Modelling Stratospheric Ozone Dynamics

MTH3024 Project

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Introduction

Despite being considered a pollutant in the lower atmosphere, ozone is essential in the stratosphere. A relatively simple molecule, of 3 bonded oxygen atoms, protects us from more harmful effects of the sun by absorbing harmful UV radiation, and undergoing photolysis into oxygen. The **Chapman equations** (1) describe the dynamics of the chemical reactions which govern these interactions between atomic oxygen, molecular oxygen, and ozone.

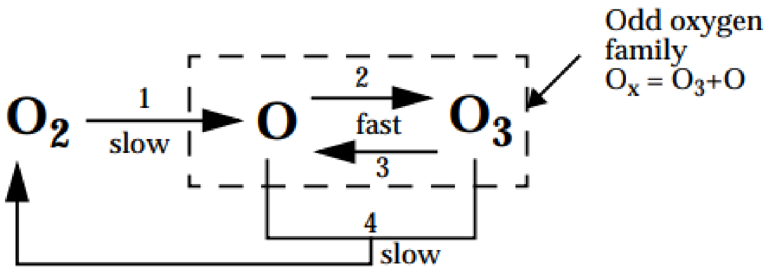

Figure 1: *A depiction of the Chapman mechanism, displaying how atomic and molecular oxygen interact with ozone.[1]*

These equations lay the foundations for a simplified yet accurate model for understanding the behaviour of these chemical processes in the stratosphere.

Questions to Address

The purpose of this report is to attempt to accurately model the dynamics between the Chapman equations, and investigate further iterations which make the model more realistic. Our main questions we wish to address are:

- **How accurate are the Chapman equations?**
  While we know a model simply using these three equations is relatively simple, does it accurately describe the interactions between atomic oxygen, molecular oxygen and ozone? And if not, what can be changed so that we have a more accurate model of these dynamics?

- **How can we improve our model's parameters?**
  The Chapman equations in their basic form take the rate of photolytic reaction to be a constant. This cannot be true in a real world-scenario, as this reaction is dependent on sunlight, which is not present at night. We will attempt to define the photolytic rate as a function of time, and examine how this affects our results.

- **How does altitude change the ozone concentration?**
  While our Chapman equations do not specify any conditions changing due to altitude, we wish to examine if the concentrations of ozone are affected by stratospheric altitude. And if so, why?

- **How does air pollution affect the ozone layer?**
  From modelling our system of Chapman equations, we can use the same process to model the presence of chlorofluorocarbons (or CFC's) in the atmosphere. Do these pollutants have any effect on the system? And if so, is it positive or negative?

Setting up our model

As previously discussed, the production and breakdown of oxygen in the atmosphere is modelled using the Chapman equations. These are defined by the following[2]:

$$\begin{aligned}
&\mathrm{O_3} + h\nu \to \mathrm{O_2} + \mathrm{O} \\
&\mathrm{O} + \mathrm{O_3} \to \mathrm{O_2} + \mathrm{O_2} \\
&\mathrm{O_2} + h\nu \to \mathrm{O} + \mathrm{O} \\
&\mathrm{O} + \mathrm{O_2} \to \mathrm{O_3}
\end{aligned} \tag{1}$$

The hv term in the first and third equations represent photolytic reactions, which depend on energy from the sun.

The Chapman equations in differential form are as follows [2]:

$$\begin{aligned}
\frac{d}{dt}n_O(t) &= 2j_{O_2}n_{O_2}(t) + j_{O_3}n_{O_3}(t) - k_{1.2}n_O(t)n_{O_2}(t)n_M - k_{1.4}n_{O_3}(t)n_O(t) \\
\frac{d}{dt}n_{O_2}(t) &= j_{O_3}n_{O_3}(t) + 2k_{1.4}n_{O_3}(t)n_O(t) - j_{O_2}n_{O_2}(t) - k_{1.2}n_O(t)n_{O_2}(t)n_M \\
\frac{d}{dt}n_{O_3}(t) &= k_{1.2}n_O(t)n_{O_2}(t)n_M - j_{O_3}n_{O_3}(t) - k_{1.4}n_{O_3}(t)n_O(t)
\end{aligned}$$

Where j_{O_2} and j_{O_3} are the photolytic rates for the respective photolysis reactions with molecular oxygen and ozone respectively, and $k_{1.2}$ and $k_{1.4}$ are the reaction rates of the equations 1.2 and 1.4 respectively.

Assumptions

The total number of atoms in the system is conserved, given by the following equations for Chapman equations and CFC system respectively:

$$\begin{aligned} f &= 3n_{O_3}(t) + 2n_{O_2}(t) + n_O(t) \\ F &= 2n_{CF_2Cl_2}(t) + n_{ClO}(t) + n_{Cl}(t) + n_{CF_2Cl}(t) \end{aligned} \tag{2}$$

However we are only taking into account the numerical value of the different chemicals as opposed to their moles. In turn, this reduces the accuracy of the model because the pressure exerted on the molecules is inversely proportional to the molar mass. It is also assumed that there is no mass transfer during the simulation and we are working with a photochemical box model, insinuating that there is a perfect mixture of all the chemicals and the changes in concentration are only due to the chemical reactions between them. A further assumption that is made on our model is that there is no albedo i.e. reflectivity or absorbance from the surface of the Earth and the clouds, which influences the rate of photolysis.

Initial Values and Parameters

To initialise the system, we had to make initial guesses for values of the concentration and rates of reactions. Our initial values for the parameters of the model, without CFCs present, were taken from David Andrews' "An Introduction to Atmospheric Physics"[3], which were calculated at mid latitudes at noon at a height of 25km during equinox. Values for the CFC's concentrations and rates were found by outsourcing which will be referenced later. Through our investigations we will alter some of these parameters and their conditions in order to more accurately describe real-life ozone dynamics.

Investigations

Initial Model

We know that molecular oxygen (O_2) is a much more stable molecule than both atomic oxygen and ozone although atomic oxygen is very reactive in comparison to the other molecules. This means that while atomic oxygen and ozone react on a much smaller time scale, molecular oxygen takes much longer to react.

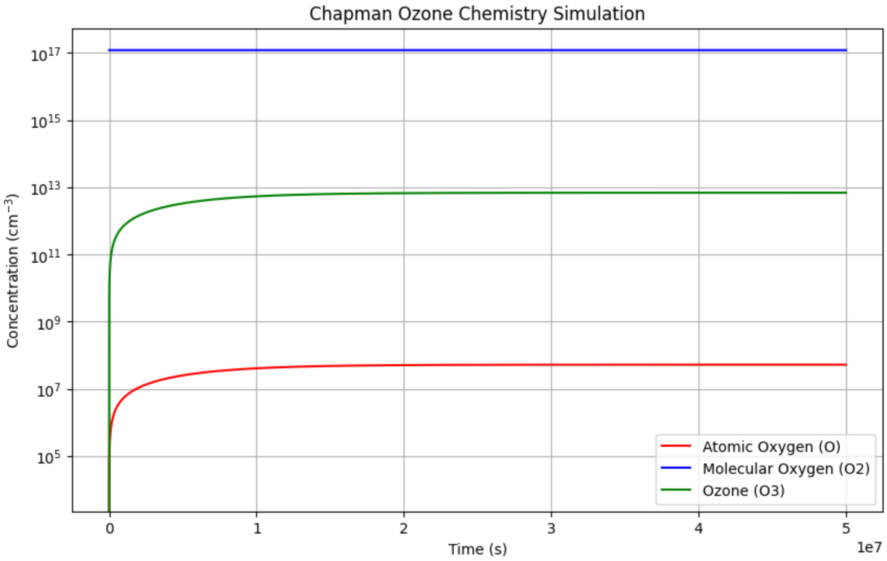

Figure 2: *Plot of concentration over time simulated for $5 * 10^7$ seconds (579 days) using champan equations, were red, blue and green represent the rate of change of concentration for atomic oxygen, molecular oxygen and ozone respectively.*

Figure 2 shows how the system reaches equilibrium with concentration of molecular oxygen as $f/2 = 1.2 * 10^{17}$ molecules cm^{-3} and the rest of the concentrations set to zero. Using the rates given by table 1 in David Andrews' "An Introduction to Atmospheric Physics"[3] we see our system produces no negative concentrations and reaches a state of equilibrium at around 150 days. This model therefore describes ozone dynamics relatively accurately. Next we wish to expand this in order to more accurately depict a realistic model of stratospheric ozone dynamics since our model assume a single photolytic rate and a single altitude.

Improving Model Accuracy

Time-Dependent Photolytic Rates

While initially we set the photolytic rate to be constants, we eventually set these rates to be the value of the function:

$$\phi(t) = \max\left(\cos\frac{2\pi t}{T_d}, 0\right) \tag{3}$$

where T_d is the amount of seconds in one day. This is more accurate to a real-life scenario since the photolysis process depends on the light emitted by the sun. The value of this rate over a 24 hour period starting at 12 noon can be seen in figure 3

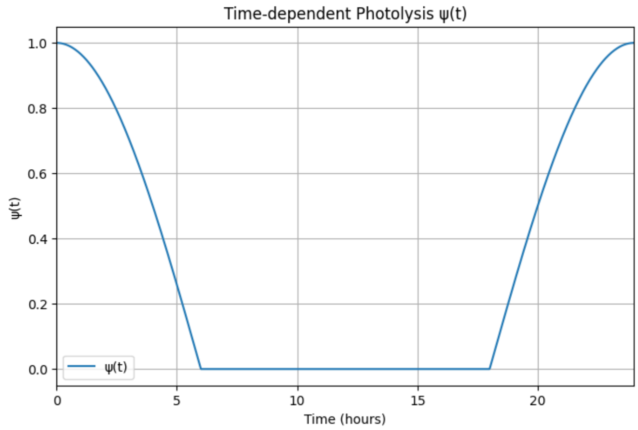

Figure 3: *The change in time-dependent photolysis over the course of 24 hours. The rate is harmonic, with the value at its highest at 12pm in the day, and decreasing to 0 over the time that the sun is down.*

We then simulate the dynamical system over the course of a year from the month of June to June, starting at 12pm on one day, and ending the following day at 12pm. We are using the same assumptions as previously stated in regards to weather conditions.

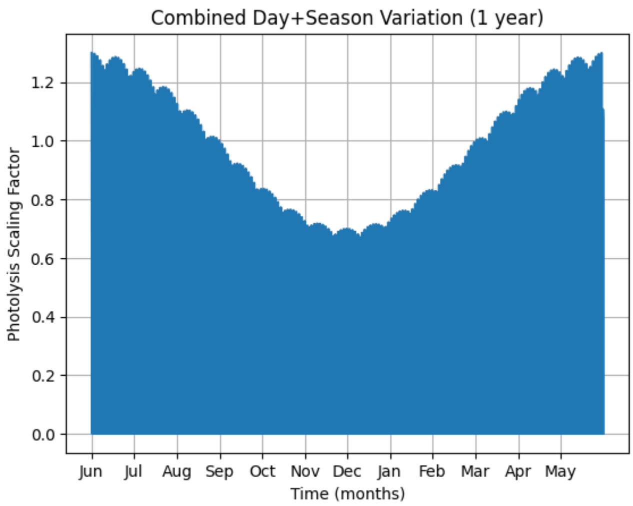

Figure 4: *The change in photolytic rate over the course of a whole year. (Summer to Summer) As we would expect, the value of the photolytic rate scales with seasonal change, with the values being lower closer to Winter as there is less heat/light from the sun in these seasons*

We then implemented our time-dependent photolysis variable to our photolytic rates for oxygen ($J_{O_2}(t) = j_{O_2}\phi(t)$) and ozone ($J_{O_3}(t) = j_{O_3}\phi(t)$). We can then simulate a full day of the dynamics of the ozone layer, which should give us a better idea of what is most affected by more realistic photolytic reactions.

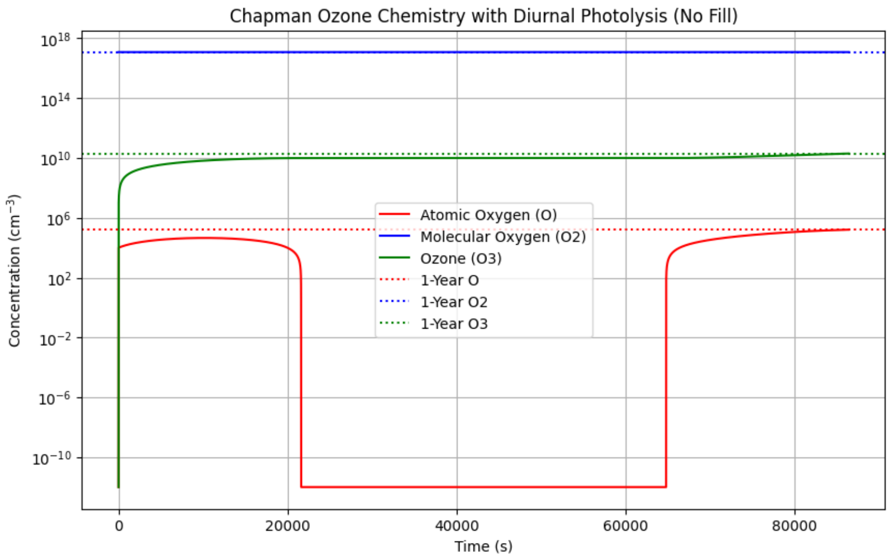

Figure 5: *Plot of concentrations of atomic oxygen (red), molecular oxygen (blue) and ozone (green) over a time of one day, with time-dependent photolytic rates. Drastic changes in atomic oxygen's concentration with changes in time-dependent photolysis.*

Figure 5 shows that the more stable molecules are far less affected by the change in photolysis than atomic oxygen, which is a much more reactive molecule. The concentration of atomic oxygen at night drops to zero, while the concentration of ozone and molecular oxygen remain relatively unchanged. We would expect the concentration of ozone to stay consistent as long as the concentration of atomic oxygen is small in comparison, and the time scale at which molecular oxygen would change is too long for there to be an effect on the concentration caused by the change in photolytic rates over a night.

Investigating Altitude Dependency

The concentration of ozone in the stratosphere also dependents on the altitude. Our original parameters were recorded at an altitude of 25km, but we swept over a range of altitudes to take a closer look at this relationship.

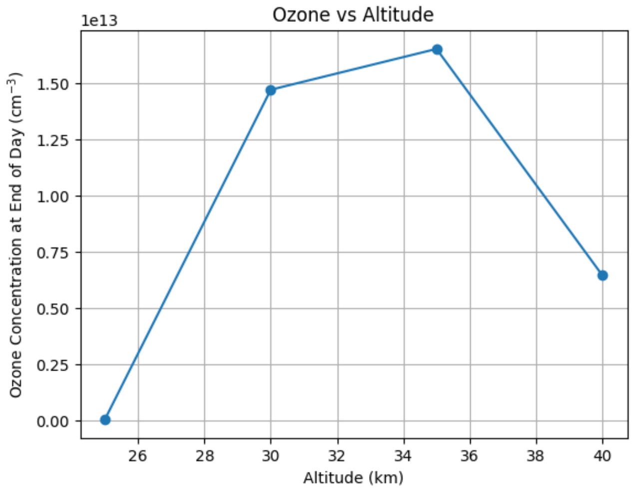

Figure 6: *Plot of concentration of ozone over varied altitudes from 25km to 40km, with a peak in concentration at 35km.*

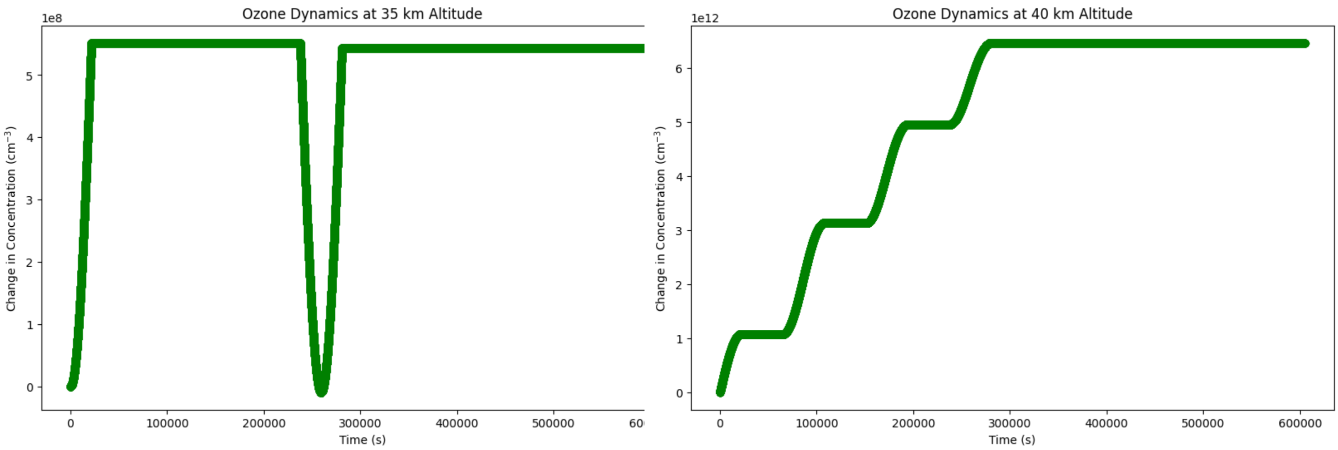

Figure 7: *Plots of concentration of ozone over time of one week for altitudes of 35km and 40km. Clearly, the altitude affects the production of ozone molecules through the Chapman mechanism, with the ozone concentration changing differently at varying altitudes.*

We can see from these figures that the altitude definitely impacts the concentration of ozone present. Our model shows the average concentration of ozone peaking at 35km. This is in line with what we would expect from the model, as experimental data gathered in Palestina, Texas [2] mirrors the shape of our graph for average ozone concentration.

Stratospheric CFC's

We extended our model by adding equations that would model the presence of CFC's in the stratosphere. CFCs undergo photolysis producing chlorine, which is a major contributor to ozone depletion, which acts like a catalyst in the system. This is the justification for choosing the following equations, as it retains a simplified model of CFC reactions in stratosphere as investigated by [4].

$$
\begin{aligned}
&\mathrm{CF_2Cl_2} + h\nu \rightarrow \mathrm{Cl_2} + \mathrm{CF_2Cl} \\
&\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \\
&\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2}
\end{aligned}
\tag{4}
$$

In these reactions, CF_2Cl_2 is Freon-12, CF_2Cl is chlorodifluoromethyl, Cl is chlorine, and ClO is chlorine oxide. Since these are inert in the lower atmosphere, they only begin to react in the stratosphere. As we would expect from pollutants, the amount of ozone in the stratosphere is reduced due to the presence of the CFC's.

Using equations (4) we expanded upon our original system of ODE's from the Chapman mechanism. Calculated by hand we derived the following:

$$
\begin{aligned}
&\frac{d}{dt}n_O(t) = 2j_{O_2}n_{O_2}(t) + j_{O_3}n_{O_3}(t) - k_{1.2}n_O(t)n_{O_2}(t)n_M - k_{1.4}n_{O_3}(t)n_O(t) - k_{4.3}n_{ClO}(t)n_O(t) \\
&\frac{d}{dt}n_{O_2}(t) = j_{O_3}n_{O_3}(t) + 2k_{1.4}n_{O_3}(t)n_O(t) - j_{O_2}n_{O_2}(t) - k_{1.2}n_O(t)n_{O_2}(t)n_M \\
&\quad k_{4.2}n_{Cl}(t)n_{O_3}(t) + k_{4.3}n_{ClO}(t)n_O(t) \\
&\frac{d}{dt}n_{O_3}(t) = k_{1.2}n_O(t)n_{O_2}(t)n_M - j_{O_3}n_{O_3}(t) - k_{1.4}n_{O_3}(t)n_O(t)k_{4.2}n_{cl}(t)n_{O_3}(t) \\
&\frac{d}{dt}n_{CF_2Cl_2}(t) = -j_{CF_2Cl_2nCF_2Cl_2}(t) \\
&\frac{d}{dt}n_{CF_2Cl}(t) = j_{CF_2Cl_2}n_{CF_2Cl_2}(t) \\
&\frac{d}{dt}n_{ClO}(t) = k_{4.2}n_{Cl}(t)n_{O_3}(t) - k_{4.3}n_{ClO}(t)n_O(t) \\
&\frac{d}{dt}n_{Cl}(t) = k_{4.2}n_{Cl}(t)n_{O_3}(t) + k_{4.3}n_{ClO}(t)n_O(t)
\end{aligned}
$$

With the addition of these CFCs we expected our system to produce less ozone, modelling a real-life scenario were CFCs undergo photolysis and produce chlorine which react with ozone.

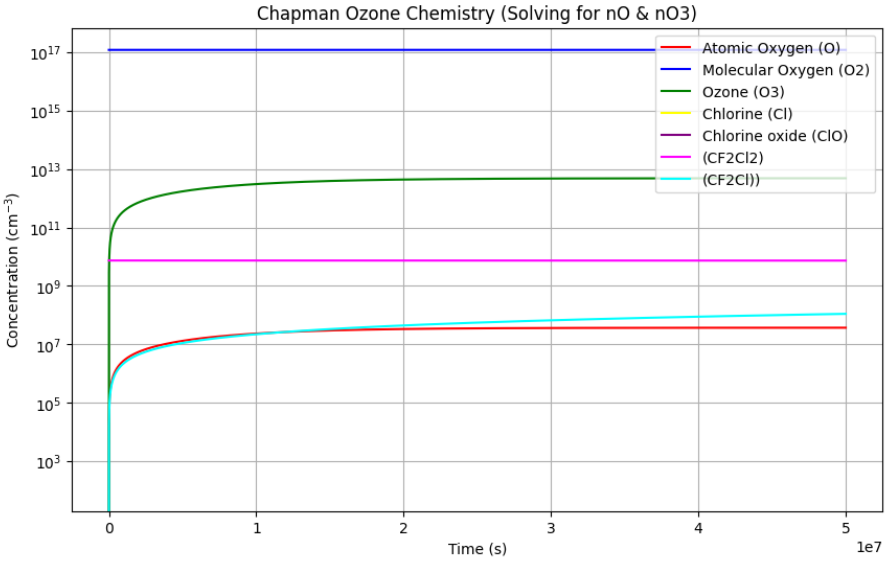

Figure 8: *Plot of concentrations of atomic oxygen (red), molecular oxygen (blue), ozone (green), chlorine (yellow), chlorine oxide (magenta), Freon-12 (pink) and chlorodifluoromethly (cyan) against time of* $5 * 10^7$ *seconds (579 days). Concentrations of Cl and ClO can't be seen as they remain at zero through whole simulation*

Figure 8 shows the the system with CFCs implemented with initial concentration of molecular oxygen as before ($f/2$) and $CF_2Cl_2 = 7.4 * 10^9$ [6] and the rest of the concentrations set to zero. The following rates for equations 4 were used, $j_{CF_2Cl_2} = 3 * 10^{-10}$, $k_{4.2} = 1.14 * 10^{-11}$ and $k_{4.2} = 3.86 * 10^{-11}$[7]. This model produces less ozone as expected, were the system has a steady-state value of $4.85 * 10^{12}$ instead of $6.86 * 10^{12}$, like we had in our initial model. Chlorine and chlorine oxide also both don't change which makes sense, since they act like catalysts in the system. We can also see this from the way we set up the ODEs, were $\frac{d}{dt}n_{ClO}(t) = -\frac{d}{dt}n_{Cl}(t)$.

Conclusion

From our investigations, we seen it is quite challenging to model such a complex system such as stratospheric ozone due to all the variable at play.

However, we've been able to accurately simulate the basic dynamics of the Chapman mechanism, and subsequently iterate upon our model to create a more accurate depiction of real-life stratospheric mechanisms, including the effect the presence of CFC's has in relation to damaging the ozone layer. From our graphs we can see that the presence of CFC's drastically reduce the concentration of ozone molecules in the stratosphere, which can be damaging to the environment, as there is less to ozone to absorb the more harmful effects of the sun's UV radiation. We also found a clear connection between altitude to the concentration of ozone.

Further work

Some possible extensions to our model stem from the goal of accurately modelling an entire atmospheric system, extending our model from the stratosphere to the lower atmosphere and taking into account more pollutants or chemical mechanisms and their effects on ozone dynamics. Examples of this include:

- Modelling ozone transportation between the stratosphere and troposphere.
- How temperature affects ozone formation, especially around polar regions. [5]
- Including the albedo due to the presence of clouds
- Changing pressure exerted on molecules

However, a model of such exhaustive detail is beyond the scope of this project, and would require a much deeper understanding of atmospheric physics and chemistry.

References

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