PROBLEMS

3. 1 **Atmospheric steady state**

A power plant emits a pollutant X to the atmosphere at a constant rate E (kg s^{-1}) starting at time $t = 0$. X is removed from the atmosphere by chemical reaction with a first-order rate constant k (s^{-1}).

1. Let m be the mass of X in the atmosphere resulting from the power plant emissions. Write an equation for $m(t)$. Plot your results. What is the steady-state value m_∞?

2. Show that the atmospheric lifetime of X is $\tau = 1/k$. What is the ratio $m(t)/m_\infty$ at time $t = \tau$? At time $t = 3\tau$?

3. If the power plant were to suddenly cease operations, how long would it take for m to decrease from its steady state value m_∞ to 5% of that value?

### 3. 2 **Ventilation of pollution from the United States**

We model the lower atmosphere over the United States as a well-mixed box extending horizontally 5,000 km in the west-east direction. The box is ventilated by a westerly wind of speed $U = 10$ m s^{-1}.

1. What is the residence time τ_{out} (in days) of air in the lower atmosphere over the United States?

2. Consider a pollutant emitted in the United States and having a lifetime τ_{chem} against chemical loss. Calculate the fraction f of the pollutant exported out of the United States box as a function of the ratio τ_{out}/τ_{chem}. Plot your result. Comment on the potential for different pollutants emitted in the United States to affect the global atmosphere.

3. 3 **Stratosphere-troposphere exchange**

The rate of exchange of air between the troposphere and the stratosphere is critical for determining the potential of various pollutants emitted from the surface to reach the stratosphere and affect the stratospheric ozone layer. One of the first estimates of this rate was made in the 1960s using measurements of strontium-90 (^{90}Sr) in the stratosphere. Strontium-90 is a radioactive isotope (half-life 28 years) produced in nuclear explosions. It has no natural sources. Large amounts of ^{90}Sr were injected into the stratosphere in the 1950s by above-ground nuclear tests. These tests were banned by international treaty in 1962. Following the test ban the stratospheric concentrations of ^{90}Sr began to

decrease as ^{90}Sr was transferred to the troposphere. In the troposphere, ^{90}Sr is removed by wet deposition with a lifetime of 10 days (by contrast there is no rain, and hence no wet deposition, in the stratosphere). An intensive stratospheric measurement network was operated in the 1960s to monitor the decay of ^{90}Sr in the stratosphere. We interpret these observations here using a 2-box model for stratosphere-troposphere exchange with transfer rate constants k_{TS} and k_{ST} (yr^{-1}) between the tropospheric and stratospheric reservoirs. The reservoirs are assumed to be individually well-mixed.
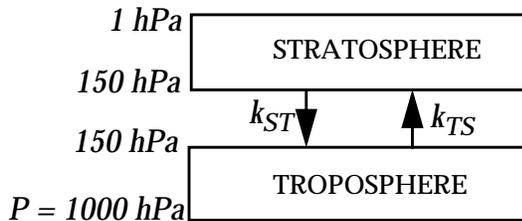
Let m_S and m_T represent the masses of ^{90}Sr in the stratosphere and in the troposphere respectively. Observations of the decrease in the stratospheric inventory for the period 1963-1967 can be fitted to an exponential $m_S(t) = m_S(0)\exp(-kt)$ where $k = 0.77$ yr^{-1}.

1. Write mass balance equations for m_S and m_T in the 1963-1967 period.

2. Assuming that transfer of ^{90}Sr from the troposphere to the stratosphere is negligible (we will verify this assumption later), show that the residence time of air in the stratosphere is $\tau_S = 1/k_{ST} = 1.3$ years.

3. Let m'_T and m'_S represent the total masses of air in the troposphere and the stratosphere, respectively. Show that the residence time of air in the troposphere is $\tau_T = \tau_S (m'_T/m'_S) = 7.4$ years. Conclude as to the validity of your assumption in question 2.

4. Hydrochlorofluorocarbons (HCFCs) have been adopted as replacement products for the chlorofluorocarbons (CFCs), which were banned by the Montreal protocol because of their harmful effect on the ozone layer. In contrast to the CFCs, the HCFCs can be oxidized in the troposphere, and the oxidation products washed out by precipitation, so that most of the HCFCs do not penetrate into the stratosphere to destroy ozone. Two common HCFCs have trade names HCFC-123 and HCFC-124; their lifetimes against oxidation in the troposphere are 1.4 years and 5.9 years, respectively. There are no other sinks for these species in the troposphere. Using our 2-box model, determine what fractions of the emitted HCFC-123 and HCFC-124 penetrate the stratosphere.

[To know more: Holton, J.R., et al., Stratosphere-troposphere exchange, *Rev.*

Geophys., 33, 403-439, 1995.]

3. 4 Interhemispheric exchange

In this problem we use observations of the radioactive gas ^{85}Kr to determine the characteristic time for exchange of air between the northern and southern hemispheres. We consider a 2-box model where each hemisphere is represented by a well-mixed box, with a rate constant k (yr^{-1}) for mass exchange between the two hemispheres. Our goal is to derive the residence time $\tau = 1/k$ of air in each hemisphere.

Krypton-85 is emitted to the atmosphere during the reprocessing of nuclear fuel. It is removed from the atmosphere solely by radioactive decay with a rate constant $k_c = 6.45 \times 10^{-2}$ yr^{-1}. The sources of ^{85}Kr are solely in the northern hemisphere and their magnitudes are well known due to regulation of the nuclear industry. Atmospheric concentrations of ^{85}Kr are fairly well known from ship observations. In 1983 the global ^{85}Kr emission rate was $E = 15$ kg yr^{-1}, the total atmospheric mass of ^{85}Kr in the northern hemisphere was $m_N = 93$ kg, and the total atmospheric mass of ^{85}Kr in the southern hemisphere was $m_S = 86$ kg.

1. Assume that the interhemispheric difference in the atmospheric mass of ^{85}Kr is at steady state, that is, $d(m_N - m_S)/dt = 0$ (we will justify this assumption in the next question). Express τ as a function of E, k_c, m_N, m_S and solve numerically using the 1983 values.

2. The global emission rate of ^{85}Kr was increasing during the 1980s at the rate of 3% yr^{-1}. Justify the assumption $d(m_N - m_S)/dt = 0$. [Hint: use the mass balance equation for $(m_N - m_S)$ to determine the time scale needed for $(m_N - m_S)$ to adjust to steady state following a perturbation.]

[To know more: Jacob, D. J., et al., Atmospheric distribution of ^{85}Kr simulated with a general circulation model, *J. Geophys. Res., 92*, 6614-6626, 1987.]

3. 5 Long-range transport of acidity

A cluster of coal-fired power plants in Ohio emits sulfur dioxide (SO_2) continuously to the atmosphere. The pollution plume is advected to the northeast with a constant wind speed $U = 5$ m s^{-1}. We assume no dilution of the plume during transport. Let $[SO_2]_o$ be the concentration of SO_2 in the fresh plume at the point of emission; SO_2 in the plume has a lifetime of 2 days against oxidation to sulfuric acid (H_2SO_4), and H_2SO_4 has a lifetime of 5 days against wet deposition. We view both of these sinks as first-order processes ($k_1 = 0.5$ day^{-1}, k_2

= 0.2 day^{-1}). Calculate and plot the concentrations of SO_2 and H_2SO_4 as a function of the distance x downwind of the power plant cluster. At what distance downwind is the H_2SO_4 concentration highest? Look up a map and see where this acid rain is falling.

3. 6 Box vs. column model for an urban airshed

Consider an urban area modeled as a square of side L and mixing height h, ventilated by a steady horizontal wind of speed U (see Figure). A gas X is emitted at a constant and uniform rate E (molecules m^{-2} s^{-1}) in the urban area. The gas is assumed inert: it is not removed by either chemistry or deposition. The air flowing into the urban area contains zero concentration of X.

constant emission E
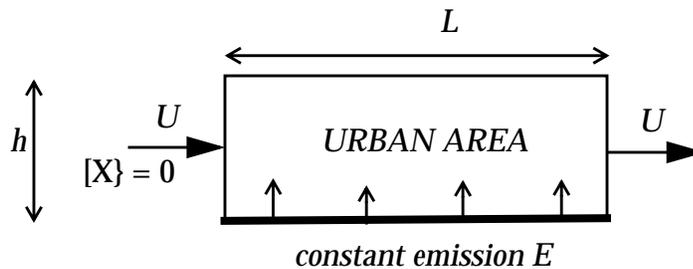
What is the mean number density of X in the urban area computed with

(a) a steady-state box model for the urban area assuming X to be well-mixed within the box?

(b) a puff (column) model for the urban area?

Explain the difference in results between the two models.

3. 7 The Montreal protocol

The 1987 Montreal protocol was the first international agreement to control emissions of chlorofluorocarbons (CFCs) harmful to the ozone layer. It was subsequently amended (London 1990, Copenhagen 1992) to respond to the increased urgency created by 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 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 = 1.0x10^{10} kg and the emission rate was $E = 4$x10^8 kg yr^{-1}.

1. The initial Montreal protocol called for a 50% reduction of CFC emissions by 1999 and a stabilization of emissions henceforth. Consider a future scenario where CFC-12 emissions are held constant at 50% of 1989 values. Show that the mass of CFC-12 in the atmosphere would eventually approach a steady-state value $m = 2$x10^{10} kg, higher than the 1989 value. Explain briefly why the CFC-12

abundance would *increase* even though its emission *decreases.*

2. 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 to the 1989 value.

3. What would have happened if the Montreal protocol had been delayed by 10 years? Consider a scenario where emissions are held constant from 1989 to 2006 and then drop to zero as of 2006. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Briefly conclude as to the consequences of delayed action.