OCE/ESS/ATM S 588 Global Carbon Cycle and Greenhouse Gases
Problem Set 2 – due in class on Thursday, February 5 2009

In this problem set you will build simple box models to determine the magnitude, partitioning, and location of methane sources. Take a look at the notes at the end of the problem set, they will help you write the mass balance equations.

1) SOURCES OF METHANE TODAY, IN PRE-INDUSTRIAL TIMES, AND DURING THE LAST GLACIAL MAXIMUM

Atmospheric and ice-core measurements have shown that the current (2000), pre-industrial (1750), and last ice age (~20,000 years ago) mixing ratios of CH_4 are: 1750 ppbv, 650 ppbv and 390 ppbv (1 ppbv = 10^{-9} v/v). Here you will infer the CH_4 sources using a simple 1-box model of the atmosphere.

   A. Calculate the mass of CH_4 in the atmosphere (in Tg, 1 Tg=10^9 kg) for each time period assuming a uniform mixing ratio in the atmosphere. Mass of the atmosphere = 5.2 10^{18} kg; molecular weight of dry air = 29×10^{-3} kg/mole; molecular weight of CH_4 = 16×10^{-3} kg/mole.

   B. Now assuming steady-state (Production=Loss) and an atmospheric lifetime of 9 years for methane, calculate the global CH_4 source for each of the time-periods.

   C. Infer the anthropogenic contribution to today's CH_4 budget. Comment.

   D. There are indications that the concentrations of the hydroxyl radical might have been 20% higher during the pre-industrial era relative to present, implying a shorter lifetime of methane at that time. Under that scenario, what would be the inferred anthropogenic sources in the current atmosphere? Comment.

2) ISOTOPIC COMPOSITION OF ATMOSPHERIC CH_4 : $\delta^{13}C$

Measurements of $\delta^{13}C$ in atmospheric CH_4 can be used to estimate the relative contributions of bacterial (wetlands, rice paddies, cattle, etc..) and non-bacterial (fossil fuel, biomass burning) CH_4 sources. Bacterial sources tend to prefer the lighter isotope and thus have a more negative $\delta^{13}C$ compared to non-bacterial sources. Here you will apply a 1-box model of atmospheric $\delta^{13}C$ (see note at the end of the problem set).

   **A.** Based on an observed $\delta^{13}C$ of –47.2‰ for atmospheric CH_4 (in today's atmosphere) calculate the average $\delta^{13}C$ isotopic composition of the CH_4 source assuming steady-state and an oxidation fractionation α=0.993.

   B. Now infer the relative contribution of bacterial and non-bacterial CH_4 sources. Use $\delta^{13}C$= -60‰ for bacterial sources and $\delta^{13}C$= -34‰ for non-bacterial sources. (hint: Assume that the average $\delta^{13}C$ isotopic composition of the CH_4 source you calculated in 2.A. is a linear combination of the bacterial and non-bacterial sources)

C. Combine your results from 2.B. and 1.D. to estimate the absolute magnitude of the fossil fuel+biomass burning source, the natural bacterial source, and anthropogenic bacterial source (rice, ruminants, landfills…). Compare your results to Table 7.6 in Chapter 7 of the IPCC report (you can look it up on the class web-site).

To learn more about methane isotopes: *"Carbon isotopic composition of atmospheric CH_4: Fossil and biomass burning source strengths" Quay, P.D. et al., Global Biogeochemical Cycles, 5, 2-47, 1991.*

3) INTER-HEMISPHERIC GRADIENT OF CH_4 AS AN INDICATOR OF SOURCE LOCATIONS
Ice core measurements in Greenland and in Antarctica show that the mixing ratios and the interhemispheric gradient of methane have changed between glacial and interglacial times, indicating changes in the magnitude and relative importance of tropical and boreal wetlands. Here you will build a 3-box model of the atmosphere to estimate the latitudinal distribution of CH_4 sources during these two time-periods. The model divides the atmosphere into three regions: 90ºS-30ºS (South, S), 30ºS-30ºN (Tropics, T) and 30ºN-90ºN (North, N). Boxes N and S each represent 25% of the total atmospheric mass, while box T represents 50% of atmospheric mass:
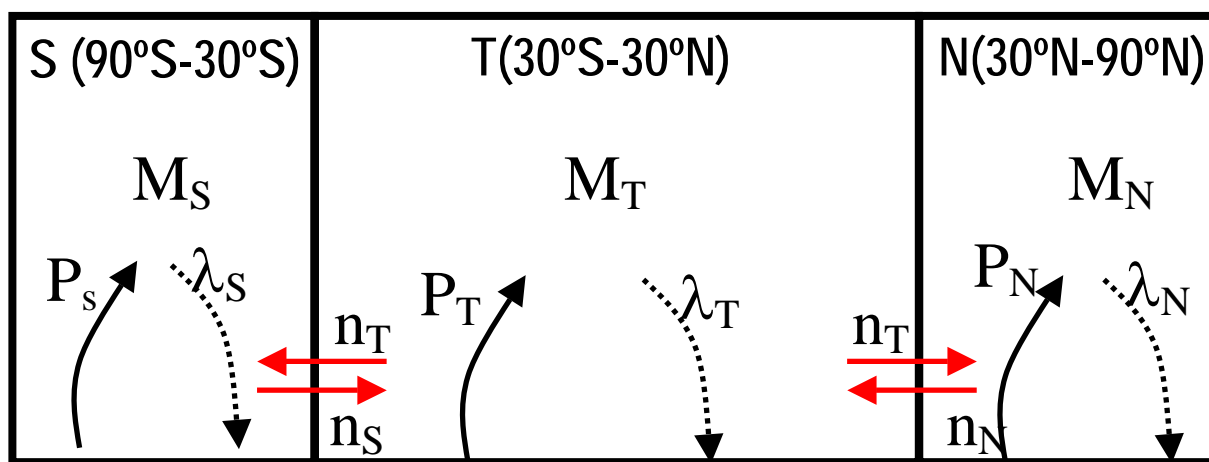
$M_{i \ (i=S,T,N)}$ mass of methane in each box [Tg]
P_i source of methane [Tg/year]
λ_i coefficient of removal [year^{-1}], defined as inverse lifetime of CH_4
n_i transport coefficient [year^{-1}], defined as inverse transport time between boxes

A. Assume that the transport coefficient between box N and T, n_n, is equal to the transport coefficient between box S and T, n_s. Show that $n_T = n_s/2 = n_n/2$

B. Write the mass balance equations controlling the mass of methane in each of the three boxes.

C. Ice core records show that methane levels during the early Holocene (~500 years ago) were equal to 710 ppbv and 675 ppbv in Greenland and in Antarctica, respectively. While during the last glacial maximum (~ 20,000 years ago), the observed values are 380 and 377 ppbv for Greenland and in Antarctica. Assume that the Greenland and

Antarctica values are representative of the Northern and Southern box and calculate the mass of methane in these two boxes for each time period. Mass of the atmosphere = 5.2 10^{18} kg.

D. You are given the following numerical values: $n_n = n_s = 1.33$ year^{-1}, $\lambda_n = 0.064$ year^{-1}, $\lambda_T = 0.15$ year^{-1}; $\lambda_S = 0.045$ year^{-1} and assume that the source of methane in the Southern box has a constant value set at 15 Tg/year. Now you have 3 equations and 3 unknowns for the equations you derived in B (M_T, P_T, and P_N). Calculate the sources of methane in the Tropical and Northern box for the Holocene and for the last glacial maximum. Comment on how climate has affected these sources and the interhemispheric CH_4 gradient.

To learn more: *"Changes in the atmospheric CH_4 gradient between Greenland and Antarctica during the Holocene" Chappellaz, J., et al., J. Geophys. Res., 102, 15987-15997, 1997.*

Notes on box models:
Here is a simple formulation for a 1-box model of atmospheric methane

$$dCH_4/dt = P - CH_4/\tau \quad [1]$$

where CH_4 is the mass of CH_4 in the atmosphere (in Tg), τ is its lifetime against oxidation (years), P is the global CH_4 source (Tg/year) and dCH_4/dt is the rate of change of atmospheric methane (Tg/year).

This 1-box model can be extended to the mass of the methane isotopes in the atmosphere. For $^{13}CH_4$:

$$d(^{13}CH_4)/dt = P \times (^{13}C/^{12}C)_s - CH_4 \times (^{13}C/^{12}C) \times \alpha/\tau \quad [2]$$

Where $^{13}CH_4$ is the mass of $^{13}CH_4$ in the atmosphere, $(^{13}C/^{12}C)$ is the $^{13}C/^{12}C$ ratio of atmospheric methane, $(^{13}C/^{12}C)_s$ is the mean $^{13}C/^{12}C$ ratio of methane sources, and α is the isotopic fractionation associated with the oxidation of CH_4. Note that the isotopic composition of atmospheric CH_4 and of its sources are often given as $\delta^{13}C$ (in per mil units):

$$\delta^{13}C = [(^{13}C/^{12}C)/(^{13}C/^{12}C)_{standard} - 1] \times 1000, \text{ with } (^{13}C/^{12}C)_{standard} = 0.011237$$