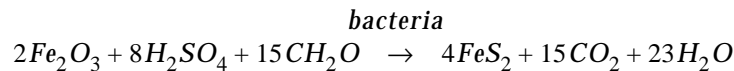


PROBLEMS

6. 1 Short questions on the oxygen cycle

1. Comment on the following statement: "Destruction of the tropical rainforests, the lungs of the Earth, menaces the supply of atmospheric oxygen"
2. A developer in Amazonia has a plan to *raise* the levels of atmospheric oxygen by cutting down the rainforest and replacing it with a managed forest. The managed forest would be cut every 20 years, the cut trees would be sealed in plastic bags loaded with weights, and the bags would be dumped to the bottom of the ocean. What is the developer's reasoning? Would the plan work? Why or why not?
3. In oxygen-depleted (*anoxic*) muds on the ocean floor, bacteria derive energy by using Fe_2O_3 and H_2SO_4 to oxidize organic material. The stoichiometry of the reaction is as follows (" CH_2O " represents the organic material):



This reaction represents an important source of atmospheric oxygen. Why? Where do Fe_2O_3 and H_2SO_4 originate from? Comment on the role of the reaction in the oxygen cycle.

4. Hydrogen atoms are produced in the upper atmosphere by photolysis of water vapor and can then escape to outer space because of their light mass. This escape of H atoms is effectively a source of O_2 to the atmosphere; explain why. The present-day rate of H atom escape to outer space is $5.4 \times 10^7 \text{ kg H yr}^{-1}$. Assuming that this rate has remained constant throughout the history of the Earth (4.5×10^9 years), calculate the resulting accumulation of oxygen. Is this an important source of oxygen?
5. Atmospheric O_2 shows a small seasonal variation. At what time of year would you expect O_2 to be maximum? Explain briefly. Estimate the amplitude of the seasonal cycle at Mauna Loa, Hawaii.

6. 2 Short questions on the carbon cycle

1. Does growth of corals ($\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(\text{s})$) cause atmospheric CO_2 to increase or decrease? Explain briefly.
2. There are no sinks of CO_2 in the stratosphere. Nevertheless, the CO_2 mixing ratio in the stratosphere is observed to be 1-2 ppmv lower than in the troposphere. Explain.

[Source: Boering, K.A., et al., Stratospheric mean ages and transport rates from observations of CO_2 and N_2O , *Science*, 274, 1340, 1996]

3. Humans ingest organic carbon as food and release CO_2 as product. As the

world population grows, will increased CO₂ exhalation from humans contribute to increasing CO₂ in the atmosphere?

4. A consequence of global warming is melting of the polar ice caps. This melting decreases deep water formation. Why? Would this effect represent a negative or positive feedback to global warming? Briefly explain.

5. Comment on the statement: “Planting trees to reduce atmospheric CO₂ is not an appropriate long-term strategy because the organic carbon in the trees will return to atmospheric CO₂ in less than a century”.

6.3 Atmospheric residence time of helium

Helium (He, atomic weight 4 g mol⁻¹) and argon (Ar, atomic weight 40 g mol⁻¹) are both produced in the Earth's interior and exhaled to the atmosphere. Helium is produced by radioactive decay of uranium and thorium; argon is produced by radioactive decay of potassium-40 (⁴⁰K). Both helium and argon, being noble gases, are chemically and biologically inert and are negligibly soluble in the ocean. Present-day atmospheric mixing ratios of helium and argon are 5.2 ppmv and 9340 ppmv, respectively.

1. Atmospheric argon has no sink and has therefore gradually accumulated since Earth's formation 4.5x10⁹ years ago. In contrast, atmospheric helium has a sink. What is it?

2. Show that the average source of argon to the atmosphere over Earth's history is $\bar{P}_{Ar} = 1.5 \times 10^7 \text{ kg yr}^{-1}$.

3. Potassium-40 has no sources in the Earth's interior and decays radioactively with a rate constant $k = 5.5 \times 10^{-10} \text{ yr}^{-1}$. Hence the source of argon has decreased gradually since Earth's formation. Let $P_{Ar}(\Delta t)$ represent the present-day source of argon, where $\Delta t = 4.5 \times 10^9$ years is the age of the Earth. Show that

$$\frac{P_{Ar}(\Delta t)}{\bar{P}_{Ar}} = \frac{k\Delta t}{\exp(k\Delta t) - 1} = 0.23$$

4. Observations in geothermal and bedrock gases show that the present-day sources of atmospheric helium and argon (kg yr⁻¹) are of the same magnitude: $P_{Ar}(\Delta t) \approx P_{He}(\Delta t)$. Deduce the residence time of helium in the atmosphere.

6.4 Methyl bromide

Methyl bromide (CH₃Br) is the principal source of bromine in the stratosphere and plays an important role in stratospheric O₃ loss. It is emitted to the atmosphere by a number of anthropogenic sources (agricultural fumigants, leaded gasoline...) and also has a natural source from biogenic activity in the ocean. There has been much recent interest in quantifying the relative magnitude of the anthropogenic vs. natural sources. This problem surveys some of the current understanding.

1. Atmospheric lifetime of CH_3Br

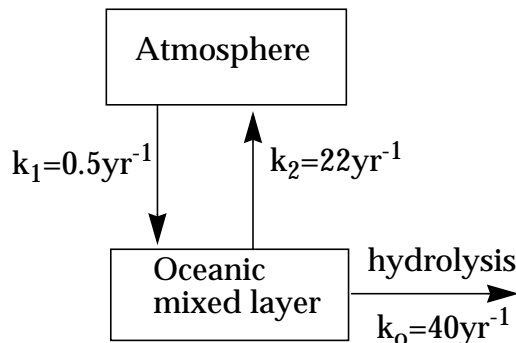
The main sinks for atmospheric CH_3Br are oxidation in the atmosphere and uptake by the ocean. The lifetime of CH_3Br against atmospheric oxidation is known with good confidence to be 2.0 years (see chapter 11). We focus here on determining the lifetime against uptake by the ocean and the implications for transport of CH_3Br to the stratosphere.

1.1 The Henry's law constant for CH_3Br in seawater is

$$K_H = \frac{[\text{CH}_3\text{Br}(aq)]}{P_{\text{CH}_3\text{Br}}} = 0.11 \text{ M atm}^{-1}$$

and the volume of the oceanic mixed layer is 3.6×10^{19} liters. Calculate the equilibrium fractionation $n_{\text{ocean}}/n_{\text{atm}}$ of CH_3Br between the atmosphere and the oceanic mixed layer, where n_{atm} is the total number of moles of CH_3Br in the atmosphere and n_{ocean} is the total number of moles of CH_3Br in the oceanic mixed layer.

1.2 You should have found in question 1.1 that the oceanic mixed layer contains only a small amount of CH_3Br compared to the atmosphere. However, ocean uptake can still represent an important sink of atmospheric CH_3Br due to rapid hydrolysis of $\text{CH}_3\text{Br}(aq)$ in the ocean. The Figure below shows a 2-box model for CH_3Br in the atmosphere-ocean system. The rate constant for hydrolysis of $\text{CH}_3\text{Br}(aq)$ is $k_0 = 40 \text{ yr}^{-1}$. The transfer rate constants for CH_3Br from the atmosphere to the oceanic mixed layer, and from the oceanic mixed layer to the atmosphere, are $k_1 = 0.5 \text{ yr}^{-1}$ and $k_2 = 22 \text{ yr}^{-1}$. Show that the atmospheric lifetime of CH_3Br against loss by hydrolysis in the oceans is $\tau = (k_0 + k_2) / k_0 k_1 = 3.3$ years.



1.3 Could significant quantities of CH_3Br be transferred from the oceanic mixed layer to the deep ocean? (That is, can the deep ocean represent a large reservoir for CH_3Br , as it does for CO_2 ?) Briefly explain.

1.4 By considering the sinks from both atmospheric oxidation and hydrolysis in

the oceans, show that the overall atmospheric lifetime of CH_3Br is 1.2 years.

1.5 Based on the answer to 1.4, and using a rate constant $k_{TS} = 0.14 \text{ yr}^{-1}$ for transfer of air from the troposphere to the stratosphere, estimate the fraction of emitted CH_3Br that enters the stratosphere and is thus active in O_3 depletion.

2. *A 2-box model for atmospheric CH_3Br*

We now use data on the tropospheric distribution of CH_3Br to constrain the importance of the anthropogenic source. Observations indicate an interhemispheric ratio $R = m_N/m_S = 1.3$ for CH_3Br , where m_N and m_S are the masses of CH_3Br in the northern and southern hemispheres respectively. Let us interpret this ratio using a two-box model for the troposphere where the northern and southern hemispheres are individually well mixed and the transfer rate constant for air between the two hemispheres is $k = 0.9 \text{ yr}^{-1}$ (problem 3. 4). We assume that CH_3Br is at steady state and is removed from the atmosphere with a rate constant $k' = 0.8 \text{ yr}^{-1}$ (corresponding to a lifetime of 1.2 years, as derived in section 1 of this problem).

2.1 If the source of CH_3Br were exclusively anthropogenic and located in the northern hemisphere, show that R would have a value of 1.9, higher than observed.

2.2 The discrepancy may be explained by the natural biogenic source of CH_3Br in the oceans. Assume that this biogenic source is equally distributed between the two hemispheres, as opposed to the anthropogenic source which is exclusively in the northern hemisphere. In order to match the observed value of R , what fraction of the global source must be biogenic?

2.3 Is the finding that the ocean represents a major source of CH_3Br contradictory with the finding in question 1.2 that the ocean represents a major sink? Briefly explain.

[To know more: Penkett, S.A., et al., Methyl bromide, in *Scientific Assessment of Ozone Depletion: 1994*, chap. 10, World Meteorological Organization, Geneva, 1995]

6. 5 Global fertilization of the biosphere

We apply here the box model of the nitrogen cycle presented in Figure 6-3 to examine the possibility of global fertilization of the biosphere by human activity over the past century.

1. What is the residence time of nitrogen in each of the reservoirs of Figure 6-3?

2. Consider a "land reservoir" defined as the sum of the land biota and soil reservoirs. What is the residence time of nitrogen in that reservoir? Why is it so much longer than the residence times calculated for the individual land biota and soil reservoirs?

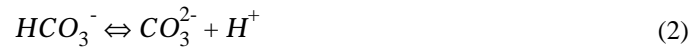
3. Human activity over the past century has affected the nitrogen cycle by

cultivation of nitrogen-fixing crops and application of industrial fertilizer to crops (increasing the land biofixation rate from 110 Tg N yr⁻¹ to 240 Tg N yr⁻¹), and by fossil fuel combustion (increasing the nitrogen fixation rate in the atmosphere from 5 Tg N yr⁻¹ to 30 Tg N yr⁻¹). Estimate the resulting percentage increases over the past century in the global nitrogen contents of the land biota reservoir and of the ocean biota reservoir. Conclude as to the extent of global fertilization of the Earth's biosphere by human activity.

[To know more: Vitousek, P.M., et al., Human alteration of the global nitrogen cycle: sources and consequences, *Ecol. Appl.*, 7, 737-750, 1997]

6.6 Ocean pH

The surface ocean is saturated with respect to CaCO₃ (this saturation is indeed necessary for the formation of sea shells). Calculate the pH of the surface ocean for present-day conditions ($P_{CO_2} = 365$ ppmv) using the observed seawater Ca²⁺ concentration [Ca²⁺] = 0.01 M and the carbonate equilibria:



Equilibrium constants are $K_H = 3 \times 10^{-2} \text{ M atm}^{-1}$, $K_1 = 9 \times 10^{-7} \text{ M}$, $K_2 = 7 \times 10^{-10} \text{ M}$, $K_W = 1 \times 10^{-14} \text{ M}^2$, $K_S = 9 \times 10^{-7} \text{ M}^2$.

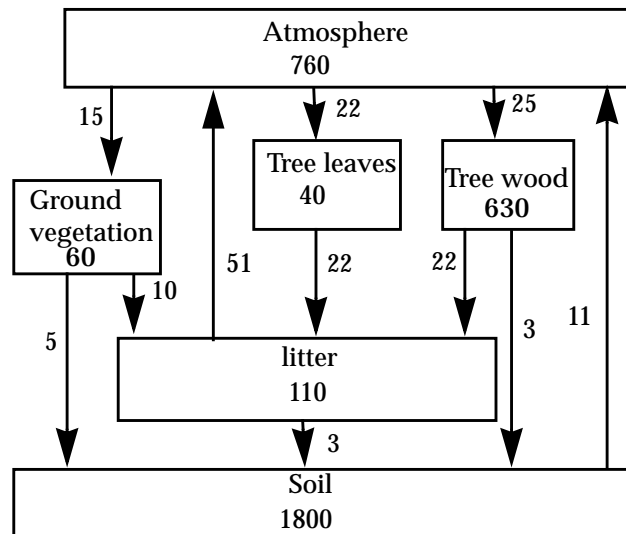
6.7 Cycling of CO₂ with the terrestrial biosphere

Consider the following global cycle of carbon between the atmosphere, the terrestrial vegetation, and the soil. Reservoirs are in units of Pg C (1 petagram = 1 × 10¹⁵ g) and flows are in units of Pg C yr⁻¹.

1. The three reservoirs "ground vegetation," "tree leaves," and "tree wood" represent collectively the "terrestrial vegetation reservoir." The flow rate of atmospheric CO₂ into this terrestrial vegetation reservoir represents the net primary productivity (NPP) of the terrestrial biosphere. Calculate the lifetime of carbon in the terrestrial vegetation reservoir against transfer to the litter and soil.

2. Tree leaves eventually fall to produce litter. What is the dominant fate of carbon in the litter? What fraction is incorporated into the soil?

3. Acid rain causes a decrease of microbial activity in the litter and in the soil. How is atmospheric CO₂ affected?



6.8 Sinks of atmospheric CO₂ deduced from changes in atmospheric O₂

Measurement of the long-term trend in atmospheric O₂ has been used to determine the fate of fossil fuel CO₂ in the atmosphere and the relative importance of uptake by the ocean and by the biosphere. We describe here the principle of the method.

1. We first examine the O₂:CO₂ stoichiometry of the individual CO₂ sources and sinks.

1.1 The mean stoichiometric composition of fossil fuel burned is CH_{1.6} (1 part carbon for 1.6 parts hydrogen). We view fossil fuel combustion as a stoichiometric reaction where CH_{1.6} is oxidized by O₂ to yield CO₂ and H₂O. Show that 1.4 moles of O₂ are consumed per mole of CO₂ emitted by fossil fuel combustion.

1.2 How many moles of O₂ are produced per mole of CO₂ taken up by the biosphere?

1.3 Is any O₂ produced or consumed when CO₂ dissolves into the ocean as CO₂:H₂O/HCO₃⁻/CO₃²⁻?

2. We are now equipped to use the method. Observations from July 1991 to July 1994 (3 years) indicate a 3.2 ppmv increase in atmospheric CO₂ and a 8.8 ppmv decrease in atmospheric O₂. Global fossil fuel combustion during this period was 6.3x10¹² kg C yr⁻¹.

2.1 If fossil fuel were the only process affecting CO₂ and O₂ concentrations during the 1991-1994 period, by how much would these concentrations have changed?

2.2 From the observed trends of atmospheric CO_2 and O_2 , determine the fraction of CO_2 emitted from fossil fuel combustion over the 3-year period that (a) was taken up by the biosphere, (b) dissolved in the oceans, (c) accumulated in the atmosphere.

[Source: Keeling, R.F., et al., Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentrations, *Nature*, 381, 218-221, 1996.]

6.9 Fossil fuel CO_2 neutralization by marine CaCO_3

We saw in chapter 6 that a fraction $f = 28\%$ of CO_2 emitted by fossil fuel combustion remains in the atmosphere once full equilibration with the ocean is achieved. We examine here how dissolution of calcium carbonate (CaCO_3) from the ocean floor can reduce f over longer time scales.

1. Explain qualitatively how dissolution of CaCO_3 from the ocean floor increases the capacity of the ocean to take up atmospheric CO_2 .

2. We assume that CaCO_3 on the ocean floor was in equilibrium with oceanic CO_3^{2-} in preindustrial times. Ocean uptake of fossil fuel CO_2 has since disrupted this equilibrium by decreasing CO_3^{2-} levels. Dissolution of CaCO_3 is a slow process, taking place on a time scale of several thousand years. By that time we will most likely have exhausted all our fossil fuel reserves. We consider a "final" state several thousand years in the future when equilibrium between CaCO_3 and oceanic CO_3^{2-} has finally been reached. Show that the oceanic CO_3^{2-} concentration in this final state is the same as in preindustrial times. [Note: the oceanic Ca^{2+} concentration is 10^{-2} M, sufficiently high not to be affected significantly by enhanced dissolution of CaCO_3 from the sea floor].

3. Show that

$$\frac{P_{\text{CO}_2, \text{final}}}{P_{\text{CO}_2, \text{preindustrial}}} = \left(\frac{[\text{HCO}_3^-]_{\text{final}}}{[\text{HCO}_3^-]_{\text{preindustrial}}} \right)^2$$

4. Global reserves of exploitable fossil fuel are estimated to be 5×10^{18} g C. Show that if all the exploitable fossil fuel were emitted to the atmosphere as CO_2 , the increase in the mass of HCO_3^- in the ocean when the "final" state is achieved would be 10×10^{18} g C. Assume as an approximation that all the emitted CO_2 enters the ocean (we will verify the quality of this approximation in the next question).

5. Infer from questions 3 and 4 the fraction of added fossil fuel CO_2 that remains in the atmosphere in the "final" state where all exploitable fossil fuel has been emitted to the atmosphere and full reequilibration of the ocean with CaCO_3 on the sea floor has been achieved. The "initial" preindustrial state is defined by a total mass of HCO_3^- in the ocean of 38×10^{18} g C and $P_{\text{CO}_2} = 280$ ppmv. Ignore

any net uptake of carbon by the biosphere.

[Source: Archer, D.H., et al., Dynamics of fossil fuel CO₂ neutralization by marine CaCO₃, *Global Biogeochem. Cycles*, 12, 259-276, 1998.]