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Evaluation of photostationary and non-photostationary operational models for NO_x pollution in a street canyon

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1 Abstract

2 To predict pollutant concentration in urban areas, it is crucial to take into
3 account the chemical transformations of reactive pollutants in operational dis-
4 persion models. In this work, we derive and discuss two photostationary (with
5 constant or varying transformation rates) and one non-photostationary chemi-
6 cal models for NO – NO₂ – O₃ pollution in a street canyon. In the analytical
7 derivation, we focus on the chemical and transport time scales to evaluate the
8 applicability of the models in different urban contexts. We then assess their
9 performance in predicting NO₂, NO and O₃ concentration at three locations
10 within an urban district by comparing the model predictions with measure-
11 ments acquired in a field campaign. The results are in line with analytical
12 speculations and highlight in which street types non-photostationary models
13 can bring substantial advantages. In courtyards with limited ventilation and
14 without direct emissions, the performance of the photostationary model with
15 meteorology-based transformation rates is satisfactory. On the other hand, the
16 application of a non-photostationary model significantly improves the predic-
17 tions in urban canyons with direct vehicular emissions. The applicability of the
18 proposed models in operational tools at the city scale is finally discussed.

19 **Keywords**

20 Photochemical smog, Urban air quality, Non-photostationary chemical model,
21 Air pollution measurement campaign

22 **Introduction**

23 The time scales related to pollutant transfer over large urban agglomerations
24 range from a few minutes to several hours. During this period, a large num-
25 ber of physico-chemical processes take place and determine the concentration of
26 pollutants in the urban atmosphere (Sillman, 1999). When the focus is on dis-
27 persion at the local district scale, the rate of turbulent transport is considerably
28 high compared to the rate of chemical transformation and most of the atmo-
29 spheric compounds can be treated as inert tracers. There are however chemical
30 reactions which are sufficiently fast to significantly affect the concentration of
31 pollutants during their residence time in the streets. This is notably the case for
32 nitrogen oxides. The nitrogen oxides that are most relevant for air pollution are
33 generally indicated as NO_x and include nitrogen dioxide (NO_2) and nitrogen
34 monoxide (NO).

35 The emissions of NO_x result from combustion processes, especially from
36 motor vehicle engines or from power stations and industries. They are there-
37 fore a tracer of anthropogenic activity in urban areas and their trends are used
38 to assess the effectiveness of regulations on air pollution, or to evaluate the
39 effects of sudden changes in emissions, such as during COVID-19 restrictions
40 (e.g., Toscano and Murena, 2020; Lovarelli et al., 2020; Misra et al., 2021).
41 It is generally assumed that the partition of NO_x at the point of emission is
42 approximately between 10% to 15% for NO_2 and 85% to 90% for NO (Ntzi-
43 achristos et al., 2000). Acute exposure to NO_x causes respiratory disease and
44 compromises lung functioning when inhaled at high concentrations. Children
45 are the most vulnerable, with a demonstrated increased incidence of childhood
46 asthma due to NO_2 emissions from vehicular traffic (Khreis et al., 2017; Anen-
47 berg et al., 2022). Despite being the major contributor to NO_x , NO is less

48 toxic than NO_2 . However, as most radicals, it is extremely unstable and forms
49 NO_2 through photochemical oxidation. Nitrogen dioxide is then converted back
50 to NO as a result of photolysis which also leads to the regeneration of ozone
51 (O_3). When the photostationary state is reached, these reactions result in a cy-
52 cle with zero net chemistry and the chemical compounds reach the equilibrium
53 composition, which can be easily derived in terms of kinetic reaction parame-
54 ters by the Leighton relation (Leighton, 1961). Deviations from this state occur
55 when (i) the residence time of pollutants in the reference volume (i.e. the street)
56 is shorter than the time needed for reaching the photostationary equilibrium,
57 (ii) turbulent motions mix the reactants so slowly that they remain segregated
58 rather than reacting (Li et al., 2021), (iii) the transformation of nitrogen monox-
59 ide into NO_2 is altered by the role of complex reactions with radicals resulting
60 from the oxidation of Volatile Organic Compounds (VOCs) and CO (Jenkin
61 and Clemmitshaw, 2000). The concentrations of NO and NO_2 are also affected
62 by reactions involving the hydroxyl radical and leading to the production of
63 nitric acid.

64 The coupling of turbulent and chemical dynamics to assess photochemi-
65 cal pollution in urban areas has been explored extensively in the past two
66 decades by means of Computational Fluid Dynamics (CFD) simulations. Baker
67 et al. (2004) extended a Large Eddy Simulation (LES) for turbulent flow in
68 a street canyon with a simple $\text{NO}_x\text{-O}_3$ chemical model. The same reaction
69 scheme was adopted by Baik et al. (2007), who instead used Reynolds-averaged
70 Navier–Stokes (RANS) simulations. By introducing a photostationary state de-
71 fect index, both studies highlighted the regions of a street canyon most prone
72 to chemical instability. The chemistry of VOC has been included in RANS sim-
73 ulations by Kwak and Baik (2012) and Kim et al. (2012), while Bright et al.
74 (2013) combined LES simulations with a detailed chemical reaction mechanism
75 (Reduced Chemical Scheme) comprising 51 chemical species and 136 reactions.
76 Similarly, Garmory et al. (2009) used the Stochastic Fields (FS) method to sim-
77 ulate turbulent reacting flows with a chemistry model comprising 28 species.
78 These studies showed that the effect of turbulent fluctuations (i.e. segregation)

79 on the chemistry is significant for species with the highest transformation rates.
80 They also showed that increasing chemical complexity (i.e. simulating VOC
81 chemistry) could contribute to additional but modest NO_2 and O_3 formation in
82 the canyon.

83 CFD simulations, coupled with detailed chemical models, provide an accu-
84 rate prediction but are computationally expensive and require a large amount of
85 detailed input data. To simulate air quality in large urban domains, consisting
86 of hundreds to thousands of streets, a more efficient way is adopting simplified
87 modelling approaches (Vardoulakis et al., 2007). These are usually Gaussian-
88 Lagrangian models integrated with box models to simulate the concentration in
89 the street canyons. In these operational tools, photostationarity is a convenient
90 assumption as it allows the modelling of O_3 and NO_x as inert tracers and to
91 subsequently apply photochemical equilibrium in the streets. This is the case of
92 the Canyon Plume Box Model (CPBM) (Yamartino and Wiegand, 1986), and
93 the street network model Sirane (Soulhac et al., 2017).

94 Another widespread approach is the adoption of empirical models to esti-
95 mate NO - NO_2 conversion (Ravina et al., 2022). These are based on a photosta-
96 tionary assumption but are optimised to fit observed concentrations. Hirtl and
97 Baumann-Stanzer (2007) investigated the performances of the two empirical
98 conversion schemes after Romberg et al. (1996) and after Derwent and Middle-
99 ton (1996), when implemented in the Gaussian model Atmospheric Dispersion
100 Modelling System (ADMS) and in the Lagrangian Simulation of Aerosol Trans-
101 port (LASAT) model. These dispersion models turned out to be quite successful
102 in predicting average concentrations measured in street canyons.

103 A step forward in modeling the interaction between the time scales of chem-
104 ical reactions and those of transport is represented by the model ADMS-Urban
105 (McHugh et al., 1997; Carruthers et al., 2000). In ADMS-Urban, NO_x chem-
106 istry can be modelled by the Generic Reaction Set (GRS) (Azzi et al., 1992;
107 Venkatram et al., 1994) photochemical scheme which includes seven chemical
108 reactions. The GRS chemical model is applied to the emitted pollutants after
109 transport and dispersion. The chemistry calculation for the receptor is split in

110 two steps: the first considers the contribution from far sources (source-receptor
111 travel time greater than 150 s), while the second one includes the contribution
112 from the nearest sources (source-receptor travel time less than 150 s) (CERC,
113 2022). In this way, the model takes into account the travel time of the pollution
114 plume and it assumes a time -or distance- dependence on the generation of NO₂.

115 Finally, the Operational Street Pollution Model (OSPM) (Palmgren et al.,
116 1996; Berkowicz et al., 1997) is a street canyon model which includes NO –
117 NO₂ – O₃ chemistry by means of a non-photostationary model that takes into
118 account the interaction between the chemical reaction rates and the residence
119 time of the pollutants in the street.

120 The overview above suggests that operational modeling of reactive pollu-
121 tant concentration at the urban scale requires an adequate description of (i) the
122 chemistry, (ii) the turbulent transport, (iii) the interaction between these two
123 processes, all while minimizing the computational cost and required input data
124 in order to be applied to hundreds to thousands of streets. To date, empirical
125 relationships and photostationary models are the most commonly used for op-
126 erational purposes while non-photostationary schemes are rarely implemented.
127 This is especially true for street network models, where, to our knowledge, the
128 non-photostationary scheme has not yet been implemented. Furthermore, the
129 existing literature lacks a coherent formulation of the different photochemical
130 models, with a clear statement of the underlying assumptions and a concurrent
131 validation with real data. To fill these gaps, in this work, we derive, com-
132 pare and validate three models for NO_x photochemical pollution that can be
133 efficiently implemented in street network models at the city scale. In the ana-
134 lytical derivation, we focus on the time scales of pollutant transformation and
135 transport in order to highlight the range of application of the different models.
136 To verify the reliability of the different schemes we compare the model outputs
137 to field data. The main objective is to evaluate whether the application of a
138 non-photostationary model can bring substantial advantages in the prediction of
139 pollutant concentration in the streets, with respect to photostationary models.

140 The formulation of a photochemical model, adopting box-model approach,

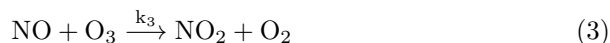
141 is presented in 1. A general presentation of the measurement campaign is given
142 in Section 2. Results are discussed in Section 3, while the conclusions are drawn
143 in Section 4.

144 1. NO – NO₂ – O₃ chemical street model

145 To maximize computational efficiency, minimize input data while providing
146 a satisfactory description of pollution in the urban area, city-scale operational
147 models, such as street network models (Soulhac et al., 2011), generally provide a
148 single concentration value for each street. This can be notably achieved adopt-
149 ing a box model at the street scale, which provides spatially averaged pollutant
150 concentration by computing a pollutant budget over the volume of the street. In
151 order to simulate photochemical pollution, the pollutant budget has to take into
152 account the terms of chemical production and of chemical destruction (Soulhac
153 et al., 2011) as well as those related to the turbulent fluxes at the street edges
154 and at the top of the street.

155

156 To write the budget of photochemical pollutants in the street, we start by
157 considering the simplified chemical scheme involving NO, NO₂ and O₃:



158 It is known (Seinfeld, 1986) that the second equation is much faster than
159 the first and the third ones, so that the constants k_1 and k_3 are the limiting
160 parameters of these chemical reactions. The constant rate k_1 (NO₂ photolysis
161 rate) depends on the intensity of solar radiation, whilst k_3 depends on air tem-
162 perature. These dependences can be modeled by the following relations (Kasten
163 and Czeplak, 1980; Seinfeld, 1986):

$$\begin{cases} k_1 = \frac{1}{60}(0.5699 - [9.056 \cdot 10^{-3}(90 - \zeta)]^{2.546}) \left(1 - 0.75 \left[\frac{Cld}{8}\right]^{3.4}\right) (\text{s}^{-1}) \\ k_3 = 1.325 \cdot 10^6 \exp\left(-\frac{1430}{T}\right) (\text{m}^3\text{mol}^{-1}\text{s}^{-1}) \end{cases} \quad (4)$$

164 where ζ is the solar elevation in degrees, T is the air temperature in Kelvin
165 and Cld is the cloud coverage in Oktas. These meteorological parameters vary
166 over time. In operational dispersion models, the time-dependence of the mete-
167 orological parameter is usually modelled assuming a quasi-steady approach, i.e.
168 assuming steady condition of time step of 1 hours. Cloud coverage and temper-
169 ature are measured during the day at meteorological stations, while the solar
170 elevation is a function of the day of the year, the local hour and the site latitude
171 (e.g., Soulhac et al., 2011). Note that k_1 is set equal to 0 at night, when the
172 solar elevation angle is negative. More sophisticated models for k_1 and k_3 are
173 available in the literature, but they are generally not adapted for operational
174 purposes (Seinfeld, 1986).

175 Referring to Eqs. 1-3, the production and destruction terms for each chem-
176 ical species are related to the molar concentration by the following expressions:

$$\begin{aligned} P_{NO} &= k_1[\text{NO}_2] & D_{NO} &= k_3[\text{NO}][\text{O}_3] \\ P_{NO_2} &= k_3[\text{NO}][\text{O}_3] & D_{NO_2} &= k_1[\text{NO}_2] \\ P_{O_3} &= k_1[\text{NO}_2] & D_{O_3} &= k_3[\text{NO}][\text{O}_3] \end{aligned} \quad (5)$$

177 where $[\cdot]$ represents the molar concentration (mol/m^3) of the compound.

178
179 We include the production and destruction terms in the street box model
180 formulated in Soulhac et al. (2011). Neglecting wet and dry deposition phenom-
181 ena, the budget of time-averaged concentration of NO_2 , NO and O_3 for a single
182 street-canyon of length L , width W and height H , can be written:

$$Q_{\text{NO}_2} - u_d \mathcal{S}_h ([\text{NO}_2] - [\text{NO}_2]^\dagger) - U \mathcal{S}_v ([\text{NO}_2] - [\text{NO}_2]^\dagger) + k_3 [\text{NO}][\text{O}_3] \mathcal{V} - k_1 [\text{NO}_2] \mathcal{V} = 0 \quad (6)$$

183

$$Q_{\text{NO}} - u_d \mathcal{S}_h ([\text{NO}] - [\text{NO}]^{\text{f}}) - U \mathcal{S}_v ([\text{NO}] - [\text{NO}]^{\text{f}}) + k_1 [\text{NO}_2] \mathcal{V} - k_3 [\text{NO}] [\text{O}_3] \mathcal{V} = 0 \quad (7)$$

184

$$-u_d \mathcal{S}_h ([\text{O}_3] - [\text{O}_3]^{\text{f}}) - U \mathcal{S}_v ([\text{O}_3] - [\text{O}_3]^{\text{f}}) + k_1 [\text{NO}_2] \mathcal{V} - k_3 [\text{NO}] [\text{O}_3] \mathcal{V} = 0 \quad (8)$$

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where $\mathcal{V} = LWH$ is the volume of the street, $\mathcal{S}_h = LW$ is its horizontal area and $\mathcal{S}_v = WH$ is its vertical cross section. The velocities U and u_d are the mean velocity along the street and the exchange rate at roof level (e.g., Soulhac et al., 2008; Salizzoni et al., 2009; Fellini et al., 2020) and they drive the longitudinal and vertical pollutant fluxes entering and leaving the street volume. For each of the three chemical compounds NO_2 , NO and O_3 , Q is the molar emission in the street, $[\cdot]^{\text{f}}$ is the concentration in the atmosphere above roofs, and $[\cdot]$ is the concentration in the flow advected within the canopy at the upwind intersection of the street. We point out that the source of ozone is not included in the budget (i.e. $Q_{\text{O}_3} = 0$) since direct ozone emissions in the streets are rare. Eqs. 6-8 can be reformulated by highlighting the time scales associated with the terms of transport and chemical reaction. For example, for NO_2 we can write:

$$\frac{Q_{\text{NO}_2}}{\mathcal{V}} - \frac{[\text{NO}_2] - [\text{NO}_2]^{\text{f}}}{\tau_v} - \frac{[\text{NO}_2] - [\text{NO}_2]^{\text{f}}}{\tau_h} + \frac{[\text{NO}]}{\tau_3} - \frac{[\text{NO}_2]}{\tau_1} = 0 \quad (9)$$

197 with

$$\begin{cases} \tau_v = \frac{H}{u_d} \\ \tau_h = \frac{L}{U} \\ \tau_1 = \frac{1}{k_1} \\ \tau_3 = \frac{1}{k_3[\text{O}_3]} \end{cases} \quad (10)$$

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To determine the order of magnitude of the different terms in Eq. 9 we can roughly estimate the time scales involved, based on the data collected and simulated for the city of Lyon (France) (Soulhac and Salizzoni, 2010; Soulhac et al., 2012). The depth H and length L of street canyons vary in the ranges 15-30 m and 20-150 m, respectively. The wind speed within the streets U and the typical turbulent exchange velocity u_d can reasonably be assumed in the ranges 0.1-5 m/s and 0.01-0.22 m/s, respectively (Salizzoni et al., 2009; Soulhac et al.,

205 2011) when the free stream wind above the city is between 1.5 m/s and 8 m/s
 206 (Météo-France data for the period 1981–2006) From these data, we obtain that
 207 τ_v ranges in 68-3000 s, and τ_h in 4-1500 s. Typical values of k_1 and k_3 can be
 208 estimated by means of Eq. 4 by varying the cloud coverage Cld between 0 and
 209 8, the temperature T in 5°C-30°C and ζ in 10°-90° (in this analysis we consider
 210 only daytime). The concentration of ozone can be taken in the range 25-75 ppb
 211 (data measured at Saint-Exupery station for the year 2008). These data provide
 212 τ_1 in the range 105-1850 s and τ_3 in the range 54-247 s. Moreover, we introduce
 213 an average time scale τ_s related to the pollutant wash-out from the street:

$$\tau_s = \left(\frac{1}{\tau_h} + \frac{1}{\tau_v} \right)^{-1} \quad (11)$$

214 and we find that τ_s varies approximately in the range 4-1000 s. This analysis
 215 shows that there is an overlap between the timescales associated to chemical
 216 reactions and the characteristic residence times of pollutants within the street.
 217 Consequently a modeling approach combining chemistry and advection-diffusion
 218 processes must be adopted, as neither of the two processes can be neglected.

219

220 Finally, we define the average background concentration $[\cdot]^b$ as:

$$[\cdot]^b = \frac{\frac{[\cdot]^c}{\tau_h} + \frac{[\cdot]^r}{\tau_v}}{\frac{1}{\tau_h} + \frac{1}{\tau_v}} \quad (12)$$

221 .

222 In this way, Eq. 9 can be simplified using only the background concentration
 223 $[\text{NO}_2]^b$:

$$\frac{Q_{\text{NO}_2}}{\mathcal{V}} - \frac{[\text{NO}_2] - [\text{NO}_2]^b}{\tau_s} + k_3[\text{NO}][\text{O}_3] - k_1[\text{NO}_2] = 0 \quad (13)$$

224 The same formulation is valid for NO and O₃ so that a system of 3 equations
 225 (Eq. 13 and the two analogous balances for NO and O₃) describes in a compact
 226 way the dynamics of the three chemical compounds. In what follows, we will
 227 examine the solution of this system of equations adopting different scenarios
 228 related to the relative importance of the different time scales involved.

229 *1.1. Passive scenario*

230 As a first step, we consider the case of a passive pollutant, whose concentra-
 231 tion is generally referred to as $[\cdot]^*$. For NO_2 Eq. 13 simplifies as:

$$\frac{Q_{\text{NO}_2}}{\mathcal{V}} - \frac{[\text{NO}_2]^* - [\text{NO}_2]^b}{\tau_s} = 0. \quad (14)$$

232 This scenario corresponds to the case of reaction times that are extremely long
 233 (i.e. $\tau_1 \rightarrow \infty$, $\tau_3 \rightarrow \infty$) so that the terms of chemical production and destruction
 234 are negligible for the budget in the street. The solution is given by:

$$[\text{NO}_2]^* = [\text{NO}_2]^b + \frac{\tau_s Q_{\text{NO}_2}}{\mathcal{V}} \quad (15)$$

235 By analogy, the relative solution for the ‘passive’ NO concentration reads:

$$[\text{NO}]^* = [\text{NO}]^b + \frac{\tau_s Q_{\text{NO}}}{\mathcal{V}} \quad (16)$$

236 and for O_3 concentration, assuming no emission of ozone:

$$[\text{O}_3]^* = [\text{O}_3]^b. \quad (17)$$

237 The concentration $[\cdot]^*$ takes into account all contributions to pollution de-
 238 riving from advective transport only, i.e. the direct emission into the street and
 239 the transport of pollutants to the street both from adjacent street and from the
 240 atmosphere above the roofs. Thus, Eqs. 15-17 can be seen as the general solu-
 241 tions for a dispersion model able to provide passively advected concentrations
 242 in the streets.

243 *1.2. Photostationary chemical model*

244 Let us now consider that the reactive pollutants in the control volume (i.e.
 245 within the street canyon) have the necessary time to reach the photochemical
 246 equilibrium. This corresponds to assume that the characteristic time scales of
 247 the chemical reactions τ_1 and τ_3 are small compared to the residence time of
 248 pollutants within the street (i.e. τ_1 and $\tau_3 \rightarrow 0$). Under these assumptions,
 249 the advective and source terms in Eq. 13 become negligible compared to the

250 production and destruction terms and the balance equation is simplified as fol-
 251 lows:

$$k_3[\text{NO}]^\infty[\text{O}_3]^\infty - k_1[\text{NO}_2]^\infty = 0 \quad (18)$$

252 where the photostationary concentrations have been referred to as $[\cdot]^\infty$. Eq. 18
 253 is known as the Leighton relationship (Leighton, 1961), whose formulation could
 254 also be obtained from the budget of NO_2 or O_3 (see Eqs. 7 and 8).

255 The conservation of N and O species lead to the following relations, which
 256 are valid for passive, photostationary or non-photostationary concentrations:

$$[\text{NO}] + [\text{NO}_2] = [\text{NO}]^* + [\text{NO}_2]^* = [\text{NO}]^\infty + [\text{NO}_2]^\infty = \phi_N, \quad (19)$$

$$[\text{O}_3] + [\text{NO}_2] = [\text{O}_3]^* + [\text{NO}_2]^* = [\text{O}_3]^\infty + [\text{NO}_2]^\infty = \phi_O, \quad (20)$$

257 where ϕ_N and ϕ_O are constants defining the proportion of the different species,
 258 whatever the chemical history of the pollutants reaching the street canyon. We
 259 note that ϕ_N and ϕ_O can be easily computed from the results of the passive
 260 model providing the concentrations $[\cdot]^*$ (Section 1.1) which take into account
 261 all the pollutant contributions reaching the canyon (i.e. both direct emissions
 262 and transported pollutants).

263 Combining Eqs. 18 to 20 (see e.g., Soulhac et al. (2011)) provides the solu-
 264 tion:

$$[\text{NO}_2]^\infty = \frac{b - \sqrt{b^2 - 4c}}{2} \quad (21)$$

265 with:

$$\begin{cases} b = \frac{k_1}{k_3} + [\text{O}_3]^* + [\text{NO}]^* + 2[\text{NO}_2]^* = \frac{k_1}{k_3} + \phi_N + \phi_O \\ c = ([\text{O}_3]^* + [\text{NO}_2]^*) ([\text{NO}]^* + [\text{NO}_2]^*) = \phi_O \cdot \phi_N \end{cases} \quad (22)$$

266 Eq. 22 illustrates that NO_2 concentration depends only on k_1/k_3 , ϕ_N and
 267 ϕ_O . This highlights that the chemical history of the background concentration,
 268 that is included in passive concentrations $[\cdot]^*$ by equations 15 to 17, has no

269 influence on the photostationary solution because this solution corresponds to
 270 an infinite reaction time, which offsets the initial repartition between NO, NO₂
 271 and O₃.

272 Once [NO₂][∞] is known, Eqs. 19 and 20 provide [NO][∞] and [O₃][∞].

273 1.3. Non-photostationary chemical model

274 To find the general solution for the full chemical street model (Eq.13), we
 275 take the difference between Eqs. 13 and 14:

$$-\frac{[\text{NO}_2] - [\text{NO}_2]^*}{\tau_s} + k_3[\text{NO}][\text{O}_3] - k_1[\text{NO}_2] = 0 \quad (23)$$

276 By introducing Eqs. 19 and 20 in Eq. 23:

$$-\frac{[\text{NO}_2] - [\text{NO}_2]^*}{\tau_s} + k_3([\text{NO}]^* + [\text{NO}_2]^* - [\text{NO}_2])([\text{O}_3]^* + [\text{NO}_2]^* - [\text{NO}_2]) - k_1[\text{NO}_2] = 0 \quad (24)$$

277 and rearranging, the equation for [NO₂] is finally:

$$[\text{NO}_2]^2 - b'[\text{NO}_2] + c' = 0 \quad (25)$$

278 with

$$\begin{cases} b' = b + \frac{1}{k_3\tau_s} \\ c' = c + \frac{[\text{NO}_2]^*}{k_3\tau_s} \end{cases} \quad (26)$$

279 We obtain the non-photostationary solution for [NO₂] is then:

$$[\text{NO}_2] = \frac{b' - \sqrt{b'^2 - 4c'}}{2} \quad (27)$$

280 This expression is very similar to the photo-chemical model implemented in
 281 OSPM (Palmgren et al., 1996; Berkowicz et al., 1997) but generalized for a
 282 street canyon with a longitudinal advection velocity U and a vertical turbulent
 283 exchange rate u_d , therefore suitable for implementation in street network mod-
 284 els. Also in this case, once [NO₂] is known, Eqs. 19 and 20 provide [NO] and
 285 [O₃].

286 The solution in Eqs. 26-27 can be discussed according to the asymptotic
 287 values for the street residence time scale τ_s , as shown in Fig. 1. If $\tau_s \rightarrow 0$ (i.e.

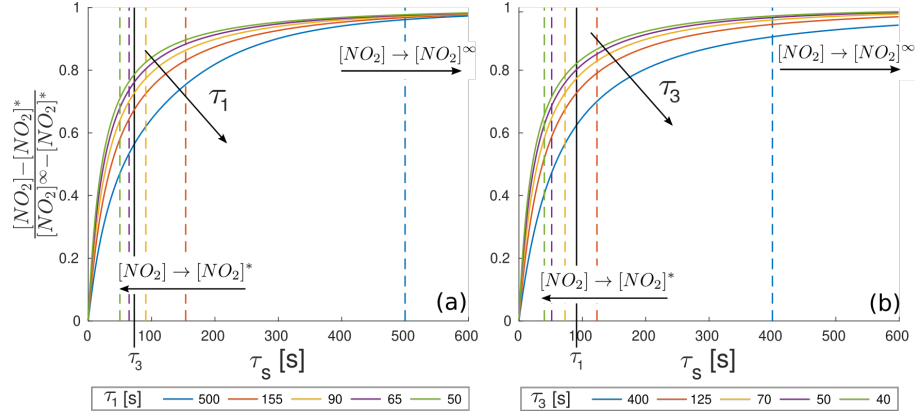


Figure 1: Trend of the non-photostationary solution ($[NO_2]$) towards the solution for the passive model ($[NO_2]^*$) and towards the photostationary solution ($[NO_2]^\infty$) as a function of the characteristic time of advective transport (τ_s), and of the two characteristic times of reaction. Panel (a) shows different curves as a function of τ_1 , indicated in the legend and by the dashed vertical lines. Similarly, panel (b) shows the curves as a function of τ_3 indicated in the legend and by the dashed vertical lines.

288 $\tau_s \ll \tau_1$ and τ_3), according to Eq. 24, we have that $[NO_2] \rightarrow [NO_2]^*$. It means
 289 that the pollutants have no time to react and the concentration of the chemical
 290 species is provided by the passive solution (Eqs. 15-17). On the other hand, if
 291 τ_s tends to infinity (i.e. $\tau_s \gg \tau_1$ and τ_3), then $b = b'$ and $c = c'$ in Eq. 26 and
 292 the concentration $[NO_2]$ tends to $[NO_2]^\infty$. It means that the pollutants have
 293 an infinite time to react and the final concentration of the chemical species is
 294 provided by the photostationary solution (Eq. 21).

295 For intermediate values of τ_s , the solution is in-between, with only a partial
 296 conversion from NO to NO_2 , compared to the photostationary limit. We can
 297 remark that, unlike the photostationary case, Eq. 26 includes $[NO_2]^*$ independ-
 298 dently of the constants ϕ_N and ϕ_O . This adds a dependence of the solution on
 299 the chemical history of the background concentration.

300

301 To provide further interpretations, Eq. 24 can be rewritten in the form:

$$\underbrace{[NO_2]^*}_{\alpha} \chi^2 - \underbrace{\left(\frac{k_1}{k_3} + [O_3]^* + [NO]^* + \frac{1}{k_3 \tau_s} \right)}_{\beta} \chi + \underbrace{\left(\frac{[NO]^* [O_3]^*}{[NO_2]^*} - \frac{k_1}{k_3} \right)}_{\gamma} = 0 \quad (28)$$

302 with

$$\chi = \frac{[\text{NO}_2] - [\text{NO}_2]^*}{[\text{NO}_2]^*} = \frac{\beta - \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha}. \quad (29)$$

303 where χ represents the rate of increase of NO_2 concentration with respect to
304 its passive value $[\text{NO}_2]^*$. The term γ can be seen as a quantification of the
305 non-photostationarity of the passive concentrations of NO , NO_2 and O_3 . Con-
306 sequently, if the passive concentrations are already close to the photostationary
307 equilibrium ($\gamma \simeq 0$), then the solution tends to $\chi \simeq 0$, which means that the
308 final concentration is close to the passive one.

309

310 1.4. Validation strategy

311 As a further step, we test the analytical solutions presented in the previous
312 sections against field data. In doing so, we will consider three different mod-
313 els: the first one (Model 1) is the photostationary model (Eq. 21) where the
314 transformation rates k_1 and k_3 are assumed to be constant with time, what-
315 ever the temperature and radiative conditions. This solution can be adopted
316 when the meteorological information (temperature, intensity of solar radiation)
317 is missing and to minimize the computational cost. The sensitivity of the model
318 to the value adopted for the k_1/k_3 ratio is discussed in the following section.
319 The second one (Model 2) is a photostationary model with transformation rates
320 that vary during the day according to the meteorological conditions. To this
321 aim, Eq. 4 is applied to estimate k_1 and k_3 with the parameters T , Cld and
322 ζ varying over the day. The third one (Model 3) is the model derived for the
323 non-photostationary conditions in Eq. 27, with parameters k_1 and k_3 again
324 varying during the day.

325 The models presented in sections 1.2 and 1.3 are designed to apply the chem-
326 ical scheme (Eqs. 1-3) as a post-calculation after the application of a transport
327 and dispersion model able to provide the advected concentrations in the street,
328 i.e. $[\text{NO}]^*$, $[\text{NO}_2]^*$, and $[\text{O}_3]^*$. In order to validate only the chemical models,
329 avoiding the influence of errors due to the dispersion simulation, we have con-
330 sidered a virtual perfect dispersion model by using the measured concentrations

331 in the streets as input data for the chemical models. According to Eqs. 21
332 and 27, the results of the photochemical models depend on k_1/k_3 , ϕ_N , ϕ_O and
333 $[\text{NO}_2]^*$. As mentioned above, the ratio k_1/k_3 can be taken as a constant or
334 estimated from meteorological data and as a function of time. Equations 19
335 and 20 show that the conserved quantities ϕ_N and ϕ_O can be computed directly
336 from the measured concentrations at the monitoring stations, which correspond
337 to $[\text{NO}]$, $[\text{NO}_2]$, and $[\text{O}_3]$. Once ϕ_O is known, $[\text{NO}_2]^*$ results from Eq. 20 by
338 subtracting the measured background concentration of ozone (see Eq. 17). The
339 other parameter of the non-photostationary model is the time scale τ_s . In the
340 validation, this parameter was adjusted to optimize the correlation coefficient
341 between the model and measured concentrations. The resulting values will be
342 discussed in the following section.

343 2. On-site measurements

344 The field data were measured during the LYON6 campaign which took
345 place between the 9th and the 24th July 2001 in the 6th arrondissement in
346 Lyon (France) and was handled by COPARLY (Comité de Coordination pour
347 le contrôle de la Pollution Atmosphérique), the local authority for traffic and air
348 pollution management, in collaboration with the Fluid Mechanics and Acous-
349 tics Laboratory (LMFA) in École Centrale de Lyon. The campaign consisted of
350 local measurements of vehicular traffic, air pollution and weather conditions.

351 The meteorological data were collected by two stations within the urban area
352 (Fig. 2) and by a third one located 7 km from the studied district, and positioned
353 away from any building that could directly influence the measurements. To have
354 a representative dataset over the study district, the measurements from the
355 three different stations were combined together. The reference temperature was
356 measured by the sensors located within the urban area. To avoid local effects,
357 cloud cover, precipitation, wind speed and wind direction were provided by the
358 station outside the urban area. However, a correction to the wind intensity to
359 take into account the difference in surface roughness was applied as detailed in

360 Soulhac et al. (2012). The temporal evolution of the resulting meteorological
361 dataset is represented in Fig. 3.

362 Hourly concentration of nitrogen monoxide, nitrogen dioxide and ozone were
363 measured by three monitoring stations, referred to as ‘Station 1’, ‘Station 2’ and
364 ‘Station 3’. Station 1 was located in a busy street canyon. Station 2 and Station
365 3 were located inside school courtyards, far away from polluting source. In this
366 regard, we point out that the models derived in Section 1 are valid for both
367 street canyons and urban courtyards as the fundamental assumption underlying
368 the box model (Eq. 6-8) is the decoupling between the dynamics in the street
369 and the dynamics above the roofs (Salizzoni et al., 2011). The urban courtyard
370 differs from the street canyon by the absence of direct emissions and street
371 intersections at the ends. For courtyards, therefore, the wash-out time scale τ_s
372 (Eq. 11) corresponds to the rate of vertical exchange at roof level (τ_h) and Q_{NO}
373 and Q_{NO_2} are equal to zero.

374 In Station 2 and 3, the analyzers were placed at 2 m from the ground and
375 in the middle of the courtyard. The concentration was measured over approxi-
376 mately 6 days (see Fig. 3). In Station 1, the analyzer was also placed 2 m off
377 the ground but a few centimeters from a building wall, and the concentration
378 was measured over 15 days. In real street canyons there are several factors
379 (e.g., traffic, vegetation, building geometries) that increase the mixing of pol-
380 lutants therefore inducing a concentration field that is more homogeneous than
381 that observed in controlled case studies in wind tunnels and numerical simula-
382 tions, where a highly spatially inhomogeneous concentration field is predicted
383 (Buccolieri et al., 2009; Marucci and Carpentieri, 2019; Fellini et al., 2020). For
384 this reason, and considering that the focus of the proposed models is on hourly
385 averaged pollution, the concentration in the canyon can be assumed sufficiently
386 homogeneous and therefore less sensitive to the positioning of the sensor within
387 the street. This is in line with previous validation studies of street network
388 models (Soulhac et al., 2012, 2017) in which an influence of the sensor position
389 on the agreement between the model and the measurements was not observed.

390 To estimate the concentration levels of background pollutants, other three

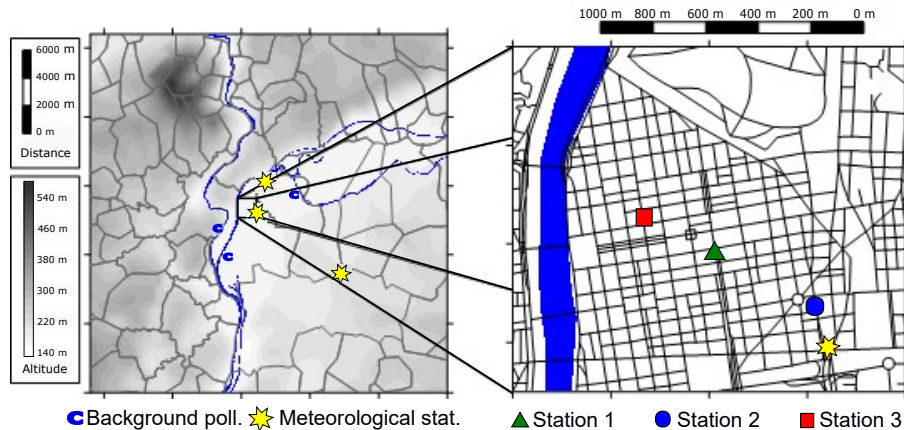


Figure 2: Location of the three meteorological stations, of the suburban stations for measuring pollution background and of the three pollution monitoring stations inside the study district.

391 monitoring stations located outside the district were used. Refer to Soulhac et al.
 392 (2012) for a complete description of the measurement campaign and simulation
 393 set-up.

394 3. Results

395 The meteorological data collected during the field campaign directly provide
 396 the temporal evolution of the ratio k_1/k_3 , estimated using Eq. 4. As shown
 397 in Fig. 4-a, this ratio is far from being constant with time, and varies from a
 398 maximum of about $0.9 \mu\text{mol}/\text{m}^3$ (20 ppb) and a minimum close to 0 during
 399 the night, with an average value of $0.3 \mu\text{mol}/\text{m}^3$ (6.8 ppb). This is due to
 400 the variation over time of temperature, cloud coverage and solar elevation (see
 401 Eq. 4). As stated in Eq. 18, this ratio equals the ratio $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ when
 402 the pollutants are in photostationary equilibrium. By using the measurements
 403 from the three pollution monitoring stations, we test this condition in Fig. 4-
 404 b and c. As usual in practical applications, concentration measurements are
 405 provided also in ppb (C_x is the concentration in ppb of the chemical compound
 406 x, while $[x]$ is the molar concentration. The relation between the two is given
 407 by the molar volume V_m , i.e. $C_x = [x]V_m 10^9$). Results show that, for Station
 408 2 and Station 3, the ratio $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ agrees well with the trend of the

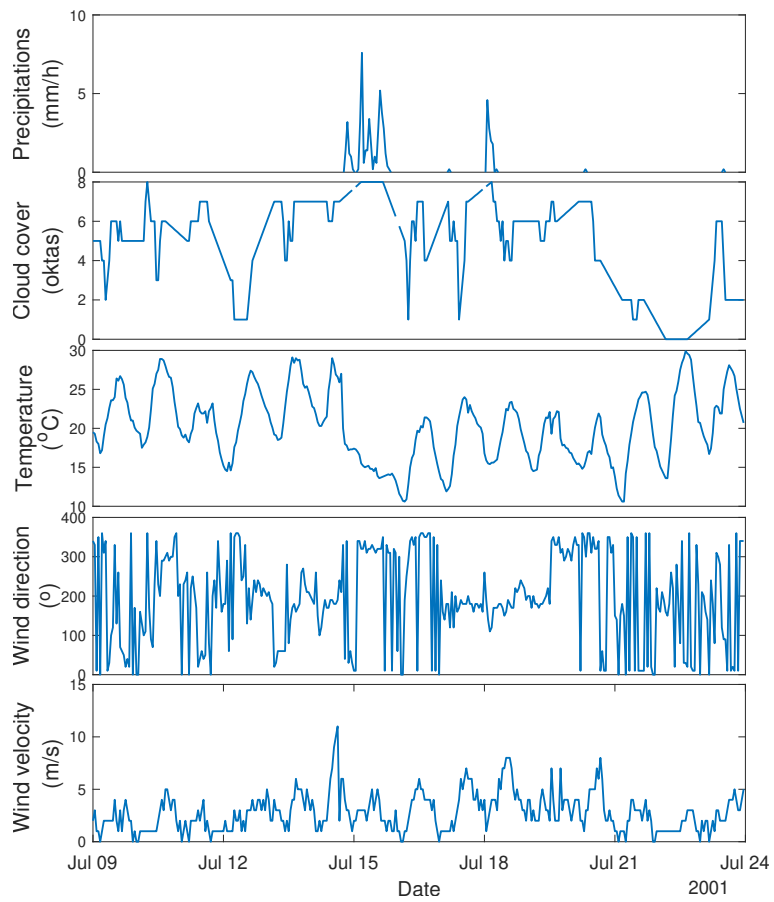


Figure 3: Temporal evolution of the meteorological parameters for the two-weeks campaign obtained by integrating the data from the different meteorological stations.

409 ratio k_1/k_3 . This is in line with the analysis performed in Fig. 1: in sites
 410 sheltered from direct vehicular emissions and with long residence times, the
 411 photostationary equilibrium (Eq. 18) is a reliable assumption. Conversely, for
 412 the busy street canyon (Station 1), the ratio $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ is generally higher
 413 than k_1/k_3 (Fig. 4-c). This is due to the fact that, at the emission, $[\text{NO}_X]$
 414 are mainly constituted by NO, that is progressively transformed in NO_2 until
 415 photostationary equilibrium is reached. For this reason, close to the source the
 416 ratio $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ is expected to be higher than that corresponding to the
 417 equilibrium.

418 This first analysis shows that the photostationary model has some limita-
 419 tions when applied to busy street canyons with direct vehicular emissions.

420

421 To clarify this point, we assess the performance of the three photochemical
 422 models (derived in Section 1 and retrieved in Section 1.4) in predicting the
 423 concentration of $[\text{NO}_2]$ in the three measurement stations. For the sake of
 424 comparison, we include in our analysis the empirical model developed by Dixon
 425 et al. (2001). Starting from the work of Derwent and Middleton (1996), Dixon
 426 et al. (2001) developed a new $\text{NO}_X - \text{NO}_2$ relationship based on a larger dataset
 427 collected across multiple sites:

$$\frac{C_{\text{NO}_2}}{C_{\text{NO}_X}} = a + b \log(C_{\text{NO}_X}) + c \log(C_{\text{NO}_X})^2 + d \log(C_{\text{NO}_X})^3 + e \log(C_{\text{NO}_X})^4. \quad (30)$$

428 where C_{NO_2} and C_{NO_X} are the concentration in ppb of NO_2 and NO_X , respec-
 429 tively, and the polynomial constants take the following values at urban sites:
 430 $a = -3.08308$, $b = +7.472477$, $c = -5.11636$, $d = +1.381938$, $e = -0.12919$.
 431 For $C_{\text{NO}_X} < 15$ ppb, one should use $C_{\text{NO}_2}/C_{\text{NO}_X} = 0.60$. The model is referred
 432 as DDM model in the following.

433

434 The four models are applied in a quasi-steady approximation, therefore de-
 435 scribing temporal evolution of all variables (meteorological, emissions, back-
 436 ground concentration) as the succession of stationary states lasting 1 hour.

437

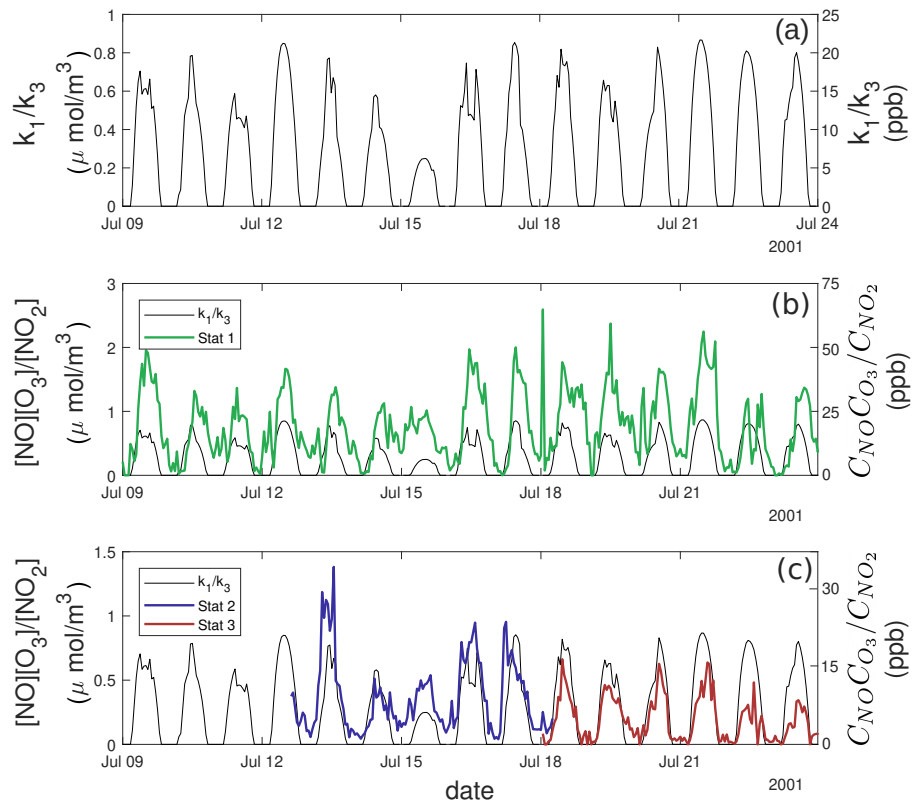


Figure 4: Evolution of the ratio k_1/k_3 as predicted by Eq. 4 (a), and comparison with the ratio $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ in $\mu\text{mol}/\text{m}^3$ ($C_{\text{NO}}C_{\text{O}_3}/C_{\text{NO}_2}$ in ppb) for the site within the street canyon -Station 1- (b) and for the two sites in the courtyards -Station 2 and Station 3- (c).

	k_1/k_3 (ppb)	2	5	10	15	20	25
Relative variation of NO ₂ concentration (%)	Station 1	14	8	Ref (0)	-7	-14	-20
	Station 2	18	11		-10	-19	-28
	Station 3	20	12		-11	-21	-31

Table 1: Sensitivity (e.g., relative variation of NO₂ concentration) of the output from Model 1 as a function of the ratio k_1/k_3 (in ppb).

438 The simplest photostationary model (Model 1) assumes that the ratio k_1/k_3
439 is constant over time and for the different urban locations. According to Seinfeld
440 (1986), we assume as a typical value for this ratio 10 ppb. This value is in line
441 with the time average of the trend estimated by means of Eq. 4 and reported in
442 Fig. 4.a. Moreover, we have tested the sensitivity of the model results to this
443 constant by calculating the relative variation of the mean NO₂ concentration
444 over the simulated period for different k_1/k_3 ratios. The results are reported in
445 Table 1. The concentration is very sensitive to variations in the ratio k_1/k_3 and,
446 as stated by Eq. 18, it increases as the ratio decreases. Moreover, the sensi-
447 tivity of the model is higher for Station 2 and Station 3 with respect to Station 1.

448
449 The results provided by the the three photo-chemical models are shown in
450 Fig. 5, where measured and simulated NO₂ concentrations are plotted for the
451 three monitoring stations. Moreover, following Chang and Hanna (2004), we
452 assessed the performance of the models by means of multiple statistical indices:

- 453 • the Relative Error: $RE = \left(\frac{2|C_m - C_p|}{C_m + C_p} \right)$;
- 454 • the Fractional Bias: $FB = 2(\overline{C_m} - \overline{C_p}) / (\overline{C_m} + \overline{C_p})$;
- 455 • the Normal Mean Square Error: $NMSE = \overline{(C_m - C_p)^2} / \overline{C_m C_p}$;
- 456 • the Mean Geometric bias: $MG = \exp[\overline{\ln(C_m)} - \overline{\ln(C_p)}]$;
- 457 • the Geometrical mean squared Variance: $VG = \exp[\overline{\ln(C_m) - \ln(C_p)}^2]$;
- 458 • the correlation coefficient: $R = \frac{\overline{(C_m - \overline{C_m})(C_p - \overline{C_p})}}{\sigma_{C_m} \sigma_{C_p}}$;
- 459 • the ‘fraction in a factor of 2’: fraction of the data for which $0.5 \leq C_p/C_m \leq$
460 2,

461 where C_m and C_p are the measured and predicted concentrations, and σ_{C_m} and
462 σ_{C_p} their standard deviations. A perfect model would have MG, VG, R and
463 FAC2=1, and FB, NMSE=0. A positive(negative) FB indicates that the model
464 tends to underpredict(overpredict) the measures. Following Chang and Hanna
465 (2004), the performances of a dispersion model can be defined as ‘good’ when
466 the following criteria are satisfied: $|\text{FB}| \leq 0.3$, $\sqrt{\text{NMSE}} \leq 2$, $0.7 \leq \text{MG} \leq 1.3$,
467 $\text{VG} \leq 1.6$, $\text{FAC2} \geq 0.5$. In Hanna and Chang (2012), the same authors suggest
468 a relaxation of these thresholds for application in urban areas. While all the
469 statistical indices are used to assess the performance of the four models, we
470 recall that only the correlation coefficient R is used as a criterion to uniquely
471 determine the value τ_s that maximizes the correlation between the results of the
472 non-photostationary model (Model 3) and the experimental data (see Section
473 1.4).

474

475 Panel a in Fig. 5 compares the measured and predicted concentrations for
476 Station 1, which corresponds to the busy urban canyon with vehicular emissions.
477 The photostationary model with constant k_1/k_3 (Model 1) predicts with a good
478 approximation the measured data but tends to overestimate NO_2 for mean to
479 high concentration values. This is confirmed by the negative fractional bias in
480 Table 3. This overestimation is also observed for low concentrations when a
481 variable k_1/k_3 ratio is implemented in the photostationary model (Model 2).
482 The slight loss of performance of Model 2 compared to Model 1 is highlighted
483 by the statistical metrics in Table 3, with the increase in the absolute value of
484 the fractional bias and the decrease in MG from 0.91 to 0.84. On the other
485 hand, a noticeable improvement in the prediction is observed by applying the
486 non-photostationary model (Model 3). The value of τ_s that maximizes the
487 correlation coefficient R is found to be equal to 89 s. This value is comparable
488 with the time scale of the chemical reactions and thus confirms the need to adopt
489 a non-photostationary solution (see Fig. 1). The scatter plot in Fig. 5 shows
490 that the dispersion of the points around the bisector decreases with respect the
491 photostationary models, as well as the relative error (RE) in Table 3. Finally, the

492 approach proposed by Dixon et al. (2001) (DDM model) fairly predicts low to
493 medium concentrations but tends to cut the highest concentration values. The
494 same trend was observed by Vardoulakis et al. (2007) by applying the model
495 by Derwent and Middleton (1996), whose prediction is almost comparable to
496 the DDM model for concentration up to 500 ppb. Vardoulakis et al. (2007)
497 suggested that this underestimation of the NO_2 concentration was because the
498 empirical relationship was derived using measures that do not always reflect the
499 typical NO_2/NO_x vehicle emission ratio of the case study.

500 Panels b and c in Fig. 5 compares the measured and predicted concentrations
501 for Station 2 and 3, which correspond to the stations located within courtyards.
502 Model 1 provides slightly scattered results and noticeably underestimates NO_2
503 concentration in Station 3 (FB=0.18 in Table 3). The adoption of a variable
504 k_1/k_3 ratio (Model 2) improves the performance of the photostationary model.
505 This is highlighted by the reduction in the relative error (RE), and by the
506 trend towards 1 of the R metric. On the other hand, the adoption of the non-
507 photostationary model (Model 3) does not bring further improvements. For both
508 monitoring stations, the value of τ_s that maximizes the correlation coefficient
509 R tends to infinity. As depicted in Fig. 1, this means that the results provided
510 by the non-photostationary model ($[\text{NO}_2]$) correspond to those provided by the
511 photostationary one ($[\text{NO}_2]^\infty$). This suggests that the pollutant concentrations
512 in these sites already reached the photochemical equilibrium, as foreseen in Fig.
513 4). Finally, the approach proposed by Dixon et al. (2001) performs worse than
514 the three physically-based models also for Station 2 and 3. Differently from
515 Station 1, here the predictions are significantly underestimated (FB=0.21 and
516 0.28) also for low to medium concentration values.

517 Despite differences in performance, we finally notice that the statistical met-
518 rics in Table 3 are within the validity ranges suggested by Chang and Hanna
519 (2004) for all models.

520 In addition to NO_2 concentrations, the models derived in Section 1 (and
521 presented in Section 1.4) provide NO and O_3 concentrations. Fig. 6 shows
522 that, in a general way, the concentrations of NO are well simulated by the

		RE	FB	NMSE	MG	VG	R	FAC2
M1	Station 1	0.18	-0.12	0.05	0.91	1.01	0.96	1.00
	Station 2	0.13	0.04	0.03	1.06	1.00	0.94	1.00
	Station 3	0.17	0.18	0.07	1.18	1.03	0.96	1.00
M2	Station 1	0.18	-0.15	0.04	0.84	1.03	0.97	1.00
	Station 2	0.07	-0.05	0.02	0.95	1.00	0.97	1.00
	Station 3	0.10	0.10	0.02	1.09	1.01	0.99	1.00
M3	Station 1	0.09	0.00	0.01	1.01	1.00	0.99	0.99
	Station 2	0.07	-0.05	0.02	0.95	1.00	0.97	1.00
	Station 3	0.09	0.10	0.02	1.09	1.01	0.99	1.00
DDM	Station 1	0.21	0.05	0.09	1.04	1.00	0.86	1.00
	Station 2	0.27	0.21	0.08	1.29	1.07	0.93	1.00
	Station 3	0.32	0.28	0.12	1.38	1.11	0.96	1.00

Table 2: Performance statistics for the four investigated models (M1, M2, M3, DDM) in predicting the measured NO₂ concentration in the three measurement stations. Station 1 is to the busy street canyon, while Station 2 and 3 are courtyards.

523 proposed models. As observed for NO₂ concentrations, the non-photostationary
524 model (Model 3) outperforms Model 2 for Station 1, while for Stations 2 and 3
525 adopting the photostationary model with variable k_1/k_3 is sufficient to maximize
526 correlation. The DDM model shows good agreement for Station 1 for high
527 concentration values, while for medium-low values (between 50 and 100 ppb)
528 the error is significant. In accordance with Eq. 19, this behaviour reflects
529 the results found for NO₂ concentrations. We also observe that for stations 2
530 and 3, the DDM model fails to reproduce low NO concentrations. Regarding
531 the prediction of ozone, the same considerations made for NO and NO₂ are
532 valid: Model 3 brings significant improvements in results for the busy street
533 canyon (Station 1), while the photostationary assumption (Model 2) holds when
534 predicting concentrations in stations far from direct emissions (Station 2 and
535 3).

536 4. Conclusions

537 In this work we have derived different box models to simulate the concen-
538 tration of NO, NO₂ and O₃ in a street canyon. Starting from a mass balance in
539 the street, we have first defined a model for a passive tracer, then for chemical
540 species at photostationary equilibrium and finally for the non-photostationary

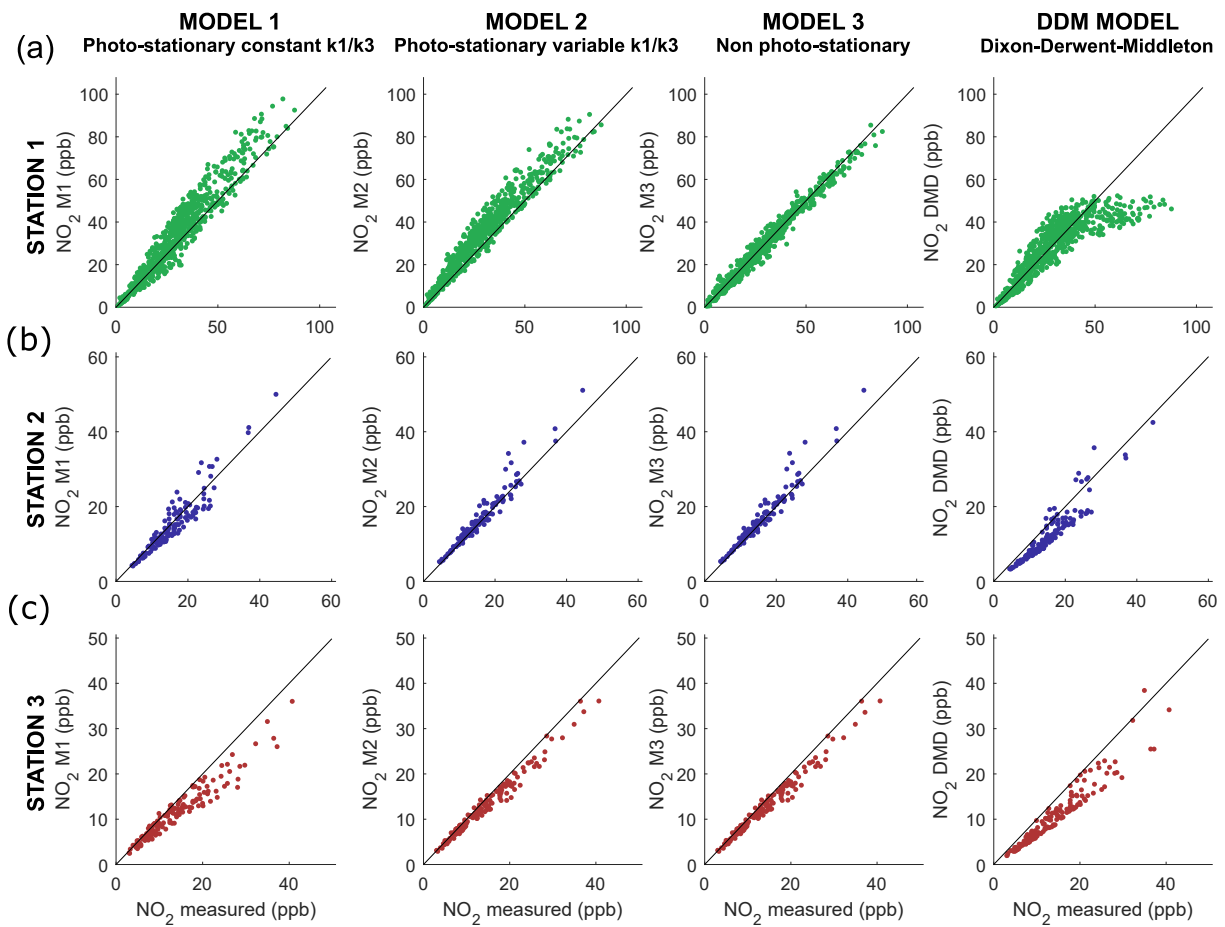


Figure 5: Comparison between the measured NO₂ concentrations in Station 1 (a), Station 2 (b) and Station 3 (c) against the concentrations computed with the three different photochemical models (M1, M2 and M3) and with the Derwent-Middleton model. Each point corresponds to one hour average concentration. Station 1 is to the busy street canyon, while Station 2 and 3 are courtyards.

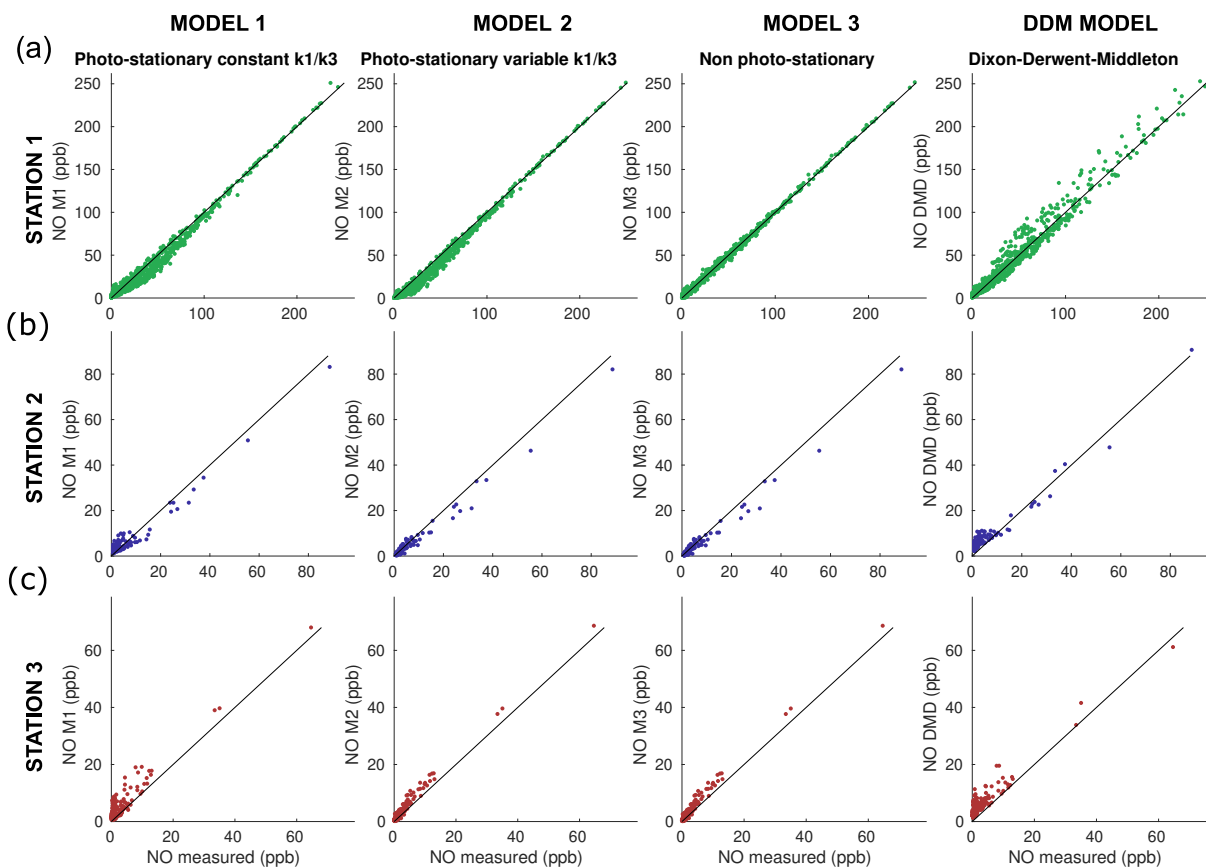


Figure 6: Comparison between the measured NO concentrations in Station 1 (a), Station 2 (b) and Station 3 (c) against the concentrations computed with the three different photochemical models (M1, M2 and M3) and with the Derwent-Middleton model. Each point corresponds to one hour average concentration. Station 1 is to the busy street canyon, while Station 2 and 3 are courtyards.

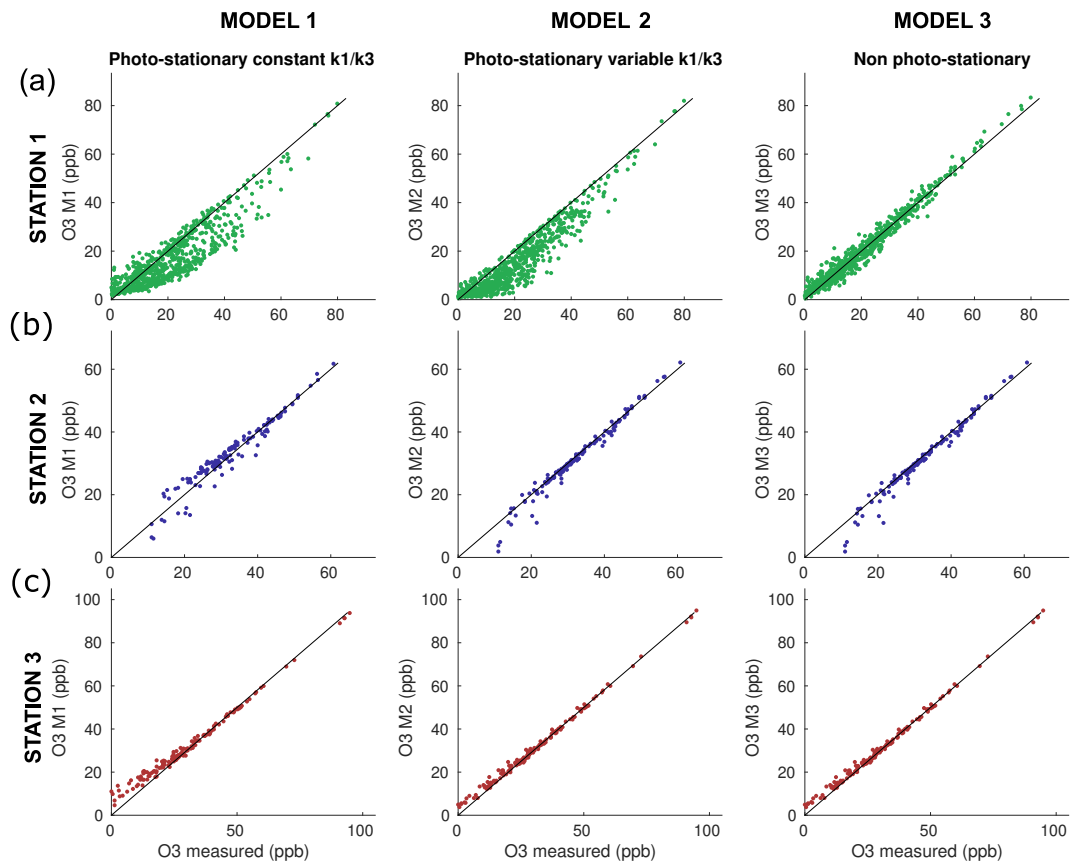


Figure 7: Comparison between the measured O_3 concentrations in Station 1 (a), Station 2 (b) and Station 3 (c) against the concentrations computed with the three different photochemical models (M1, M2 and M3). Each point corresponds to one hour average concentration. Station 1 is to the busy street canyon, while Station 2 and 3 are courtyards.

541 state. Prediction from the simulations were compared with concentration mea-
542 surements acquired during a field campaign. Results showed that the photosta-
543 tionary models adequately reproduce the pollutant concentration in canyons far
544 from direct vehicular emissions. However, the implementation of a parameteri-
545 zation for the reaction rates according to the meteorological conditions is crucial.
546 In busy streets, the photostationary equilibrium is not yet fully achieved and
547 the non-photostationary model performs better. Finally, empirical models such
548 as Dixon-Derwent-Middleton relationship fail to reproduce concentration peaks
549 in busy canyons and underestimate NO_2 concentrations at photochemical equi-
550 librium. These results show that the photostationary model with meteorology-
551 based parameters is satisfactory in reproducing the concentrations in different
552 urban scenarios. However, the non-photostationary model brings significant
553 improvements in busy street canyons.

554 Differently from previous studies, the chemical models presented here in-
555 clude a description of the longitudinal and vertical ventilation processes and are
556 therefore suitable for application to a network of streets with pollutant fluxes at
557 street intersections. This paves the way for their implementation in operational
558 street network models such as Sirane.

559 Furthermore, the adoption of a coherent formulation and the analysis of the
560 balance equations in terms of characteristic transport and reaction times clarify
561 the processes involved, the physico-chemical assumptions, and the limits of their
562 validity. This information is critical to understanding, developing, and improv-
563 ing the parametric models used in existing air quality simulation software. In
564 this regard, a desirable development is the treatment of non-photostationarity
565 outside the urban canopy, i.e. over rooftops or on high-emission roads in open
566 terrain.

567 Finally, we notice that the diffusion of low-cost sensors provides nowadays
568 large databases of pollutant concentration in cities. The inclusion of more accu-
569 rate transport and reaction models in operational tools for urban air pollution
570 is in line with this growing availability of data that can be used for validation
571 and data assimilation. In this sense, this work highlights the feasibility of im-

572 plementing non-photostationary models in simulation tools at the city scale and
573 paves the way for further application and validation.

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