Delft University of Technology

Aircraft Emissions and Climate Effects
AE4462-17

Assignment 1: Emissions & Chemical Regimes

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1 Part A: NO_X Evolution

1.1 Question 1

The differential equation for NO_X is shown by Equation 1 [1], where P_{NO_X} is the emission term of NO_X in $[molec/cm^3/s]$ and L is the loss term in $[1/s]$. Whereas NO_X is given in $[molec/cm^3]$.

$$\frac{d[\mathrm{NO_X}]}{dt} = P_{\mathrm{NO_X}} - L[\mathrm{NO_X}] \tag{1}$$

1.2 Question 2

The volume mixing ratio is defined by the following equation, where M_{air} is the mean molar mass of air (approx. 29 kg/kmol), C is the concentration in molecules/cm^3, N_{avo} is Avogadro's constant ($6.02 \cdot 10^{26}$), and ρ is the air density (1 kg/m^3).

$$VMR = M_{air} \cdot C \cdot 10^6 \cdot N_{avo}^{-1} \cdot \rho^{-1} = 29 \cdot C \cdot 10^6 \cdot \frac{1}{6.02 \cdot 10^{26}} = \frac{29 \cdot C}{6.02 \cdot 10^{20}} \tag{2}$$

The air density in molec/cm^3 can be calculated by converting the molecular weight of air (29 kg/kmol). Note that ρ_{air} is given in $[kg/m^3]$.

$$\rho = (\frac{M_{air}}{n})^{-1} \cdot N_{avo} \cdot \rho_{air} = \frac{6.02 \cdot 10^{26}}{29} \text{ molec/kg} \cdot \frac{1}{10^6} \text{ kg/cm}^3 = \frac{6.02 \cdot 10^{20}}{29} \approx 2.076 \cdot 10^{19} \text{ molec/cm}^3 \tag{3}$$

1.3 Question 3

To solve the differential equation in question 1, semi-implicit Euler-Scheme is used shown in Equation 4 [1], where $[\widetilde{\mathrm{NO_X}}]$ is the discrete numerical solution from Equation 1.

$$[\widetilde{\mathrm{NO_X}}](t+1) = \frac{[\widetilde{\mathrm{NO_X}}](t) + P_{\mathrm{NO_X}} \cdot dt}{1 + L \cdot dt} \tag{4}$$

For the first 5 days and the last 10 days, as the 1 km^3 box is transported over the ocean hence the emission term P equals to 0. Whereas the 15 days in between has a P value of 0.12 $[kgN/day]$, and the conversion to $[molec/cm^3/s]$ is shown in Equation 5. Whereas NO_X has a lifetime of 1.5 days, meaning it has a loss term of $1/(1.5 \cdot 24 \cdot 3600)$ $[1/s]$.

$$P[molec/cm^3/s] = P[kgN/day] \cdot N_{avo} \cdot \frac{1}{24} \cdot \frac{1}{10^{15}} \cdot \frac{1}{24 \cdot 3600} \tag{5}$$

To get the value of concentration of NO_X from the value of NO_X in $[pptv]$ to $[molec/cm^3]$ and from $[molec/cm^3]$ to $[kgN/box]$ Equation 6 is used.

$$\mathrm{NO_X}[molec/cm^3] = \rho_{air}[molec/cm^3] \cdot \mathrm{NO_X}[pptv] \cdot 10^{-12} = \mathrm{NO_X}[KgN/box] \cdot N_{avo} \cdot \frac{1}{24} \cdot \frac{1}{10^{15}} \tag{6}$$

The time step of 1 hour is used for the simulation as proposed from the assignment reader [1], leading to the concentration of NO_X $[kgN/box]$ throughout the 30 days shown in Figure 1.

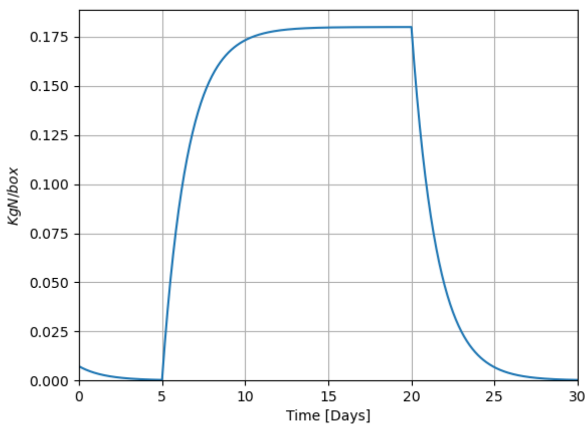

Figure 1: NO_X Concentration throughout 30 day

1.4 Question 4

For the box being transported through the ocean for both CH_4 and CO will be relatively constant as the lifetime of of CH_4 is approximately 7-12 years [2] and the lifetime of CO is approximately 2 months [3]. For the box being transported over land, both CH_4 and CO will increase greater than NO_X as the emission over land for CH_4 and CO is higher than NO_X. Additionally, the increase in mass will close to a linear increase, as the lifetime of both CH_4 and CO is greater than the simulation time.

2 Part B: NO to NO_2 Ratio

2.1 Question 1

The differential equation for NO is based on two production equations and one loss equation: In the equations provided, the first equation is a reaction that transforms NO into NO_2, hence a loss of NO, but the following equations transform NO_2 into NO, thus production equations. The differential equation would thus be difference between them:

$$\frac{d\{NO\}}{dt} = k_2[\mathrm{hv}][\mathrm{NO_2}] + k_3[\mathrm{O}][\mathrm{NO_2}] - k_1[\mathrm{O_3}][\mathrm{NO}] \tag{7}$$

where k_1, k_2, and k_3 are the reaction rate constants.

2.2 Question 2

Since the reactions are assumed to be steady-state, $\frac{d\{NO\}}{dt}$ is equal to 0. The ratio NO : NO_2 can be expressed as follows:

$$0 = k_2[\mathrm{hv}][\mathrm{NO_2}] + k_3[\mathrm{O}][\mathrm{NO_2}] - k_1[\mathrm{O_3}][\mathrm{NO}] \tag{8}$$

$$k_1[\mathrm{O_3}][\mathrm{NO}] = k_2[\mathrm{hv}][\mathrm{NO_2}] + k_3[\mathrm{O}][\mathrm{NO_2}] = [\mathrm{NO_2}](k_2[\mathrm{hv}] + k_3[\mathrm{O}]) \tag{9}$$

$$\frac{[\mathrm{NO}]}{[\mathrm{NO_2}]} = \frac{k_2[\mathrm{hv}] + k_3[\mathrm{O}]}{k_1[\mathrm{O_3}]} \tag{10}$$

NO_x is the sum of NO and NO_2. Thus the ratio NO : NO_x is:

$$\frac{[\mathrm{NO}]}{[\mathrm{NO}_x]} = \frac{[\mathrm{NO}]}{[\mathrm{NO}] + [\mathrm{NO_2}]} = \frac{1}{1 + \frac{[\mathrm{NO_2}]}{[\mathrm{NO}]}} \tag{11}$$

2.3 Question 3

The ratio of NO : NO_2 is calculated through the reaction rate constants k_1, k_2, and k_3. Using the given temperature of 298K and the reaction rate constants equations provided, k_1 is equal to $1.955 \cdot 10^{-14}$, k_2 is equal to $5.000 \cdot 10^{-3}$, and k_3 is equal to $1.032 \cdot 10^{-11}$. Furthermore, the concentrations of [hv] is assumed to be 1 because it is the solar radiation present in the atmosphere in its natural state. The concentration of O_3 is assumed to be the initial value of 40 ppbv. This is converted to molecules per cm^3 by dividing by the molecular weight of air, and multiplying by the air density, to give a value of $8.306 \cdot 10^{11}$ $[molec/cm^3]$. The ratio of $\frac{[\mathrm{O}]}{[\mathrm{O_3}]}$ is given as $5 \cdot 10^{-6}$.

$$\frac{[\mathrm{NO}]}{[\mathrm{NO_2}]} = \frac{8.166 \cdot 10^{-12}[\mathrm{hv}]}{1.955 \cdot 10^{-14}[\mathrm{O_3}]} + \frac{1.032 \cdot 10^{-11}}{1.955 \cdot 10^{-14}}\frac{[\mathrm{O}]}{[\mathrm{O_3}]} = \frac{8.166 \cdot 10^{-12}}{1.955 \cdot 10^{-14} \cdot 8.306 \cdot 10^{11}} + \frac{1.032 \cdot 10^{-11}}{1.955 \cdot 10^{-14}} \cdot 5 \cdot 10^{-6} \tag{12}$$

$$\frac{[\mathrm{NO}]}{[\mathrm{NO_2}]} = 0.3107 \tag{13}$$

The ratio of $\frac{[\mathrm{NO}]}{[\mathrm{NO}_x]}$ is:

$$\frac{[\mathrm{NO}]}{[\mathrm{NO}_x]} = \frac{1}{1 + \frac{1}{0.3107}} = 0.2370 \tag{14}$$

3 Part C: Ozone Net-Production

3.1 Question 1

Using the same approach as in the previous question, we can distinguish between one production equation and two loss equations.

$$\frac{d[\mathrm{O_3}]}{dt} = k_6[\mathrm{HO_2}][\mathrm{NO}] - k_7[\mathrm{HO_2}][\mathrm{O_3}] - k_8[\mathrm{OH}][\mathrm{O_3}] \tag{15}$$

3.2 Question 2

Using the given temperature of 298K, the reaction rate for k_6, k_7 and k_8 are $8.166 \cdot 10^{-12}$, $1.931 \cdot 10^{-15}$ and $7.253 \cdot 10^{-14}$ $[molec/cm^3/s]$ respectively. Additionally, the concentration ratio between NO and NO_X is approximately 0.23. Adapting the the semi-implicit Euler scheme shown in Equation 4 to the differential equation above, where P is the next change of ozone production. Combining the differential equation to the previous simulation, and neglecting the days where the box is transported over the ocean. The production and loss rate of ozone can be shown in Figure 2.

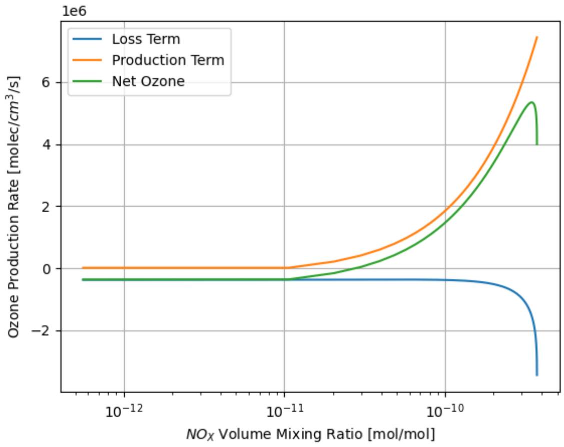

Figure 2: Production and Loss Rate of Ozone

3.3 Question 3

The 3 different chemical regimes are the low NO_X regime, high NO_X and the transition regime [4]. The low NO_X regime is related to the production of ozone purely based on NO_X, which is more focused on $NO + HO_2 \longrightarrow NO_2 + OH$. Whereas for the high NO_X regime, the 3 reaction equations affect this, as higher the concentration of NO_X the greater the production of ozone layer. However the depletion of ozone is also greater as the concentration of ozone layer increase. Lastly, the transition regime is the stage transforming between the low and high NO_X regime.

4 Part D: General Ozone Production

There are both positive and negative arguments towards Ozone production. However in order to differentiate, it is necessary to define two separate types of Ozone, namely *stratospheric Ozone* and *tropospheric Ozone*. Stratospheric Ozone is produced in the stratosphere and is created through natural processes. Tropospheric Ozone is produced at ground-level and tends to be created through artificial processes.

4.1 Positive Arguments

Stratospheric Ozone Layer: Production of Ozone in the stratosphere is a critical element to maintain a livable environment on Earth. The Ozone layer is able to absorb and shield a large influx of the sun's ultraviolet radiation. A depletion of stratospheric Ozone would cause a significant observable augmentation in skin cancers, eye cataracts, and immunology deficiencies. Furthermore, marine ecosystem disruption would be caused due to reduced motility and production of phytoplankton, thus severely cutting the marine food chain [5].
Tropospheric Ozone: Ground production of Ozone is used to purify the air through removal of pollutants and neutralization of odors. This is significantly used for water sanitation, contributing to improved public health in certain environments [6].

4.2 Negative Arguments

Tropospheric Ozone: A major contributing factor to smog production, overexposure (breathing in significant amounts) to Ozone causes inflammation of the respiratory airways, trapping air in the alveoli and causing shortness of breath. This can cause (and aggrevate people prone to) bronchitis, emphysema, and asthma [7]. Furthermore, and in contrast to the aforementioned points, an increased exposure to Ozone also harms vegetational environments by reducing photosynthesis, and drastically reducing plant growth. This has a consequent effect on humans and wildlife, as it creates reduced dioxygen production (through means of photosynthesis), affecting water and nutrient cycles, and diversity of plantation [8].

References

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