

# Analytical Solution for a Pollutant Dispersion Model with Photochemical Reaction in the Atmospheric Boundary Layer

Guilherme Jahnecke Weymar<sup>1,\*</sup>, Bardo Ernst Josef Bodmann<sup>1</sup>, Daniela Buske<sup>2</sup>,  
Jonas da Costa Carvalho<sup>2</sup>, Marco T. M. B. Vilhena<sup>1</sup>

<sup>1</sup>Pos-Graduate Program in Mechanical Engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil

<sup>2</sup>Pos-Graduate Program in Mathematical Modelling, Federal University of Pelotas, Pelotas, Brazil

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**Abstract** This paper presents an analytical solution for the three-dimensional advection-diffusion equation applied to the dispersion of pollutants that form in the Atmospheric Boundary Layer (ABL). Some substances, when emitted in ABL suffer photochemical reactions producing secondary pollutants, so that a source term is included in the advection-diffusion equation to represent this reaction. The model was applied to simulate the dispersion and transport of ozone (O<sub>3</sub>) produced by photochemical reactions from nitrogen dioxide (NO<sub>2</sub>), pollutant emitted by burning fossil fuels by automotive vehicles. The pollutant concentration fields obtained by the proposed solution are compared with mixing ratio data obtained by monitoring the air quality in the metropolitan area of Porto Alegre. From the analysis of the results one verifies that the inclusion of the term proposed to represent a photochemical reaction of a reactive pollutant allows to predict ozone concentrations in the ABL.

**Keywords** Advection-diffusion equation, Photochemical reaction, Analytical solution, GILTT method

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## 1. Introduction

The interest in preserving the air quality is growing considerably in recent years due to increased emission of pollutants in the atmosphere caused by the increase of industrial development and the burning of fossil fuels by automotive vehicles. Thus, to control the air quality one needs an interpretive tool, such as a mathematical model that is able to link the cause (pollution source) with the effect (pollutant concentration distribution). The use of certain mathematical models in addition to the observed measurements produce a qualitative as well as quantitative progress in the management of air pollution, because the models allow a more complete description of the development of the transport phenomenon with respect to spatial distributions and forecast the concentration distribution evolution [1], whereas measurements are typically restricted to a small set of points.

Today, one can say that one of the biggest problems caused by air pollution in urban areas are caused by photochemical oxidants, these are formed in the atmosphere

by reaction between volatile organic compounds (VOC's) and nitrogen oxides (NO<sub>x</sub>) in the presence of sunlight, where the principal component is ozone (O<sub>3</sub>). Therefore, the pollutant of interest in this work is ozone, which is classified a secondary pollutant that appears as a bluish reactive gas and approximately 1.6 times heavier than oxygen molecules. The oxidizing character of this gas can cause extensive damage to fauna and flora. Furthermore, ozone contributes to the greenhouse effect since the compound presents an absorption band at "9.6" μm [2].

According to [3], cars are the main sources of emissions of ozone precursors. Even knowing the complexity of atmospheric chemistry, when the atmosphere has predominance of nitrogen compounds the formation of tropospheric ozone is well known. However, when there is the presence of hydroxyl radicals (OH) and hydrocarbons these cause an atmospheric disequilibrium, resulting in increased ozone formation.

Thus, this work presents an analytical solution for three-dimensional advection-diffusion equation applied to the dispersion of pollutants formed from a photochemical reaction in the Atmospheric Boundary Layer (ABL), the resolution of the problem is done with the use of techniques of Laplace transform and GILTT (Generalized Integral Laplace Transform Technique) [5].

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\* Corresponding author:

daniela.buske@ufpel.edu.br (Guilherme Jahnecke Weymar)

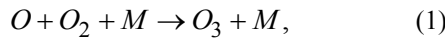
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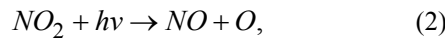
## 2. Photochemical Reaction and Ozone Production

Ozone (O<sub>3</sub>) performs a fundamental role in stratospheric chemistry, because it reacts with ultraviolet light behaving as a protective shield against the harmful effects of radiation. However, ozone is a highly reactive and toxic species, and when present in the troposphere has prejudicial effects to many living beings.

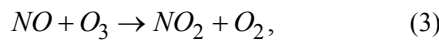
According to [4], the most important reaction in the production of ozone in the atmosphere is between atomic oxygen and molecular:



where *M* is a third element, such as N<sub>2</sub> or O<sub>2</sub>, which removes the energy of reaction and stabilizes O<sub>3</sub>. At high altitudes (above 20km), oxygen atoms are produced by photo dissociation of molecular oxygen by absorption of deep ultraviolet radiation. At lower altitudes, where there is only radiation with wavelengths longer than 290nm, the only source of atomic oxygen is the photo dissociation of nitrogen dioxide:

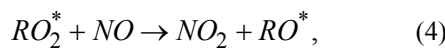


where the photon *hν* has a wavelength between 290nm and 430nm. An ozone removal process is its reaction with nitric oxide:

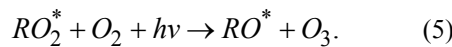


The three reactions (1), (2) and (3) occur rapidly, establishing a stable concentration of ozone. However, only these reactions do not justify the ozone levels found in polluted urban atmospheres. In the latter reaction, an ozone molecule is required for the generation of NO<sub>2</sub>, consuming a molecule of NO.

A reaction that converts the NO to NO<sub>2</sub> without consuming the molecule O<sub>3</sub> may cause accumulating of ozone. This reaction occurs in the presence of hydrocarbons. In particular, peroxy radicals RO<sub>2</sub><sup>\*</sup>, where "R" is an alkyl group and produced in the oxidation of hydrocarbon molecules react with the NO to form the NO<sub>2</sub>, allowing an increased production of ozone:



Thus, the liquid process of the reactions (2), (1) and (4) is:



To determine solar radiation that reaches the troposphere the knowledge of the solar radiation that reaches the top of the atmosphere is of need. Measurements made at high altitudes from aircraft campaigns [6] resulted in the establishment of standard values of constant solar energy, terrestrial solar energy and spectral irradiance. These measurements have been adopted as standard by the American Association for Testing and Materials (ASTM) and as design values for the National Aeronautics and Space Administration - NASA.

To determine a function that represents the solar spectral

irradiance depending on the wavelength one uses the spectral distribution established by Planck equation:

$$E_\lambda = \frac{2\pi c_v^2 \bar{h} \lambda^{-5}}{\left( \frac{\bar{h} c_v}{\lambda k_B T} - 1 \right)} \quad (6)$$

where *c<sub>v</sub>*=3.00×10<sup>8</sup> m/s is the speed of light, *ħ*=6.62×10<sup>-34</sup> Js is Planck's constant, *k<sub>B</sub>*=1.381×10<sup>-23</sup> J/K is Boltzmann constant. From equation (6), a curve fitting was performed using the method of least squares and a Padè approximation 4-5 and 4-6. Figure 1 shows the graph of the set of the adjusted solar irradiance function:

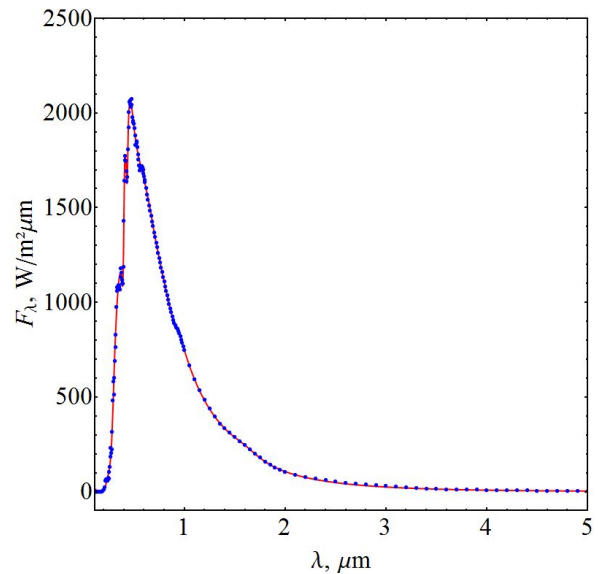


Figure 1. Function of Solar Spectral Irradiance

The radiation passing through the atmosphere suffers losses, that is, the spectral radiance is reduced by the presence of gases and aerosols in the atmosphere due to absorption and scattering. The radiation transport through the atmosphere can be evaluated by the Beer-Lambert law [7],

$$dI_\lambda = -k_\lambda I_\lambda ds, \quad (7)$$

where *I<sub>λ</sub>* is the spectral radiance along a path in the direction *s* and *k<sub>λ</sub>* is called the extinction coefficient. The extinction coefficient is represented by

$$k_\lambda = \sigma_{ext}(\lambda) \rho(s), \quad (8)$$

where *ρ(s)* is the density of gases (which may vary along the path *s*) and *σ<sub>ext</sub>* is the extinction cross section at the wavelength *λ*. Extinction is the sum of the cross sections of absorption and scattering (*σ<sub>ext</sub>*=*σ<sub>a</sub>*(*λ*)+*σ<sub>e</sub>*(*λ*)). In this study, we considered only the absorption of gases, thus *σ<sub>ext</sub>*=*σ<sub>a</sub>*(*λ*) and therefore:

$$k_\lambda = \sum_{i=1}^N \sigma_{a,i}(\lambda) \rho_i(s), \quad (9)$$

where  $\sigma_{a,i}$  and  $\rho_i(s)$  are the cross-section of absorption and the density at the height  $s$  of gas  $i$ , respectively ( $N$  is the number of gases that composes the atmosphere).

According to [8], the spectrum region from  $0.2\mu\text{m}$  to  $0.7\mu\text{m}$ , most of the solar radiation is absorbed by gases  $\text{O}_2$  and  $\text{O}_3$ .

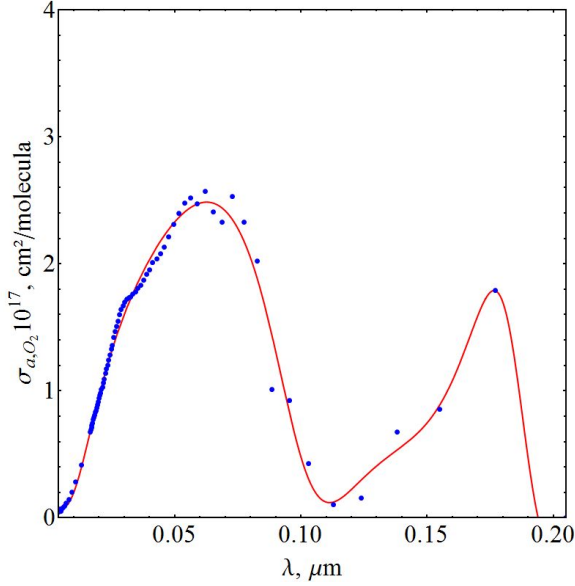


Figure 2. Cross section of oxygen absorption

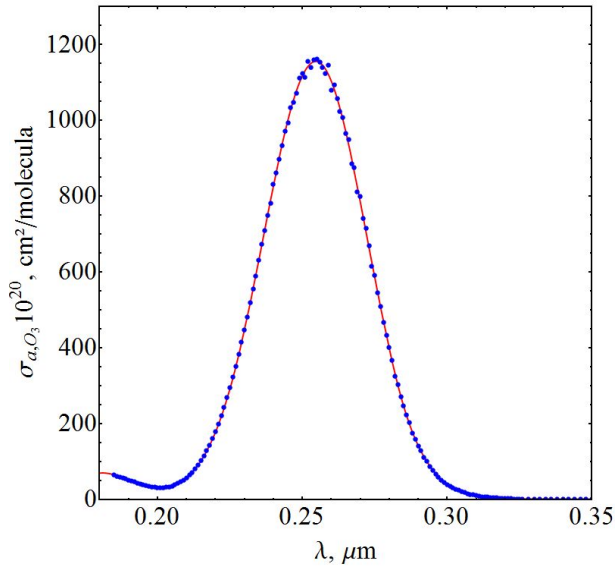


Figure 3. Cross section of ozone absorption

Therefore, to calculate the solar radiation reaching the PBL, one considers only the oxygen and ozone absorption:

$$k_\lambda = \sigma_{a,o_2}(\lambda)\rho_{o_2} + \sigma_{a,o_3}(\lambda)\rho_{o_3}. \quad (10)$$

Using the data from [10] and [9], and curve fitting with the least squares method one obtains the parametrized cross sections of oxygen and ozone absorption, Figures 2 and 3, respectively.

For simplicity, one assumes a uniform distribution of

these gases throughout the atmosphere. Thus, the solution to the Beer-Lambert equation (7) is:

$$I_\lambda = I_0(\lambda)e^{-\int_0^z (\sigma_{a,o_2}(\lambda)\rho_{o_2}(s) + \sigma_{a,o_3}(\lambda)\rho_{o_3}(s))ds} \quad (11)$$

Using the function shown in Figure 1 as the radiation reaching the top of the atmosphere, one determines the solar radiation that reaches the boundary layer, shown in Figure 4.

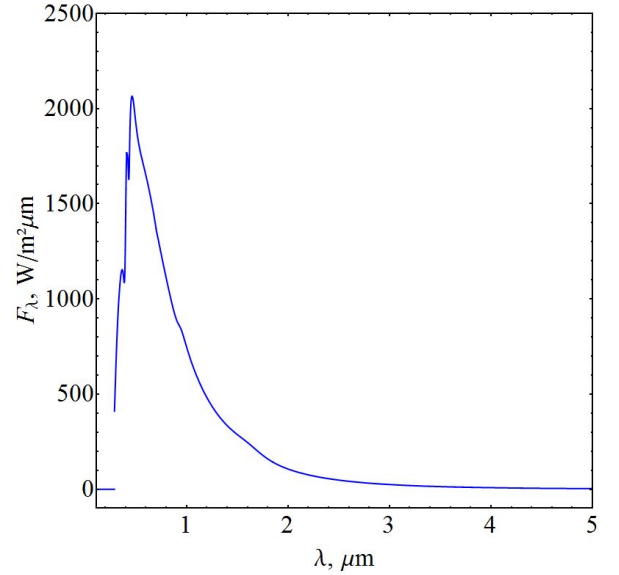


Figure 4. Solar Spectral Irradiance Function that reaches ABL

The atmosphere, although appearing transparent to visible radiation, performs a crucial role in the Earth's energy balance, as it controls the amount of solar radiation that actually reaches the Earth's surface, and also controls the amount of terrestrial radiation that escapes into space. In addition, it influences on chemical processes.

For reactions (2), (1) and (4) it follows that the formation of ozone in the lower atmosphere is due to the photolysis of  $\text{NO}_2$ .

According to [11], the rate (or frequency) of atmospheric photolysis ( $J$ ) are of fundamental interest in the study of atmospheric chemistry processes.

Photo dissociation of the  $\text{NO}_2$  is described as a first order process [9], represented by:

$$\frac{dc_{NO_2}}{dt} = -J_{NO_2}c_{NO_2}, \quad (12)$$

Valid for photons with wavelength between  $290\text{nm} < \lambda < 430\text{nm}$ , the frequency of photolysis of  $\text{NO}_2$  is represented by the coefficient  $J_{NO_2}$  was calculated as follows [27],

$$J_{NO_2} = \int F_\lambda(\lambda)\sigma_{a,NO_2}(\lambda,T,P)\Phi_{NO_2}(\lambda,T,P)d\lambda, \quad (13)$$

where  $F_\lambda$  ( $1/\text{cm}^2\text{s}\mu\text{m}$ ) is the local flux, that is, the amount of light available in the atmosphere,  $\sigma_{a,NO_2}$  ( $\text{cm}^2$ ) is the cross section of absorption of the molecule, or it is the intensity of light available at a given wavelength that the

molecule can absorb and  $\Phi_{NO_2}$  (molecule/photon) is the quantum yield, that represents the probability with which a compound absorbs light of a certain wavelength.

For simplicity one considers the absorption cross section and the quantum yield  $NO_2$  depending only on the wavelength ( $\lambda$ ), and with the available data from [12], one obtains  $\sigma_{a,NO_2}$  and  $\Phi_{NO_2}$ , as shown in Figures 5 and 6, respectively.

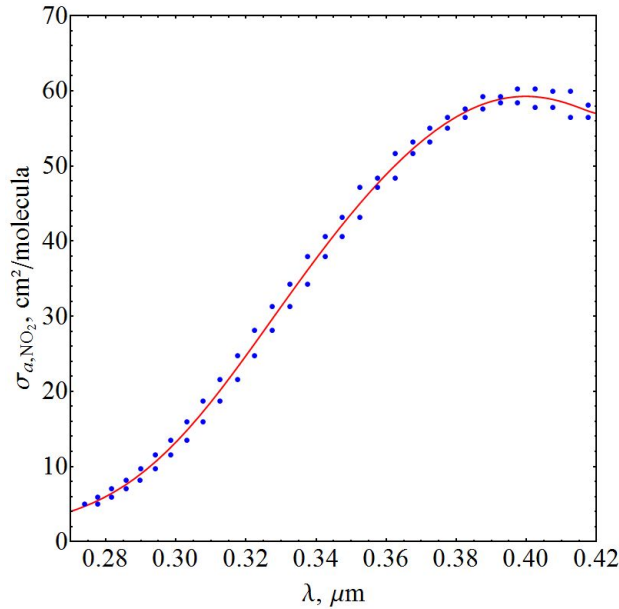


Figure 5. Absorption cross section function of  $NO_2$

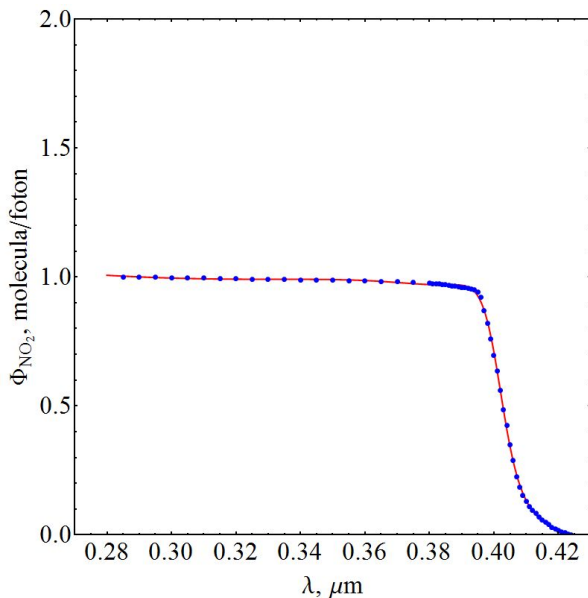


Figure 6. Quantum yield function of  $NO_2$

Thus, for calculating the photolysis rate of nitrogen dioxide, one performs the integration in the spectral range in which the photochemical reaction takes place:

$$J_{NO_2} = \int_{290nm}^{430nm} F_{\lambda}(\lambda) \sigma_{a,NO_2}(\lambda, T, P) \Phi_{NO_2}(\lambda, T, P) d\lambda. \quad (14)$$

### 3. Solution of Three-Dimensional Advection-Diffusion Equation

To model the ozone concentration distribution the transient three-dimensional advection-diffusion equation was employed and a photochemical reaction term added (first-order process), this term is the photo dissociation  $NO_2$  in  $O_3$ :

$$\frac{\partial \bar{c}}{\partial t} + \bar{v} \nabla \bar{c} = \nabla \cdot (K \cdot \nabla \bar{c}) = J_{NO_2} c_{NO_2}. \quad (15)$$

Here  $\bar{c}$  the average concentration of the pollutant (ozone),  $\bar{v} = (\bar{u}, \bar{v}, \bar{w})$  the average wind speed,  $K$  the matrix of diffusion coefficients  $K = \text{diag}(K_x, K_y, K_z)$ . The domain of interest is a cube with dimensions  $L_x$ ,  $L_y$  and  $h$ , where  $h$  is the height of PBL. Equation (15) is subject to zero-flow boundary conditions on the faces of the cube, zero initial concentration (at  $t = 0$ ) and source condition  $\bar{c}(0, y, z, t) = 0$ . Observe that the production of ozone takes place only by photochemical reactions.

To solve the proposed problem, we apply the spectral method in the variable  $y$ , that is, the pollutant concentration is expanded in a series with terms of eigenfunctions of an associated Sturm-Liouville problem and making use of the integral operator  $\int_0^{L_y} (\cdot) Y_n(y) dy$ , thus transforming the equation (15) in a transient system of two-dimensional advection-diffusion equations, and the following simplifying assumptions: The advection is dominant along the  $x$ -axis direction  $[\bar{u} \frac{\partial \bar{c}}{\partial x} \gg \frac{\partial}{\partial x} (K_x \frac{\partial \bar{c}}{\partial x})]$ ; the wind direction is oriented in the  $x$ -axis  $[\bar{v} = (\bar{u}, 0, 0)]$  and for the coefficient of lateral turbulent diffusivity,  $K_y = K_y(z)$ , one obtains the following equation:

$$\begin{aligned} & \frac{\partial \bar{c}_m(x, z, t)}{\partial t} + u \frac{\partial \bar{c}_m(x, z, t)}{\partial x} \\ & = K_z \frac{\partial^2 \bar{c}_m(x, z, t)}{\partial z^2} + K_z' \frac{\partial \bar{c}_m(x, z, t)}{\partial z} \\ & - \beta_m^2 K_y \bar{c}_m(x, z, t) + J_{NO_2} c_{NO_2} \int_0^{L_y} Y_n(y) dy, \end{aligned} \quad (16)$$

Equation (16) is solved by GILTT technique. For this purpose, we apply the Laplace transform in the time variable resulting in a two-dimensional stationary problem [13]:

$$\begin{aligned} -u \frac{\partial \bar{C}_m(x, z, r)}{\partial x} & = K_z \frac{\partial^2 \bar{C}_m(x, z, r)}{\partial z^2} + K_z' \frac{\partial \bar{C}_m(x, z, r)}{\partial z} \\ & - (\beta_m^2 K_y + r) \bar{C}_m(x, z, r) + \frac{J_{NO_2} c_{NO_2}}{r} \int_0^{L_y} Y_n(y) dy. \end{aligned} \quad (17)$$

Upon applying the spectral method in variable  $z$ , we obtain a first order ordinary differential equation:

$$BZ'(x, r) + EZ(x, r) = H, \quad (18)$$

where  $Z(x,r)$  is the vector of components  $\hat{C}(x,r)$ ,  $B=(b_{l,j})$ ,  $E=(e_{l,j})$  e  $H=(h)$  are arrays whose entries are:

$$b_{l,j} = \int_0^h \bar{u} \psi_l(z) \psi_j(z) dz, \quad (19)$$

$$e_{l,j} = \alpha_l^2 \int_0^h K_z \psi_l(z) \psi_j(z) dz - \int_0^h K_z' \psi_l'(z) \psi_j(z) dz \quad (20)$$

$$+ \int_0^h (K_y \beta_m^2 + r) \psi_l(z) \psi_j(z) dz$$

$$h_l = \frac{J_{NO_2} c_{NO_2}}{r} \int_0^{L_y} Y_n(y) dy \int_0^h \psi_l(z) dz. \quad (21)$$

It should be noted that, when applying the integral operators, these have been normalized, so the ordinary differential equation (18) is analytically solved by Laplace transform and diagonalization, one obtains  $Z(x,r)=\bar{C}_{m,l}(x,r)$ , so that  $\bar{C}_m(x,z,r)$  is well established. To obtain  $\bar{c}_m(x,z,t)$  one applies the inverse Laplace transform in  $\bar{C}_m(x,z,r)$ , where the inversion is done numerically by the use of Gauss quadrature.

Once  $\bar{c}_m(x,z,t)$  is known, the final solution of the advection-diffusion equation (15) is given by the equation:

$$\bar{c}(x,y,z,t) = \sum_{m=0}^M \bar{c}_m(x,z,t) Y_m(y). \quad (22)$$

## 4. Validation against Experimental Data

For an adequate prediction of transport and diffusion models in the atmosphere validation against experimental data are of need. To this end besides some measured data also topographical properties and typical meteorological conditions of the area to be analyzed [25] shall be employed.

To this end, this section presents the parameterization of turbulent diffusion coefficients, wind profile, the observed data used in this study and the numerical results obtained with the model.

### 4.1. Physical Model Parameterization

In atmospheric diffusion problems, the choice of a turbulent parameterization represents a fundamental decision to model the dispersion of pollutants. The parameterization of turbulence is an approximation of nature in the sense to try to represent the physical phenomena by parametrized expressions. The reliability of a model is strongly related to the way in which the parameters are calculated and related to the PBL [26].

#### 4.1.1. Turbulent Diffusion Coefficients

We used the following vertical and lateral diffusion coefficients as suggested by [14] and derived from [15] for

unstable conditions ( $L < 0$ ):

$$\frac{K_z}{w_* h} = 0.22 \left( \frac{z}{h} \right)^{\frac{1}{3}} \left( 1 - \frac{z}{h} \right)^{\frac{1}{3}} \left[ 1 - e^{-\left( \frac{4z}{h} \right)} - 0.0003 e^{-\left( \frac{8z}{h} \right)} \right], \quad (23)$$

$$K_y = \frac{\sqrt{\pi} \sigma_v}{16 (f_m)_v q_v}, \quad (24)$$

where  $\sigma_v$  is the Eulerian standard deviation of longitudinal turbulent velocity given by:

$$\sigma_v^2 = \frac{0.98 c_v}{(f_m)_v^{\frac{2}{3}} \left( \frac{\psi_\varepsilon}{q_v} \right)^{\frac{2}{3}} \left( \frac{z}{h} \right)^{\frac{2}{3}} w_*^2} \quad (25)$$

where  $(f_m)_v = 0,16$  is the vertical component of the normalized frequency of the spectral peak,  $q_v = 4,16 \frac{z}{h}$  is the stability function,  $\psi_\varepsilon$  is molecular dissipation rate function expressed by [16], [17]:

$$\psi_\varepsilon^{\frac{1}{3}} = \left[ \left( 1 - \frac{z}{h} \right)^2 \left( \frac{z}{-L} \right)^{-\frac{2}{3}} + 0.75 \right]^{\frac{1}{2}}, \quad (26)$$

#### 4.1.2. Wind Profile

In a first approximation and to describe the wind field for the simulations of the dispersion of pollutants, the equation used for wind parameterization is described by a power law expressed by [18],

$$\frac{\bar{u}}{u_1} = \left( \frac{z}{z_1} \right)^\alpha,$$

where  $\bar{u}$  and  $\bar{u}_1$  are the horizontal average wind speeds in the heights  $z$  and  $z_1$ , respectively, and  $\alpha$  is an exponent which is related to the intensity of turbulence [19].

### 4.2. Observed Data

The FEPAM (“*Fundação Estadual de Proteção Ambiental Henrique Luiz Roessler*”) is a Brazilian institution responsible to evaluate, monitor and disseminate information about environmental quality. This organization has a monitoring station in the Metropolitan Region of Porto Alegre (MRPA). In January of 2006, a monitoring campaign of air quality in the MRPA was performed, and the measurements among others yielded the mean concentrations of ozone and nitrogen dioxide. The location of the monitoring station close to the town of Esteio is represented by the red dot in Figure 7.

Weather conditions in the period 05-09 of January of 2009 was under clear sky conditions and light winds at the surface.

Table 1 shows the meteorological data of the day January 05 in the period from 11 am to 7 pm used in the model for the numerical results. In Table 1,  $\bar{u}_r$  is the reference speed (m/s),  $u_*$  is the friction velocity (m/s),  $L$  is the length of

Monin-Obukhov (m),  $w_*$  is the convective vertical speed scale (m / s) and  $h$  is the PBL height (m).

**Table 1.** Meteorological parameters of January 05 - Esteio Station

Hour (h)	(ref) (ms <sup>-1</sup> )	$u_*$ (ms <sup>-1</sup> )	$w_*$ (ms <sup>-1</sup> )	L (m)	h (m)
11 am	2,00	0,27	0,50	-305	801
12 am	2,60	0,35	0,65	-397	921
1 pm	1,60	0,21	0,40	-244	641
2 pm	2,30	0,31	0,58	-351	921
3 pm	3,10	0,41	0,78	-473	1240
4 pm	3,30	0,44	0,83	-503	1320
5 pm	4,20	0,56	1,05	-641	1680
6 pm	4,60	0,61	1,15	-702	1840
7 pm	5,70	0,76	1,43	-870	2280

The meteorological data presented in Table 1 are calculated by equations from the literature. The length of Monin-Obukhov can be written as [20]:

$$L = -\frac{h}{\kappa} \left( \frac{u_*}{w_*} \right)^3, \quad (27)$$

where " $\kappa$ " is the constant of Von-Kármán ( $\kappa \approx 0,4$ ) and  $w_* \approx 0,25\bar{u}$  [21]. The speed friction  $u_*$  is obtained by  $u_* = \frac{\kappa\bar{u}}{\ln(\frac{z_r}{z_0})}$ , where  $z_r = 10$  m (reference height) and  $\bar{u}$  is the

wind speed. The CLP height  $h$  is obtained from the relationship  $h = 0,3 \frac{u_*}{f_c}$  [22], [23], wherein  $f_c = 10^{-4}$  (Coriolis force).

### 4.3. Numerical Results

To perform statistical comparisons between the model and observed data we consider the set of statistical indices described by [24] and defined as follows:

$$NMSE = \frac{\overline{(C_o - C_p)^2}}{C_p \overline{C_o}},$$

$$COR = \frac{\overline{(C_o - \overline{C_o})(C_p - \overline{C_p})}}{\sigma_o \sigma_p},$$

$$FS = \frac{(\sigma_o - \sigma_p)}{0.5(\sigma_o + \sigma_p)},$$

where the subscripts  $o$  and  $p$  refer to the observed and predicted concentration, respectively, and the bar represents the mean value. The best results are expected to have values close to zero for NMSE and FS indexes, and close to 1 for the correlation index COR.

Table 2 presents the results of statistical indexes, where one observes that predicted concentrations of the model reproduces satisfactorily the experimentally findings.

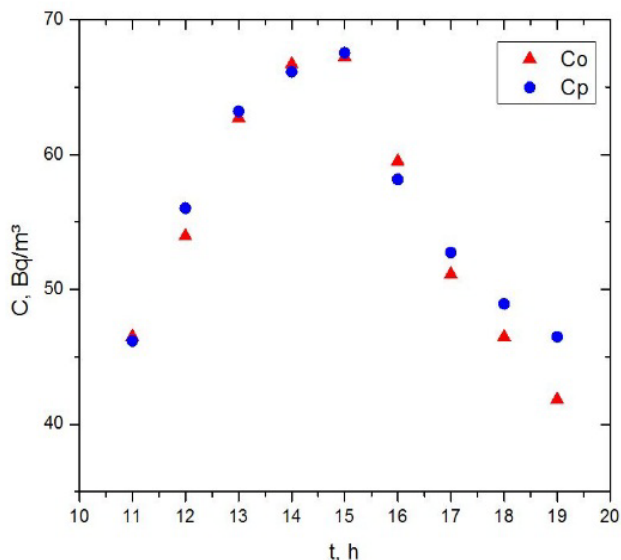
**Table 2.** Statistical comparison between the model results and the FEPAM dataset

Model	NMSE	COR	FS
3D-GILTT	0.00	0.98	0.22



**Figure 7.** Location of the monitoring station in Esteio (FEPAM)

Figure 8 shows comparisons between the concentrations of the  $O_3$  simulated  $C_p$  and observed  $C_o$  data. One observes fairly good agreement between the predicted and observed concentrations in the period from 11 am to 7 pm to January 05, 2009.



**Figure 8.** Comparison between the mean hourly concentrations during the days of January simulated and observed for Esteio station (FEPAM)

It is noteworthy that results show fairly good agreement with observation despite the simplified approach adopted for the wind field and with respect to the topography of the MRPA region. In future work, we intend to improve these results considering the values found for the wind profile for mesoscale codes, where characteristics of the terrain topography are expected to enter.

## 5. Conclusions

This paper presents a new analytical representation for the solution of the advection-diffusion equation with small error in the numerical inversion of the inverse Laplace transform, for the dispersion problem of a secondary pollutant. The model in question considers photochemical reaction of a primary pollutant released into the atmosphere which gives rise to ozone prediction. Analytical solutions are of fundamental importance to understand and describe physical phenomena, as they take into account explicitly all the parameters involved in the problem, so that their influence can be reliably investigated. In the proposed model, a photochemical reaction of a primary pollutant in the atmosphere is considered in order to improve forecasting and understanding the dispersion of ozone formed in the planetary boundary layer. Even with adopted simplifications presented in this work, the model was able to reproduce the behavior of the ozone concentration during the period from 11 am to 7 pm with a fairly good fidelity.

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## REFERENCES

- [1] D.M. Moreira, T. Tirabassi, “Modelo matemático de dispersão de poluentes na atmosfera: um instrumento técnico para gestão ambiental”, in Portuguese, *Ambiente & Sociedade*, vol. 7, pp. 169-171, 2004.
- [2] I. Colbeck, A.R. Mackenzie, *Air pollution by photochemical oxidants*, Elsevier Science, New York, 1994.
- [3] C. Athinson-Palombo, J.A. Miller, J. Balling, C. Robert, “Quantifying the ozone “weekend effect” at various locations in Phoenix, Arizona”, *Atmos. Environ.*, vol. 40, pp. 7644-7658.
- [4] B.J. Finlayson-Pitts, J.N. Pitts, “Tropospheric air pollution ozone, airborne toxics, polycyclic aromatic hydrocarbons and particles”, *Science*, vol. 276, pp. 1045-1051, 1997.
- [5] D. Buske, M.T. Vilhena, T. Tirabassi, B. Bodmann, “Air pollution steady-state advection-diffusion equation: the general three-dimensional solution”, *JEP*, vol. 3, pp. 1124-1134, 2012.
- [6] M.P. Thekaekara, “Solar energy motion in space (SEMIS)”, *Symp. Solar Radiation Meas. And Instrumentation*, pp. 414-442, 1973.
- [7] B.J. Finlayson-Pitts, J.N. Pitts, “Spectroscopy and photochemistry fundamentals”, In *Chemistry of the Upper and Lower Atmosphere*, pp. 43-85. Academic Press, 2000.
- [8] M.A. Mélières, C. Maréchal, *Climate Change: Past, Present and Future*, CRDP de l’Académie de Grenoble: Grenoble, 2010.
- [9] B.J. Finlayson-Pitts, J.N. Pitts, “Photochemistry of Important Atmospheric Species”, In *Chemistry of the Upper and Lower Atmosphere*, pp. 86-129. Academic Press, 2000.
- [10] H.K. Rudek, G.K. Moortgat, R. Sander, R. Sorensen, “The mpi-mainz uv/vis spectral atlas of gaseous molecules of atmospheric interest”, *Earth System Science Data*, pp. 365-373, 2013.
- [11] R.E. Shetter, W. Junkermann, W.H. Swartz, G.J. Frost, “Photolysis frequency of  $NO_2$ : Measurement and modeling during the International Photolysis Frequency Measurement and Modeling Intercomparison (IPMMI)”, *Geophysical Research*, 108(D16), 8544, in press, 2003.
- [12] B.J. Finlayson-Pitts, J.N. Pitts, *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press, 2000.
- [13] S. Wortmann, M.T. Vilhena, D.M. Moreira, D. Buske, “A new analytical approach to simulate the pollutant dispersion in the PBL”, *Atmos. Environ.*, vol. 39, pp. 2171-2178, 2005.

- [14] G.A. Degrazia, H.F. Campos Velho, J.C. Carvalho, "Nonlocal exchange coefficients for the convective boundary layer derived from spectral properties", *Contr. Atmos. Phys.*, vol. 70, pp. 57-64, 1997.
- [15] G.K. Batchelor, "Diffusion in a field of homogeneous turbulence, Eulerian analysis", *Australian Journal of Scientific Research*, vol.2, pp. 437-450, 1949.
- [16] J. Hojstrup, "Velocity spectra in the unstable boundary layer", *Journal of Atmospheric Sciences*, vol. 39, pp. 2239-2248, 1982.
- [17] S.J. Caughey, *Diffusion in the convective boundary layer, Atmospheric Turbulence and Air Pollution Modelling*, Edited by F.T.M. Nieuwstadt and H. Van Dop, 1982.
- [18] H.A. Panofsky, J.A. Dutton, *Atmospheric Turbulence*, John Wiley & Sons, New York, 1984.
- [19] J.S. Irwin, "A theoretical variation of the wind profile power-law exponent as a function of surface roughness and stability", *Atm. Environ.*, vol. 13, pp. 191-194, 1979.
- [20] P. Zannetti, *Air Pollution Modeling, Computational Mechanics Publications*, Southampton, 1990.
- [21] G.A. Briggs, "Plume dispersion in the convective boundary layer. Part II: analyses of CONDORS field experimental data", *Journal of Applied Meteorology*, vol. 32, pp. 1388-1425, 1992.
- [22] S.S. Zilitinkevich, "On the determination of the height of the Ekman boundary layer", *Boundary-Layer Meteorology*, vol. 3, pp. 141-145, 1972.
- [23] S.S. Zilitinkevich, V.M. Gryanik, V.N. Lykossov, D.V. Mironov, "Third-order transport and nonlocal turbulence closures for convective boundary layers", *Journal of Atmospheric Sciences*, vol. 56, pp. 3463-3477, 1999.
- [24] S.R. Hanna, "Confidence limit for air quality models as estimated by bootstrap and jackknife resampling methods", *Atmos. Environ.*, vol. 23, pp. 1385-1395, 1989.
- [25] D.M. Moreira, M.T. Vilhena, J.C. Carvalho, "Tritium dispersion simulation in the atmosphere from ANGRA I Nuclear Power Plant", *International Journal of Nuclear Energy Science and Technology*, vol. 3, pp. 118-130, 2007.
- [26] C. Mangia, D.M. Moreira, I. Schipa, G.A. Degrazia, T. Tirabassi, U. Rizza, "Evaluation of a new eddy diffusivity parametrisation from turbulent eulerian spectra in different stability conditions", *Atmospheric Environment*, vol. 36, pp. 67-76, 2002.
- [27] M.Z. Jacobson, *Fundamentals of Atmospheric Modeling*, Cambridge University Press, Cambridge, 2<sup>nd</sup> edition, 2005.