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AN APPROXIMATE DISPERSION MODEL OF NITROGEN COMPOUNDS IN THE ATMOSPHERE WITH CHEMICAL REACTION

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Abstract. The dispersion of chemical compounds emitted into the atmosphere from point sources has drawn the attention of states and society. The release of nitrogen compounds (NOx) and volatile organic compounds (VOC) into the atmosphere in the presence of solar radiation generates what is called photochemical smog. This article presents an approximate model for estimating NOx compounds and a comparison of two procedures for solving the system of ordinary differential equations for the set of chemical reactions. The approximate model separates the transport mechanisms (advection and diffusion) from the chemical reaction mechanisms in the diffusion equation. The transport mechanisms are solved by the analytical solution of the diffusion equation generating a quantity of air entering the rectangular shaped "puff". The system of chemical reactions is solved by considering the volume of the "puff" constant at each displacement. The results of emissions from a chimney of a coal-burning thermoelectric plant show the formation of nitrogen compounds, ozone gas and nitric acid over distance. The main conclusion obtained is that the approximate model can represent a release into the atmosphere with chemical reactions.

Keywords: atmosphere, dispersion, nitrogen compounds, chemical reaction

1. INTRODUCTION

In recent decades, air pollution has drawn attention due to its harmful effect on the environment. One of the sources of gas emissions is industrial chimneys, (Fenger, 1999), and (USEPA, 2019). These gases can undergo chemical transformations in the atmosphere and produce products that will interact with the environment, according to the work of (Yamartino et al., 1992), (Seinfeld and Pandis, 2006), and (USEPA, 2019). The propagation is represented by an approximate model for the gases emitted from a coal-fired power plant in this work. The approximate model of gas propagation separates the mechanisms of dispersion and chemical reactions as will be described. Also shown are the numerical results obtained for the concentrations of NOx compounds and a comparison of an approximate analytical solution for the system of differential equations for chemical reactions with the most rigorous solution.

2. METHODOLOGY

2.1 The source of gas emissions

The main gases involved in atmospheric pollution NOx, SOx, Carbon Monoxide (CO) and Volatile Organic Compounds (VOC) have their flows estimated from the emission factors of the "AP-42" inventory, (USEPA, 2012) and the elemental analysis of coal burned in the boiler, (Rodrigues, 2004).

2.2 The approximate propagation and diffusion model

The approximate propagation model (advection, dispersion and chemical reaction) of the gases emitted from the chimney is a combination of instantaneous releases (called "puffs"). It separates the mechanisms of chemical reaction

and propagation (displacement and diffusion) at each displacement time of the "puffs" released in series, (Orlandi, 2004).

The instantaneous release is approximated by a model of homogeneous properties, called box models, according to (Seinfeld and Pandis, 2006). The shape of a prism with a rectangular base is adopted for this "puff", as shown in Figure 1. A local solution of the diffusion equation is used to determine the concentration profile for the total mass of gases and also the air intake for the "Puff".

The "puff" has the following variables that characterize it: the total mass of gas (m_{gp}), the position of its center in relation to the emission source ($X_{C,i}$), the longitudinal dimension ($L_{x,i}$), the transverse dimension ($L_{y,i}$), the vertical dimension ($L_{z,i}$), the atmospheric displacement time (t_p), and the total release time from the source (t_t). The volume of the "puff" is determined by the relationship:

$$V_i = L_{x,i} L_{y,i} L_{z,i}, \tag{1}$$

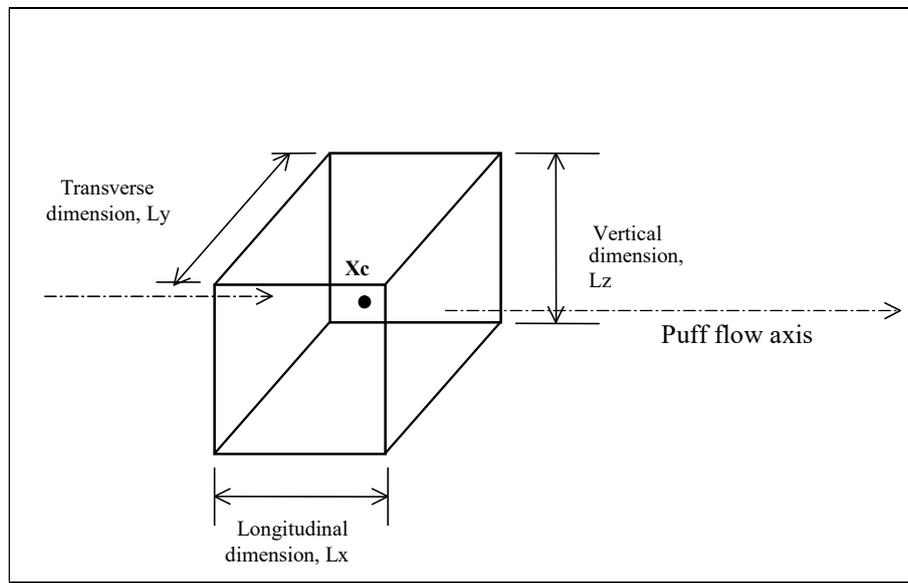Where i refers to the displacement time "i".

Figure 1. "Puff" prism with rectangular base.

The total concentration of all gases in the puff is given by the relationship:

$$\rho_{gp,i} = \frac{m_{gp,i}}{L_{x,i} L_{y,i} L_{z,i}}, \tag{2}$$

Where m_{gp} is the total mass of gases released in the chimney.

The position of the "puff" center is determined at each time displacement of the "puff" by:

$$x_{C,i} = x_{C,i-1} + u_{m,i-1} t_p, \tag{3}$$

Where $x_{C,i}$ is the position of the center of the "puff" after displacement number "i", $+u_{m,i-1}$ is the average wind speed of the "puff" after displacement "i-1 ", and t_p is the displacement time.

The average wind speed is given by the logarithmic wind speed profile

$$u_{m,i}(z) = \frac{u_*}{k} \left[\ln\left(\frac{z+z_0}{z_0}\right) - \varphi\left(\frac{z}{L}\right) \right], \tag{4}$$

Where $u_{m,i}(z)$ is the average wind speed at height z, u_* is the friction speed with the ground, k is the von karman constant, z is the height of the center of the puff in the vertical direction, z_0 is the soil roughness, φ is the atmospheric stability function, and L is the Monin-Obukov length.

The air intake rate for the "puff" is given by the relationship:

$$\Delta V_{Ar,i} = \frac{-V_{i-1}\frac{\left(\rho_{mg,i}-\rho_{mg,i-1}\right)}{t_p}}{\rho_{mg,i-1}},$$

(5)

Where $\Delta V_{Ar,i}$ is the air intake volume for the "puff" at its displacement "i", V_{i-1} is the volume of the "puff" at "i-1", and $\rho_{mg,i}$ is the average total concentration at displacement "i".

The average concentration of the "puff" is obtained through the instantaneous Gaussian model

$$\rho_{mg,i} = \frac{m_{gp,i}}{\sigma_{x,i}\sigma_{y,i}\sigma_{z,i}(2\pi)^{1,5}}e^{\frac{-\left(x_{C,i}-u_{m,i}t_{t,i}\right)^2}{2\sigma_{x,i}^2}}e^{\frac{-y_i^2}{2\sigma_{y,i}^2}}\left[e^{\frac{-(z_i-h)^2}{2\sigma_{z,i}^2}}+e^{\frac{-(z_i+h)^2}{2\sigma_{z,i}^2}}+\right],$$

(6)

Where $t_{t,i}$ is the total displacement time of "puff" i, y_i is the transverse position of "i", z_i is the vertical position, h is the height of the chimney, $\sigma_{x,i}$ is the dispersion coefficient in the longitudinal direction of "i", $\sigma_{y,i}$ is the dispersion coefficient in the cross direction, and $\sigma_{z,i}$ is the dispersion coefficient in the vertical direction. The dispersion coefficients are estimated from the atmospheric parameters, shown in the work of Irwin (1979).
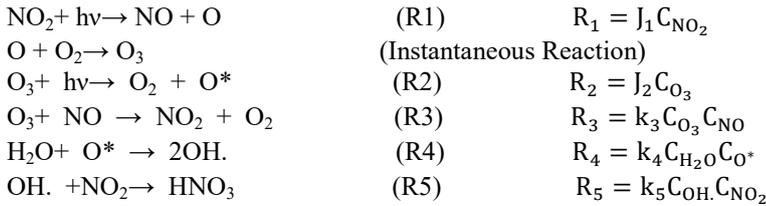
The gas "puff" incorporates this amount of air volume, at each displacement interval, and has its volume corrected by the relation:
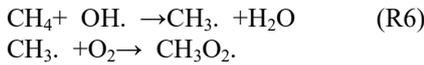
$$V_i = V_{i-1} + \Delta V_{Ar,i},$$

(7)

2.3 The approximate model of chemical reactions

In this work, a simplified model was adopted for the evaluation of Nitric Acid formed in the atmosphere from Nitrogen compounds released in a Thermoelectric Power Station. The set of reactions was decoupled from the reactions of Volatile Organic Compounds (VOC) for an evaluation of the results obtained and a greater ease of solving the set of ordinary differential equations that present a problem of numerical instability, according to (Yamartino et al., 1992) and (Sander et al., 2010). The reaction set used is shown:

The chemical of the Nitrogen compounds:

$NO_2 + hv \rightarrow NO + O$	(R1)	$R_1 = J_1 C_{NO_2}$
$O + O_2 \rightarrow O_3$	(Instantaneous Reaction)	
$O_3 + hv \rightarrow O_2 + O^*$	(R2)	$R_2 = J_2 C_{O_3}$
$O_3 + NO \rightarrow NO_2 + O_2$	(R3)	$R_3 = k_3 C_{O_3} C_{NO}$
$H_2O + O^* \rightarrow 2OH.$	(R4)	$R_4 = k_4 C_{H_2O} C_{O^*}$
$OH. + NO_2 \rightarrow HNO_3$	(R5)	$R_5 = k_5 C_{OH.} C_{NO_2}$

The chemistry of the Methane:

$CH_4 + OH. \rightarrow CH_3. + H_2O$ (R6)
$CH_3. + O_2 \rightarrow CH_3O_2.$

This set of reactions forms the following system of ordinary differential equations, which describe the mass balance in a constant volume system, for NOx gases (Methane chemistry was not considered)

$$\frac{dC_{NO_2}}{dt} = -J_1 C_{NO_2} + k_3 C_{NO} C_{O_3} - k_5 C_{NO_2} C_{OH},$$

(8)

$$\frac{dC_{NO}}{dt} = J_1 C_{NO_2} - k_3 C_{NO} C_{O_3},$$

(9)

$$\frac{dC_{O_3}}{dt} = J_1 C_{NO_2} - J_2 C_{O_3} - k_3 C_{NO} C_{O_3},$$

(10)

$$\frac{dC_{O^*}}{dt} = J_2 C_{O_3} - k_4 C_{O^*} C_{H_2O},$$

(11)

$$\frac{dC_{H_2O}}{dt} = -k_4 C_{O^*} C_{H_2O}, \tag{12}$$

$$\frac{dC_{OH}}{dt} = 2k_4 C_{O^*} C_{H_2O} - k_5 C_{NO_2} C_{OH}, \tag{13}$$

$$\frac{dC_{HNO_3}}{dt} = k_5 C_{NO_2} C_{OH}, \tag{14}$$

$$\frac{dC_{O_2}}{dt} = -J_1 C_{NO_2} + J_2 C_{O_3} + k_3 C_{O_2} C_{NO}, \tag{15}$$

The system of seven coupled ordinary differential equations, for the seven components, describes the mass balance of Nitrogen (NOx) compounds in a constant volume, that is, treating it independently of atmospheric dispersion (dilution with atmospheric air) at each displacement time of the "Puff". The system is solved at each displacement time of the "puff" by the implicit method of numerical integration "Backward Differentiation Formula" fourth order BDF

$$C_{i,n} = \frac{48}{25} C_{i,n-1} - \frac{36}{25} C_{i,n-2} + \frac{16}{25} C_{i,n-3} - \frac{3}{25} C_{i,n-4} + h \frac{12}{25} f(C_{i,n}, t_n), \tag{16}$$

Where $C_{i,n}$ is the concentration value of component "i" at time "t_n", h is the numerical integration step and $f(C_{i,n}, t_n)$ is the derived function of the concentration "$C_{i,n}$" calculated in the current time. The integration step is a very small value due to rigidity problems, due to the difference in the reaction speeds of the components, faster reactions and slower reactions. The discretization generates a system of non-linear equations for the concentrations. It is solved by the successive substitution method at each integration step.

2.4 Approximate solution of the chemical reaction system

Considering an approximation to solve the differential equations coupled (the system of chemical reactions). The approximations are that the concentration of the derivative component is first order (in the derivative function on the right side of the equation) at each integration period, and the concentrations of the other components are assumed to be constant. Therefore, the differential equations for the components take the form

$$\frac{dC_{i,t}}{dt} = k_1 C_{i,t} + k_0, \tag{17}$$

Where k_0 and k_1 are approximate constants.

This differential equation has the following analytical solution

$$C_{i,t} = \left(C_{i,0} + \frac{k_0}{k_1}\right) e^{k_1 t_p} - \frac{k_0}{k_1}, \tag{18}$$

Where $C_{i,0}$ is the concentration of component "i" at the beginning of the displacement time.

3. RESULTS AND DISCUSSION

The model was used for an emission source, according to the data cited by the company (CGTEE, 2012) for the so-called phase "B", for a sunny day and with the characteristics of an unstable atmosphere. These data are shown in Table 1. The concentration results for compounds NO, O_3, NO_2 and HNO_3 are shown in Figures 2, 3, 4 and 5, respectively. The graphs show the concentration values, on the ordinate axis, against the distance from the emission point, on the abscissa axis. The full line shows the result of the BDF numerical method, and the dashed line shows the approximate analytical result. These results show the formation of Ozone gas and Nitric Acid from a NOx source. The model using an analytical solution to evaluate the air intake results in a faster approximation and avoids the convergence problems of numerical solution methods.

Table 1. Data used in the simulation.

Emission Source Data	
Flow, in kg s-1	0.275560
Height of the chimney, in m	150.0
Chimney diameter, in m	5.0
Atmosphere data	
Pressure, in atm	1.0
Temperature, in ^{o}C	25.0
Relative air humidity, in %	30.0
Wind speed at 10 m, in m s^{-1}	7.0
Convective speed, m s^{-1}	1.64
Length of the convective boundary layer, m	780.0
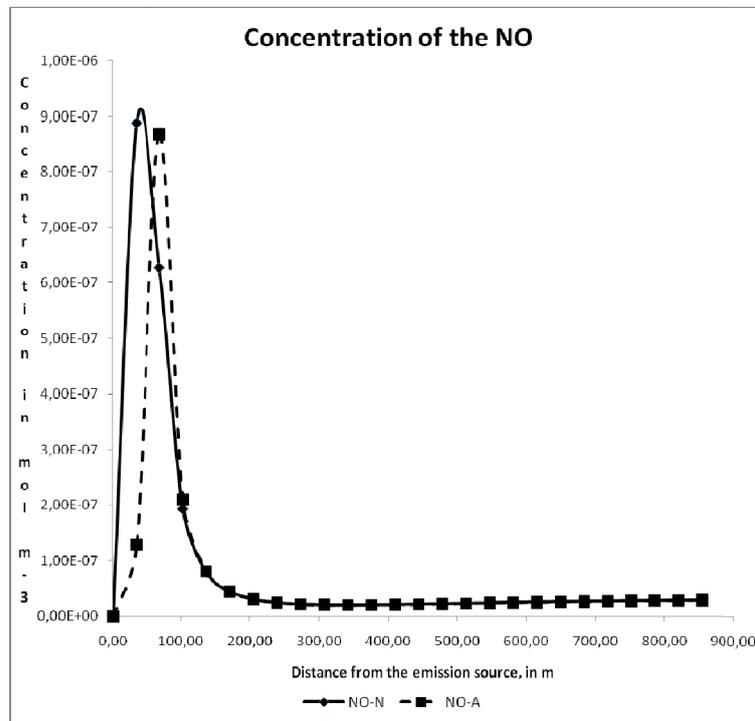
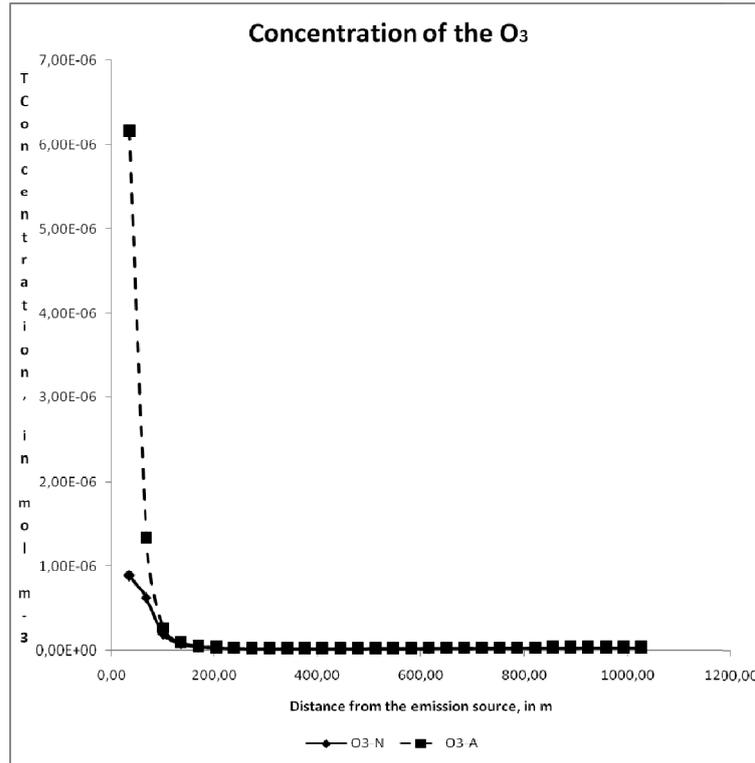Figure 2. Concentration profile for the compound NO.
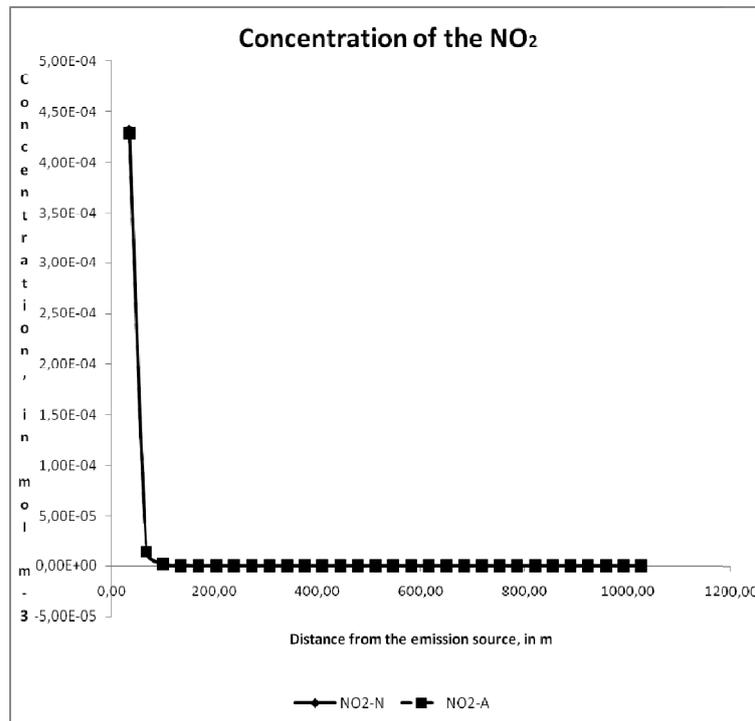
Figure 3. Concentration profile for the compound O_3.

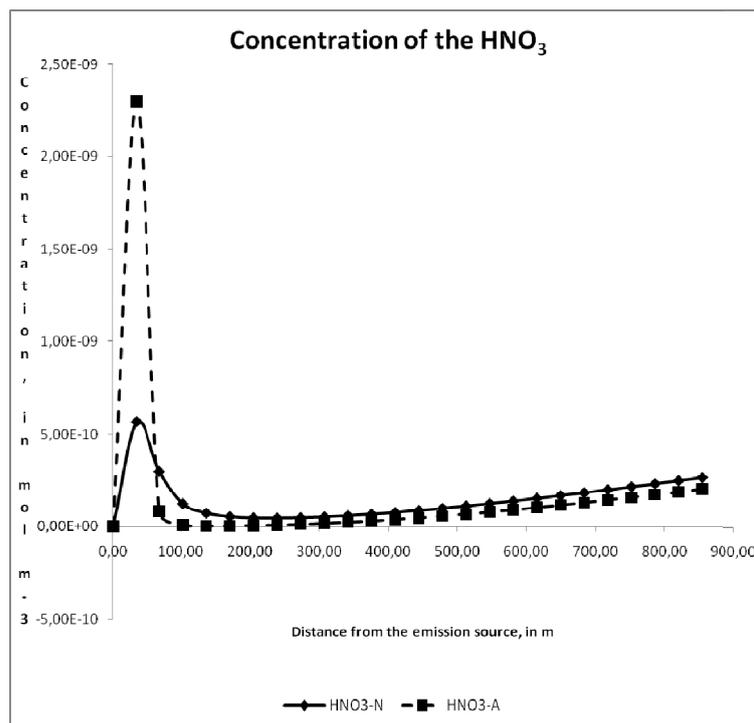Figure 4. Concentration profile for the compound NO_2.

Figure 5. Concentration profile for the compound HNO_3.

4. CONCLUSION

The results of the numerical procedure for integrating the equations and the procedure will show concordant results for distances from 100 m from the source and will differ for smaller distances (closer to the source). The processing time was 1Hs 33 min for the numerical procedure and only 3 min for the analytical approach.

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