A Mathematical Study of a Simplified Kinetic Model for the Tropospheric Ozone Cycle

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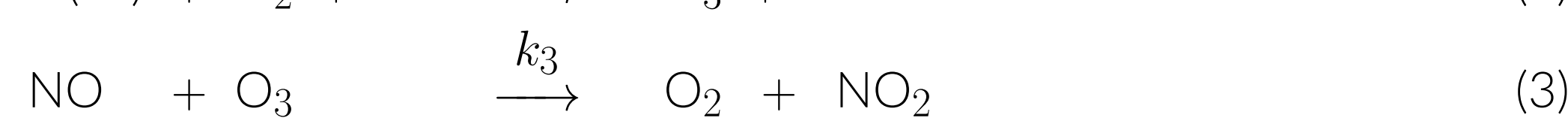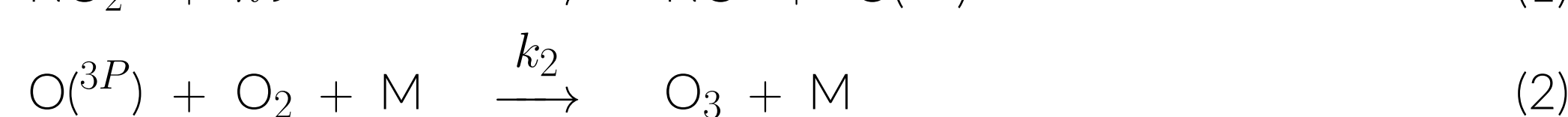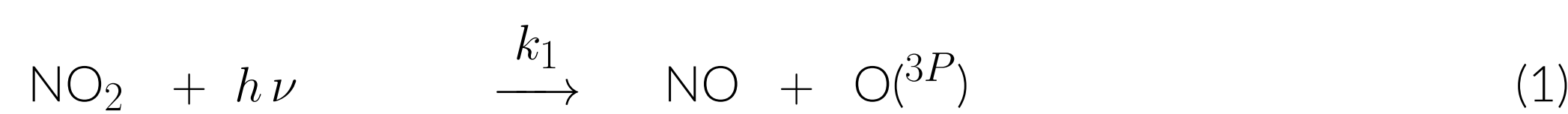School of Technology, UNICAMP, Limeira, SP, Brazil

Abstract

A variety of mathematical or computational models have been developed and used to better understand the dynamics of atmospheric pollutants. Among the pollutants of interest are those related to the tropospheric ozone (O_3) formation cycle, which involves nitrogen oxides (NO_x). In this process, there is a sequence of chemical reactions whose most elementary modeling can be described in terms of ordinary differential equations (ODEs). In this study, we consider the concentrations (in $\mu g/m^3$) of the gases (O, NO, NO_2, and O_3) over time. We present a qualitative study of the model in which we verify that the equilibrium state is non-hyperbolic. To study it, we use the Center Manifold Theory to determine its stability analytically. These analytical results demonstrate its local asymptotic stability, which is also confirmed numerically. In addition to this stability result, another conclusion is that the simplified ozone kinetics model with fixed kinetic parameters does not allow the behavior of sustained oscillatory solutions for the aforementioned pollutant concentrations.

Model

In this study, the tropospheric ozone cycle is analyzed as a closed system, i.e. without the contribution of pollutant emission sources. The concentrations (in $\mu g/m^3$) of the following gases over time are taken into account: $O(^3P)$, NO, NO_2 and O_3, where $O(^3P)$ denotes the oxygen atom in its ground state. In the troposphere, these gases react according to the following physical-chemical reactions [1, 2, 3]:

$$NO_2 \ + \ h\,\nu \quad \xrightarrow{k_1} \quad NO \ + \ O(^3P) \tag{1}$$

$$O(^3P) \ + \ O_2 + M \quad \xrightarrow{k_2} \quad O_3 \ + \ M \tag{2}$$

$$NO \ + \ O_3 \quad \xrightarrow{k_3} \quad O_2 \ + \ NO_2 \tag{3}$$

In (1), (2) and (3), k_i ($i = 1, 2, 3$) denotes the kinetic parameters of these physicochemical reactions.

The dynamics of the chemical kinetics given by the reactions (1), (2) and (3) can be described by the following system of ordinary differential equations:

$$\begin{cases} \dfrac{d\,[O(^3P)]}{dt} &= \ k_1\,[NO_2] \ - \ k_2\,[O(^3P)] & (4) \\[2mm] \dfrac{d\,[NO]}{dt} &= \ k_1\,[NO_2] \ - \ k_3\,[NO]\,[O_3] & (5) \\[2mm] \dfrac{d\,[NO_2]}{dt} &= \ k_3\,[NO]\,[O_3] \ - \ k_1\,[NO_2] & (6) \\[2mm] \dfrac{d\,[O_3]}{dt} &= \ k_2\,[O(^3P)] \ - \ k_3\,[NO]\,[O_3] & (7) \end{cases}$$

With, $[O(^3P)] \geq 0$, $[NO_2] \geq 0$, $[NO_2] \geq 0$, $[O_3] \geq 0$.

Existence and Uniqueness of the Solution

Let $y(t) = ([O(^3P)](t), [NO](t), [NO_2](t), [O_3](t))$, $f(y) = (f_1(y), f_2(y), f_3(y), f_4(y))$ where $f_1 = k_1[NO_2] - k_2[O(^3P)]$, $f_2 = k_1[NO_2] - k_3[NO][O_3]$, $f_3 = k_3[NO][O_3] - k_1[NO_2]$ e $f_4 = k_2[O(^3P)] - k_3[NO][O_3]$. Thus, the system (4)-(7) can be written as:

$$\frac{dy}{dt} = f(t, y), \tag{8}$$
$$y(t_0) = y_0 \quad \text{e} \quad t \in [t_0, t_f]. \tag{9}$$

Theorem

We consider the initial value problem (IVP) (8)-(9) where $f(t, y) \ : \ [t_0, t_f] \to \mathbb{R}^4 \times \mathbb{R}^4$ is continuous on $[t_0, t_f] \times \mathbb{R}^4$ and verifies the Lipchitz condition with respect to the variable y, which means that there is a positive constant L such that $\forall t \in [t_0, t_f]$ and $\forall y_1, y_2 \in \mathbb{R}^4$ there is

$$||f(t, y_1) - f(t, y_2)|| \ \leq \ L||y_1 - y_2||. \tag{10}$$

Therefore, the IVP (8)-(9) has a unique solution.

Equilibrium Solution

We denote the concentrations of each chemical species at time t as $C_1(t) \doteq [O(^3P)](t)$, $C_2(t) \doteq [NO](t)$, $C_3(t) \doteq [NO_2](t)$ e $C_4(t) \doteq [O_3](t)$. The equilibria of (4)-(7) are those at which the rates of change of $[O(^3P)]$, $[NO]$, $[NO_2]$, and $[O_3]$ are all zero, resulting in the following system of algebraic equations:

$$\begin{cases} k_1\,C_3^* \ - \ k_2\,C_1^* \ = \ 0 & (11) \\ k_1\,C_3^* \ - \ k_3\,C_2^*\,C_4^* \ = \ 0 & (12) \\ k_3\,C_2^*\,C_4^* \ - \ k_1\,C_3^* \ = \ 0 & (13) \\ k_2\,C_1^* \ - \ k_3\,C_2^*\,C_4^* \ = \ 0 & (14) \end{cases}$$

Thus, the non-trivial equilibrium solution of the system is given by,

$$E = \left(\frac{k_3}{k_2}C_2^*C_4^*, \ C_2^*, \ \frac{k_3}{k_1}C_2^*C_4^*, \ C_4^* \right), \tag{15}$$

Eigenvalues

Theorem

The equilibrium solution E is non-hyperbolic.

The characteristic polynomial is:

$$\lambda^2\,[a\,\lambda^2 + b\,\lambda + c], \tag{16}$$

where $a = 1$, $b = [k_1 + k_2 + k_3(C_2^* + C_4^*)]$, and $c = k_1k_2 + k_2k_3(C_2^* + C_4^*) + k_1k_3C_2^*$.

Discriminant	Condition	Eigenvalues
$\Delta > 0$	$\dfrac{1}{k_1k_3C_2^*}\left(\dfrac{(k_1 + k_3C_4^*) - (k_2 - k_3C_2^*)}{2}\right)^2 > 1$	$\lambda_{1,2} = 0, \ \lambda_{3,4} = \dfrac{-b \pm \sqrt{\Delta}}{2a}$
$\Delta = 0$	$\dfrac{1}{k_1k_3C_2^*}\left(\dfrac{(k_1 + k_3C_4^*) - (k_2 - k_3C_2^*)}{2}\right)^2 = 1$	$\lambda_{1,2} = 0, \ \lambda_{3,4} = \dfrac{-b}{2a}$
$\Delta < 0$	$\dfrac{1}{k_1k_3C_2^*}\left(\dfrac{(k_1 + k_3C_4^*) - (k_2 - k_3C_2^*)}{2}\right)^2 > 1$	$\lambda_{1,2} = 0, \ \lambda_{3,4} = \dfrac{-b \pm i\sqrt{\Delta}}{2a}$

Table 1. Eigenvalues associated with the equilibrium solution E.

Local Stability

Theorem

The equilibrium solutions E for the fixed components are locally stable.

To show this theorem for the model, we use the Local Center Manifold Theorem [4]:

Theorem

(Local Center Manifold Theorem). Let $f \in C^r(K)$, where $r \geq 1$ and K is an open subset of $\mathbb{R}^n$ containing the origin. Suppose that $f(0) = 0$ and that $f'(0)$ has c eigenvalues with zero real part and s eigenvalues with negative real part, where $c + s = n$. The system (4)-(7) can be written in a diagonal form as,

$$\begin{cases} \dfrac{dx}{dt} = Cx + F(x, y), & (17) \\[2mm] \dfrac{dy}{dt} = Py + G(x, y), & (18) \end{cases}$$

where $(x, y) \in \mathbb{R}^c \times \mathbb{R}^s$, C is a square matrix with c eigenvalues with zero real part, P is a square matrix with s eigenvalues with negative real part, $F(0) = G(0) = 0$, and $F'(0) = G'(0) = 0$. Therefore, there is a $\delta > 0$ and a function $h \in C^r(N_\delta(0))$ which defines a local center manifold given by

$$W_{local}^c = \{(x, y) \in \mathbb{R}^c \times \mathbb{R}^s | y = h(x) \quad \text{for} \quad |x| < \delta\}, \tag{19}$$

where W^c is tangent to the center subspace $E^c = \{(x, y) \in \mathbb{R}^c \times \mathbb{R}^s | y = 0\}$ and satisfies

$$h'(x)[Cx + F(x, h(x))] - Ph(x) - G(x, h(x)) = 0, \tag{20}$$

for $|x| < \delta$, and the flow on the center manifold $W^c(0)$ is defined by the system of equations

$$\frac{dx}{dt} = Cx + F(x, h(x)), \tag{21}$$

$\forall x \in \mathbb{R}^c$, with $|x| < \delta$.

Numerical Results

The system was treated as an initial value problem in which the initial concentration of $O(^3P)$, NO, NO_2 and O_3 was chosen to be zero, 10^{12}, 10^{10} and zero molecules/cm³, respectively [1]. For a temperature $T = 298$ K [1], the values assigned for the kinetic parameters were: $k_1 = 1.7 \cdot 10^{-2}$ s⁻¹, $k_2 = 1.4 \cdot 10^3 \cdot$ e$^{\left(\frac{1175}{T}\right)}$ cm³ molecules⁻¹ s⁻¹ and $k_3 = 1.8 \cdot 10^{-12} \cdot$ e$^{\left(\frac{-1370}{T}\right)}$ cm³ molecules⁻¹ s⁻¹. We used the `ode` routine from the `deSolve` package of `R`, which can identify and numerically solve rigid systems (*stiff*).
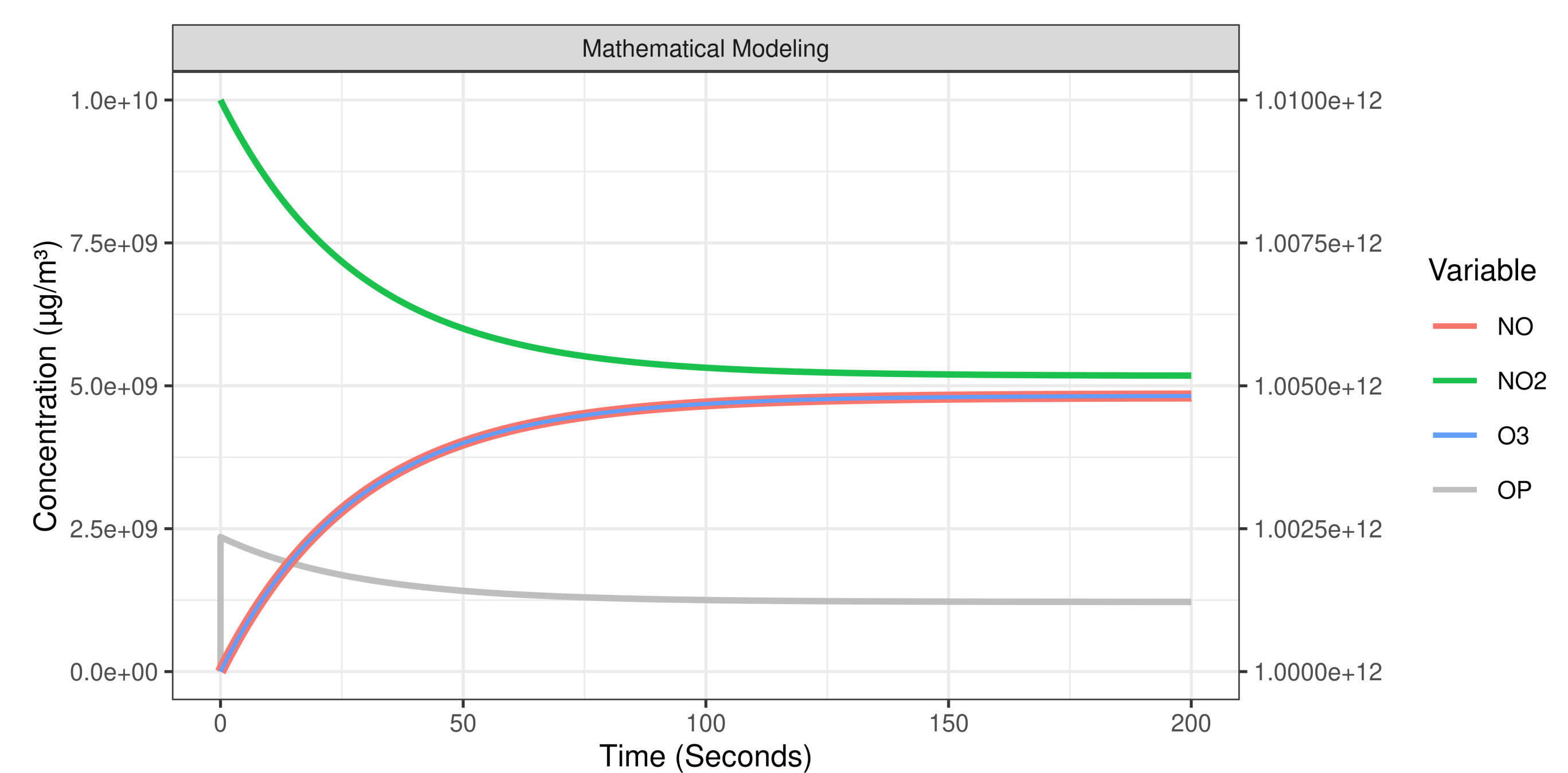

Figure 1. Numerical solution of the mathematical model presented and defined by equations (4), (5), (6) and (7) for the tropospheric ozone cycle. The scale of [NO] is the vertical axis on the right, and the value of $[O(^3P)]$ is shown with a multiplicative factor of 10^6.

Using the initial conditions and parameter values, we obtained the stationary numerical solution shown in Figure 1: $(1.2194 \cdot 10^3, 1.0048 \cdot 10^{12}, 5.1786 \cdot 10^9, 4.8213 \cdot 10^9)$, and the equilibrium solution given by (15) is $(1.2173 \cdot 10^3, 1.0048 \cdot 10^{12}, 5.1699 \cdot 10^9, 4.8213 \cdot 10^9)$. Using the information Table 1, the inequality is less than unity, and so the eigenvalues are $\lambda_{1,2} = 0$, $\lambda_3 = -10573.3$ and $\lambda_4 = -61625.7$. According to the theoretical results, this equilibrium solution is locally stable. Thus, with this numerical solution, we can verify the theoretical result derived analytically.

Conclusion

In this work, we present a qualitative study of a mathematical model of ordinary differential equations in time that characterizes the kinetics of the chemical reactions of the ozone cycle in the troposphere. The only non-trivial equilibrium state of the system is non-hyperbolic. Using the Center Manifold Theory, we have proved that this state is locally stable.

Acknowledgements

References

[1] Mark Z. Jacobson.
Fundamentals of Atmospheric Modeling.
Cambridge University Press, 2 edition, 2005.

[2] Stefano Marsili-Libelli.
Simplified kinetics of tropospheric ozone.
Ecological Modelling, 84(1-3):233–244, 1996.

[3] Daniel Vallero.
Fundamentals of Air Pollution.
Academic Press, Oxford, 5 edition, 2014.

[4] Lawrence Perko.
Differential Equations and Dynamical Systems.
Springer New York, NY, 3 edition, 2001.