \quad \frac{\partial[OH]}{\partial t} = P_{OH} - \sum_X k[OH][X]. \quad (7)$$

499 Where  $P_{OH}$  is the total rate of production of OH, and  $-k [OH] [X]$  represents the chemical loss of OH  
 500 through reaction with X. The dominant OH chemical production and loss terms for each location  
 501 (rates of reaction, here expresses in ppt  $s^{-1}$ ) are given in Table 2. Primary OH production ( $O_3$   
 502 photolysis) predictably falls with reduced  $O_3$  abundance from the background into the canyon (NO  
 503 titration), but comprises a small fraction of the total production rate. NO-driven radical cycling  
 504 dominates OH production, with a significant (up to 22 %) contribution from HONO photolysis. The  
 505 lifetime of HONO is comparable to the timescale of the vortex circulation and mixing (photolysis  
 506 lifetime of 8 minutes), thus HONO must be explicitly considered in understanding OH abundance  
 507 (cannot be assumed to be in steady state). No heterogeneous sources of HONO were implemented  
 508 within this model – see discussion below. Going from the background to leeward (within-canyon)  
 509 locations, the OH sink increases from  $2.8 s^{-1}$  to  $96 s^{-1}$ , a factor of 30, while the dominant OH  
 510 production rate,  $HO_2 + NO$ , increases from 1.1 to  $11.7 ppt s^{-1}$  (total OH production increases by a  
 511 factor of 8.8); accordingly within-canyon OH levels are much lower than in the overlying boundary  
 512 layer. The local maximum in OH in the vortex centre arises from the semi-isolated nature of this part  
 513 of the domain; at the centre, OH production rates are comparable with those at the leeward site (total  
 514 production rate of 11.5 vs.  $13.6 ppt s^{-1}$ , dominated by  $HO_2 + NO$ ), but the OH sink is much lower than  
 515 that directly downwind of the emission source –  $61 vs. 96 s^{-1}$  – and OH levels are correspondingly *ca.*  
 516 31 % higher.

517  
 518 Within the street canyon, gas phase chemistry is dominated by  $NO_x$  and as such it is often useful to  
 519 consider the temporal and spatial variation in  $NO_x$  levels. The chemical interaction of  $NO_x$  with  $O_3$   
 520 plays a key role in determining  $NO_2$  levels observed in the urban environment. As a result of this  
 521 interaction, another useful measure to consider is defined as the total oxidant ( $O_x = O_3 + NO_2$ ).  
 522 Considering only NO- $NO_2$ - $O_3$  reactions,  $O_x$  is conserved whilst partitioning between the component  
 523 forms of  $O_3$  and  $NO_2$  is determined by overall levels of  $NO_x$ ,  $O_3$  and solar radiation. Figs. 5(b) and (c)  
 524 illustrate the spatial variation in  $NO_x$  and  $O_x$  within and above the canyon domain. The mixing ratios  
 525 of  $NO_x$  and  $O_x$  are both greater within the canyon (236 and 79 ppb respectively) compared to the  
 526 background atmosphere where  $NO_x = 9 ppb$  and  $O_x = 50 ppb$ . The spatial distribution of  $NO_x$  (Fig  
 527 5(b)) is similar to that of the passive scalar (Fig. 3(d)) demonstrating the effective conservation of  
 528  $NO_x$  on the canyon residence timescale. The change in mixing ratio of  $NO_x$  and  $O_x$  with height  
 529 within the canyon ( $0.0 \leq z/H \leq 2.0$ ) at five sites across the street is illustrated in Fig. 6 using a  
 530 logarithmic scale. The highest concentration of  $NO_x$  occurs at street level toward the leeward wall  
 531 downwind of the two line emission sources located in the centre of the street. Figs. 5 and 6 also  
 532 indicate that the lowest levels of  $O_x$  occur toward street level on the upper windward wall with the  
 533 highest concentrations close to street level toward the leeward wall. Elevated  $O_x$  in this region arises  
 534 from the 5 % primary  $NO_2$  emission within the  $NO_x$  source term. The lowest ratios of  $NO_2$  to NO  
 535 (Fig. 5d) occur at street level downwind of the emission sources toward the leeward wall. The



536 decrease in the NO<sub>2</sub>/NO ratio within the canyon primarily reflects the predominance of NO in the  
 537 primary NO<sub>x</sub> emission term. Table 3 illustrates that the ratio of NO<sub>2</sub> to NO is higher for the box  
 538 model case indicating greater (mean) simulated conversion of NO to NO<sub>2</sub> when dynamical effects are  
 539 neglected (i.e. assuming instant mixing). This arises as a number of cells within the LES model have  
 540 very little or no O<sub>3</sub> present (Fig. 3) hence NO to NO<sub>2</sub> conversion is precluded at many locations.

541

#### 542 *4.2 Atmospheric composition and exchange rate effects*

543 The change in the canyon averaged concentration of the passive scalar over time is compared between  
 544 the LES and box model results (Fig. 7). Fluctuations in the concentration of the averaged passive  
 545 scalar inherent in the LES results are caused by large scale variations of the flow and the variable  
 546 nature of canyon ventilation caused by the unsteady fluctuations in the shear layer at roof level, as  
 547 observed by Louka et al. (2000) and reproduced by the model. The optimum value of exchange  
 548 velocity,  $\omega_t$ , can be determined by minimising the difference between the passive scalar results for the  
 549 LES and box model. As shown in Fig. 7, for the final 60 minute averaging period a value of  $\omega_t =$   
 550  $0.021 \text{ m s}^{-1}$  applied to the box model best represents the LES values and is therefore applied to the box  
 551 model simulations for comparison with canyon averaged LES results of other chemical species.

552 The sensitivity of the canyon averaged concentrations derived from the box model output to the value  
 553 of the exchange velocity,  $\omega_t$ , between the canyon air and the background atmosphere was  
 554 investigated. The effect of increasing  $\omega_t$  from  $0.021 \text{ m s}^{-1}$  to  $0.022 \text{ m s}^{-1}$  is illustrated in Table 4. This  
 555 increase in the exchange velocity results in a decrease in mean within canyon averages of NO<sub>x</sub> and O<sub>x</sub>  
 556 by 4.5 % and 2 % respectively. The concentration of O<sub>3</sub> increases with  $\omega_t$ , partially due to an increase  
 557 in O<sub>3</sub> rich background air entering the canyon from above, and partly due to lower NO levels reducing  
 558 the titration of O<sub>3</sub> to NO<sub>2</sub>. For OH and HO<sub>2</sub>, increasing  $\omega_t$  reduces the modelled levels due to a  
 559 reduction in the concentration of VOCs, as increased mixing leads to increased ventilation out of the  
 560 canyon. In the case of the passive scalar, we have  $\omega_t \cdot (\bar{c} - c_B) = \text{constant}$ , and thus

$$561 \quad \frac{\bar{c}^{(b)} - c_B}{\bar{c}^{(a)} - c_B} = \frac{\omega_a}{\omega_b}, \quad \text{and} \quad \frac{\bar{c}^{(b)} - \bar{c}^{(a)}}{\bar{c}^{(a)}} \cong -0.045.$$

$$562 \quad \text{Whereas for NO}_x \text{ where } c_B \ll \bar{c}^{(a)} \text{ then } \frac{\bar{c}^{(b)} - \bar{c}^{(a)}}{\bar{c}^{(a)}} \cong -\frac{\omega_b - \omega_a}{\omega_a} = -0.048.$$

563 The similarity of these results (and those in table 4) indicates that (on this timescale) NO<sub>x</sub> is  
 564 approximately passive in nature.

565

#### 566 *4.3 Temporal changes and segregation effects within the canyon*

567 The variation with time of the spatially averaged ‘within canyon’ concentrations of a number of  
 568 species simulated by the LES-RCS model is compared with their equivalents simulated using the box

569 model (with equal emissions and net external mixing applied) in Fig. 8. Significant differences  
570 between the concentrations of key chemical species simulated using the box and LES approaches are  
571 apparent. In general, the LES results show much greater dynamically-driven variability, and with  
572 some net deviations from the within-canyon mixing ratios taken from the box model. For NO, over  
573 the final 60 minutes of the simulation, the box model results are around 1 % higher than those of the  
574 LES simulation. Levels of NO<sub>2</sub> are also higher in the box model than the LES, throughout the  
575 simulation, with a mean difference of 10 % over the final hour of the modelled period ( $150 \leq t \leq 210$   
576 min), while ozone levels are correspondingly lower, by 6 % over the final hour of the simulation. Fig.  
577 8(a) illustrates the change in mixing ratio of NO<sub>x</sub> and O<sub>x</sub> over time. Over the final hour of the model  
578 run, levels of NO<sub>x</sub> and O<sub>x</sub> simulated by the box model are higher than those from the LES by 3 and  
579 8 % respectively (Table 3) – thus the changes in abundance reflect chemical impacts upon NO<sub>x</sub> and  
580 O<sub>x</sub> abundance, rather than solely perturbations to the NO-NO<sub>2</sub>-O<sub>3</sub> photochemical steady state  
581 partitioning. Following the initial spin up of each model run, a large initial peak in both OH and HO<sub>2</sub>  
582 is observed directly after emissions are introduced. These peaks are followed by a rapid decline to  
583 equilibrium, which is achieved *ca.* 30 minutes after emission initiations. In contrast to the LES, the  
584 box model simulations approach equilibrium much more rapidly, reflecting the slower mixing  
585 processes inherent in the LES when compared to the fast and perfectly mixed conditions of the box  
586 model – as would be expected, segregation effects cause a reduction in the rate at which canyon-  
587 averaged concentrations approach the equilibrium levels simulated in a single-compartment model,  
588 i.e. street canyons respond more slowly to perturbations than a single-box model would suggest. OH  
589 and HO<sub>2</sub> levels simulated by the box model in steady state are higher than those in the LES  
590 simulation, with mean differences of 11 % and 8 % respectively over the final 60 minutes of the  
591 simulation. The assumption of instant mixing inherent to the box model leads to overestimates of the  
592 concentrations of NO, NO<sub>2</sub> and OH, and an underestimate for O<sub>3</sub>, relative to the LES-RCS approach.  
593 Segregation effects, spatial inhomogeneity in composition due to incomplete mixing, reduce the  
594 canyon-averaged rate at which O<sub>3</sub> reacts with NO to produce NO<sub>2</sub> (i.e. the dominant pathway for NO  
595 to NO<sub>2</sub> conversion), due to limited or near-zero quantities of O<sub>3</sub> in a number of cells within the LES  
596 model domain, as is apparent in Fig. 3. In terms of HO<sub>x</sub>, it is clear that segregation effects also play  
597 an important role in determining composition; the higher OH abundance within the box model implies  
598 an overestimate of the extent of OH-driven processing of reactive emissions within the canyon,  
599 compared with the more accurate LES scheme. While the comparison shown in Fig. 8(b) suggests a  
600 deviation of the order of 11 %, the actual difference will be greater, as the OH levels experienced by  
601 the majority of emitted air parcels within the canyon will reflect the circumference of the vortex,  
602 rather than the centre (where OH levels are approximately 30 % higher).

603

604 *4.4 VOC oxidation chemistry and atmospheric composition: RCS v a simple chemistry case*

605 To further ascertain the effect of the detailed VOC oxidation chemistry, the results obtained using the  
 606 RCS mechanism (51 chemical species and 136 reactions) were compared with those obtained using a  
 607 3 reaction scheme ( $O_3$ - $NO_x$  chemistry alone, *i.e.* reactions 8 - 10, below), as used by previously by  
 608 Baik et al. (2007), Baker et al. (2004) and Grawe et al. (2007).



612 Comparisons were performed using both the LES and box-model dynamical frameworks. The initial  
 613 conditions ( $NO_x$  and  $O_3$  levels) were identical to those applied using the full chemical scheme in both  
 614 cases, and within the LES construct the simulated dynamics were identical to those used with the full  
 615 chemical scheme. It is important to note that photochemical steady state was not in fact achieved (or  
 616 assumed) in any cells of the model domain – as the dynamical residence time was too short (typically  
 617 fractions of a second, *vs.* the 1 - 2 minute time constant for the  $NO$ - $NO_2$ - $O_3$  system under sunlit  
 618 conditions). Fig. 9 shows a comparison of the  $O_3$ - $NO_x$ -only case with the full RCS reaction scheme.  
 619 Going from the simple to the full scheme, levels of  $NO_2$  and  $O_3$  are higher and  $NO$  lower, reflecting  
 620 additional  $NO$  to  $NO_2$  conversion (and net ozone production) in the more detailed chemistry.  
 621 Correspondingly, levels of  $O_x$  are higher, while  $NO_x$  levels are slightly lower (again, going from the  
 622 simple to the full scheme), reflecting the presence of  $NO_x$  loss processes (e.g. formation of nitric acid,  
 623  $HNO_3$ ) and partitioning to other  $NO_y$  species (e.g.  $HONO$ ,  $HO_2NO_2$ ). The differences between the  
 624 full RCS scheme, and  $O_3$ - $NO_x$ -only case, are similar but not identical between the box and LES  
 625 dynamical frameworks – the changes in  $NO$ ,  $NO_2$ ,  $NO_x$ ,  $O_3$  and  $O_x$  are all less between the two LES  
 626 models (dashed lines in Fig. 9), than the two box models (solid lines in Figure 9). For example, for  
 627  $NO$  the box models show a decrease of ca. 8 % going from the  $O_3$ - $NO_x$ -only to the full chemical  
 628 approaches, while the reduction is only 5 % for the LES models. For  $NO_2$ , the corresponding  
 629 increases are ca. 18 % for the box models and 12 % for the LES approaches; changes in ozone are  
 630 (proportionately) similar. Within the LES dynamical framework, the system is less sensitive to the  
 631 additional chemical processes included in the RCS, compared with the  $O_3$ - $NO_x$ -only scheme. In much  
 632 of the domain,  $O_3$  levels are very low / zero, such that the  $NO:NO_2$  ratio is increased, and impacts of  
 633  $NO_x$  removal and partitioning in the full chemical scheme are reduced, while ozone production is  
 634 immediately repartitioned into  $NO_2$  – effectively, segregation effects in the LES simulations make the  
 635 canyon-averaged model composition less sensitive to the chemical simplifications attendant in  
 636 moving from the RCS to the basic  $O_3$ - $NO_x$  only chemical mechanism. These results are consistent  
 637 with those of Garmory et al. (2009), who found only a modest sensitivity of the predicted  $NO_x$  and  $O_3$   
 638 levels towards the level of detail in the chemical mechanism used, but do not agree with the findings  
 639 of Kim et al. (2012), who reported substantial (> 100 %) changes in ozone levels with the inclusion of  
 640 VOC oxidation chemistry, in comparison with an  $O_3$ - $NO_x$  only type approach. It is surprising that  
 641 Kim et al. observed such substantial increases in ozone, as observed photochemical ozone production

642 rates are typically of the order of 5-20 ppb per hour (e.g. Cazorla et al., 2012), so increases of the  
643 order reported would imply canyon residence times of the order of hours. The study of Kim et al.  
644 successfully reproduced observed levels of essentially conserved species such as CO, suggesting that  
645 the general canyon circulation / residence time / ventilation rate were well simulated, but noted that  
646 levels of NO were substantially greater than those observed, pointing to differences in emissions from  
647 those occurring in reality – substantial discrepancies between predicted and observed vehicular  
648 emissions, particularly for NO<sub>x</sub>, are widely observed (e.g. Carslaw et al., 2011). Alternatively, this  
649 may reflect different model approaches to implementing photochemical steady state within the model  
650 – if it is assumed that photochemical steady state is actually achieved within each cell (in contrast to  
651 the present work), a different distribution between NO + O<sub>3</sub> and NO<sub>2</sub> would result – one which,  
652 relative to the approach used here, would be expected to favour NO<sub>2</sub> in the near-source region within  
653 the canyon, and NO + O<sub>3</sub> in the canyon outlet. It is not clear from the descriptions given if  
654 photochemical steady state was in fact adopted by Kim et al.

655

#### 656 *4.5 Within-Canyon Chemical Processing*

657 Fig. 10 illustrates the change in mixing ratio of O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>x</sub> with height at the canyon  
658 inlet ( $x/W = -0.5$ ) and canyon outlet planes ( $x/W = +0.5$ ). Increases are observed in the level of NO,  
659 NO<sub>2</sub>, NO<sub>x</sub> and O<sub>x</sub> leaving the canyon, indicating the combined effect of primary emissions and  
660 chemical processing on the abundance of pollutants escaping to the wider background atmosphere. In  
661 order to evaluate the extent of within-canyon processing further, the change in vertical flux of a  
662 number of species with height was calculated based on Equation 5 for the final hour of the model  
663 simulation (shown in Fig. 11). The calculated resolved-scale flux near roof level ( $z/H = 1$ ) can be  
664 used to determine a representative flux of pollutants out of the canyon and into the background  
665 atmosphere. This may then be compared with raw emission rates to evaluate the within-canyon  
666 processing (although given the turbulent nature of the canyon-background interface (e.g. Figs 1, 3) the  
667 choice of height at which to evaluate this is somewhat arbitrary). A peak in the resolved-scale  
668 turbulent flux profile is apparent at  $z/H \approx 0.1$  and a decrease in total flux is seen for  $z/H < 0.1$  in all  
669 flux profiles. This is the result of the elevation of the line emission source located within the centre of  
670 the canyon 1 m above street level. For the passive scalar, the profile differs from that expected a priori  
671 for a conserved quantity which should remain constant with height. At roof level ( $z/H \approx 1$ ) the flux of  
672 the passive scalar into the background atmosphere is equal to 933 ppb m<sup>-2</sup> s<sup>-1</sup> i.e. 93 % of that emitted  
673 is escaping into the wider atmosphere. The maximum flux of the passive scalar of 1000 ppb m<sup>-2</sup> s<sup>-1</sup> is  
674 observed slightly below roof level. This observed decrease in the flux of passive scalar with height  
675 arises from the sub-grid scale turbulent dispersion not resolved explicitly within the LES model (the  
676 sub-grid scale flux is not included here). Because of this, the fluxes of NO<sub>x</sub> and O<sub>x</sub> out of the canyon  
677 discussed below are obtained at a height slightly below the roof level,  $z_f = 0.933 H$ , where the

678 contribution of sub-grid scale dispersion is minimised and at which height the flux of passive scalar  
679 reaches 99.6% of its theoretical value.

680

681 A positive upward total flux of both NO and NO<sub>2</sub> from within the street to the overlying background  
682 atmosphere is observed with a negative (downward) flux of O<sub>3</sub>, with a significant effect of within-  
683 canyon chemical processing upon pollutant flux escaping the canyon apparent for NO and NO<sub>2</sub>. The  
684 maximum total flux of NO (798 ppb m<sup>-2</sup> s<sup>-1</sup>) occurs near street level ( $z/H \approx 0.2$ ). At  $z = z_f$ , the flux of  
685 NO is equal to 752 ppb m<sup>-2</sup> s<sup>-1</sup> compared to a raw emission rate equivalent to 900 ppb s<sup>-1</sup>. Therefore  
686 there is an approximately 16.5 % chemical conversion of NO within the canyon when compared to the  
687 raw emission rate. The maximum flux of NO<sub>2</sub> (248 ppb m<sup>-2</sup> s<sup>-1</sup>) occurs just below roof level and is  
688 approximately 2.5 times that of the raw emission rate of 100 ppb s<sup>-1</sup>, again indicating within-canyon  
689 processing affecting the level of NO<sub>2</sub> escaping into the wider urban boundary layer. In terms of O<sub>3</sub>  
690 the maximum downward flux into the canyon of 135 ppb m<sup>-2</sup> s<sup>-1</sup> occurs just above roof level as O<sub>3</sub>  
691 rich background air enters the canyon from above, and O<sub>3</sub> is removed within the canyon by reaction  
692 with NO. At  $z = z_f$  (near roof level), the flux of NO<sub>x</sub> is 989 ppb m<sup>-2</sup> s<sup>-1</sup> or 1.1% lower than that  
693 emitted; O<sub>x</sub> is 130 ppb m<sup>-2</sup> s<sup>-1</sup> at  $z = z_f$ , or 30% higher than the 100 ppb s<sup>-1</sup> of NO<sub>2</sub> emitted. Therefore  
694 NO<sub>x</sub> release into the boundary layer is almost the same as that emitted, but oxidant release increases  
695 significantly, in part as a result of the chemical processing taking place within the canyon. These  
696 findings demonstrate the value in considering the modelled (and observed) levels of NO<sub>x</sub> and of  
697 oxidant (O<sub>x</sub>), alongside NO / NO<sub>2</sub> / O<sub>3</sub>, which can be used to disaggregate the effects of NO<sub>x</sub>-O<sub>3</sub>  
698 photochemical steady state from net photochemical ozone production. Garmory et al. (2009) report  
699 values of simulated OH levels along a vertical profile through the centre of the canyon of the order of  
700 0.003 – 0.006 ppt, significantly lower than the mean within-canyon value determined here (0.08 ppt;  
701 Table 3); however differences in the emissions profiles (total NO<sub>x</sub> emission used here *ca.* 60 % of that  
702 of Garmory et al. (with differing fractions of primary NO<sub>2</sub>: 5 % vs. 1 % respectively), and a much  
703 lower VOC:NO<sub>x</sub> emission ratio (*ca.* 10 % of that used by Garmory et al., by volume, excluding CO)  
704 probably accounts for much of this difference – lower OH levels reflecting the much larger VOC sink,  
705 not compensated for by equivalently enhanced NO-driven HO<sub>x</sub> cycling. Kim et al. (2012) showed  
706 that OH-driven oxidation (of SO<sub>2</sub> and NO<sub>2</sub>) could result in measurable secondary aerosol production  
707 of up to 0.7 μg m<sup>-3</sup> within the street canyon, which may be compared with roadside PM<sub>10</sub> levels of 25  
708 – 47 μg m<sup>-3</sup> (whole UK roadside site annual average, and Marylebone roadside annual average -  
709 AQEG, 2005). Kim et al. do not report their simulated OH levels, and no condensed phase processes  
710 were considered in this work; however an upper estimate for comparison may be obtained: The mean  
711 flux through the OH + NO<sub>2</sub> reaction (Table 2, *i.e.* neglecting that only a fraction of this will partition  
712 to the particulate phase within the canyon) equates to 56 μg m<sup>-3</sup> of HNO<sub>3</sub> production, supporting the

713 conclusion of Kim et al. that significant secondary aerosol production may occur on the canyon  
714 timescale.

715

716 Several studies have examined the partition of total flux of a scalar ( $F_{total}$ ) between mean advective  
717 flux ( $F_{adv}$ ) and turbulent flux ( $F_{turb}$ ) for a street canyon. Based on the results of their RANS  
718 renormalisation group (RNG)  $k$ - $\varepsilon$  turbulence model for a passive scalar, Liu et al. (2011) analysed  
719 roof level fluxes, *i.e.*,  $F(z=H)$ , where  $F(z)$  as defined by Equation 5 can be either  $F_{adv}$  or  $F_{turb}$  (denoted  
720 by  $\overline{PCH}$  or  $PCH''$  in their paper). Our results (Fig. 11) demonstrate that both  $F_{adv}(z)$  or  $F_{turb}(z)$  are  
721 very sensitive to height near the roof level. The 2D fields of  $F_{adv}(x,z)$  and  $F_{turb}(x,z)$  for a passive scalar  
722 derived from LES simulations conducted by Cheng and Liu (2011) support this observation.  
723 Therefore the analysis of vertical profiles of  $F_{adv}$  and  $F_{turb}$  is necessary and useful. As seen in Fig. 11,  
724 the dominant vertical flux observed within the canyon from the street level up to  $z/H \approx 0.8$  is the mean  
725 advective flux which transports all pollutants (except for  $O_3$ ) upwards toward roof level throughout  
726 the canyon. Between  $z/H \approx 0.8$  and roof level, the mean advective flux decreases rapidly to become  
727 negative just above the top of the canyon ( $1.0 \leq z/H \leq 1.2$ ) indicating that the mean flow (averaged  
728 across the domain) acts to entrain pollutants downwards toward the canyon at this height. For all  
729 species included in Fig. 11, a large increase in the resolved-scale turbulent flux is observed toward  
730 roof level indicating the importance of the shear layer associated turbulent processes in pollutant  
731 exchange at this level. For all species except  $O_3$ , the resolved-scale turbulent flux at roof level is at a  
732 maximum and is positive, indicating that there is more pollutant escaping out of the canyon at this  
733 height through turbulent transport than entering from the background atmosphere above. The mean  
734 flux of all species excluding  $O_3$  and  $O_x$  becomes close to zero at a height of  $z/H \approx 1.4$  *i.e.* toward the  
735 free flowing boundary layer above, which is unaffected by the dynamical processes taking place  
736 within and just above the canyon itself. For  $O_3$  however, a negative mean flux is observed until well  
737 above roof level indicating net downward transport of  $O_3$  rich air towards the canyon. These results  
738 are consistent with those of Baik et al. (2007), who adopted an RNG  $k$ - $\varepsilon$  turbulence model but applied  
739 it to simple  $NO_x$ - $O_3$  chemistry; they showed 2D fields of  $-\partial F(x,z)/\partial z$  instead of  $F(x,z)$  for the purpose  
740 of budget analysis, in which  $F(x,z)$  was either  $F_{adv}(x,z)$  or  $F_{turb}(x,z)$  of  $NO$ ,  $NO_2$ , and  $O_3$ .

741

## 742 5. Conclusions

743 A reduced chemical scheme has been developed based upon a subset of a near explicit chemical  
744 mechanism, and implemented within an LES simulation of urban street canyon dynamics. The  
745 resultant LES-RCS model has been used to investigate urban street canyon atmospheric composition  
746 by simulating the combined effects of emissions, mixing and chemical processing on pollutant  
747 concentration within an idealised canyon. Pollutants within and above the canyon were found to  
748 show a clear spatial variation, with  $NO_x$  levels close to the leeward wall over double those of the

749 windward wall; such variations are of importance in assessing the potential exposure of receptors to  
750 air pollutants. Through comparison of simulations using the LES dynamical framework with those  
751 using a simple zero-dimensional box model approach, the effects of segregation on canyon  
752 atmospheric chemistry and composition are evident. Compared with a single-box canyon model, the  
753 LES scheme responds more slowly to chemical perturbations, and (after quasi-equilibrium is  
754 established) the box model simulated levels of NO, NO<sub>2</sub> and OH were found to be higher than their  
755 (canyon-averaged) equivalents in the more realistic LES scheme, while levels of O<sub>3</sub> were  
756 underestimated compared with the LES approach. The assumption of instant mixing inherent to the  
757 box model leads to overestimates of the concentrations of NO, NO<sub>2</sub> and OH, and an underestimate for  
758 O<sub>3</sub>, relative to the LES approach. Segregation effects, due to spatial inhomogeneity in composition  
759 due to incomplete mixing, reduce the canyon-averaged rate at which O<sub>3</sub> reacts with NO to produce  
760 NO<sub>2</sub> (i.e. the dominant pathway for NO to NO<sub>2</sub> conversion), due to limited quantities of O<sub>3</sub> present in  
761 a number of cells within the LES model domain (Fig. 3). Segregation effects also affect HO<sub>x</sub> levels;  
762 the higher OH abundance within the box model implies an overestimate of the extent of OH-driven  
763 processing of reactive emissions within the canyon, compared with the more realistic LES approach.  
764 While the comparison shown in Fig. 8(b) suggests a deviation of the order of 11 %, the actual  
765 difference will be greater, as the OH levels experienced by the majority of emitted air parcels within  
766 the canyon will reflect the circumference of the vortex, rather than the centre (where OH levels are  
767 approximately 30 % higher). Through comparison of the comprehensive RCS and O<sub>3</sub>-NO<sub>x</sub>-only  
768 chemical mechanisms, a clear effect of the inclusion of detailed oxidation chemistry is also evident.  
769 Going from the O<sub>3</sub>-NO<sub>x</sub> only system to the RCS mechanisms, levels of NO<sub>2</sub> and O<sub>3</sub> are higher and NO  
770 lower, reflecting additional NO to NO<sub>2</sub> conversion (and net ozone production) under the more detailed  
771 chemistry. Segregation effects reduced the sensitivity of the model outputs to the increase in  
772 chemical complexity when comparing the box model dynamical framework to the LES approach.

773

774 Chemical processing of emissions takes place within the canyon, contributing to an increase in O<sub>x</sub> (O<sub>3</sub>  
775 + NO<sub>2</sub>) of 30 % (compared to the primary NO<sub>2</sub> component of the emission source), for the moderately  
776 polluted emission scenario considered. This result shows that the atmospheric “pre-processing” of  
777 primary emissions taking place within street canyons can be significant in terms of atmospheric  
778 composition and the flux of pollutants from street canyon level to the wider urban boundary layer  
779 above. These processes are likely to be dependent upon the nature of the domain (canyon aspect  
780 ratio), prevailing meteorology and emission / pollution scenario considered. Further research to  
781 average the extent of these effects across a representative parameter space will determine the  
782 modification to raw emission rates which might be applied to account for within canyon processing of  
783 raw emissions in larger scale regional and neighbourhood models.

784

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794



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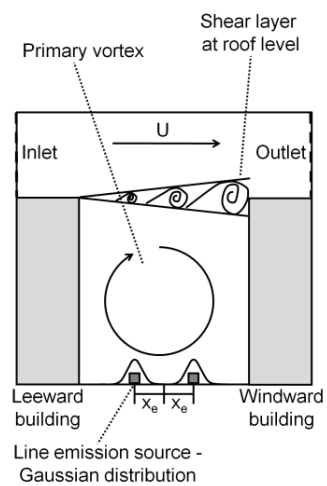
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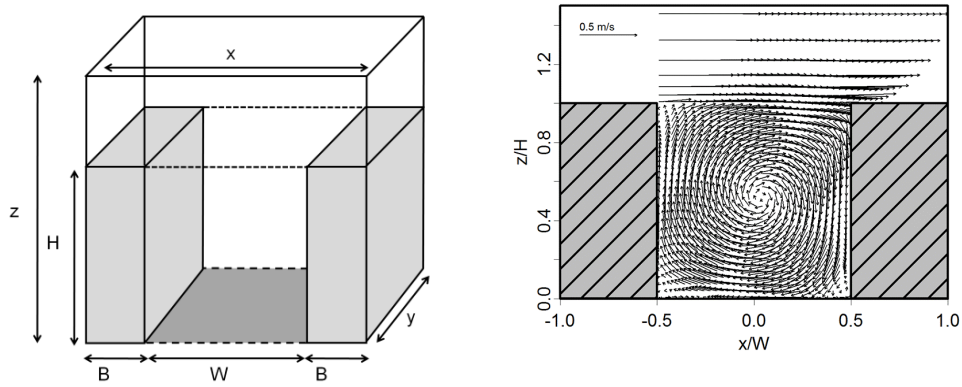


Figure 1



**Fig. 1.** Schematic diagram illustrating the main components of an idealised street canyon, as used in this study.

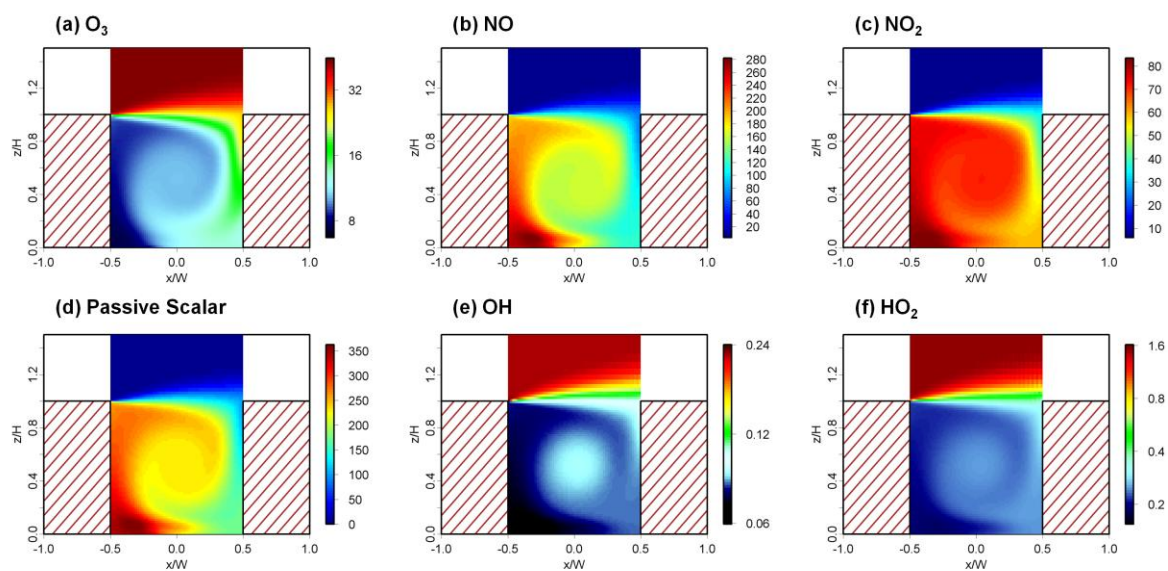
Figure 2



**Fig. 2.** (a) Schematic illustration of the LES model domain where  $x = 24$  m,  $y = 40$  m and  $z = 94$  m with canyon dimensions  $W = 18$  m,  $H = 18$  m and  $B = 3$  m and (b) Mean flow field diagram, showing temporally and spatially (along the  $y$  axis) averaged wind vectors ( $u$ ,  $w$ ). Averages were taken over the final hour of the model simulation ( $150 \leq t \leq 210$  min), when the canyon circulation was fully developed.

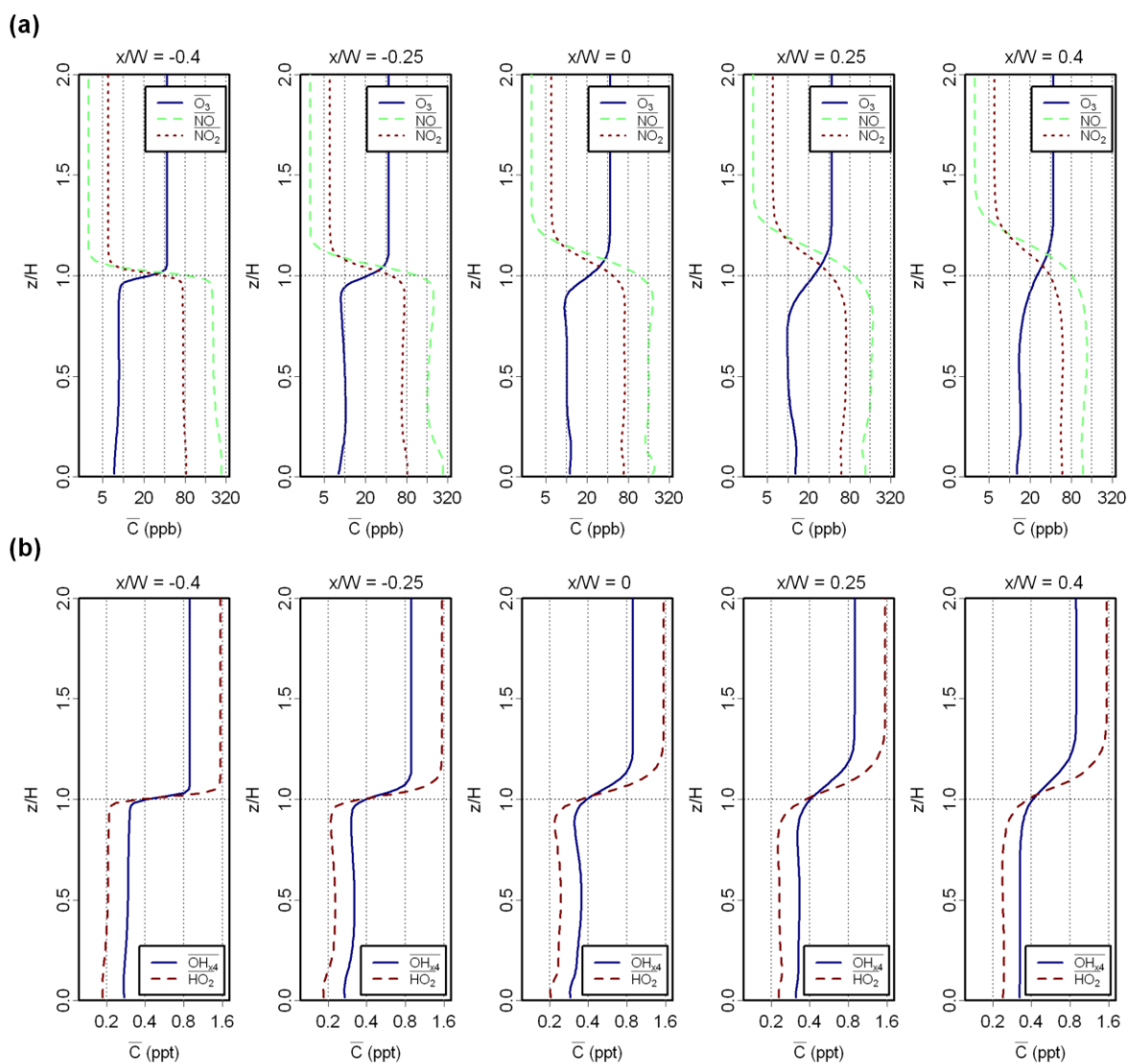


Figure 3



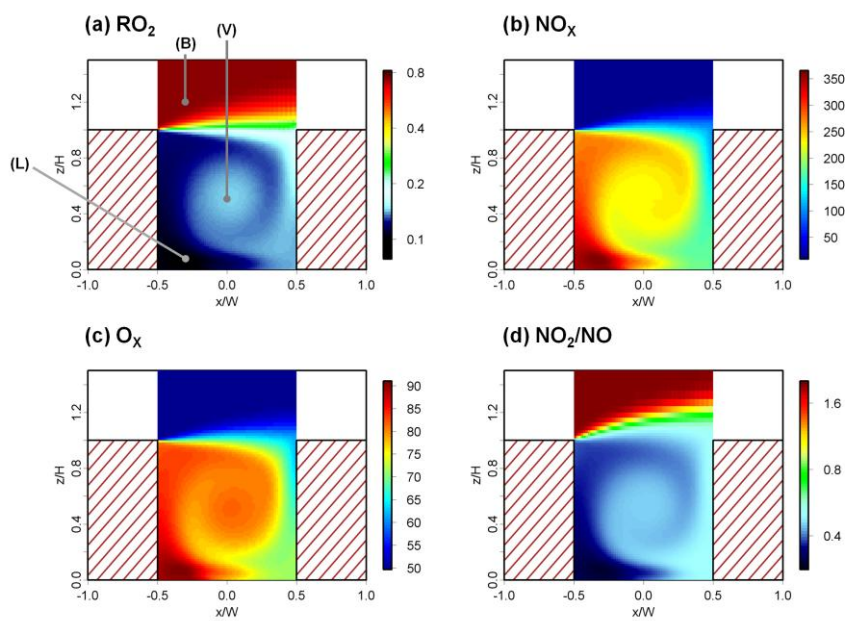
**Fig. 3.** Mean (time averaged) mixing ratios (ppb) of (a)  $O_3$ , (b) NO, (c)  $NO_2$ , (d) passive scalar, (e) OH (ppt) and (f)  $HO_2$  (ppt) from the LES-RCS simulations. Data averaged over the final hour of the model simulation ( $150 \leq t \leq 210$  min).

Figure 4



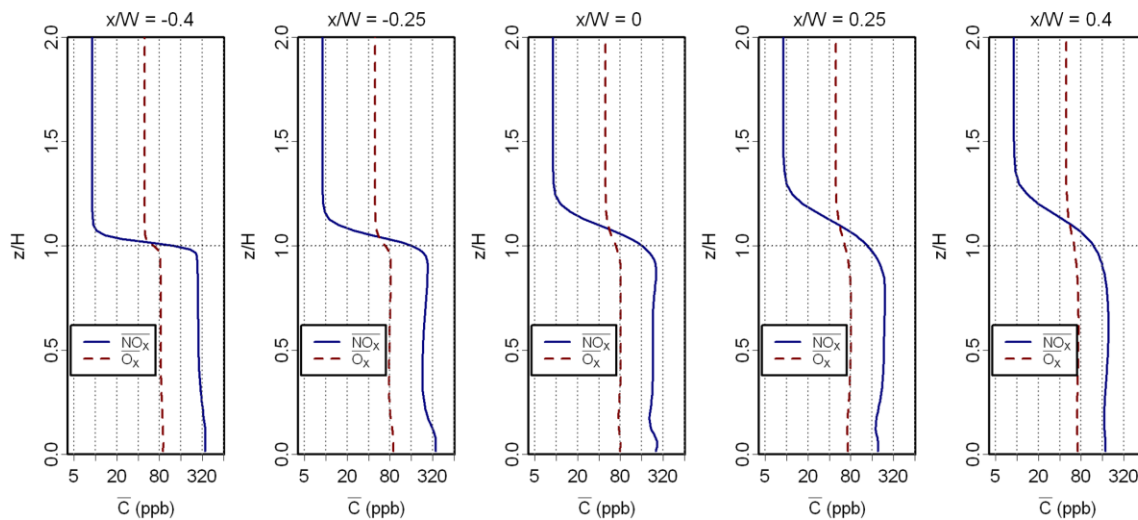
**Fig. 4.** Variation in the mean and time averaged mixing ratios of (a) O<sub>3</sub>, NO, NO<sub>2</sub>, and (b) OH<sub>x4</sub> (4 × OH) and HO<sub>2</sub> with height within the canyon (0.0 ≤ z/H ≤ 2.0) at x/W = -0.4, 0.25, 0.0, 0.25, 0.4, from the LES-RCS simulation.

Figure 5



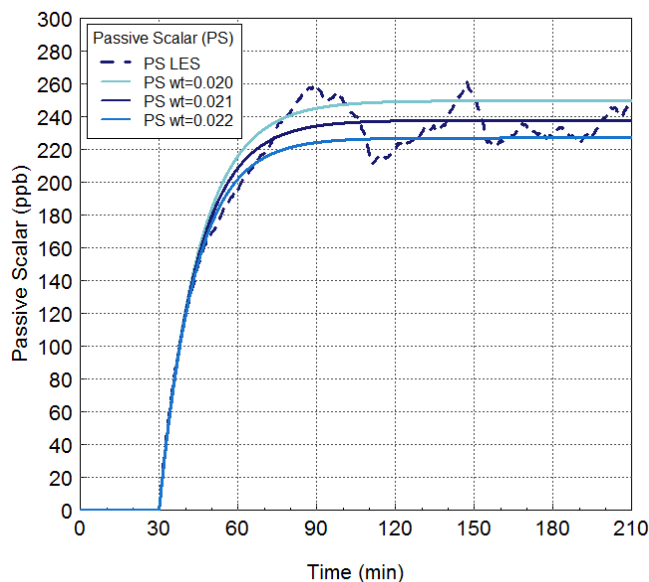
**Fig. 5.** Mean and time averaged mixing ratios of (a)  $\text{RO}_2$  (ppt), (b)  $\text{NO}_x$  (ppb), (c)  $\text{O}_x$  (ppb) and (d)  $\text{NO}_2/\text{NO}$  ratio from the LES-RCS simulation.

Figure 6



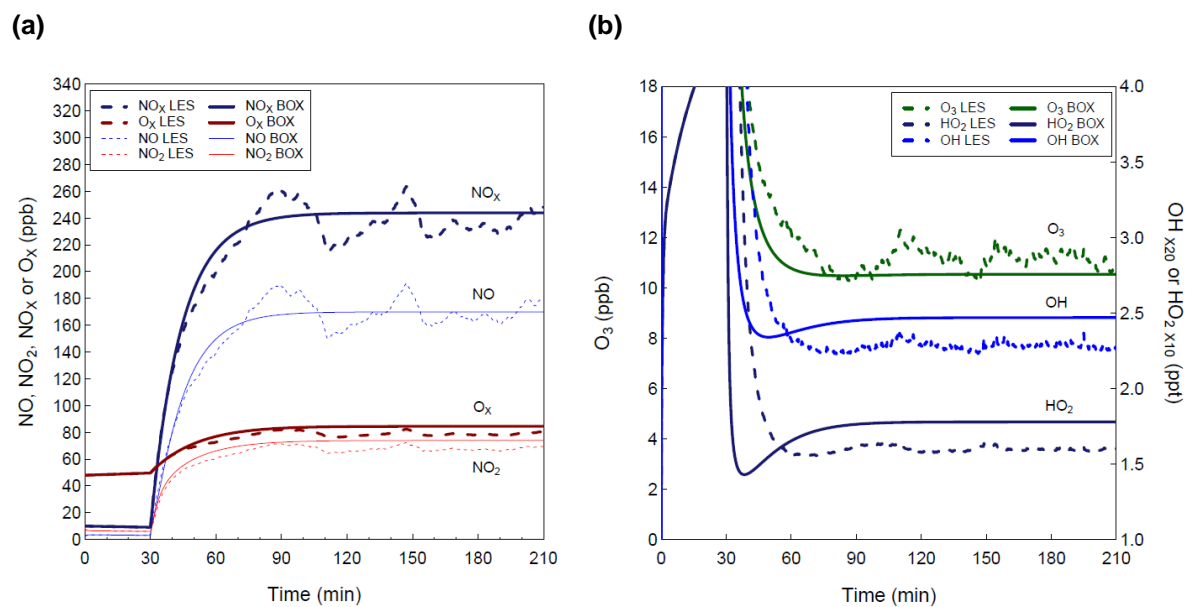
**Fig. 6.** Time averaged vertical mixing ratio profiles on a logarithmic scale of  $NO_x$  and  $O_3$  at  $x/W = -0.4, -0.25, 0.0, 0.25, 0.4$  within and above the canyon ( $0.0 \leq z/H \leq 2.0$ ), from the LES-RCS simulation.

Figure 7

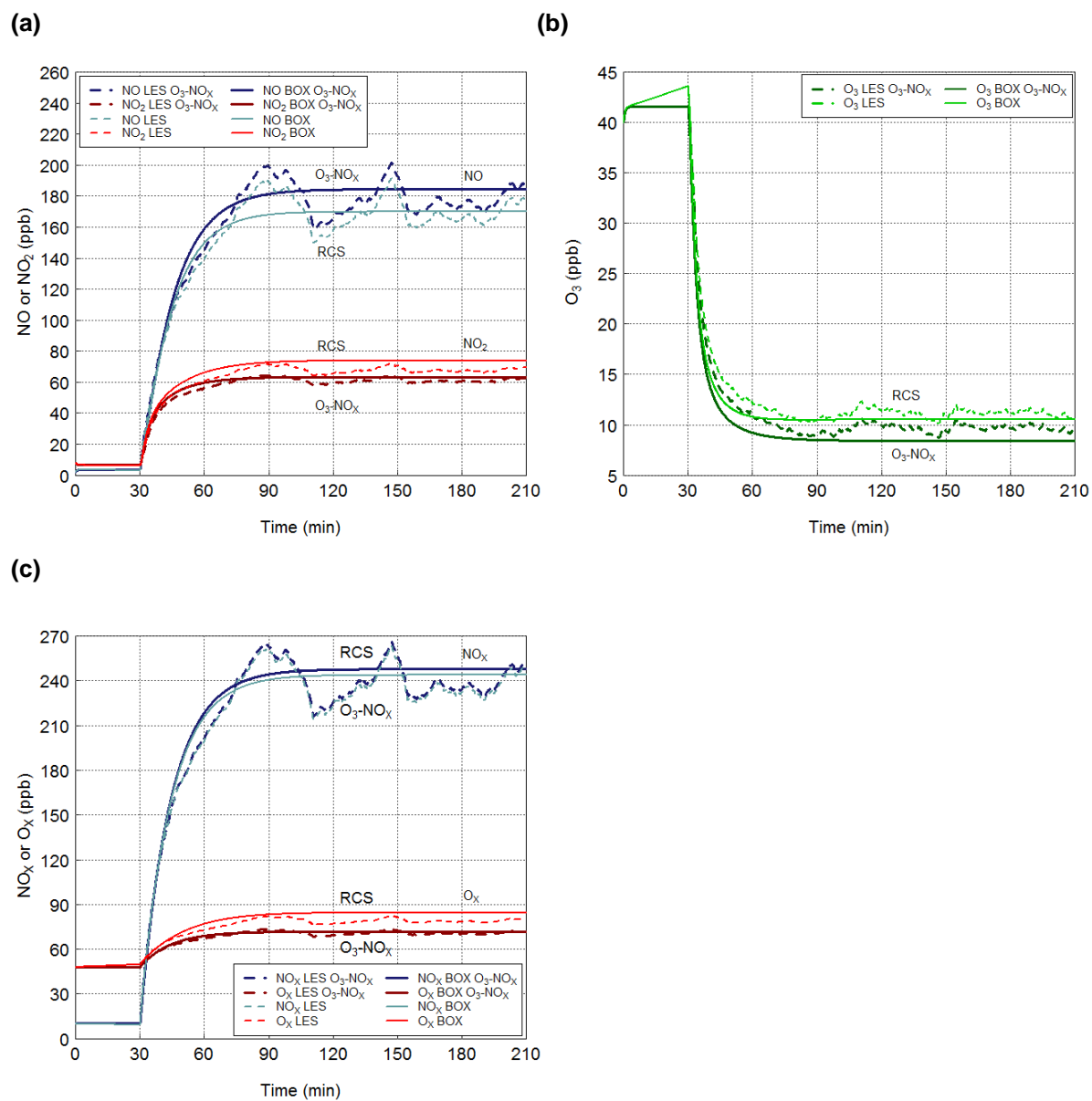


**Fig. 7.** Time evolution of the canyon averaged mixing ratio of the (chemically conserved) passive scalar calculated using the LES and box model dynamical frameworks, as a function of the exchange velocity ( $\omega_t$ ) – values in  $ms^{-1}$ .

Figure 8

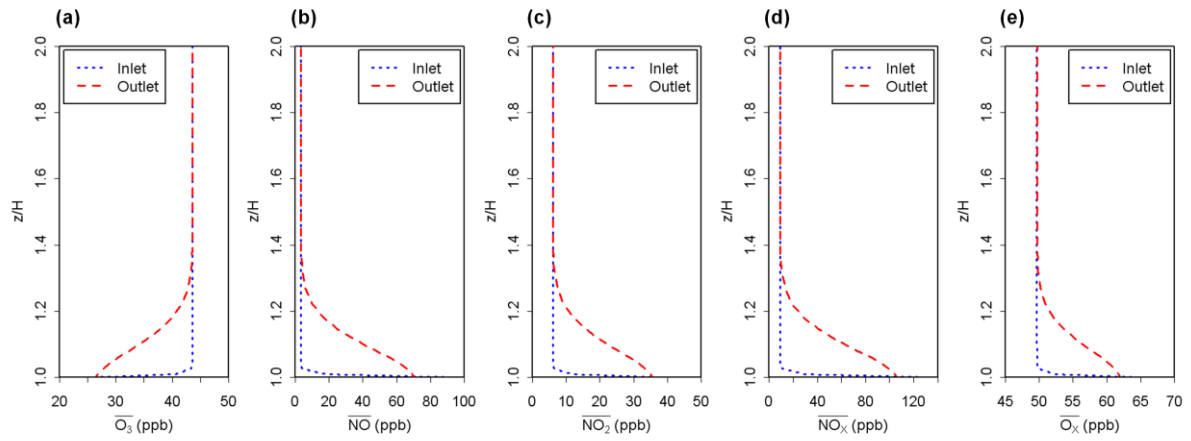


**Fig. 8.** Time evolution of the canyon averaged mixing ratio of (a) NO<sub>x</sub>, O<sub>x</sub>, NO, NO<sub>2</sub> (ppb) and (b) O<sub>3</sub> (ppb), OH<sub>x20</sub> (20 × OH) (ppt), HO<sub>2x10</sub> (10 × HO<sub>2</sub>), calculated using the LES-RCS and Box-RCS simulations.



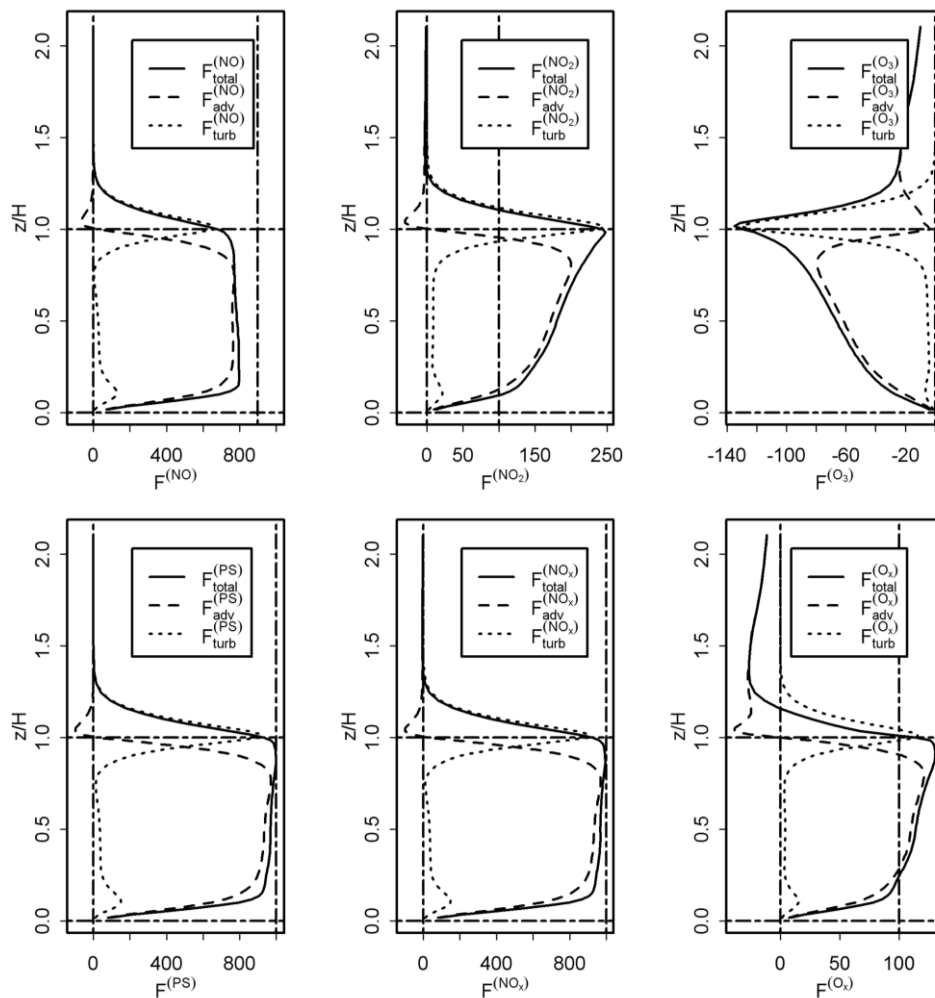
**Fig. 9.** Time evolution of canyon averaged mixing ratio (ppb) of (a) NO, NO<sub>2</sub>; (b) O<sub>3</sub> and (c) NO<sub>x</sub>, O<sub>x</sub>, using the LES and box model dynamical frameworks, and the RCS and O<sub>3</sub>-NO<sub>x</sub>-only chemistry cases.

Figure 10



**Fig. 10.** Time averaged vertical mixing ratio profiles ( $1.0 \leq z/H \leq 2.0$ ) of (a)  $O_3$ , (b)  $NO$ , (c)  $NO_2$ , (d)  $NO_x$  and (e)  $O_x$  (ppb) at the canyon inlet ( $x/W = -0.5$ ) and canyon outlet ( $x/W = 0.5$ ), from the LES-RCS simulations.

Figure 11



**Fig. 11.** Vertical profiles of advective, turbulent and total flux (ppb m<sup>-2</sup> s<sup>-1</sup>) averaged across the canyon (-0.5 ≤ x/W ≤ 0.5), from the LES-RCS simulation.



**Table 1**

Initial mixing ratios (ppb) used in the RCS model simulations

Species	Chemical formula	Mixing ratio / ppb
Nitric oxide	NO	2
Nitrogen dioxide	NO <sub>2</sub>	8
Ozone	O <sub>3</sub>	40
Carbon monoxide	CO	200
Nitric acid	HNO <sub>3</sub>	2
Methane	CH <sub>4</sub>	1800
Water vapour	H <sub>2</sub> O	2 %
<b>VOCs</b>		
Ethene	C <sub>2</sub> H <sub>4</sub>	0.91
Propene	C <sub>3</sub> H <sub>6</sub>	0.29
Formaldehyde	HCHO	3.14
Acetaldehyde	CH <sub>3</sub> CHO	2.98
Isoprene	C <sub>5</sub> H <sub>8</sub>	0.28
Methanol	CH <sub>3</sub> OH	7.38
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	2.37
Peroxyacetyl nitrate	PAN	0.46

**Table 2**

The dominant OH production and loss rates calculated for the LES-RCS simulation. Average concentrations taken over the final hour of the model simulation ( $150 \leq t \leq 210$  min) and at three locations (Fig. 5): within the canyon vortex (V), toward the lower leeward wall (L) and in the background atmosphere (B).

	(V) Vortex	(L) Lower leeward wall	(B) Background atmosphere
	Rate of production / loss (ppt s <sup>-1</sup> )		
<b>Production</b>			
$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	100	174	4.8
$\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$	27	25	0.74
$\text{O}_3 + h\nu \rightarrow \text{OH} + \text{OH}$	0.79	0.78	1.3
$\text{O}_3 + \text{VOC} \rightarrow \text{OH} + \text{products}$	0.35	0.57	0.0060
<b>Loss</b>			
$\text{OH} + \text{VOC} \rightarrow \text{products}$	-61	-96	-2.8
$\text{OH} + \text{NO} \rightarrow \text{HONO}$	-41	-71	-0.78
$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$	-22	-26	-1.9
$\text{OH} + \text{CO} \rightarrow \text{HO}_2$	-5.0	-7.4	-1.0

**Table 3**

Canyon- and time-averaged mixing ratios calculated using the LES-RCS and Box-RCS model approaches

	(a) LES	(b) Box	(b) - (a)	[(b) - (a)] / (a)
	Mixing ratio (ppb)			%
O <sub>3</sub>	11.2	10.5	-0.7	-5.9
NO	168	170	2	1.2
NO <sub>2</sub>	68	74	6	9.5
OH*	0.08	0.09	0.01	11.3
HO <sub>2</sub> *	0.23	0.25	0.02	8.1
NO <sub>x</sub>	236	244	8	3.3
O <sub>x</sub>	79	85	6	8.0
NO <sub>2</sub> /NO	0.40	0.44		

\*Mixing ratios of OH and HO<sub>2</sub> are given in ppt.

**Table 4**

Effect of exchange velocity: canyon and time averaged mixing ratios for the Box-RCS simulation with  $\omega_t = 0.021 \text{ m s}^{-1}$  and  $\omega_t = 0.022 \text{ m s}^{-1}$ .

	(a) Box $\omega_t = 0.021 \text{ m s}^{-1}$	(b) Box $\omega_t = 0.022 \text{ m s}^{-1}$	(b) - (a)	[(b) - (a)] / (a)
	Mixing ratio (ppb)			%
O <sub>3</sub>	10.54	10.76	0.22	2.1
NO	169.9	161.8	-8	-4.8
NO <sub>2</sub>	74.0	71.6	-2	-3.2
OH*	0.089	0.088	-0.0012	-1.3
HO <sub>2</sub> *	0.247	0.246	-0.0006	-0.3
NO <sub>x</sub>	244	233	-11	-4.5
O <sub>x</sub>	85	82	-3	-3.5

\*Mixing ratios of OH and HO<sub>2</sub> are given in ppt.

**Table 5**

Comparison of mean (canyon- and time-averaged) mixing ratios, for the RCS and O<sub>3</sub>-NO<sub>x</sub>-only mechanisms, using the LES and Box model dynamical frameworks. .

	(a) LES RCS	(b) Box RCS	(c) LES O <sub>3</sub> -NO <sub>x</sub>	(d) Box O <sub>3</sub> -NO <sub>x</sub>	[(a) - (c)] / (c)	[(b) - (d)] / (d)
	Mixing ratio (ppb)				%	
O <sub>3</sub>	11.2	10.5	9.7	8.4	15.5	25.0
NO	168	170	177	185	-5.1	-8.1
NO <sub>2</sub>	68	74	61	63	11.5	17.5
NO <sub>x</sub>	236	244	238	248	-0.8	-1.6
O <sub>x</sub>	79	85	70.7	71.4	11.7	19.0
NO <sub>2</sub> /NO	0.40	0.44	0.34	0.34		