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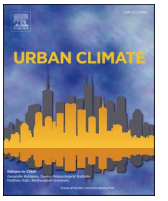
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Effect of emission variability on concentration fluctuations in idealised deep urban street canyons

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ABSTRACT

The level of air pollution in a street canyon depends on the non-trivial interplay between vehicular exhaust emissions, atmospheric transport, and physico-chemical transformation of pollutants. In this study, we investigate the temporal dynamics of air pollutant concentration in a deep street canyon orthogonal to the wind direction using a two-box model. Simulations provide insights into both steady-state mean concentrations and the magnitude of concentration fluctuations as pollutant nature (inert or reactive), emission signal stochasticity, and the fundamental rates of turbulent transport and chemical transformations vary. Beyond elucidating the role of different parameters on mean pollution levels, the results reveal that extreme air pollutant concentrations are more likely to occur when the characteristic time scale of vehicular exhaust emissions significantly exceeds the ventilation time scale of the street canyon. The innovative modelling approach paves the way for various applications, particularly in the field of optimal traffic management and the study of citizens' exposure to air pollution.

1. Introduction

Nowadays, urban areas face significant challenges related to the urban microclimate and especially to air pollution. According to the latest WHO (World Health Organization) report (WHO, 2023), almost all of the global population (99%) breathe air that exceeds WHO guideline limits. This is responsible for around 7 million premature deaths per year (Murray et al., 2020). The vulnerability of cities to air pollution is due, on one hand, to the high number and magnitude of polluting emissions in densely populated areas and, on the other hand, to the intricate urban geometry that limits ventilation (Li et al., 2021; Fellini et al., 2020b, 2021). In urban street canyons, turbulent transport is inhibited and the wind-induced flow field depends on several factors such as the geometry of the canyon (e.g., Jeong and Andrews, 2002; Xiaomin et al., 2006), its orientation with respect to the wind (Soulhac et al., 2008), the presence of obstacles such as trees (Gromke and Ruck, 2012; Fellini et al., 2022; Carlo et al., 2023; Del Ponte et al., 2024), and thermal effects that induce buoyancy flows (Marucci and Carpentieri, 2019; Fellini et al., 2020a). Typically, the attention is directed towards street canyons oriented perpendicular to the wind direction, as this configuration exhibits the highest air pollutant concentrations. This is primarily attributed to the formation of one or multiple recirculating vortices within the canyon, as numerically and experimentally evidenced in previous literature (e.g., Sini et al., 1996; Lee and Park, 1994; Jeong and Andrews, 2002; Assimakopoulos et al., 2003; Louka et al., 2002; Liu et al., 2004; Allegrini et al., 2013; Marucci and Carpentieri, 2019; Fellini et al., 2020a). These recirculating

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structures restrict the transport of pollutants and confines them at street level, where they are emitted.

Vehicular traffic stands out as the predominant source responsible for surpassing air quality standards in city centres (EEA, 2021). The combustion processes by motor vehicles are mainly responsible for the emissions of nitrogen oxides (NO_x) which, upon acute exposure, can lead to respiratory ailments and impair lung function. Children are particularly susceptible, as evidenced by an elevated occurrence of childhood asthma attributed to NO_x emissions from vehicular traffic (Khreis et al., 2017; Anenberg et al., 2022). The repartition of NO_x at the emission is approximately between 10% to 15% for nitrogen dioxide (NO_2) and, thus, 90% to 85% for nitrogen monoxide (NO) (Ntziachristos et al., 2000). While NO is the primary contributor to NO_x, it is less toxic than NO_2. However, due to its inherent instability as a radical, NO readily undergoes photochemical oxidation to form NO_2. Nitrogen dioxide can subsequently undergo photolysis, converting back to NO and leading to the generation of ozone (O_3) (Oke et al., 2017). These chemical transformations can be succinctly represented by a minimalistic 3-reaction scheme involving NO_2-NO-O_3 (Soulhac et al., 2011). However, a more comprehensive depiction encompasses the intricate interactions involving radicals resulting from the oxidation of volatile organic compounds (VOC) and carbon monoxide (CO) (Jenkin and Clemitshaw, 2000), as well as interactions with hydroxyl radicals, ultimately leading to the production of nitric acid.

The fate of pollutants emitted at street level relies thus on both complex chemical transformations as well as transport dynamics governed by the turbulent flow. Previous studies have shown that, within busy street canyons, chemical reactions occur on a timescale similar to that of canyon air circulation and residence time of pollutants (Soulhac et al., 2023). Therefore, it is crucial to model both dynamics (chemical and turbulent) in order to accurately simulate air pollutant concentrations.

Extensive research has been conducted over the past two decades to investigate the interplay between turbulent and chemical dynamics in assessing photochemical pollution in urban areas, as reviewed by Zhong et al. (2016a). Especially, Computational Fluid Dynamics (CFD) has played a key role in providing insights into this domain (e.g., Garmory et al., 2009; Kwak and Baik, 2012; Kim et al., 2012). By means of CFD simulations, both the turbulent flow field and the chemical reactions can be reproduced with great accuracy. Nevertheless, the range of scenarios to be simulated in an urban environment is extensive, given the diverse street geometries, meteorological conditions, and emission modes. Since the domain and model configurations should be tailored on a case-by-case basis, employing CFD models for such a wide range of scenarios is computationally demanding and resource-intensive. For these reasons, a more efficient way is adopting simplified modelling approaches as box models (Vardoulakis et al., 2007).

Box models partition a street canyon into one or several regions (referred to as boxes), with each box associated with a mass balance equation. One-box models for non-reactive pollutants have been widely studied (Berkowicz, 2000; Soulhac, 2000; Kukkonen et al., 2001; Caton et al., 2003). However, both experimental observations and numerical simulations have shown that air pollutant concentration is far from being spatially uniform in street canyons (e.g., Assimakopoulos et al., 2003; Marucci and Carpentieri, 2019), and more than one time scale is involved in the ventilation process (Salizzoni et al., 2009; Fellini et al., 2020a). Therefore, a comprehensive understanding of the wash-out process requires the adoption of multi-box models (Salizzoni et al., 2009; Murena et al., 2011). Regarding chemical transformations, photochemical smog has been incorporated into a one-box chemistry model by Liu and Leung (2008) and into a two-box model by Zhong et al. (2015) and Zhong et al. (2016b). Furthermore, the investigation conducted by Soulhac et al. (1) validated the outcomes of a box model employing the simplified NO-NO_2-O_3 cycle through field measurements conducted in three urban canyons in the city of Lyon (France).

Historically, box models have predominantly been employed to assess steady-state air pollutant concentrations within street canyons, offering valuable approximations for operational models at the urban scale (Carruthers et al., 2000; Soulhac et al., 2011). Nevertheless, these models can also be effectively employed to delve into transient behaviors and investigate the influence of diverse parameters on the system's dynamics. Such analyses become particularly intriguing when the system's external forces exhibit temporal variability, as is often the case with vehicular emissions.

The passage of a single car, traffic flow regulated by traffic lights, or daily traffic patterns are characterized by a temporal scale that can range from seconds to hours. The variability in emission rates over time significantly influences concentration trends and, consequently, the levels of pollution to which residents are exposed. Moreover, the presence of chemical reactions introduces non-linear behaviors that can further amplify traffic-induced variations in pollutant concentrations. The evaluation of peak concentration values is crucial as short-term exposure to high peaks is associated with respiratory and cardiovascular health issues (Cassiani et al., 2020).

In this framework, the objective of this study is to adopt a box model for a street canyon with either inert or reactive pollutant emissions to evaluate how the typical time scales of canyon ventilation and chemistry interact with the time scale of traffic emissions at the street level. The study aims to analyze concentration transients in different regions of the canyon and quantify peculiar behaviors deviating from the mean steady-state values.

The study is organized as follows. Section 2.1 presents the box model accounting for both transport and chemical dynamics. The results for the case of an inert gas emission with different time forcings at the source are presented in Section 3.1. The analysis will then extend to the emission of NO_x 3.2. Finally, the conclusions of this work will be discussed in Section 4.

2. Methods

2.1. Model description

In European urban environments, street geometries commonly exhibit height to width aspect ratios (H/W) ranging from 0.5 to 2 (Soulhac and Salizzoni, 2010). Considering that the most elevated pollution levels occur in deep streets, our study specifically focuses on the upper limit of this range, which corresponds to a narrow canyon with an aspect ratio of $H/W = 2$. For this geometry, and for a

perpendicular incoming wind, the flow field (Fig. 1.a-b) is characterized by two overlapping vortices as well-documented by previous experimental (Fellini et al., 2020a) and numerical studies (Kovar-Panskus et al., 2002). The works of Salizzoni (2006); Salizzoni et al. (2009); Murena et al. (2011); Fellini et al. (2020a) have shown that a model with two degrees of freedom is suitable to describe pollutant exchanges within these types of canyons. This implies that the cavity wash-out can be accurately modelled by means of a sequence of pollutant transfers between three regions (Fig. 1.c-d): (i) the external flow, (ii) the recirculating cell at the top of the cavity (box 1) exchanging pollutants with the external flow, and (iii) the cell at the bottom of the cavity where pollutants are released (box 2).

Following this modelling approach, and assuming an absence of lateral street intersections (i.e., considering the canyon to be indefinitely long), the mass balance for the two boxes within the canyon reads:

$$\begin{cases} V_1 \dfrac{dC_1}{dt} = & S_{1e}u_{1e}(C_e - C_1) + S_{12}u_{12}(C_2 - C_1) + P_1 - D_1 \\ V_2 \dfrac{dC_2}{dt} = & S_{12}u_{12}(C_1 - C_2) + P_2 - D_2 + Q, \end{cases} \tag{1}$$

where S_{1e} is the exchange surface between box 1 and the external flow and S_{12} is the exchange surface between box 1 and box 2; V_1 and V_2, C_1 and C_2, P_1 and P_2, and D_1 and D_2, are the volume, mean concentration, production and destruction terms of box 1 and box 2, respectively. The emission Q is located in the lower box (box 2). The bulk exchange velocities (see Appendix A for the definition) between box 1 and the external flow and between box 1 and box 2 are denoted as u_{1e} and u_{12}, respectively. In this model, the street properties are assumed to be fairly uniform along the longitudinal axis of the canyon, and thus the geometry and the dynamics are assumed to be two-dimensional. Volumes and surfaces will then be considered per unit length along the canyon axis.

Setting the volume of each box as a function of the total volume of the cavity by means of a single geometrical parameter β (i.e., $V_1 = \beta V$, $V_2 = (1-\beta)V$), and replacing the exchange surfaces (per unit length) S_{1e} and S_{12} equal to the width of the canyon, W, the characteristic time for pollutants to exit box 1 and box 2 can be defined as:

$$T_1 = \frac{\beta V}{W u_{1e}}, T_2 = \frac{(1-\beta)V}{W u_{12}}. \tag{2}$$

These equations show that the characteristic washout times depend on the exchange rates at the interfaces (u_{1e} and u_{12}) and on the flow field topology inside the canyon, i.e. the size of the two recirculation cells that is described by the repartition parameter β. Recent studies (Salizzoni et al., 2009; Fellini et al., 2020a) have revealed that the vertical exchange rate at the canyon roof (u_{1e}) is governed by the intensity of the turbulent kinetic energy in the shear layer that develops at the interface between the external atmospheric flow and the flow in the cavity. The exchange between the two cells (u_{12}), instead, mainly depends on the turbulent kinetic energy that penetrates inside the canyon from the external flow. The exchange time T_1 can thus be considered as representative of the external atmospheric forcing and is in general shorter than T_2. For fixed external conditions, the ratio T_2/T_1 depends on the turbulent flow field inside the canyon: a high T_2/T_1 ratio occurs when the intensity of the turbulent kinetic energy entering the canyon is low compared to the turbulence intensity in the shear layer. This could be due to the presence of obstacle in the streets (such as tree crowns) or buoyancy effects a the lateral walls (Fellini et al., 2020a). Under these conditions, the washout time is much longer at pedestrian level where high levels of pollution will occur. Conversely, a low T_2/T_1 ratio reveals the presence of efficient turbulent transport within the canyon and

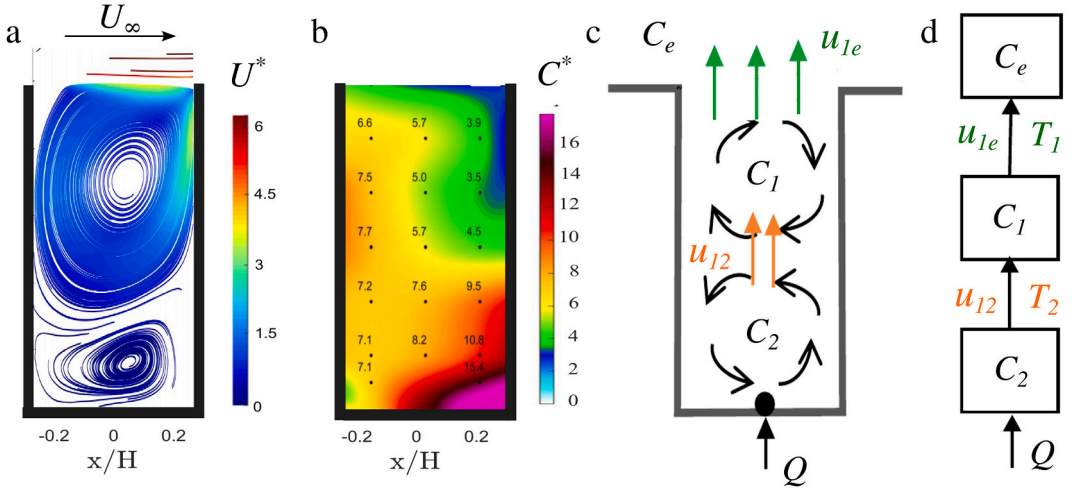


Fig. 1. a) Streamlines of the mean dimensionless velocity field $U^* = \left(U^2 + W^2\right)^{0.5}/u^*$ (U and W are the mean horizontal and vertical velocities, u^* and U_∞ are the friction and free stream velocities of the external boundary layer) and b) mean dimensionless concentration field ($C^* = Cu^*HL/Q$, where L is the canyon longitudinal length) within a street canyon with height to width aspect ratio $H/W = 2$ from the experimental work of (Fellini et al., 2020a). c) Simplified representation of pollutant transfer dynamics inside the canyon with street emission Q. d) Schematic representation of the two-box model.

therefore more effective ventilation at street level.

By replacing Eqs. 2 in the concentration budgets (Eqs. 1), the two-box model becomes:

$$\begin{cases} \dfrac{dC_1}{dt} = & \dfrac{C_e - C_1}{T_1} + \dfrac{\alpha}{T_2}(C_2 - C_1) + p_1 - d_1 \\ \dfrac{dC_2}{dt} = & \dfrac{1}{T_2}(C_1 - C_2) + p_2 - d_2 + q, \end{cases} \tag{3}$$

where $\alpha = (1-\beta)/\beta$, while q, p and d are the source, chemical production and destruction per unit volume, respectively.

To introduce chemical transformations of nitrogen oxides in the box model, we use a minimalistic 3-reaction cycle for NO-NO_2-O_3 (see Appendix B). Despite the model's simplicity, its effectiveness in capturing the essential aspects of chemical dynamics has been confirmed in prior research. For instance, Bright et al. (2013) employed Large Eddy Simulation (LES) initially coupled with a basic 3-reaction scheme and later with a detailed chemical reaction mechanism (Reduced Chemical Scheme) involving 51 chemical species and 136 reactions. Their findings showed that increasing chemical complexity, such as simulating VOC chemistry, led to additional but modest formation of NO_2 and O_3 in the canyon. This numerical outcome aligns with the results presented in Soulhac et al. (1), where the outcomes of the 3-reaction chemical model were compared with measurements conducted in three urban canyons in the city of Lyon. Modelling the photolysis of NO_2 into NO and O_3 by means of the kinetic constant of reaction k_1, and the regeneration of NO_2 from NO and O_3 by means of the kinetic constant of reaction k_3, the production (p) and destruction (d) terms can be written according to the expressions reported in Eqs. B.12 in Appendix B. The mass balance for each chemical species (NO_2, NO, O_3) in the two boxes of the cavity results:

$$\begin{cases} \dfrac{d[NO_2]_1}{dt} = & -\dfrac{[NO_2]_1}{T_1} + \dfrac{\alpha}{T_2}\left([NO_2]_2 - [NO_2]_1\right) + k_3[NO]_1[O_3]_1 - k_1[NO_2]_1 \\ \dfrac{d[NO_2]_2}{dt} = & \dfrac{1}{T_2}\left([NO_2]_1 - [NO_2]_2\right) + k_3[NO]_2[O_3]_2 - k_1[NO_2]_2 + q_{NO_2} \\ \dfrac{d[NO]_1}{dt} = & -\dfrac{[NO]_1}{T_1} + \dfrac{\alpha}{T_2}\left([NO]_2 - [NO]_1\right) + k_1[NO_2]_1 - k_3[NO]_1[O_3]_1 \\ \dfrac{d[NO]_2}{dt} = & \dfrac{1}{T_2}\left([NO]_1 - [NO]_2\right) + k_1[NO_2]_2 - k_3[NO]_2[O_3]_2 + q_{NO} \\ \dfrac{d[O_3]_1}{dt} = & \dfrac{[O_3]_e - [O_3]_1}{T_1} + \dfrac{\alpha}{T_2}\left([O_3]_2 - [O_3]_1\right) + k_1[NO_2]_1 - k_3[NO]_1[O_3]_1 \\ \dfrac{d[O_3]_2}{dt} = & \dfrac{1}{T_2}\left([O_3]_1 - [O_3]_2\right) + k_1[NO_2]_2 - k_3[NO]_2[O_3]_2 + q_{O_3}, \end{cases} \tag{4}$$

where $[\cdot]$ represents the molar concentration (mol/m^3) of the compound, and their subscript 1, 2 and e indicate the concentration in box 1, in box 2, and in the external flow, respectively. The emissions q_{NO_2}, q_{NO} and q_{O_3} are the emission rates per unit volume of NO_2, NO, and O_3, respectively. Since ozone is a secondary pollutant, its direct emission in the street can be neglected ($q_{O_3} = 0$) while the contribution from the external atmosphere (where indirect formation of O_3 occurs) is significant. For this reason, its concentration above roof level ($[O_3]_e$) is included in the model. Nitrogen monoxide and dioxides are instead directly emitted by the vehicular traffic and, in busy street canyons, this emission dominates with respect to the background contribution, that is here neglected. Their emission rates can be estimated as a function of the total NO_x emissions ($q_{NO_x} = q_{NO_2} + q_{NO}$) by means of the repartition ratio $a = q_{NO_2}/q_{NO_x}$.

2.2. Simulated street canyon and emission scenarios

We focus on a realistic 10 m wide (W) street canyon, flanked by 20 m high buildings (H), with a main recirculating vortex occupying 70% (β) of the upper canyon volume (box 1), and a second smaller vortex in the bottom of the canyon (box 2). The vertical exchange velocities u_{1e} and u_{12} are fixed equal to 0.1 and 0.05 m/s, respectively, which are reasonable values for this geometry and are in accordance with previous experimental measurements (Fellini et al., 2020a). According to Eqs. 2, the ventilation times for the two boxes are $T_1 = 140$ s and $T_2 = 120$ s.

We examine a scenario characterized by clear skies ($Cld = 0$), a temperature of $\Theta = 20^{\circ}C$, and a solar elevation angle (χ) of 45°. The background O_3 concentration is 170 $\mu g/m^3$. This setting is representative of a typical sunny day in Southern European cities during the spring season. According to Eq. B.11, the chemical transformation rates are computed as $k_1 = 8 \times 10^{-3}\,s^{-1}$ and $k_3 = 2.1 \times 10^{-4}\,m^3\mu g^{-1}s^{-1}$. Two characteristic time scales associated with the chemical transformations are then defined: $\tau_1 = 1/k_1$ and $\tau_3 = 1/(k_3[O_3]_e)$. In this scenario, τ_1 is 125 s ($\tau_1/T_1 = 0.9$) and τ_3 is 28 s ($\tau_3/T_1 = 0.2$). It is worth noting that these time scales are comparable to the characteristic ventilation times of the canyon (T_1 and T_2). Under these conditions, it becomes crucial to model both the transport and chemical transformation dynamics to obtain an accurate estimation of the pollution levels within the canyon.

The pollutant source is ground-level NO_x vehicular emission, assumed to range from 0.5 to 300 $\mu g/m/s$. This range has been established based on findings from two prior studies related to traffic within street canyons in European city centers. The first study,

conducted by Soulhac et al. (2012), estimated NO_x emissions in a district of Lyon, France, by employing traffic simulation and data derived from direct traffic measurements. Subsequently, the COPERT III model was applied. The second study, detailed in Li et al. (1) and Grylls et al. (2019), estimated NO_x vehicular emissions in the urban district of South Kensington, London, through the coupling of VISSIM traffic microsimulation (Bloomberg and Dale, 2000) and the emission model developed by Panis et al. (2006). The emission per unit length estimated from these studies is then converted into an emission per unit volume (with the mean denoted as q_0 in the following). This conversion involves dividing by the volume of the bottom box (V_2) of the canyon, as specified by Eq. 3. The repartition of NO_x at the emission is taken constant in this study and described by the repartition coefficient $a = q_{NO_2}/q_{NO_x}$ equal to 0.2 (Carslaw et al., 2016).

To replicate vehicular emissions, we progressively introduce emission models with increasing complexity in this study. Initially, we consider a constant emission over time. Subsequently, we shift to periodic emission signals, as vehicular emissions exhibit periodic patterns influenced by factors such as the typical travel time of a single car along the street (under low traffic conditions) or the regulation of a traffic light (under heavy traffic conditions).

For simulating this periodicity, we first model the emission as a sinusoidal function:

$$q(t) = q_0\left(1 + A sin\left(\frac{2\pi}{\tau}t\right)\right), \tag{5}$$

where τ is the period of the signal and A is the coefficient that controls the amplitude of the periodic variations. The mean and the standard deviation of the sine function are $\mu = q_0$ and $\sigma = q_0 A/\sqrt{2}$, respectively. The parameters of the periodic emission are set as $\tau = 120$ s and $A = \sqrt{2}/3$. The period of the source τ is chosen as representative of the cycle length of a traffic light, while the amplification coefficient A is fixed to match realistic emission variations around the mean and to facilitate the comparison with the stochastic emission scenario. Adopting this value for A, the standard deviation and the coefficient of variation (CV $= \sigma/\mu$) of the source are $\sigma = q_0/3$ and CV $= 1/3$, respectively.

Finally, we take into account the non-deterministic nature of vehicular emissions due to many unpredictable factors like driving behavior, variations in the intensity of the vehicular traffic, and the turbulent nature of the wind in the street canyon. To address these variabilities, the source signal is forced with a coloured Gaussian noise $X(t)$, (i.e)

$$q(t) = q_0 + X(t), \tag{6}$$

Table 1
Street canyon parameters and variability ranges simulated in this study.

Geometrical parameters				
Width & Height	W [m]	10	H [m]	20
Flow dynamics parameters				
Topology of cells	β [·]	0.7	α [·]	0.43
Vertical bulk velocities	u_{1e} [m/s]	0.1	u_{12} [m/s]	0.05
Ventilation times	T_1 [s]	140	T_2 [s]	120
Emission parameters				
Emission mean for inert gas	Q_0 [μg/m/s]	45	q_0 [$\mu g/m^3/s$]	0.75
Emission mean for NO_x	Q_0 [$\mu g/m/s$]	60	q_0 [$\mu g/m^3/s$]	1
Repartition coefficient for NO_x	a [·]	0.2		
Emission period	τ [s]	120		
Emission time variability	σ_q [$\mu g/m^3/s$]	$q_0/3$	CV_q [·]	1/3
Chemical parameters				
Reaction rates	k_1 [s^{-1}]	8×10^{-3}	k_3 [$m^3/\mu g/s$]	2.1×10^{-4}
Reaction time scales	τ_1 [s]	125 s	τ_3 [s]	28 s
Background O_3 concentration	C_{O3} [$\mu g/m^3$]	170		
Range of varying parameters				
Emission mean (unit length)	Q_0 [$\mu g/m/s$]	0.5–300		
Emission mean (unit volume)	q_0 [$\mu g/m^3/s$]	0.01–5		
Ventilation time (bottom box)	T_2 [s]	35–130		
Emission period	τ [s]	40–220		
Reaction time scale 1	τ_1 [s]	14 - 1.4×10^4		
Reaction time scale 3	τ_3 [s]	14–280		
Range of time ratios				
Ventilation time ratio	T_2/T_1 [·]	0.25–0.93		
Emission period	τ/T_1 [·]	0.3–1.6		
Reaction time scale 1	τ_1/T_1 [·]	0.1–100		
Reaction time scale 3	τ_3/T_1 [·]	0.1–10		

which accounts for random fluctuations at the emission but maintains a characteristic temporal scale. The noise is obtained from the Ornstein-Uhlenbeck process and its main parameters are the relaxation time, τ, and the diffusion constant of the process, ε. The diffusion constant amplifies the noise, while the relaxation time is representative of the autocorrelation of the signal, that mimics the periodicity of vehicle transits. For $\tau \to 0$ the signal tends to a Gaussian white noise, i.e. a completely uncorrelated noise. The stochastically perturbed emission is obtained by summing the noise $X(t)$ to the mean emission q_0. As a result, the emission is characterized by a Gaussian NO_x function, with mean q_0 and variance $\varepsilon\tau/2$ (see Appendix C for details). To limit negative entries for the source signal, we choose the diffusion constant ε in such a way that nearly all values lie within three standard deviations of the mean:

$$3 \cdot \mathrm{std}\{X(t)\} = q_0 \to \varepsilon = \frac{2}{9}\frac{q_0^2}{\tau}. \tag{7}$$

As a further control, rare negative occurrences for q are forced to be equal to zero. Thus, the source term has mean q_0, standard deviation $q_0/3$ and CV $= 1/3$, as the sinusoidal emission described above.

The parameter values considered in this study are summarized in Table 1. To explore the impact of different characteristic time scales for both transport and chemistry on concentration dynamics within the canyon, we systematically vary the characteristic exchange time between the bottom and upper boxes (T_2), the characteristic emission period (τ), and the timescales associated with chemical reactions (τ_1 and τ_3). Additionally, we examine the variation in emission intensity (q_0). The specified parameter ranges are presented at the end of Table 1. For emissions, we referred to the same studies mentioned above (e.g., Soulhac et al., 2012). Regarding the ventilation time T_2, we considered a reasonable sensitivity based on previous experimental works (Fellini et al., 2020a). For reaction times, we took into account the reasonable sensitivity of meteorological parameters determining k_1 and k_3.

3. Results

3.1. Inert gas

3.1.1. Deterministic emissions

We begin by examining a straightforward scenario in which there are no chemical transformations ($p = d = 0$), the emission remains constant over time ($q = q_0$), and the air pollutant concentration above roof level is significantly lower than the pollution inside the canyon (i.e., $C_e - C_1 \simeq -C_1$). This condition is valid for pollutants primarily emitted directly into the streets (e.g., NO_2 and NO from vehicular traffic), where the atmosphere above the rooftops acts as a dilution factor. However, this assumption may not be applicable to other pollutant types, such as ozone or particulate matter, where external deposition into the canyon is not negligible.

Under these assumptions, the numerical solution of the system in Eq. 3 provides the temporal pattern of the concentration in the two boxes (Fig. 2.a). The coloured lines depict the concentration transient from an initial state ($C_1(0),\ C_2(0)$) as a function of the source intensity and show that the concentration of pollutants can reach a maximum value during the transient phase greater (even by a factor of two) than the initial or final state. The concentration values at final solution lie on straight lines with slope $1 + T_2/(\alpha T_1) = 1 + u_{1e}/u_{12}$. These are represented for different T_1/T_2 ratios as dashed and continuous lines in Fig. 2.a. This result correspond to the analytical solution of Eq. 3 at steady state:

$$\begin{cases} C_{0,1} = & \alpha T_1 q_0 \\ C_{0,2} = & (\alpha T_1 + T_2) q_0. \end{cases} \tag{8}$$

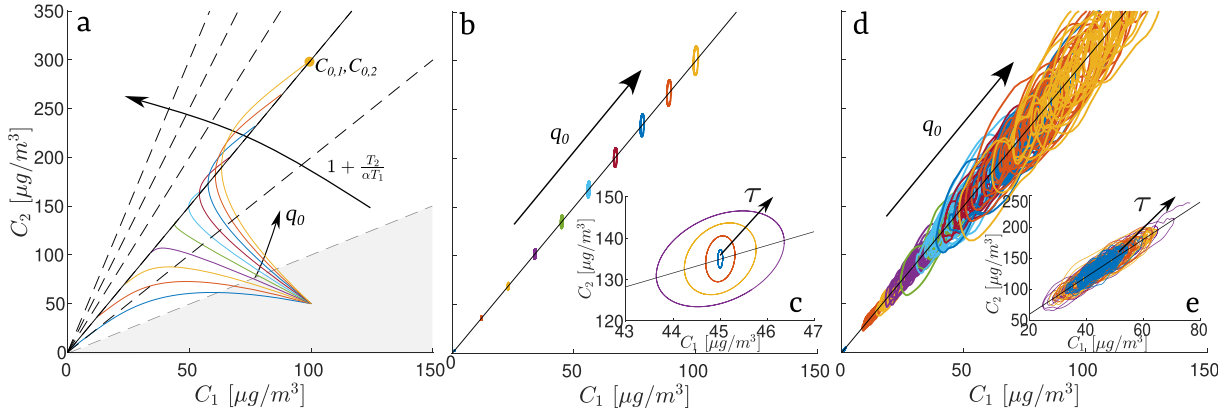
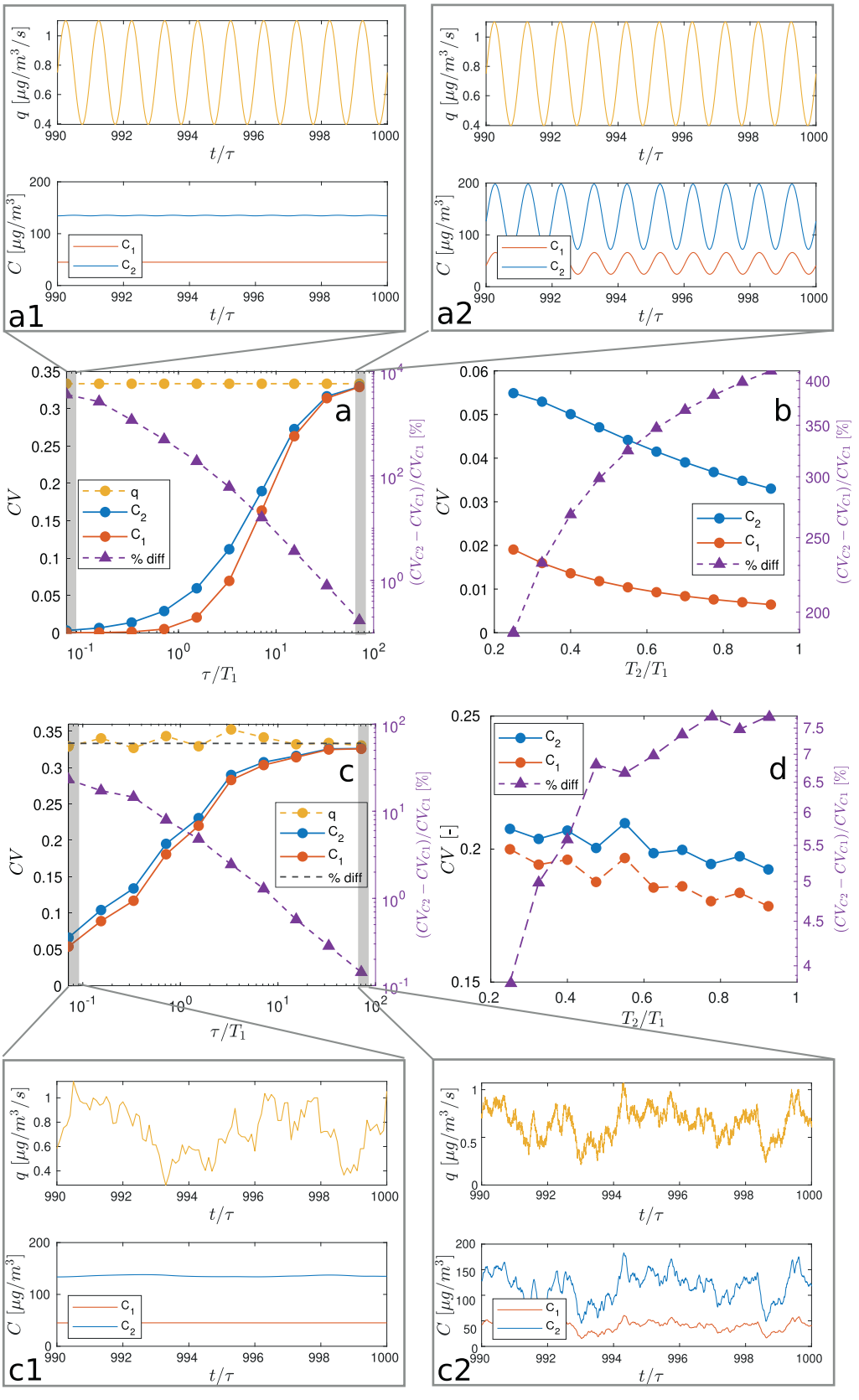


Fig. 2. (a) Concentration transients in the space $\{C_1, C_2\}$ for a constant emission with varying intensity q_0. The steady state solutions lie on straight lines with slope $1 + T_2/(\alpha T_1)$ (continuous line for the case study, dashed lines for the possible solutions with varying $T_2/(\alpha T_1)$). (b-c) Steady state limit cycles in the space $\{C_1, C_2\}$ for (b) periodic emissions with constant τ and varying intensity q_0, and for (c) periodic emissions with constant q_0 and varying period τ. (d-e) Noisy solution for (d) stochastic emissions with constant τ and varying intensity q_0, and for (e) stochastic emissions with constant q_0 and varying period τ.



(caption on next page)

Fig. 3. Inert gas. a) Coefficient of variation (CV) of the source (q) and concentration signals (C_1 and C_2) as a function of τ/T_1 for a periodic emission. Panels (a1) and (a2) show the emission and concentration signals over time for $\tau/T_1 = 0.07$ and 10^2. b) CV as a function of T_2/T_1 for a periodic emission. c) CV as a function of τ/T_1 for a stochastic emission. Panels (c1) and (c2) show the emission and concentration signals over time for $\tau/T_1 = 0.07$ and 10^2. d) CV as a function of T_2/T_1 for a stochastic emission. In a and b, the grey dashed line is the theoretical CV from the derived distributions for C_1 and C_2.

When the level of turbulent kinetic energy within the street canyon is so high that the internal ventilation rate is comparable with the exchange rate in the shear layer (i.e. $u_{12} \approx u_{1e}$), the ratio $T_2/(\alpha T_1)$ approaches 1, resulting in the concentration in the bottom box being twice that in the upper box. The scenario with equal concentrations in both boxes (a solution that aligns with the bisector of the graph, grey dashed line in Fig. 2) is realized when the ratio $T_2/(\alpha T_1)$ approaches zero. In this context, the exchange between the two boxes occurs so rapidly that the ratio T_2/T_1 tends to 0. Conversely, as the internal transfer of pollutants is inhibited (low u_{12}), the concentration at street level (C_2) increases with respect to the concentration in the upper part of the canyon, i.e. the steady solution $(C_{0,1}, C_{0,2})$ lies on a straight line with increasing slope.

To simulate emissions from vehicular traffic, a non-constant emission pattern with a periodic trend (refer to section 2.2) is incorporated into the system described by Eq. 3 and subsequently numerically solved. The obtained results are illustrated in Fig. 2.b. The solution is asymptotically stable and forms a limit cycle in the space $\{C_1, C_2\}$. As q_0 increases, both the mean concentration and the amplitude of the concentration oscillations in the two boxes increase, and the centroid of the ellipse moves along the straight line with slope $1 + T_2/(\alpha T_1)$. When q_0 is fixed and τ is increased, the amplitude of the concentration fluctuations increases as well, as shown by the growing size of the limit cycles in Fig. 2.c. This is confirmed by Fig. 3.a that reports the trend in the coefficient of variation (CV) for the source and for the concentration in the two boxes as a function of the source period, τ. The source signal (yellow line) is characterized by the highest CV (equal to 1/3, see section 2.2), while concentration fluctuations (blue and orange lines) are damped by the dynamics in the two boxes. These damping effects are maximized when the source emission is high frequency, while they decrease as τ/T_1 increases. When the period of the source is very short compared to the characteristic time of the system (low τ/T_1), the system does not "have the time" to react to the source fluctuations and settles on the mean concentration value and the coefficient of variation for the concentration tends to zero. This behavior is evident from the temporal patterns of both emission and concentration, as depicted in panel a1 of Fig. 3. On the other hand, when the source oscillations are very slow (high τ/T_1), the system follows the emission variations and the concentrations in the two boxes vary with the emission as a succession of stationary states, as shown in panel a2. In this case, the coefficient of variation for the concentration tends to that of the source. The graph also highlights that the CV for the concentration increases with τ/T_1 following a sublinear trend (approximately logarithmic for intermediate values of the τ/T_1 range).

The bottom box (i.e. box 2 where the source is located) acts as an additional low-pass filter for the upper box (box 1) that experiences weaker concentration variations. It is worth noting that for the concentration coefficient of variation (CV) to be approximately equal in both boxes and equivalent to that of the emission, the period of the source should be at least two orders of magnitude greater than the exchange time T_1 (i.e., $\tau/T_1 \gtrsim 100$).

The analysis also reveals that the concentration signals have the same period of the source but, as τ increases, the time shift (Δt) between C_2 and q and between C_1 and C_2 increases as well, while the phase shift ($\Delta\Phi = \Delta t 2\pi/\tau$) decreases (Fig. 4). For $\tau \to \infty$ the three signals tend to be synchronized since both T_1 and T_2, that govern the dynamics between boxes, become negligible with respect to the forcing period. Synchronized concentration signals implies that the maximum (and the minimum) pollution intensity for the two

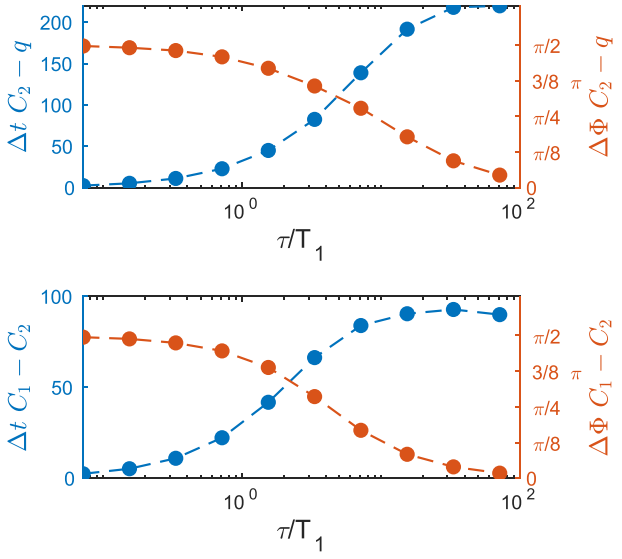


Fig. 4. Time (left axis) and phase (right axis) shift between q and C_2 (first panel) and between C_1 and C_2, as a function of the emission period τ, for an inert gas.

regions of the canyon is reached at the same time, i.e. at the time of maximum release from the source. The clockwise rotation of the ellipse axis in Fig. 2.c is another marker of the change in the phase shift between C_1 and C_2 with τ. As τ increases, the ellipse stretches over the straight line with slope $1 + T_2/(\alpha T_1)$. This indicates that the period of the source is so long that the concentration in the two boxes reaches intermediate states that correspond to the concentration that would occur with steady emissions with intensity varying between $q_0(1 - A)$ and $q_0(1 + A)$, that is the range of variation of the sinusoidal emission.

The effect of the wash-out times is significant for the mean pollution levels but not for the concentration oscillations (Fig. 3.b). In this regards, Fig. 3.b reveals that the inhibition of the vertical mixing between the two boxes (i.e. the increase of T_2/T_1) tends to reduce the coefficient of variation in the entire canyon and to increase the damping effect of box 2 on box 1 (see the right axis in Fig. 3.b).

These results show that, for a deterministic emission, the mean pollution level within the street canyon depends on the mean release at the source and the characteristic wash-out times of the canyon. On the other hand, concentration peaks increase both with amplitude and the period of the emission. For a given source emission, air pollutant concentration significantly varies with distance from the street. In the lower part of the canyon, i.e. at the lower building floors, air pollutant concentrations are higher on mean and show the greatest peaks. On the upper floors both mean and peak concentrations are attenuated.

3.1.2. *Stochastic emissions*

To simulate realistic emissions from vehicular traffic, influenced by variations in driving behavior and dispersion in a turbulent wind environment, the stochastic emission pattern with autocorrelation τ (refer to section 2.2) is incorporated into the system described by Eq. 3 and subsequently numerically solved. The solution (Fig. 2.d) provides noisy concentration signals that (after an initial transient) are statistically stable in the space $\{C_1, C_2\}$. As q_0 increases, both the mean concentration and the amplitude of the concentration oscillations in the two boxes increase. The mean concentrations of C_1 and C_2 define a point in the space that moves along the straight line with slope $1 + T_2/(\alpha T_1)$. When q_0 is fixed and τ is increased the amplitude of the concentration fluctuations increases as well, as shown in Fig. 2.e. This effect is however less significant with respect to the case of the sinusoidal forcing (panel c). These results are confirmed by Fig. 3.c. The coefficient of variation for the concentration increases with τ/T_1 with a non-linear trend (approximately logarithmic for $\tau/T_1 < 10$), and its value is significantly higher for the stochastic source than for the sinusoidal source when τ/T_1 is lower than 30, so that the gradient of the curve is less marked.

As already found for the sinusoidal emission, the effect on the concentration fluctuations of the ratio T_2/T_1 at fixed τ is not marked (Fig. 3.d). Finally, we observe that the damping effect of box 2 on box 1 (right axis of panel c and d) is still noticeable and follows the same trends seen for the sinusoidal source (right axis of panels a and b). However, this dampening effect is considerably weaker, indicating that the stochastic nature of the emission tends to equalize the magnitude of fluctuations in the two boxes. As a result, the CV curves for the concentration in the two boxes are much closer when the stochastic source is considered.

To gather further insights into the dynamics of concentration within the canyon, we report in Fig. 5 the probability density function (*pdf*) of the source emissions, and of the concentrations C_1 and C_2, for different ratios τ/T_1. While the Gaussian distribution is invariant for the source, the occurrence of extreme values for the concentration increases with τ/T_1, while the mean value of the distribution remains the same, in line with the results found in Fig. 2.e and 3.c. For $\tau/T_1 \to \infty$, the ventilation process is much faster than the emission timescale, ε approaches zero (see Eq. 7), and the emission noise varies so slowly that the concentration response of the system becomes independent of the period itself and the amplitude of the concentration variations follows the amplitude of the emission variations. As a consequence, the *pdf* of the concentration collapses onto that of the emission. Notice that in this case the *pdf* of the concentrations can be analytically found (see Appendix D) and are reported as dotted grey line in Fig. 5.b-c. On the other hand, for $\tau \to 0$, the system behaves as a filter for the noise at the source, and the coefficient of variation for the concentration tends to 0, i.e. the concentration tends to be steady over time (see also panel c1 in Fig. 3).

These results highlight that the stochastic nature of the source has no influence on the stability of the system that still provides a single (statistically) stable solution for the concentration in the two boxes. The concentration solution follows a noisy path around the mean value that is the same already found for the constant and sinusoidal source. The amplitude of the fluctuations around the mean

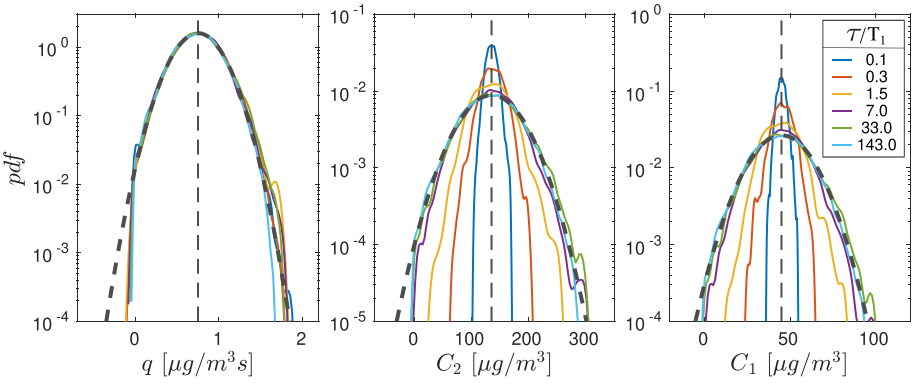


Fig. 5. Probability density function of the source and concentration signals for different values of the ratio τ/T_1 (see the legend). The dotted curves are the Gaussian distributions found for $\tau/T_1 \to \infty$ (see Eqs. D.20-D.23). The dotted vertical lines are the means found from these distributions.

(described by the coefficient of variation) is greater the longer the memory of the signal. Moreover, the stochastic fluctuations noticeably amplify the concentration variations with respect to a deterministic emission with same periodicity (τ), mean intensity (q_0) and standard deviation, while they tend to homogenize the coefficient of variation in the two boxes.

3.2. Reactive gas

3.2.1. Deterministic emissions

For vehicular emissions constant in time (i.e., $q_{NO_x} = q_{NO} + q_{NO_2} = q_0$), the numerical solution of the system in Eq. 4 provides the steady and transient concentration of NO_2, NO, and O_3 in the two boxes, as reported in Fig. 6.a and b. The steady concentration (panel a) does not vary linearly with the emission intensity and O_3 is progressively depleted as NO_x emissions increase. This is in line with previous works (e.g., Li et al., 2023) showing that the steady concentrations of the three chemical compounds follow a non-linear trend with the source emission when the background O_3 concentration is different from zero. Moreover, as expected, concentrations at street level (dashed lines) are about twice those at the top of the canyon (continuous lines) for NO and NO_2, while O_3 follows an inverse trend. The concentration of O_3 above roofs acts as a source that feeds the upper box, while the amount of O_3 transferred to street level is limited by the exchange between the two boxes (governed by the characteristic time T_2) and by the depletion of O_3 by reaction with the NO_x emissions from vehicular traffic. Fig. 6.b reports the concentration transients for the three pollutants, starting from a fixed initial condition but varying the emission rate (q_0). Due to nonlinear chemical reactions, unlike the results shown for the passive scalar (see Fig. 2.a), the ratio between the steady concentrations in the two boxes is not constant, i.e. the steady concentration in the two boxes lies on curved lines in the space $\{C_1, C_2\}$ (see the dashed grey lines).

When the emission at the source is periodic (Fig. 6.c), the solution for each chemical species follows a limit cycle in the space $\{C_1,C_2\}$, in line with the results found for the inert gas (see Fig. 2.b-c). When the mean (q_0) and - as a consequence - the standard deviation ($\sigma = q_0/3$) of the emission of NO_x increase, the mean and standard deviation of the concentration fluctuations increase for NO_2 and NO in the two regions of the canyon (blue and red circles in panel c of Fig. 6). On the other hand, the size of the ellipses representing the variations in O_3 concentration reaches a maximum for intermediate emission intensities of NO_x since O_3 oscillations

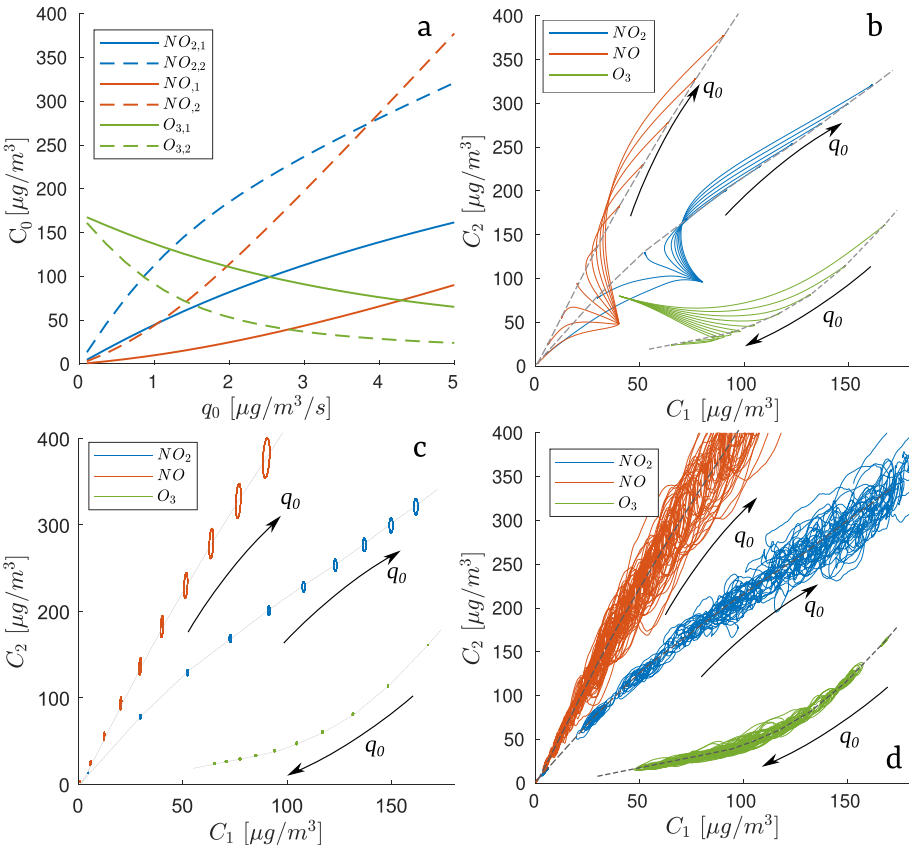


Fig. 6. a) Steady-state concentration of $NO_2 - NO - O_3$ as a function of the vehicular emissions q_0 in the upper part of the canyon (continuous lines) and at the bottom (dashed lines). b) Concentration transients in the space $\{C_1,C_2\}$ for varying q_0 ($q_0 = q_{NO} + q_{NO_2}$). The grey dashed lines correspond to the steady solution in the two boxes for varying q_0. c) Steady-state limit cycles in the space $\{C_1,C_2\}$ for periodic emissions with constant τ and varying q_0. d) Steady-state limit cycles in the space $\{C_1,C_2\}$ for stochastic emissions with constant τ and varying q_0.

are, on one hand, driven by the growing amplitude of NO_x emissions (with q_0), but, on the other hand, they are constrained by the reduction of the mean O_3 concentration, due to chemical transformations.

Focusing on the effect of the source periodicity, we observe that, as τ/T_1 increases, the mean concentration of the three chemical compounds does not change (Fig. 7.a), while their coefficient of variation (Fig. 8.a) increase significantly. This is in line with the results found for the inert pollutant in Fig. 3. It is interesting to observe in Fig. 8.a that concentration fluctuations of NO exceed those of the source when the period of the emission is very long compared to the characteristic time of street ventilation (i.e. $\tau \gg T_1$). This suggests that the chemical transformations reduce the mean concentration of NO which would settle in the canyon if it were an inert gas. This reduction of the mean implies an increase in the CV with respect to that observed in Fig. 3.a for an inert pollutant, which instead remains always below the CV of the source. Moreover, while the bottom box (where the source is located) acts as a low-pass filter for NO and O_3 concentrations, this is not always the case for NO_2.

As previously observed in the case of inert pollutants, when the vertical exchange between the lower and upper boxes slows down (increasing T_2/T_1), the concentration of the pollutants emitted by the source (NO and NO_2) increases in the bottom box (dashed lines in Fig. 7.b). This is responsible for the slight decrease in CV observed in Fig. 8.b. Mirroring NO_x, the mean O_3 concentration in the bottom box decreases with T_2/T_1 and the CV becomes three times larger. In the upper box, the mean concentration of the three chemical species remains unchanged with T_2/T_1 (continuous lines in Fig. 7.b), while the CV slightly decreases with it (Fig. 8.b). This suggests that the longer residence time of the pollutants in the bottom box, dampens the fluctuations transmitted to the upper box.

The time scales of the chemical reactions affect especially the mean concentration in the two boxes. The photolysis of NO_2 into NO and $O^{\bullet}$ (Eq. B.10) slows down τ_1 increases. As a consequence, the mean concentration of NO_2 increases with τ_1/T_1 at the expense of a reduction in NO and O_3 (see Fig. 7.c). As τ_3 increases, the regeneration of NO_2 from NO and O_3 reaction is inhibited, the mean concentration of NO_2 decreases while O_3 and NO increase (see Fig. 7.d). These variations of the mean are reflected in the trends for the CV of the three chemical compounds (Figs.8.c-d).

The analysis of the probability density function (*pdf*) of air pollutant concentration for the three chemical compounds reveals additional interesting behaviors associated with the periodicity of the emission source, as depicted in Fig. S2 and Fig. S3 in the supplementary material (SM, hereafter). As expected for a system forced by a sinusoidal signal, the *pdf* of the concentration is bimodal with two peaks occurring at the maximum and minimum concentration values. Despite the emission being driven by a symmetric sinusoidal signal, the concentration distributions display asymmetry with respect to the mean as τ/T_1 increases. This departure from symmetry is certainly due to the non-linearity introduced by the chemical transformations and is confirmed by the non-zero skewness

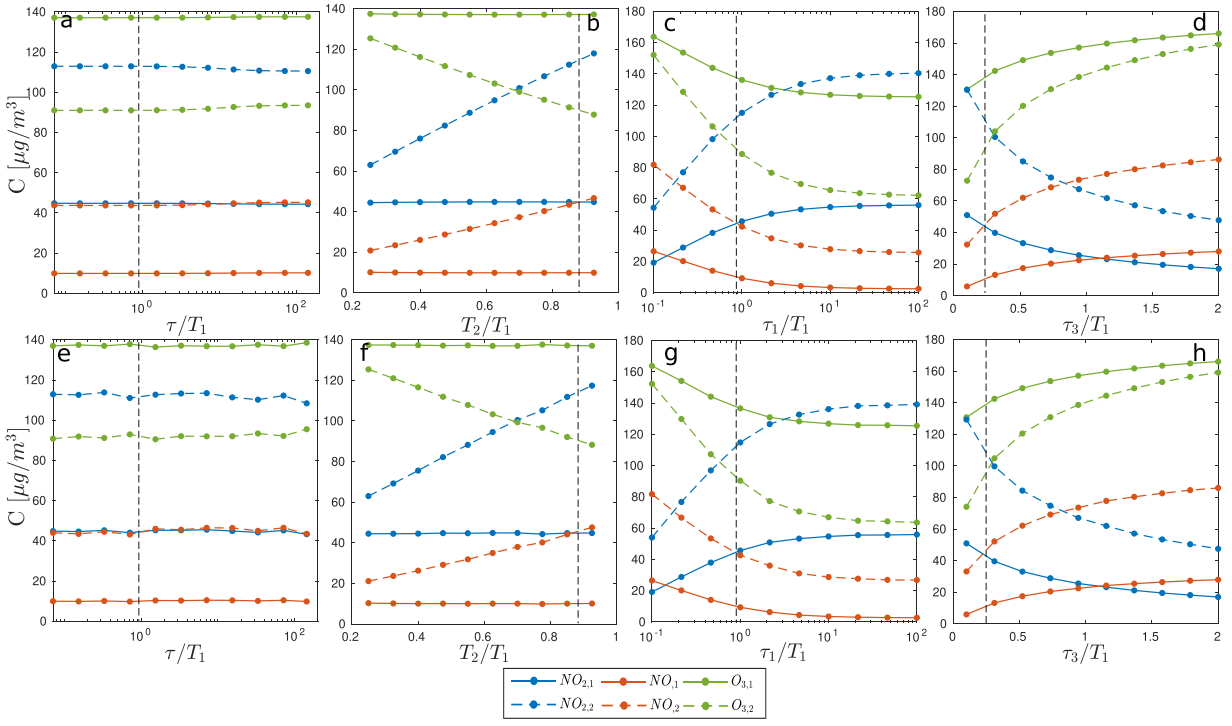


Fig. 7. Mean concentration for the three chemical species in the bottom box (dashed lines) and upper box (continuous lines) of the canyon. The first row reports the mean concentration as a function of τ/T_1 (a), T_2/T_1 (b), τ_1/T_1 (c), and τ_3/T_1 (d) for a deterministic periodic emission. The second row reports the mean concentration as a function of τ/T_1 (e), T_2/T_1 (f), τ_1/T_1 (g), and τ_3/T_1 (h) for a (coloured) stochastic emission. The graphs of the standard deviation are reported in the Supplementary Material. The characteristic times of the system (see Table 1) are reported as vertical dashed black lines.

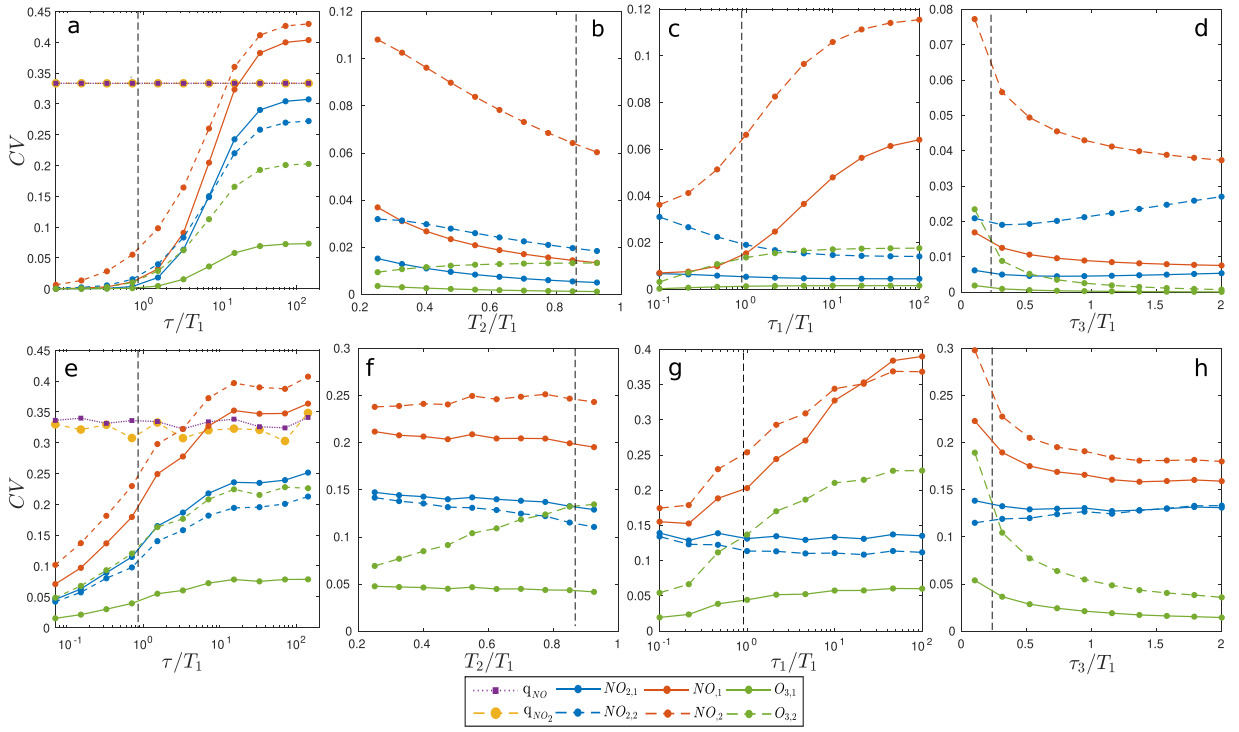


Fig. 8. Coefficient of variation (CV) of the source (q_{NO} and q_{NO2}) and concentration signals in the bottom box (dashed lines) and upper box (continuous lines) of the canyon. The first row reports the CV as a function of τ/T_1 (a), T_2/T_1 (b), τ_1/T_1 (c), and τ_3/T_1 (d) for a deterministic periodic emission. The second row reports the CV as a function of τ/T_1 (e), T_2/T_1 (f), τ_1/T_1 (g), and τ_3/T_1 (h) for a (coloured) stochastic emission. The characteristic times of the system (see Table 1) are reported as vertical dashed black lines.

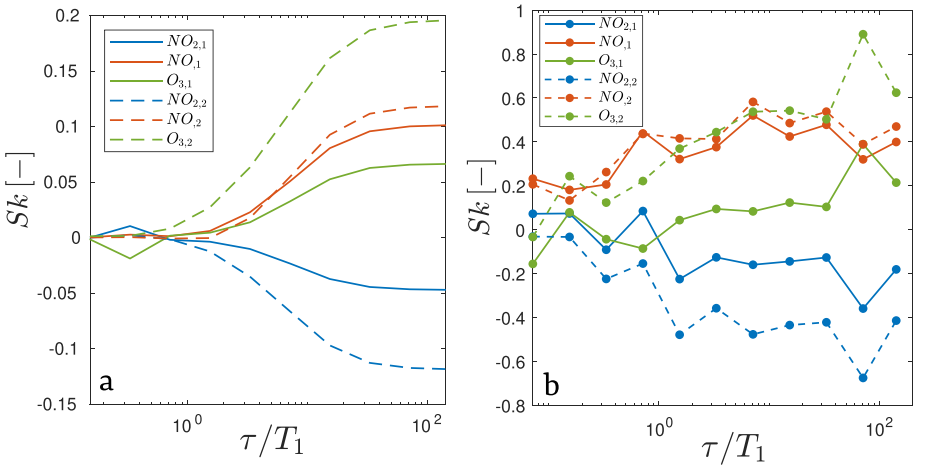


Fig. 9. Skewness of NO_2 (blue line), NO (orange line), and O_3 (green line) in the bottom box (dashed lines) and upper box (continuous lines) of the canyon, for different emission timescales (τ/T_1). a) Sinusoidal forcing. b) Stochastic forcing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the concentration signal (Fig. 9). More specifically, the distributions for NO_2 tend to exhibit negative skewness, indicating a higher frequency of lower concentrations. On the other hand, the distributions for NO and O_3 tend to have a right tail, i.e. high concentrations of pollutants become more frequent with respect to the mean. It is expected that this behavior becomes more pronounced as τ/T_1 increases since, as mentioned earlier, the system is more sensitive to oscillations when the emission has a long characteristic period. Conversely, when τ/T_1 is very small, the system filters out the oscillations at the source, resulting in little deviation of the pollutant concentration from its mean value.

3.2.2. Stochastic emissions

The emission of NO and NO_2 are randomly and independently perturbed with a coloured Gaussian noise (see section 3.1.2).

The simulation results in Fig. 6.d show that the concentration in the two regions of the canyon forms noisy limit cycles in the space $\{C_1, C_2\}$. The temporal scale of the source (τ) has no effect on the mean concentration in the canyon (Fig. 7.e) but it considerably affects the amplitude of the concentration fluctuations around the mean (Fig. 8.e). The results are qualitatively similar to those found for the periodic source: (i) the concentration fluctuations increase with τ/T_1, and (ii) the coefficient of variation of NO exceeds that of the source, (iii) the bottom box (where the source is located) acts as a low-pass filter for NO and O_3 concentration fluctuations, but not for NO_2. However, as already observed for the inert case (Fig. 3), the increase in the standard deviation (Fig. S1.e in the SM) and in the coefficient of variation (Fig. 8.e) with τ/T_1 is much more rapid for the stochastic forcing than for the deterministic sinusoidal one (Fig. 8.a).

When the slowing down of the vertical exchange between the lower and upper boxes occurs (i.e., increase of T_2/T_1), the pollutants emitted by the source (NO and NO_2) accumulate in the bottom box (dashed lines in Fig. 7.f). However, differently from the deterministic case, also the standard deviation (dashed lines in Fig. S1.f in the SM) increases significantly with T_2 so that the CV is almost unaltered (Fig. 8.f). Mirroring NO_x, the mean O_3 concentration in the bottom box (dashed line in Fig. 7.f) decreases with T_2/T_1. The standard deviation (see Fig. S1.f in the SM) increases but less rapidly, so that the coefficient of variation (panel f in Fig. 8) increases up to three times when $T_2 \sim T_1$. In the upper box (continuous lines in Fig. 7.f) the mean concentration of the three chemical species remains unchanged with T_2/T_1, the standard deviation very slightly decreases and the CV with it (continuous lines in Fig. 8.f).

Beyond the trends observed with T_2/T_1, panel f, when compared to the sinusoidal source case (panel b), highlights that the coefficient of variation exhibits significantly higher values in the stochastic scenario (approximately three times higher). This finding aligns with the patterns observed in panel e when contrasted with panel a, as well as for the inert gas case, as indicated by the CV values in panels a and b compared to c and d in Fig. 3. This phenomenon can be attributed to the distinct shapes of the two probability distributions for source emission. Given the same CV, the stochastic case demonstrates longer tails, as illustrated in Fig. S5 in the SM. These extended tails indicate the presence of extremely low or high emission values, triggering a nonlinear system response that results in concentration extremes within the canyon. This, in turn, amplifies the standard deviation and, consequently, the CV of concentrations. This shows that the system's nonlinearity, coupled with random emission fluctuations, does not significantly impact the mean concentration but exerts notable effects on concentration extremes and, consequently, on citizens' exposure. We also remark that the stochastic fluctuations at the source tend to reduce the differences in standard deviation (and therefore in CV) between the two boxes, as already observed for non-reactive pollutants.

The effect of the time scales of the chemical reactions on the mean concentration is almost identical to that observed for the deterministic periodic source (see Fig. 7.g-h) while the standard deviation follows similar but not identical trends (Fig. S1.g-h in the SM). The non-trivial interplay of variations in standard deviation along with those in the mean is reflected in the trend of the coefficient of variation reported in panels g and h of Fig. 8. In this case as well, the CV values highlight the greater variability of concentrations in the stochastic source scenario (panels g-h) compared to the sinusoidal one (c-d).

The analysis of the probability density functions of the time series (Fig. S4 in the SM) reveals interesting patterns. First, it's worth noting that the *pdf*s are unimodal, unlike the bimodal distributions observed for the deterministic sinusoidal source. Secondly, as mentioned above, the tails of the stochastic emission distribution are much longer than those of the deterministic source (see Fig. S5 in the SM). Thirdly, the probability distributions in Fig. S4 extend over increasing ranges of values as τ increases. This confirms the results found in Fig. 8, namely that as emissions occur with longer time scales compared to the characteristic ventilation time, the concentration fluctuations in the street canyon become larger. Finally, similar to the deterministic case, Fig. S4 reveals a growing asymmetry in concentration values with respect to the mean as τ increases. This behavior is well summarized by the skewness of the distributions in Fig. 9.b. The trend, albeit more noisy, is consistent with the findings for the sinusoidal emission case.

4. Conclusions

This study has enhanced our understanding of the transport and transformation dynamics of reactive and inert pollutants in street canyons through a simplified modelling approach and innovative analysis using phase diagrams.

For a constant emission of an inert pollutant, we were able to evaluate the transient behavior leading to the steady-state concentration. The results showed that the ratio between the two characteristic exchange times (T_2/T_1), together with the intensity of the source (q_0), determine the level of pollution in the bottom and upper part of the canyon. In the case of a sinusoidal periodic source, the analysis revealed an increase in the amplitude of concentration oscillations as a function of the source period, as well as the damping of concentration peaks with vertical distance from street level. The introduction of stochastic noise to the emission was found to considerably enhance concentration fluctuations with respect to deterministic periodic behavior. This phenomenon is mainly attributed to the role of the tails of the *pdf* distribution at emission, capable of amplifying the non-linear effects of the system.

Simulations concerning reactive pollutants have brought attention to the non-linear relation between the mean concentrations in the two regions of the canyon, depending on the source intensity and the background O_3 concentration. Also, statistical analysis of concentration time series highlighted that the source period not only affects the second moment of the distribution but also its asymmetry, thereby influencing the occurrence of rare concentration peaks.

While the impact of street parameters on the mean air pollutant concentration is something that, although not extensively explored, aligns with previous studies, the stochastic analysis and the examination of higher-order statistics are innovative and provide crucial insights into extreme pollution levels which dramatically affect the exposure and, consequently, the health implications for citizens. Furthermore, the findings from this study can enhance the information provided by operational urban air quality models, e.g., SIRANE.

These results cover the standard deviation of concentration in street canyons, offering a more comprehensive understanding beyond temporal means, and reveal the spatial distribution of concentrations, through the application of multi-box models.

Despite the model being grounded in previously validated studies on both ventilation dynamics, experimental validation of the obtained results for inert gases through wind tunnel experiments would be desirable. On the other hand, validating the chemical aspects would require pollution measurements within an urban canyon and temporal trends in traffic flows.

The proposed methodology is highly adaptable and can be easily extended and refined. For instance, a natural progression of the work involves exploring various canyon geometries and wind directions. In both scenarios, ventilation times would be significantly influenced, and suitable multi-box models should be carefully implemented to represent recirculation zones within the canyon.

In addition, more comprehensive chemical models could be incorporated to account for the interaction of NO_x with VOCs and hydrocarbons.Expanding the model's scope to simulate particulate matter dynamics is also feasible, requiring integration with sedimentation flow from the atmosphere above roofs and particle deposition to the ground.

Furthermore, this approach can be adapted to investigate the effect of various forcings exhibiting random components, such as atmospheric variability (different irradiation conditions, ventilation, or atmospheric stability), emissions (multiple sources within the canyon), or dynamics-related forcings (turbulence injection at street level due to vehicular traffic). Such scenario studies are crucial for assessing the impact of urban microclimate variations resulting from climate change on pollution levels and peak concentrations in the streets.

Finally, the model is particularly suitable for examining the effect of different strategies for regulating vehicular traffic, such as optimizing the cycle length of traffic signals.

CRediT authorship contribution statement

Sofia Fellini: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Pietro Salizzoni:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis. **Luca Ridolfi:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Vertical bulk exchange velocity in box models

The bulk exchange velocity between the upper part of the canyon and the external flow, u_{1e}, is defined (e.g., Fellini et al., 2020a) as the ratio between the vertical mass flux from the street cavity towards the external flow and the concentration difference $\langle C - C_e \rangle$:

$$u_{1e}(C - C_e)WL = \int_0^L \int_0^W [\langle wc \rangle]_{z=H} dydx, \tag{A.9}$$

where W, L and H are the width, length and height of the street canyon (in the direction x, y, and z of the reference system), while $\langle wc \rangle$ is the ensemble mean of the total flux of pollutants in the vertical direction. Similarly, the velocity u_{12} can be defined by considering the vertical mass flux between the two cells within the canyon and the difference in mean concentration between them.

Appendix B. NO-NO_2-O_3 reaction cycle

The nitrogen cycle in the urban atmosphere involves numerous complex reactions. However, the main chemical transformations can be reliably reduced to the following scheme (e.g., Soulhac et al., 2011):

$$\begin{cases} NO_2 + h\nu \xrightarrow{k_1} NO + O^\bullet \\ O^\bullet + O_2 \xrightarrow{k_2} O_3 \\ NO + O_3 \xrightarrow{k_3} NO_2 + O_2, \end{cases} \tag{B.10}$$

where NO_2, NO and O_3 are nitrogen dioxides, nitrogen oxides and ozone, respectively, O_2 and $O^\bullet$ are oxygen and oxygen radicals, while k_1, k_2 and k_3 are kinetic constants of reaction. The reactivity of the radical $O^\bullet$ is so high that the second transformation is much faster than the first and the third ones (Seinfeld, 1986). The constants k_1 and k_3 are thus the limiting parameters of the cycle. The rate k_1 (NO_2 photolysis rate) mainly depends on the solar light intensity whereas k_3 mainly depends on the atmospheric temperature. These

dependences can be modelled by the following relations (Seinfeld, 1986; Soulhac et al., 2023):

$$\begin{cases} k_1 = \dfrac{1}{60}\left(0.5699 - \left[9.056 \cdot 10^{-3}(90-\chi)\right]^{2.546}\right)\left(1 - 0.75\left[\dfrac{\mathrm{Cld}}{8}\right]^{3.4}\right)(\mathrm{s}^{-1}) \\ k_3 = 1.325 \cdot 10^{6} exp\left(-\dfrac{1430}{\Theta}\right)(\mathrm{m}^3\mathrm{mol}^{-1}\mathrm{s}^{-1}), \end{cases} \tag{B.11}$$

where χ is the solar elevation (in degrees), *Cld* is the cloud coverage (in Okta) and Θ is temperature (in Kelvin). Thus, the production and destruction terms per unit volume for each chemical species can be related to the molar concentration by the following expressions:

$$p_{NO2} = k_3[NO][O_3], \qquad d_{NO} = k_1[NO_2] \tag{B.12}$$

$$p_{NO} = k_1[NO_2], \qquad d_{NO} = k_3[NO][O_3] \tag{B.13}$$

$$p_{O3} = k_1[NO_2], \qquad d_{O3} = k_3[NO][O_3], \tag{B.14}$$

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

Appendix C. Coloured Gaussian noise

To mimic a realistic emission due to vehicular traffic, the source signal can be forced with a coloured Gaussian noise $X(t)$, which accounts for random fluctuations at the emission but maintains a characteristic temporal scale. The noise is obtained from the Ornstein-Uhlenbeck process and evolves over time according to:

$$\frac{dX(t)}{dt} = -\frac{1}{\tau}X(t) + \varepsilon^{1/2}\Gamma(t), \tag{C.15}$$

where τ and ε are the relaxation time and the diffusion constant of the process, and $\Gamma(t)$ is a Gaussian white noise. The diffusion constant amplifies the noise, while the relaxation time is representative of the autocorrelation of the signal, that mimics the periodicity of vehicle transits. For $\tau \to 0$ the signal tends to a Gaussian white noise, i.e. a completely uncorrelated noise. The coloured noise is added to the mean emission q_0, so that:

$$q(t) = q_0 + X(t). \tag{C.16}$$

According to Gillespie (1996), the exact updating formula for X at each time increment Δt in a numerical simulation is:

$$X(t+\Delta t) = X(t)\mu + \sigma n \tag{C.17}$$

where n are statistically independent unit random numbers and

$$\mu = e^{-\Delta t/\tau}, \tag{C.18}$$

$$\sigma^2 = (\varepsilon\tau/2)\left(1-\mu^2\right). \tag{C.19}$$

After a sufficiently long time ($t \gg \tau$), the mean and variance of $X(t)$ are 0 and $\varepsilon\tau/2$, respectively. As a consequence, the mean and variance of q (see Eq. C.16) are q_0 and $\varepsilon\tau/2$.

Appendix D. Probability density functions of concentration for a sinusoidal source with long period

For $\tau/T_1 \to \infty$, the ventilation process is much faster than the emission timescale, ε approaches zero (Eq. 7), and the emission noise varies so slowly that the system behaves like a succession of stationary states. As a consequence, the relation between emission and concentration is independent on time and follows the same relations found in Eqs. 8 for the solution with steady emission. In this case, the *pdf* of the concentrations can be analytically found as derived distribution of the source *pdf*:

$$p(C_1, \tau\to\infty) = p(q)\frac{dq}{dC_1} = \tag{D.20}$$

$$= \frac{1}{\alpha T_1\sqrt{\pi\varepsilon\tau}} exp\left[-\frac{\left(\frac{C_1}{\alpha T_1} - q_0\right)^2}{\varepsilon\tau}\right] \tag{D.21}$$

$$p(C_2, \tau\to\infty) = p(q)\frac{dq}{dC_2} = \tag{D.22}$$

$$= \frac{1}{(\alpha T_1 + T_2)\sqrt{\pi\varepsilon\tau}} exp\left[-\frac{\left(\frac{C_1}{\alpha T_1 + T_2} - q_0\right)^2}{\varepsilon\tau} \right]. \quad (D.23)$$

As mentioned above, these distributions are valid only for $\tau/T_1 \to \infty$ and are reported in Fig. 5.b-c as dotted grey line. The distributions for the concentration are again Gaussian distributions, as for the emission. For C_1, the variance is $\frac{\varepsilon\tau}{2}\alpha^2 T_1^2$ and the mean is $\alpha T_1 q_0$. For C_2, the variance is $\frac{\varepsilon\tau}{2}(\alpha T_1 + T_2)^2$ and the mean is $(\alpha T_1 + T_2)q_0$. Thus the coefficient of variation in both cases is $\sqrt{\frac{\varepsilon\tau}{2}}\ \frac{1}{q_0}$, i.e. the same as the source distribution. This confirms the results found in Fig. 3.c for $\tau/T_1 \to \infty$.

Appendix E. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.uclim.2024.101952.

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