ENV-320 - Graded assignment - Julia Schmale's part: Solution

Instructions

- You can work in groups of up to three people. Only one person per group should submit the assignment on Moodle, but all group members need to be listed on the document.
- Please submit the solution as one pdf file (i.e. not a zip folder) on Moodle. If you submit a hand-written solution, make sure that it is well readable (there are scan apps available for phones, e.g. Microsoft lens).
- Provide details of your calculations for all answers.
- For open questions to be answered with text, please respect the line limit.
- **Deadline: Thursday, 14 May 2025**.

1 Radiation and radiative transfer (15 points)

1.1 Energy flux (3 points)

What fraction of the flux of energy emitted by the Sun does Mars intercept? (*Provide a sketch of the geometry*). Consider a Mars-Sun distance of $1.5AU = 228 \times 10^6\,\mathrm{km}$ and the radius of Mars $R_M = 3390\,\mathrm{km}$.

The Sun emits over $4\pi sr$ whilst Mars receives radiation proportional to the solid angle it subtends to the Sun That solid angle is $\frac{\pi R_M^2}{D^2}$, where R_M is the radius of Mars ($3390\,\mathrm{km}$), and D is the Mars-Sun distance ($1.5AU = 228 \times 10^6\,\mathrm{km}$) The ratio of the energy flux is therefore the ratio of the solid angle Mars subtends to the total solid angle into which the radiation is directed, or $\frac{R_M^2}{4 \cdot D^2}$. Substitution yields the ratio to be 5.5×10^{-11}.

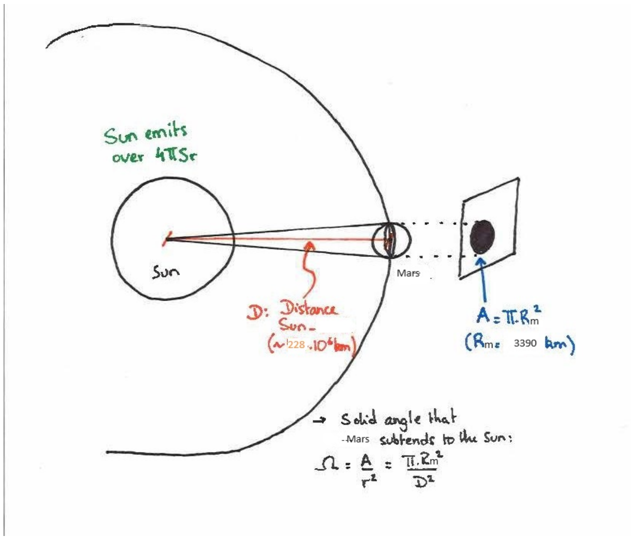

Figure 1: Possible sketch of the geometry

1.2 Irradiance fluxes (5 points)

Figure 2 shows the **seasonal** cycles of broadband radiation measurements observed at the surface of a given site.

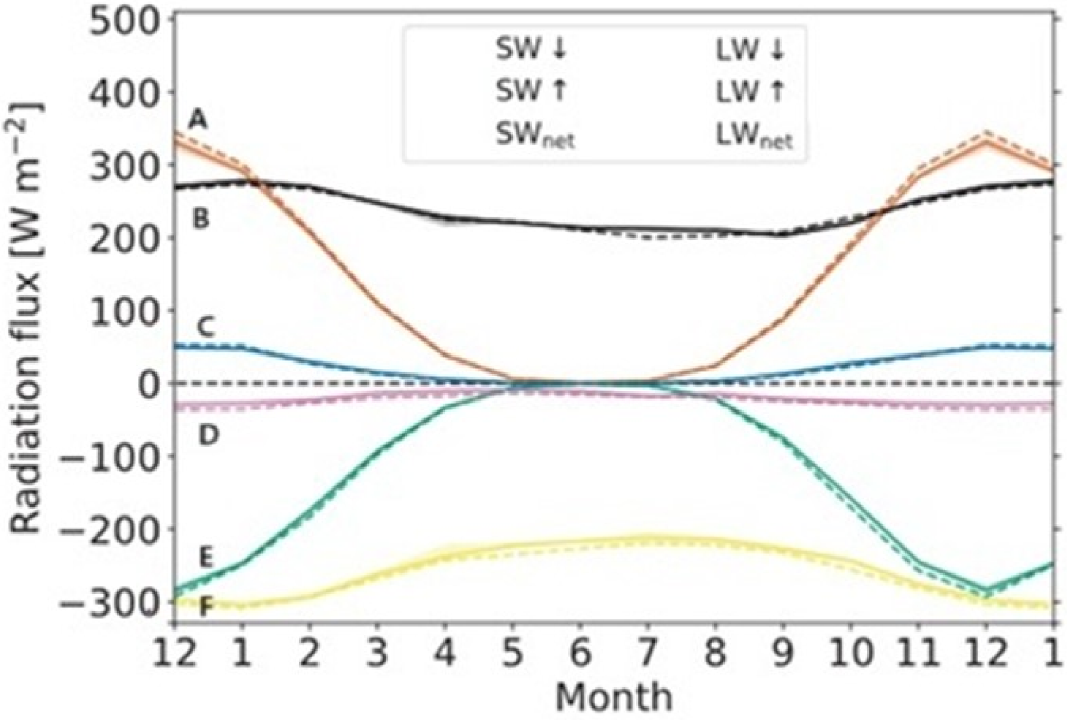

Figure 2: Broadband radiation measurements at the surface for a given site

a) In Figure 2, identify each radiation shortwave and longwave flux components labeled A–F and explain your reasoning (maximum 2 lines per component). Ignore the dashed lines. (3 p)

(A) SW downwards because it is positive and has a strong seasonal variability

(E) SW upwards because it is negative and has strong seasonal variability

(C) SW net because it is the difference of the previous ones and can be calculated. Also, it had to be positive because the reflected component cannot be higher than the downward one.

(B) LW downward because it is positive with little variability throughout the year

(F) LW upward because it is negative with little variability. It has a larger magnitude because otherwise the surface of the earth would be at almost 0 K (Stefan–Boltzmann law)

(D) LW net because is the difference

b) In which hemisphere were these measurements collected? Is the site located at the equator or in a polar region, and why? (1 p) (maximum 4 lines)

Data are collected in the southern hemisphere because the solar component is max in Dec-Jan and min in June-July. The site is in a polar region since the variation of the solar component is particularly marked, with winter months experiencing polar night (0 Wm^{-2} of downward solar irradiance)

c) Assuming that the cloud cover and type are constant throughout the entire year, alternatively, which one of the longwave flux components (LW downward, LW upward, LW net) you would use to answer the previous question and why? (1 p) (maximum 5 lines)

Hint: Base your reasoning on the Stefan-Boltzmann law to obtain/infer the temperature.

Under this assumption, the longwave downward component can be used to make a rough estimate of the location, reversing the Stefan–Boltzmann law to obtain a temperature value. This would show a higher temperature in Dec-Jan, and lower in June-July, identifying summer and winter, and therefore the hemisphere. At the equator, temperature fluctuations would be very small, while the changes here indicate a marked difference between the seasons, and hence a polar area.

1.3 Radiance and transmittance (7 points)

The MODerate resolution atmospheric TRANsmission (MODTRAN) code solves the radiative transfer equation and computes line-of-sight (so for example as seen from a satellite sensor) atmospheric spectral transmittance and radiance. Use the MODTRAN webversion `http://modtran.spectral.com/modtran_home` to answer the following questions.

a) As a climate scientist, you are analyzing satellite images of Arctic landscapes and notice that a once snow-covered region in Northern Canada has experienced a significant change: its bright, reflective snow has given way to a darker, exposed tundra surface. Intrigued, you decide to investigate how this shift has affected the radiative energy balance of the region.
How did these changes impact the radiative fluxes? Briefly explain how and why the fluxes changed (or did not change) by answering the following specific questions (3 p): (maximum 4 lines per component)

(i) Why do the fluxes change?

(ii) What happens to the direct solar flux at 100 and 0 km? Why?

(iii) What happens to the upward diffuse fluxes at 100 and 0 km? Why?

(iv) What happens to the downward flux and why?

Hint: Choose the mode "radiance" and use all defaults for "Sub-Arctic summer". Only vary the one parameter that strongly changed according to the description and interpret the changes in the flux figure and table. Keep the settings so the figures are displayed from 0.4 µm *to* 1 µm.

The surface cover change from snow cover to a darker, exposed tundra surface strongly changes the albedo. Figure 3 shows simulated shortwave radiative fluxes with an albedo of 0.8 (which could resemble glacier ice or older snow) vs. an albedo of 0.2, a possible value for a darker surface.

- The direct solar flux (at both 100 km and at 0 km) does not change, since we do not change the atmosphere in the idealized simulation.
- The upward diffuse fluxes (100 km and at 0 km) are strongly reduced due to the albedo changes: the higher absorption with a dark ground (low albedo) leads to a decrease in upward diffuse fluxes.
- The downward diffuse flux (from scattering in the atmosphere) is also reduced (but less than the upward fluxes) due to the lower reflection from the surface, and less "re-scattering" in the atmosphere.

b) While conducting fieldwork in Northern Canada, you observe a sudden change in the atmosphere—a strong windstorm lifts fine particles of dust and soot from the exposed tundra, reducing visibility to just 2 km. You decide to analyze how this dust storm influences radiative fluxes. How does the presence of airborne dust impact the radiative fluxes? Briefly explain how and why the fluxes changed (or did not change) by answering the following specific questions (2.5 p): (maximum 3 lines per component)

(i) What happens to the direct solar flux at 100 and 0 km? Why?

(ii) What happens to the upward diffuse fluxes at 100 and 0 km? Why?

(iii) What happens to the downward flux and why?

Hint: Only vary one parameter according to the description and compare with the simulation of your fieldtrip in a.

With the dust storm, the visibility reduces to 2 km, which you can directly specify in the MODTRAN input. Figure 4 shows a comparison of your field trip (albedo=0.2, visibility=23 km) and the dust storm (albedo=0.2, visibility = 2 km).

- The direct solar flux at 100 km stays the same since the dust storm only occurs near the surface (below 2 km, as indicated in the model infobox for low visibility).

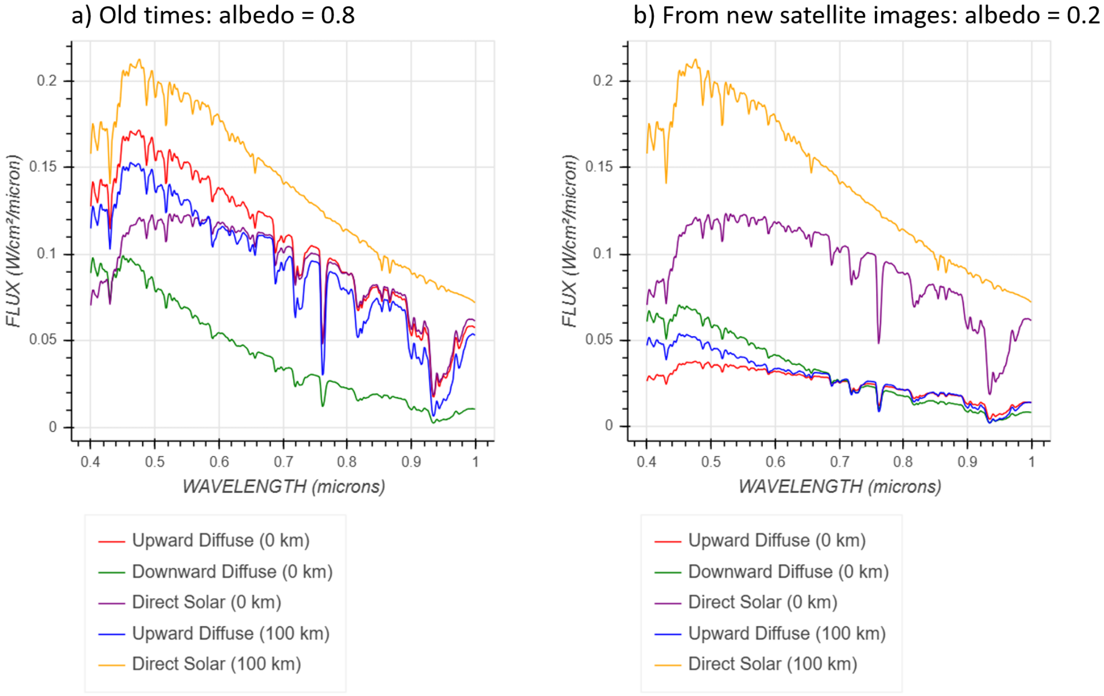

Figure 3: Flux comparison - high and low albedo

- The direct solar flux at the surface is strongly reduced since the aerosol leads to radiation extinction due to scattering and absorption. (Note: the aerosol size distribution and scattering/absorbing properties are highly simplified here, since the "rural" scheme used for this figure has likely different properties than an actual high latitude dust storm).
- The upward diffuse flux at the surface is reduced, since less radiation reaches the surface, and less radiation is reflected back to space.
- The upward diffuse flux at 100 km is higher with the dust storm, as the properties of the haze layer are more reflective than the underlying surface and radiation is scattered higher up in the atmosphere.
- The downward diffuse flux is higher with the dust storm as atmospheric scattering is increased due to the presence of aerosols, and more diffuse (and less direct) radiation reaches the surface.

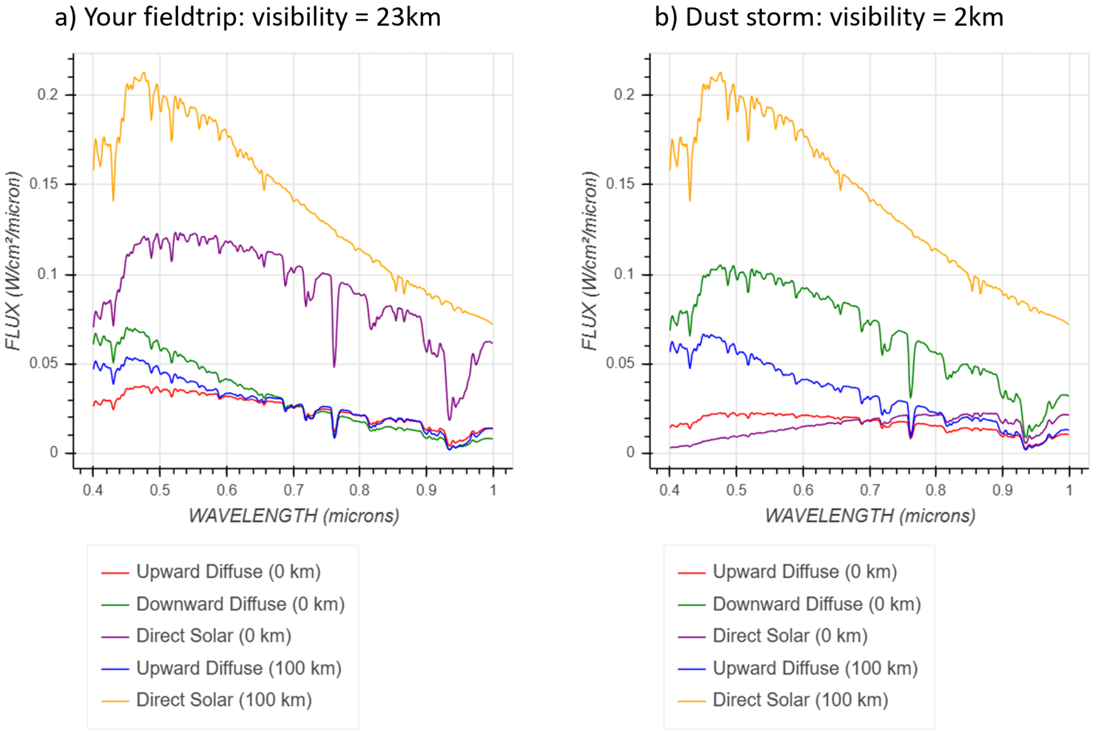

Figure 4: Flux comparison - clear atmosphere and dust storm

c) Since the field observations sparked your curiosity about radiative transfer, you run the MODTRAN model and compare the transmittance of two very different places on Earth: the tropics and the wintertime sub-Arctic as shown in the Figure 3. However, you forgot to label them... (1.5 p) (maximum 3 lines per component)

(i) Which figure corresponds to which region?

(ii) In which wavelength range do you observe the most significant changes?

(iii) What do you think is the primary source of this difference?

(Hint: You don't need to run the MODTRAN model to answer these questions.)

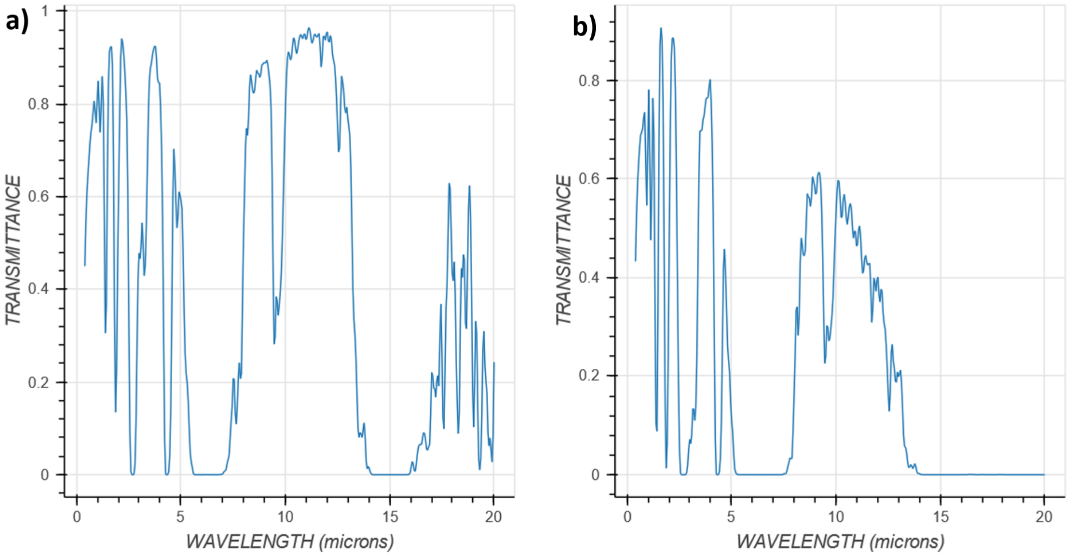

Figure 5: Transmittance

- Figure 5 a) sub-Arctic winter, b) Tropics
- Most changes are observed in the infrared range between 7 µm to 20 µm (particularly > 15 µm).
- The higher water vapour concentrations in the tropics compared to the dry wintertime sub-Arctic atmosphere are the main reason for the different transmittance. As shown in Figure 6, water vapour strongly absorbs in the wavelengths where we see large differences.

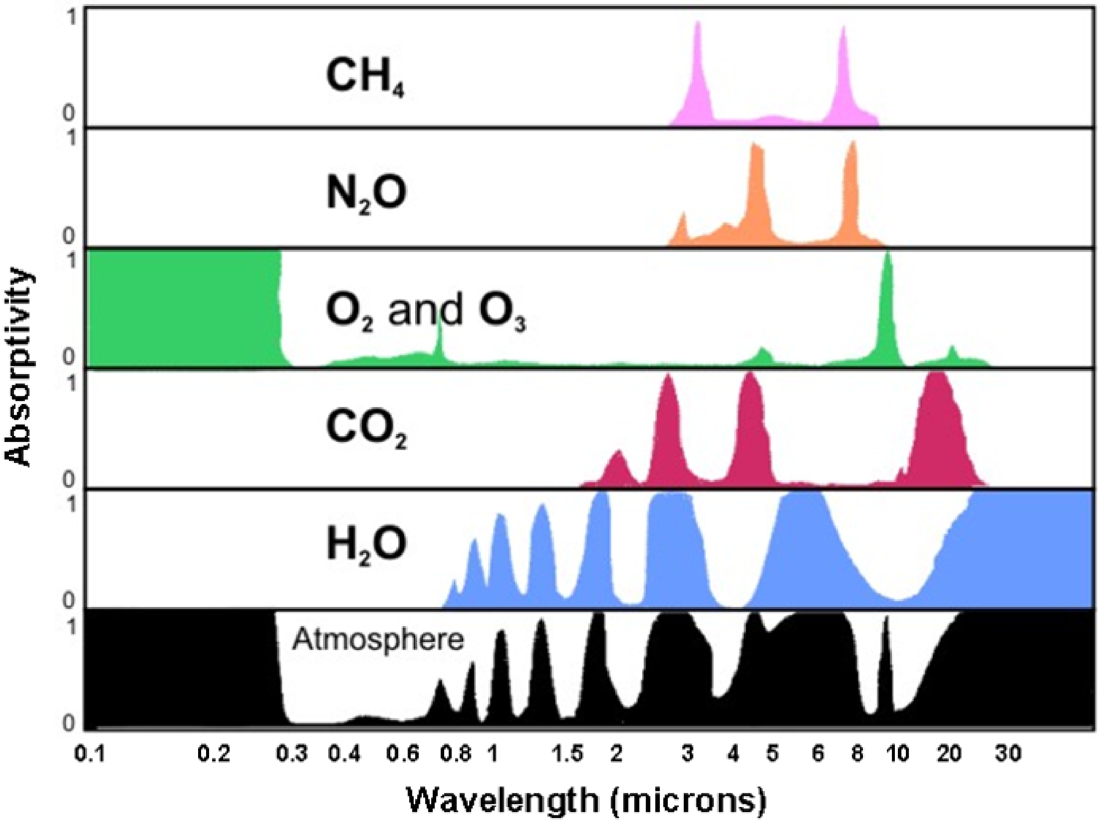

Figure 6: Absorptivity

2 Atmospheric composition (8.5 points)

2.1 Unit conversion (3 points)

a) The worldwide concentration of atmospheric carbon dioxide (CO_2) is progressively rising each year due to human activities. In 2000, the average global CO_2 level in the atmosphere stood at 370 ppm, which has now increased to 424.5 ppm. Determine the additional number of molecules per cubic meter [$\mathrm{molecule\,m^{-3}}$] present in the atmosphere today compared to 2000 at 1 atm and 10°C. Calculate the increase in concentration this represents in milligrams per cubic meter [$\mathrm{mg\,m^{-3}}$]. (2 points)

From the ideal gas law:

$$PV = nRT$$

The number of moles per $\mathrm{m^3}$ of air at $1\,\mathrm{atm}$ and $283.15\,\mathrm{K}$ are given by:

$$C = \frac{n}{V} = \frac{P}{RT} = \frac{1\,\mathrm{atm}}{8.205 \times 10^{-5}\,\mathrm{m^3\,atm\,mol^{-1}\,K^{-1}} \cdot 283.15\,\mathrm{K}} = 43.04\,\mathrm{mol\,m^{-3}}$$

Converting to units of molecules per volume [$\mathrm{molecule\,m^{-3}}$]:
Avogadro constant : $6.022 \times 10^{23}\,\mathrm{molecule\,mol^{-1}}$

$$C = 43.04\,\mathrm{mol\,m^{-3}} \cdot\ 6.022 \times 10^{23}\,\mathrm{molecule\,mol^{-1}} = 2.59 \times 10^{25}\,\mathrm{molecule\,m^{-3}}$$

Calculate the number of molecules per $\mathrm{m^3}$ in 2000 and 2024 and the difference between the two values:
C_{2000} = 370 ppm = 370×10^{-6}
C_{2025} = 424.5 ppm = 424.5×10^{-6}

$$C_{2000} = 370 \times 10^{-6} \cdot 2.59 \times 10^{25}\,\mathrm{molecule\,m^{-3}} \ = 9.58 \times 10^{21}\,\mathrm{molecule\,m^{-3}}$$

$$C_{2025} = 424.5 \times 10^{-6} \cdot 2.59 \times 10^{25}\,\mathrm{molecule\,m^{-3}} \ = 1.1 \times 10^{22}\,\mathrm{molecule\,m^{-3}}$$

Difference :

$$C_{\mathrm{diff}} = 1.1 \times 10^{22}\,\mathrm{molecule\,m^{-3}} - 9.58 \times 10^{21}\,\mathrm{molecule\,m^{-3}} = 1.42 \times 10^{21}\,\mathrm{molecule\,m^{-3}}$$

Converting the difference to units of moles per volume [$\mathrm{mol\,m^{-3}}$] and then milligrams per volume [$\mathrm{mg\,m^{-3}}$]:

Molar mass CO_2 : $\mathrm{mm}_{\mathrm{CO2}} = 44.01\ \mathrm{g\,mol^{-1}}$

$$C_{\mathrm{diff}} = \frac{1.42 \times 10^{21}\,\mathrm{molecule\,m^{-3}}}{6.022 \times 10^{23}\,\mathrm{molecule\,mol^{-1}}} = 0.00236\mathrm{mol\,m^{-3}}$$

$$C_{\mathrm{diff}} = 0.002\,36\,\mathrm{mol\,m^{-3}} \cdot 44.01\,\mathrm{g\,mol^{-1}} = 0.1034\,\mathrm{g\,m^{-3}} = 103.4\,\mathrm{mg\,m^{-3}}$$

b) The World Health Organization (WHO) has established guidelines on outdoor (ambient) air pollution levels, which are widely used as reference tools by policymakers across the world to set standards and goals for air quality management. The guidelines provide evidence and health-based standards for specific air pollutants that cities should adopt as air quality targets.
The recommended guideline level for nitrogen dioxide (NO_2) is 25 $\mu g\, m^{-3}$ over a 24-hour average. What would its mixing ratio be in ppbv at 1 atm and 25°C ? (1 point)

From the ideal gas law and the partial pressure of NO_2 (P_{NO2}) we can calculate the mixing ratio:

$$PV = nRT$$

$$\xi_{NO2} = \frac{P_{NO2}}{P_{tot}}$$

Conversion of $\mu g\, m^{-3}$ to units of $mol\, m^{-3}$:
Molar mass NO_2 : $mm_{NO2} = 46.01\ [g\, mol^{-1}]$

$$C_{NO2} = \frac{25 \times 10^{-6}\, g\, m^{-3}}{46.01\, g\, mol^{-1}} = 5.43 \times 10^{-7}\, mol\, m^{-3}$$

Using the ideal gas law, the partial pressure can be calculated:

$$\begin{aligned} P_{NO2} &= \frac{n_{NO2} \cdot R \cdot T}{V} = \frac{n_{NO2}}{V} \cdot R \cdot T = C_{NO2} \cdot R \cdot T \\ &= 5.43 \times 10^{-7}\, mol\, m^{-3} \cdot 8.205 \times 10^{-5}\, m^3\, atm\, mol^{-1}\, K \cdot 298.15\, K = 1.33 \times 10^{-8}\, atm \end{aligned}$$

Partial pressure :

$$\xi_{NO2} = \frac{P_{NO2}}{P_{tot}} = \frac{1.33 \times 10^{-8}\, atm}{1\, atm} = 1.33 \times 10^{-8} = 13.3 \times 10^{-9} = 13.3\, ppbv$$

2.2 Atmospheric lifetime (2 points)

a) Explain the concept of atmospheric lifetime for trace gases and outline the various factors that must be considered to calculate the atmospheric lifetime of a specific compound. (Hint: a verbal description is fine.) (10 lines max.)

The atmospheric lifetime is the average e-folding time or half-lifetime that a molecule resides in the atmosphere before it is removed by chemical reaction or deposition. Atmospheric lifetimes can range from a few years to thousands of years.
When considering atmospheric processes, we often analyze a specific parcel of air rather than the entire atmosphere. In this conceptual air parcel considered as a well-mixed

box , the key components to take into account are the inflow and outflow of the compound, emissions and chemical production, as well as chemical losses and deposition mechanisms.

b) The gas-phase decomposition of dinitrogen pentoxide $N_2O_5(g) \longrightarrow 2\,NO_2(g) + \frac{1}{2}\,O_2(g)$ is a reaction of first-order kinetics with the following temperature dependent rate constants :

T (K)	k (s^{-1})
338	4.9×10^{-3}
318	5.0×10^{-4}
298	3.5×10^{-5}

Table 1: Temperature dependent rate constants.

Calculate the atmospheric half-lifetime of N_2O_5 at 65°C, 45°C and 25°C.

$$\mathrm{T}_{1/2}(338K) = \frac{ln(2)}{k} = \frac{ln(2)}{4.9 \times 10^{-3}} = 141.5\,\mathrm{s}$$

$$\mathrm{T}_{1/2}(318K) = \frac{ln(2)}{k} = \frac{ln(2)}{5.0 \times 10^{-4}} = 1386.3\,\mathrm{s}$$

$$\mathrm{T}_{1/2}(298K) = \frac{ln(2)}{k} = \frac{ln(2)}{3.5 \times 10^{-5}} = 19\,804.2\,\mathrm{s}$$

2.3 Nitrogen cycle and cascade (3.5 points)

Answer the following questions:

1. Since some bacteria have the ability to fix N_2 directly from the atmosphere, and can then start the process of nitrogen cascading in the different environmental compartments, why should we then care about anthropogenic emissions of reactive nitrogen? (10 lines max.) (2 points)

   Through mainly fossil fuel consumption and agricultural nitrate fertilization, human activities introduce a considerable amount of reactive nitrogen species in the different environmental compartments (directly to the atmosphere, directly to terrestrial ecosystems and indirectly to freshwater/marine ecosystems through leaching in the soils). These excess inputs of reactive nitrogen can temporarily accumulate in some environmental compartments with diverse harmful impacts on the environment, for example in the hydrosphere where enhanced reactive nitrogen concentrations lead to eutrophication problems or in the atmosphere where N_2O is an important greenhouse gas or where NO_x and its oxidation products contribute to the formation of photochemical smogs in cities with implication for urban air quality and health.

2. Why is ammonia (NH_3) such an important nitrogen-containing compound in the atmosphere and where does it come from? (5 lines max.) (1 point)

   Ammonia is one of the very few basic gas in the atmosphere and therefore plays a crucial role in neutralizing acids (mainly the oxidation products of SO_2 and NO_2) and hence has a determining role in controlling the aerosols' acidity. *EXTRA: Its conversion to ammonium-containing aerosols can occur via, for example, the following reaction:*

   $$2\,\mathrm{NH_3}\,(\mathrm{g}) + \mathrm{H_2SO_4}\,(\mathrm{g}) \longrightarrow (\mathrm{NH_4})_2\mathrm{SO_4}\,(\mathrm{p})$$

   Ammonia primarily originates from soils, biogenic, fertilizers, biomass burning, and fossil fuel combustion emissions.

3. Which process releases N_2 back into the atmosphere? (0.5 points)

   Denitrification is the process by which fixed nitrogen returns to the atmosphere (through bacterial reduction).

3 Stratospheric chemistry (9.5 points)

3.1 Oxygen chemistry in the stratosphere (3.5 points)

a) Two "oxygen only" reactions destroy ozone in the middle stratosphere:

$$O(^1D) + O_3 \xrightarrow{k_1} 2\,O_2 \tag{1}$$

$$O + O_3 \xrightarrow{k_2} 2\,O_2 \tag{2}$$

where O stands for non-excited oxygen atoms while $O(^1D)$ is the excited singlet state. In the middle stratosphere, at about 30 km, T = 230 K, typical noontime concentrations of $O(^1D)$ and O are 50 molecule cm^{-3} and 7.5×10^7 molecule cm^{-3}, respectively. The reaction rate coefficients are given as:
$k_1 = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}
$k_2 = 8 \times 10^{-12} exp(-2060/T)$cm^3 molecule^{-1} s^{-1}.
Evaluate the rates of both ozone loss processes at this altitude and write down the relative loss rate in terms of the ratio of the two. Which loss dominates and why? (1 point)
Hint: The reaction can be approximated to be of pseudo-first order, considering that only one of the reactant has a variable concentration. Here you can consider $[O(^1D)]$ and $[O]$ constant.

First calculate k_2:

$$k_2 = 8 \times 10^{-12} exp(\frac{-2060}{230}) = 1.03 \times 10^{-15}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$$

$$\frac{\frac{d[O_3]}{dt} = -k_1[O(^1D)][O_3]}{\frac{d[O_3]}{dt} = -k_2[O][O_3]} \approx 0.078$$

The reaction with O dominates the loss, due to the much larger concentration of O relative to $O(^1D)$

b) Fig. 7 shows the calculated ozone profiles according to the Chapman cycle, where ozone is destroyed by the reactions from a). Why are the observed ozone concentrations so much lower? Explain shortly (max. 3 lines). (0.5 points)

The observed concentrations are lower because there are additional ozone sinks. O_3 is also destroyed by catalytic NO_x, HO_x and halogen cycles
(Extra: the calculated ozone profile also neglects the role of the equator-to-pole stratospheric circulation (known as the *Brewer-Dobson circulation*) in transporting ozone from its primary source in the tropical stratosphere poleward and downward into the extratropical lower stratosphere)

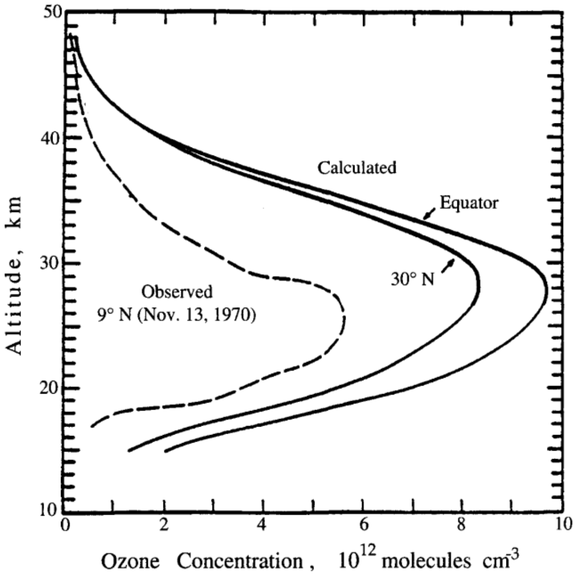

Figure 7: Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9°N) on November 13, 1970 (Seinfeld and Pandis, 2006).

c) Let us now consider a higher altitude in the stratosphere at 40 km, and a temperature of 250 K. What would be the change (as a ratio) in the rate of removal of O_3 by the reaction with O (equation (2)) at 40 km compared to 30 km? Assume the concentrations of the reactants are the same at 40 km than at 30 km. (0.5 points)

As shown in a), the reaction with O is dominant, so we focus on this one for the rate of removal of O_3. Assuming that the concentrations of reactants are the same at 40 km than at 30 km, then the only variable is the reaction rate k_2, which depends on temperature:

$$\frac{\frac{d[O_3]}{dt}_{40km}}{\frac{d[O_3]}{dt}_{30km}} = \frac{k_{2,40km}}{k_{2,30km}} = 2.05$$

The rate of removal of O_3 at 40 km increases by a factor of 2 compared to the one at 30 km.

d) In reality, the assumption of unchanged O concentration with altitude doesn't hold. What change in O concentration do you expect with increasing altitude in the stratosphere and why? How will that affect the value you calculated in (c)? (1.5 points)

The concentration of atomic oxygen (O) increases with altitude because the main sink of the O-atom is through the following fast reaction: $O + O_2 + M \xrightarrow{k_0} O_3 + M$. As the concentration of O_2 and M decrease with increasing altitude (because the pressure is decreasing), the O-atom has a longer lifetime at higher altitudes, which results in higher concentrations.

It follows that for the question (c), the rate of O_3 destruction via the reaction $O + O_3 \xrightarrow{k_2} 2\,O_2$ will be even greater at 40km compared to 30km than previously calculated in (c).

Note : Although the photodissociation rate of O_2 increases with altitude, at 30–40 km it remains on the order of 10^{-11} to $10^{-9}\,s^{-1}$, which is too low to significantly contribute to increased [O]. Therefore, the observed increase in [O] is primarily linked to the reduced efficiency of its removal via the $O + O_2 + M \xrightarrow{k_0} O_3 + M$ reaction.

3.2 Montreal protocol and ozone hole(s) (6 points)

3.2.1 Chlorofluorocarbons as long-lived species (3 points)

The 1987 Montreal protocol was the first international agreement to control emissions of chlorofluorocarbons (CFCs) harmful to the ozone layer. It was subsequently amended to respond to the increased urgency created by the discovery of the Antarctic ozone hole. In this problem we compare the effectiveness of the original and amended protocols. We focus on CFC-12, which has an atmospheric lifetime (τ) of 100 years against loss by photolysis in the stratosphere. We start our analysis in 1989 when the Montreal protocol entered into force. In 1989 the mass of CFC-12 in the atmosphere was $m = 1.0 \times 10^{10}$ kg and the emission rate was $E = 4 \times 10^{8}$ kg year^{-1}.

a) The initial Montreal protocol called for a 50 % reduction of CFC emissions by 1999 and a stabilization of emissions thereafter. Consider a future scenario where CFC-12 emissions are held constant at 50 % of the 1989 values. After a while, CFC-12 would reach a steady-state equilibrium. Calculate the mass of CFC-12 at the steady-state equilibrium. Would that mitigation strategy have worked in the long term (infinity)? (2 points)
Hint:

$$\frac{dm}{dt} = E - km \tag{3}$$

From integration of Equation 3, we get

$$\begin{aligned}
m(t) &= m_0 \cdot e^{-kt} + (1 - e^{-kt})\frac{E}{k} \\
m_{t\to\infty} &= \frac{E}{k} \text{ (as } e^{-kt} \text{ tends to 0)} \\
k &= \frac{1}{\tau} = \frac{1}{100} = 0.01\,\text{year}^{-1} \\
m(\infty) &= \frac{2 \times 10^{8}\,\text{kg year}^{-1}}{0.01} = 2 \times 10^{10}\,\text{kg}
\end{aligned}$$

This strategy would not work because the steady-state value would be at a higher concentration than initially.

b) The subsequent amendments to the Montreal protocol banned CFC production completely as of 1996. Consider a scenario where CFC-12 emissions are held constant from 1989 to 1996 and then drop to zero as of 1996. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Compare with the 1989 value. (1 point)

1989-1996 (7 years): $m = m_0 \cdot e^{-kt} + (1 - e^{-kt})\frac{E}{k}$ so $m(1996) = 1.2 \times 10^{10}\,\text{kg}$
1997-2050 (53 years): $m = m_{1996} \cdot e^{-kt} = 7.1 \times 10^{9}\,\text{kg}$ (71 % of $m(1989)$)
1997-2100 (103 years): $m = m_{1996} \cdot e^{-kt} = 4.3 \times 10^{9}\,\text{kg}$ (43 % of $m(1989)$)

3.2.2 Chlorine-catalyzed ozone destruction (3 points)

a) Once in the stratosphere, CFCs photodissociate to release chlorine. For CFC-12 (CF_2Cl_2), this happens via the following reaction:

$$CF_2Cl_2 + h\nu \longrightarrow CF_2Cl + Cl \tag{4}$$

In 1974, Mario Molina and Sherwood Rownland postulated the following catalytic chain reaction involving the chlorine atom:

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{5}$$

$$ClO + O \longrightarrow Cl + O_2 \tag{6}$$

Write down the net reaction from reactions (5) and (6). (0.5 points)

$O_3 + O \longrightarrow 2\,O_2$

b) Figure 8 shows the time evolution of main processes associated with the development of the Antarctic ozone hole. (I.) Why is the denitrification and dehydration (see panel (a) in the figure) so important for the ozone hole formation? (II.) Further your argumentation to explain how the abundances of the inactive reservoir species and active

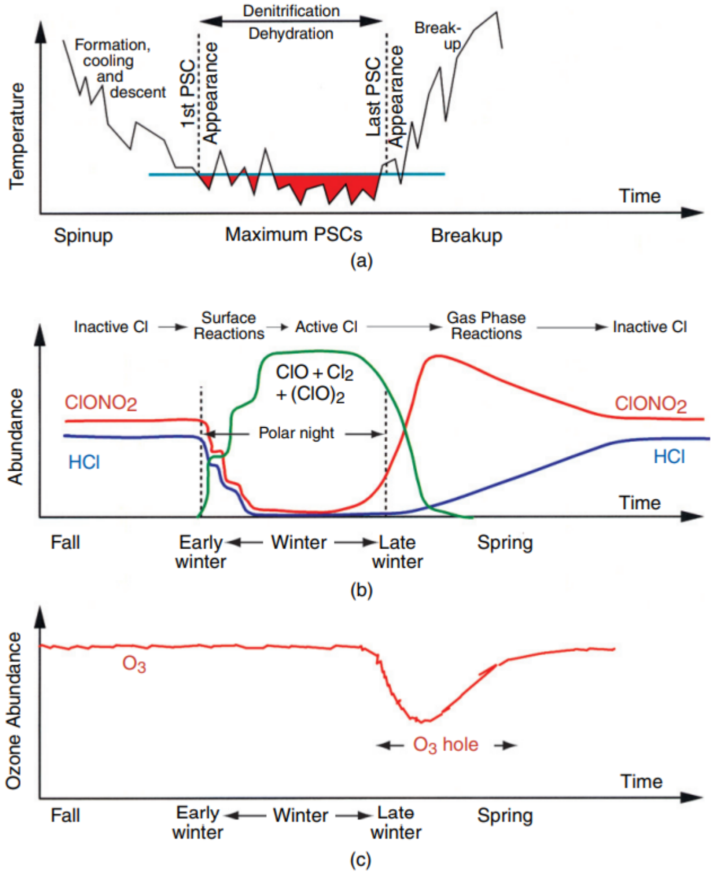

Figure 8: Schematic illustrating time evolution of the main processes associated with the development of the Antarctic ozone hole (Wallace and Hobb, 2006, Fig. 5.22)

chlorine compounds in the lower stratosphere over Antarctica change over time between fall/early winter and spring (see panel (b) in the figure). (III.) Finally, how does this affect the ozone concentrations in panel (c)? (max. 18 lines) (1.5 points)

Denitrification removes HNO_3 from the atmosphere, and dehydration removes H_2O. This means that the reactions that lead to reactive halogen compounds plus HNO_3 and H_2O are losing products, which pushes the equilibrium of the reaction to the products side, hence more reactive ozone-depleting compounds are produced. The polar vortex starts to form in the fall, with cold temperatures below $-80\,°C$ that enable the formation of Polar Stratospheric Clouds (PSCs). On the surface of the PSCs, heterogeneous chemical reactions convert the reservoir species to Cl_2, HOCl, and $ClNO_2$, which build up during the polar night as they are only destroyed by UV radiation. These reactions are enhanced by the denitrification and dehydration processes mentioned above. When sunlight reaches the pole in austral spring, the active chlorine species are rapidly photolyzed to Cl and ClO and the catalytic cycle of ozone destruction starts, leading to the drop of ozone concentrations and the ozone hole. With the weakening and breakup of the polar vortex and warmer stratospheric temperatures, PSCs are no longer present and the concentration of the reservoir species increases again.

c) Why do we speak of an Antarctic, and not an Arctic ozone hole? Explain shortly. (max. 8 lines) (1 point)

In the Antarctic, the polar vortex is much stronger and longer persisting which enables cold stratospheric temperatures and the formation of PSCs, which lead to substantial ozone destruction by heterogeneous chemistry. In the northern Hemisphere, the polar vortex is weaker and shorter lived and stratospheric temperatures are warmer, so PSC formation and substantial ozone depletion occur only rarely.

Additional info: By convention, over Antarctica the ozone hole is the region with total ozone of 220 DU or lower. In March 2019/2020, there was strong ozone depletion in the Arctic, so it could be termed ozone hole. Yet, the term "depletion" is prefered over the Arctic, since the ozone loss is still much less than the annual ozone "hole" over Antarctica in austral spring.

4 Tropospheric chemistry: gas and aerosol-phase (12 points)

During the lectures, the sources and sinks of the OH radical were discussed in detail and the reservoir molecule HONO (nitrous acid) was introduced. HONO is a dominant source of OH in many polluted environments and therefore it is important to understand the formation of HONO in highly polluted environments in order to understand the concentration and distribution of key atmospheric radical species, as well as secondary products such as secondary organic aerosols and ground level ozone which are associated with reduced air quality.

4.1 HONO (1 point)

The sources of HONO depend on the environment and are both gas and aerosol phase. While the gas phase sources of HONO are fairly well constrained, there is still debate and work being done to identify and constrain heterogeneous sources of HONO both in urban and non-urban and marine environments.

a) An example of one such proposed heterogeneous source would be bacterial production of nitrates on soil surfaces. By looking at the literature articles within peer-reviewed journals (using *Google Scholar* for example), please provide 3 tropospheric heterogeneous sources of HONO. Please also provide the bibliographic reference(s) for your answer. (0.5 points)

Conversion of nitric acid on ground or canopy surfaces, particulate nitrate photolysis, photo-enhanced NO_2 conversion on surfaces like soot or humic acid; photolysis of PAN, production from biomass burning aerosols, HONO production from blowing snow/snow and ice.

b) Why is night-time HONO chemistry important with regards to the formation of the OH radical? (3 lines max.) (0.5 points)

Because there is no sunlight for photolysis, HONO accumulates during the night. The accumulated HONO is rapidly photolyzed when the sun rises, which releases OH radicals.

4.2 HNO_3 aerosols in the marine boundary layer (4 points)

In recent years, interest in particulate nitrate as a source of HONO in the remote marine boundary layer (MBL) has increased. The concentrations of HONO are lower in the marine boundary layer due to the very low concentration of NO_x (NO + NO_2). The combination of low NO_x, in addition to high concentrations of water vapour and halogen compounds (for example Cl and Br radicals) results in net daytime ozone destruction.

a) Why do low concentrations of: i) Water vapour, ii) NO_x and iii) halogens each contribute

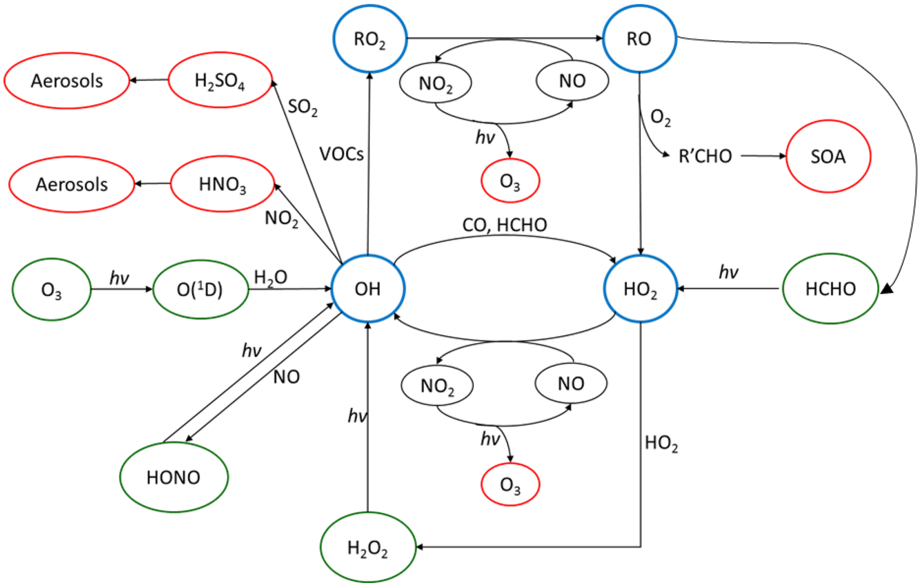

Figure 9: Generic HOx cycle as shown in lecture

to the net daytime loss of OH from the troposphere (i.e., how the sources of OH vary when varying these conditions).
Hint 1: Consider the question within the stratospheric portion of the assignment and how halogens, in a similar way to this, effect the sources of OH in the troposphere.
Hint 2: Using the HO_x cycle (in your lecture slides) and how halogens can affect it, provide a short explanation and relevant equations to fully answer i), ii), and iii) (3 points)

The idea of this question is to show understanding of the HO_x cycle by explaining what would happen to ozone if i, ii, iii were changed.

i) Less water vapour means less production of OH from O(^{1}D), i.e, the main production source of OH from ozone is reduced.

$$O_3 + h\nu \longrightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \longrightarrow 2\,OH$$

ii) The second largest source of OH is HONO but with less NO to form HONO, the OH source will be less. Less NO, means less HONO. More NO_x also increases titration of O_3, leading to less OH. Less NO also reduces the reaction of HO_2 leading back to OH. (We are looking for at least one of these answers)

$$HONO + h\nu \longrightarrow OH + NO$$

$$\mathrm{OH + NO \longrightarrow HONO}$$

iii) Halogens remove O_3 from the atmosphere. Less O_3, means the main source of OH is reduced. (Any halogen used in the equations below is okay)

$$\mathrm{X + O_3 \longrightarrow XO + O_2}$$

$$\mathrm{XO + O \longrightarrow X + O_2}$$

$$\mathrm{O_3 + h\nu \longrightarrow O_2 + O(^1D)}$$

$$\mathrm{O(^1D) + H_2O \longrightarrow 2\,OH}$$

b) A sink of HONO in the marine boundary layer is the reaction with NO_2. The concentrations of NO_x in the MBL are controlled by the oxidation of NO_2 by OH to give HNO_3. Other gas phase sinks of NO_x in the MBL are listed below, along with the aerosol phase sinks:

$$\mathrm{NO_2 + OH + M \longrightarrow HNO_3 + M} \tag{7}$$

$$\mathrm{HNO_3 + h\nu \longrightarrow OH + NO_2} \tag{8}$$

$$\mathrm{HNO_3 + OH \longrightarrow NO_3 + H_2O} \tag{9}$$

$$\mathrm{HNO_{3(g)} + aerosol \longrightarrow HNO_{3(aer)}} \tag{10}$$

$$\mathrm{N_2O_5 + H_2O_{(aer)} \longrightarrow 2\,HNO_{3(aer)}} \tag{11}$$

The rate of partitioning of HNO_3, $K_p = \frac{[\mathrm{HNO_3}]_{aerosol}}{[\mathrm{HNO_3}]_{gas}}$ describes the equilibrium between the gas and aerosol phases of HNO_3.

i) Name 2 factors that influence the partitioning of HNO_3? (0.5 points)

Relative humidity and temperature.

ii) How would you study the partitioning behaviour of HNO_3 experimentally? Please answer within 6 lines. (0.5 points)

Any of these answers are reasonable though only one is required:
1. Chamber/lab studies looking at the concentration of all reactants and products in both phases as a function of time, concentration of NO_2/OH, temperature/humidity, etc. (understanding that you can study kinetics in the lab or field).
2. In the field taking ambient measurements and analysing them for gas vs. aerosol phase HNO_3.

4.3 Aerosol Solubility (5 points)

The amount of a volatile gas that will dissolve in a condensed phase aerosol is directly proportional to the partial pressure of the gas in equilibrium with the aerosol, as stated in Henry's law which is commonly expressed as (in the case of HNO_3):

$$[\mathrm{HNO_3}] = H_{\mathrm{HNO_3}} \cdot p_{\mathrm{HNO_3}} \tag{12}$$

where $H_{\mathrm{HNO_3}}$ is the Henry's law constant for HNO_3 and $\rho_{\mathrm{HNO_3}}$ is the partial pressure of HNO_3.

a) Explain under what conditions Henry's law applies. (0.25 points)

Henry's law applies to ideal-dilute solutions.

b) Raoult's law also pertains to aqueous phase chemistry, such as that which occurs on the surface of aqueous aerosols. Give a short description of Raoult's law and state under what conditions it applies. (0.5 points)

Raoult's law states that the equilibrium partial pressure of species A over an ideal solution is equal to the saturation vapour pressure of this species in pure form times its mole fraction in solution. This law applies for ideal solutions and is commonly used to describe the vapour pressure of volatile compounds in solution.

c) What assumption do both Raoult's and Henry's law make? Describe one other assumption/limitation for each of the laws (0.75 points).

Both laws make the assumption that the solution is ideal. Raoult's law applies only under constant temperature AND pressure, whereas Henry's law applies under constant temperature only. Henry's law assumes there is no chemical reaction between the gas and the solvent in the system.

The effective Henry's law constant, K_H^*, describes the solubility of a gas in a solution, accounting for reactions and equilibria. Strong acids such as HNO_3 dissociate nearly fully into solution so the concentration of the undissociated acid is negligible compared to that of the dissociated ions (in this case H^+ and $NO_3{}^-$). This means there is no need to consider dissociation equilibrium, making it experimentally easier to determine K_H, which for strong acids is equal to K_H^*.

Weak acids, such as HO_2, however, do not dissociate fully into solution. This means that the pH of the aerosol can have an effect on the equilibrium of the dissociation of HO_2 to give $O_2{}^-$ and H^+, meaning that the pH of the aerosol will determine how much HO_2 can enter the aqueous aerosol phase. This is due to Le Chateliers principle. Le Chateliers principle states that if a system in equilibrium is subjected to a change in environment, the system will adjust to counteract this change.

$$K_H^* = H_{\mathrm{HO_2}}(1 + \frac{K_{eq}}{[\mathrm{H}^+]}) \tag{13}$$

The K_{eq} for $\mathrm{HO_2}$ is shown below:

$$K_{eq} = \frac{[\mathrm{H}^+][\mathrm{O_2}^-]}{[\mathrm{HO_2}]}) \tag{14}$$

d) At high aerosol acidity, i.e., low pH, will the solubility of $\mathrm{HO_2}$ be higher or lower than at pH 7, and why? Please give your answer within 4 lines. (0.5 points)

   At low pH, there are more H^+ ions in solution. This unbalances the equilibrium with $\mathrm{HO_2}$'s conjugate base, and forces the reaction back in the direction of $\mathrm{HO_2}$ (i.e., out of solution) to counteract the increase in H^+, and less $\mathrm{HO_2}$ will enter the aqueous phase. Therefore at low pH, the solubility of $\mathrm{HO_2}$ is lower than at pH 7.

e) Use Raoult's law to calculate the vapour pressure reduction (in %) over a water drop of a 0.2 µm radius with a NaCl particle dissolved in it. (3 points)

   The dissolved aerosol particles have a diameter of 0.15 µm. The influence of the radius of curvature on the vapour pressure can be neglected in this example.

   Raoult's law :

$$p_A = x_A \cdot p_A^* \tag{15}$$

with: p_A : vapour pressure above solution
p_A^* : vapour pressure of the pure solvent
x_A : mole fraction of the solvent in the solution

Mole fraction:

$$x_A = \frac{n_{water}}{n_{water} + n_{salt}} \tag{16}$$

with:

$$n_{water} = \frac{\rho_{water} \cdot \frac{4}{3}\pi r_{droplet}^3}{18.015\,\mathrm{g\,mol^{-1}}} \tag{17}$$

$$n_{salt} = \frac{\rho_{salt} \cdot \frac{\pi}{6} D_{particle}^3}{M_{m,salt}} \tag{18}$$

with $\rho_w = 1\,\mathrm{g\,cm^{-3}}$
$M_{m,water} = 18.015\,\mathrm{g\,mol}$

$\rho_{\mathrm{NaCl}} = 2.17\,\mathrm{g\,cm^{-3}}$
$M_{m,\mathrm{NaCl}} = 58.443\,\mathrm{g\,mol}$
$\rho_{\mathrm{NH_4NO_3}} = 1.72\,\mathrm{g\,cm^{-3}}$
$M_{m,\mathrm{NH_4NO_3}} = 80.043\,\mathrm{g\,mol}$

0.2 µm droplets with NaCl particle:

$$n_{water} = \frac{10^6\,\mathrm{g\,m^{-3}} \cdot \frac{4}{3}\pi \cdot (2 \times 10^{-7}\,\mathrm{m})^3}{18.015\,\mathrm{g\,mol^{-1}}} = 1.8601 \times 10^{-15}\,\mathrm{mol} \tag{19}$$

$$n_{salt} = \frac{2.17 \times 10^6\,\mathrm{g\,m^{-3}} \cdot \frac{\pi}{6} \cdot (1.5 \times 10^{-7}\,\mathrm{m})^3}{58.443\,\mathrm{g\,mol^{-1}}} = 6.5614 \times 10^{-17}\,\mathrm{mol} \tag{20}$$

$$x = \frac{n_{water}}{n_{water} + n_{salt}} = 0.966 \tag{21}$$

The vapour pressure reduction due to the dissolved NaCl is $-3.4\,\%$.

4.4 Aerosol data (2 points)

Aerosol particles in the atmosphere can undergo transformations in size and composition through various processes, such as condensation, coagulation, and deposition. Condensation occurs when vapor-phase molecules adhere to an existing particle, causing it to grow in size. Coagulation involves the collision of aerosol particles, which results in their merging to form larger particles. Deposition, on the other hand, refers to the process where particles settle onto surfaces.

In the lecture series you were introduced to aerosol number, surface area and volume size distributions and the concept of lognormal distributions and why these are used when dealing with aerosol data.

The table shows a measured size distribution of aerosol particles.

Size range (μm)	0-3	3-5	5-8	8-9	9-11	11-14	14-16	16-20	20-32	32-44	>44
Count ($\mathrm{cm^{-3}}$)	94	150	250	90	170	155	59	75	92	18	0

a) Plot a histogram of counts in $\mathrm{cm^{-3}}$ versus particle diameter. (0.5 points)
Hint: you will need to calculate the geometric mean diameter of each bin, assuming a lower bin value of 0.2 μm and the highest bin uppermost diameter is 62 μm.

Plots shown on next page (Fig. 10).

b) Plot a histogram of the so-called $\frac{dN}{d\log D_p}$ where the bin count is divided by the logarithm of the upper bin boundary minus the logarithm of the lower bin boundary and plotted against particle size with a logarithmic x-axis. (0.5 points)

Plots shown on next page (Fig. 11).

c) Consider a scenario where ambient aerosol particles are growing by condensation while coagulation processes are present but without deposition processes. How would you expect the aerosol size distribution to evolve over time for number and surface area? Please answer this question within 8 lines. (1 point)

Number Size Distribution: Initially, smaller particles will dominate due to higher condensation rates. However, as particles grow, coagulation will lead to the formation of larger particles, causing a shift towards larger particle sizes in the distribution over time.

Surface Area Size Distribution: While condensation contributes to an increase in surface area, coagulation tends to decrease it as smaller particles combine into larger ones. Thus, the surface area distribution may initially increase but then reach a plateau or even decrease as coagulation becomes dominant.

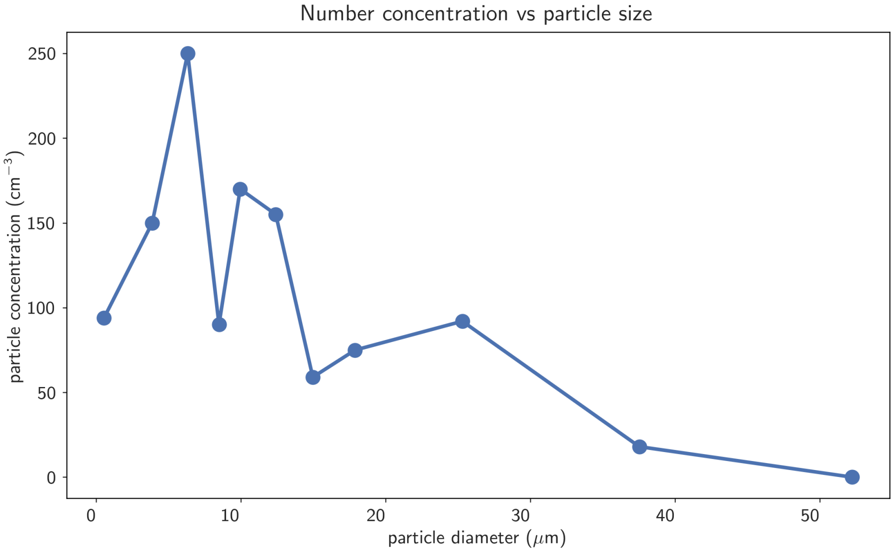

Figure 10: Count vs Particle Size

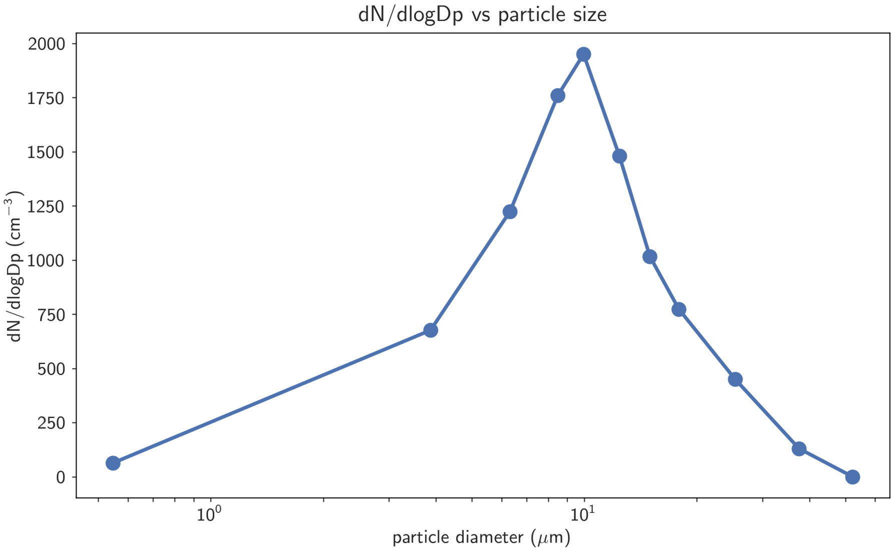

Figure 11: dNdlogDp vs Particle Size