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# **Energy and Environment**

## **能源與環境**

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## *Consider a Spherical Cow*

➤ *A Course in Environmental Problem Solving*

➤ *John Harte*

*University of California, Berkeley*



John Harte holds a joint professorship in the **Energy and Resources Group** and the **Ecosystem Sciences Division** of the College of Natural Resources. He received a BA in physics from **Harvard University** in 1961 and a PhD in theoretical physics from the University of **Wisconsin** in 1965.

*It is the mark of an instructed mind to rest satisfied with the degree of precision which the nature of the subject permits and not to seek an exactness where only an approximation of the truth is possible.*

--- **Aristotle**



**Aristotle** (384 BC – March 7, 322 BC) was an ancient Greek philosopher. Student of **Plato** and teacher of **Alexadar** the Great. Aristotle and Plato are often considered as the two most influential philosophers in Western thought. He wrote many books about physics, poetry, zoology, logic, government, and biology.

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## Content

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➤ **Chapter II Tools of the Trade**

- a. Steady-state box models and residence times
- b. Thermodynamics and energy transfer
- c. Chemical reactions and equilibria
- d. Non-steady-state box models

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# Chapter I

## *Warm-up Exercise*



### ***1. Counting Cobblers and/or Dentists (1/2)***

**How many (A) cobblers and/or (B) dentists are there in United States and/or in Taiwan ?**

**A. How many cobblers are there in United States ?**

- One cobbler does 15 repair jobs in a work day;  
repair jobs in a year =  $15 \times 5 \times 4 \times 12 = 3600$
- People in United States =  $2.3 \times 10^8$  (1980)
- Shoes repaired about every four years. So repair jobs needed to be carried out for each year  
 $= 2.3 \times 10^8 / 4 = 5.75 \times 10^7$ .
- ***Cobblers in United States*** =  $5.75 \times 10^7 / 3600 = 15972$   
**~ 16000 (or 15000) ~ Approximate Answer ~ (1980)**

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## ***1. Counting Cobblers and/or Dentists (2/2)***

### **B. How many dentists are there in Taiwan ?**

- Population in Taiwan is 23 millions. Assuming people go to see the dentists four times per year in average.
- The dentist works 8 hours in a day and five days in a week. If consider holidays there are 44 weeks to work in a year.
- Assume one patient or one job takes 0.5 hour (30 min).
- So the total number of jobs done by a dentist per year  
 $= 8 \times 2 \times 5 \times 44 = 3520$
- Thus, *Dentists in Taiwan*  $= 2.3 \times 10^7 \times 4 / 3520 =$   
 $26136 \sim \mathbf{26000 \text{ or } 25000} \quad \sim \text{Approximate Answer} \sim$

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## ***2. Measuring Molecules (1/2)***

- **Benjamin Franklin dropped oil on a lake's surface and noticed that a given amount of oil could not be induced to spread out beyond a certain area. If the number of drops of oil was doubled, then so was the maximum area to which it would spread. His measurements revealed that  $0.1 \text{ cm}^3$  of oil spread to a maximum area of  $40 \text{ m}^2$ .**
- *How thick is such an oil layer?*

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## ***2. Measuring Molecules (2/2)***

- Denote the thickness of layer by the symbol  $d$  (m).
- If  $d$  is expressed in unit of meter, then the volume of that layer is  $(40d) \text{ m}^3$ .
- $(40d) = 0.1 \text{ cm}^3 = 10^{-7} \text{ m}^3$
- $d = 25 \times 10^{-10} \text{ m} = 25 \text{ Å} \sim 12\text{-}25 \text{ atoms}$

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## ***3. The Size of an Ancient Asteroid (1/3)***

It has been proposed that dinosaurs and many other organisms became extinct 65 million years ago because Earth was struck by a large asteroid (Alvarez et al. 1980). The idea is that dust from the impact was lofted into the upper atmosphere all around the globe, where it lingered for at least several months and blocked the sunlight reaching Earth's surface. On the dark and cold Earth that temporarily resulted (Pollack et al. 1983), many forms of life then became extinct. Available evidence suggests that about 20% of the asteroid's mass ended up as dust spread uniformly over Earth after eventually settling out of the upper atmosphere. This dust amounted to about  $0.02 \text{ g/cm}^2$  of Earth's surface. The asteroid very likely had a density of about  $2 \text{ g/cm}^3$ . How large was the asteroid?

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### ***3.The Size of an Ancient Asteroid (2/3)***

- Dust amount to about  $0.02 \text{ g/cm}^2$ ,
- The asteroid had a density of about  $2 \text{ g/cm}^3$
- Suggesting that about 20% of the asteroid's mass ended up as dust spread uniformly over Earth.
- Earth has an area of  $5.1 \times 10^{14} \text{ m}^2$
- The asteroid had a mass  $= 1.02 \times 10^{17} \text{ g} / 0.2 = 5.1 \times 10^{17} \text{ g}$
- The spherical asteroid mass
- $M = \rho V = \rho \times \frac{4}{3} \pi R^3 \Rightarrow 5.1 \times 10^{17} \text{ g}$   
 $= 2 \text{ g/cm}^3 \times \frac{4}{3} \pi R^3 \Rightarrow R^3 = 0.61 \times 10^{17} \text{ cm}^3 \Rightarrow \mathbf{R \sim 4 \text{ km}}$

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### ***3.The Size of an Ancient Asteroid (3/3)***

➤ *Roughly,  $R$  equals 4 km. Given the rounded-off estimates that went into the problem, it suffices to say that the diameter of the asteroid was about 10 km.*



#### 4. *Exhausting Fossil Fuel Resources (I)*

**At the 1980 global consumption rate of petroleum, how long will it take to use up the estimated worldwide resource of this fuel?**

- Using data in the Appendix:
  1. Earth's petroleum resources:  $10^{22}$  J (1980)
  2. Rate of consumption  $1.35 \times 10^{20}$  J/yr (1980)
- The lifetime of Earth's petroleum resources is

$$\begin{aligned} T &= \frac{\text{quantity of resource}}{\text{rate of consumption in 1980}} \\ &= \frac{1.0 \times 10^{22} \text{ J}}{1.35 \times 10^{20} \text{ J/yr}} = \underline{74 \text{ yr.}} \end{aligned}$$

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#### 5. *Getting Denser (1/3)*

**If the global human population continues to grow at the rate it averaged between 1950 and 1980, how long will it take for the average human population density on Earth's land to equal the present population density in typical urban areas of the world?**

- Although the problem doesn't state that **the human population has been growing exponentially**, this is a reasonable starting assumption. Hence, Let's assume that between 1950 and 1980 the population,  $N(t)$ , behaved as  $N(t) = N(0) e^{rt}$ . (1)

where  $t$  is time,  $t=0$  is 1950,  $N(0)$  is the population in 1950, and  $r$  is a parameter called the rate constant.

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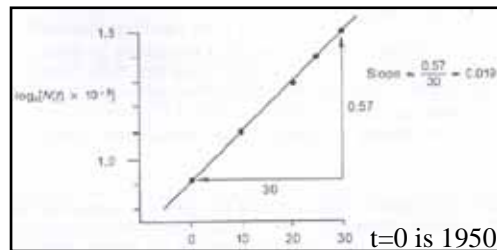
## 5. Getting Denser (2/3)

- To begin, take the natural logarithm of Eq.(1):

$$\log_e [N(t)] = \log_e [N(0)] + rt \quad (2)$$

Eq.(2) tells us that if  $\log_e [N(t)]$  is plotted as a function of  $t$ , then the relation between  $\log_e N$  and  $t$  is that of a straight line with slope  $r$ .

- A slope of about 0.019/yr is obtained. Thus **the rate constant for human population growth is about 1.9% per year.**



- The population density has to be guessed. (There's no "correct" answer.) Very large cities contain on the order of  $10^7$  people and occupy perhaps  $10^3 \text{ km}^2$ , so **let's take the urban density to be  $10^4 \text{ people/km}^2$ .**

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## 5. Getting Denser (3/3)

- If the total land area of Earth ( $1.5 \times 10^8 \text{ km}^2$ ) is potentially accessible, then the estimated 1980 population of  $4.5 \times 10^9$  people dwelled at an average density about **30 people/km<sup>2</sup>**.
- Because land area is fixed, density grows at the same rate as population. Therefore, we need only calculate how long it will take for 30 (present density) to increase exponentially to  $10^4$  (urban density) at a rate constant of 0.019/yr. Letting  $T$  denote the time period in question, we must solve the equation:

$$10^4 = 30e^{0.019T}$$

$$\Rightarrow T = \underline{\underline{305 \text{ yr}}}$$

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## 6. The Greens We Eat (1/3)

**What fraction of the total annual plant growth on Earth was eaten by humans in 1983 ?**

You must make several choices before you can calculate this fraction.

- **First, Choose your units.** You can determine the numerator and denominator in units of heat energy (e.g., calories) or in grams of carbon, dry-weight biomass, or wet-weight biomass.
- **Second, decide what is meant by annual plant growth.** Will you take the green-plant production rate to be the gross primary productivity (total photosynthetic activity) or the net primary productivity (gross productivity minus losses due to plant respiration)? The answer will depend on which you choose.
- **Third, be specific about the interpretation of human food consumption.** Specially, you can count meat consumption on the same caloric or weight basis as plant matter, or you can estimate how much plant matter it took to produce a unit of meat matter.

## 6. The Greens We Eat (2/3)

- We'll solve the problem using **energy units** and **net primary productivity (npp)**.
- From the Appendix, the rate of human net food consumption is  $1.8 \times 10^{19}$  J/yr, and the primary productivity is  $7.5 \times 10^{16}$  (C)/yr.

**This is the net amount of carbon converted from CO<sub>2</sub> to carbon-containing organic molecules each year.**

- We need the unit conversion formula to convert (C)/yr to J/yr.

**From Appendix, energy content of dry biomass is  $1.6 \times 10^4$  J/g(biomass)**

$$\text{npp (J/yr)} = \frac{\text{npp [g(C)/yr]} \times \text{energy content [J/g(biomass)]}}{\text{carbon content [g(C)/g(biomass)]}} = 3.0 \times 10^{21} \text{ J/yr}$$

The carbon content of dry biomass can be estimated by looking at Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and using its fractional carbon content as an approximation.

$$\text{carbon content} = \frac{\text{g(C)}}{\text{g(biomass)}} = \frac{72}{180} = 0.4$$

## 6. The Greens We Eat (3/3)

- The fraction of npp consumed by humans is

$$f = \frac{\text{rate of human food consumption (J/yr)}}{\text{npp (J/yr)}}$$

$$= \frac{1.8 \times 10^{19} \text{ J/yr}}{3.0 \times 10^{21} \text{ J/yr}} = \underline{0.006}$$

In words, the rate at which energy is consumed by humans as food is about 0.6% or 1/160 of the net rate at which energy is incorporated as plant matter in photosynthesis. How close was your guess?

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## 7. Sulfur in Coal

**How many tonnes and how many moles of sulfur were contained in the coal consumed worldwide in 1980?**

- tonnes of sulfur from coal combustion in 1980  
 = tonnes of coal consumed in 1980 × sulfur fraction of coal  
 =  $3.1 \times 10^9 \text{ tonnes(C)} \times 0.025 \text{ tonnes(S)/tonnes(C)}$   
 =  $7.7 \times 10^7 \text{ tonnes(S)}$
- The following units conversion is used to convert tonnes to moles:

$$\text{moles(S) from coal combustion in 1980} = \frac{\text{tonnes(S)} \times [10^6 \text{ g(S)/tonne s(S)}]}{M [\text{g(S)/mole(S)}]}$$

$$= \frac{[7.7 \times 10^7 \text{ tonnes(S)}] \times [10^6 \text{ g(S)/tonne s(S)}]}{32 \text{ g(S)/mole(S)}} = \underline{2.4 \times 10^{12} \text{ moles(S)}}$$

## Chapter II

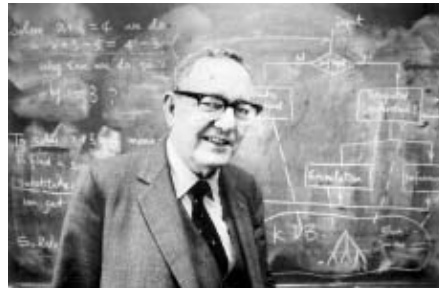
### *Tools of the Trade*

#### *A. Steady-State Box Models and Residence Times*

*...having a good question, a fundamental question, and having some tools of inquiry that allow you to take the first step toward an answer —those are the conditions that make for exciting science.*

*---Herbert A. Simon*

Here you will be handed some of the tools that form the core of environmental science. They include residence-time methods and box models, practical methods in thermodynamics and chemical equilibrium kinetics, and a few relatively simple differential equations.



## 1. School as a Steady-State System

**A college has a constant undergraduate enrollment of 14,000 students. No students flunk out or transfer in from other colleges and so the residence time of each student is four years. How many students graduate each year?**

$$\text{Steady - State condition : } F_{\text{in}} = F_{\text{out}} = \frac{M \text{ (total stock)}}{T \text{ (residence time)}}$$

$$\begin{aligned} \text{graduation rate} &= \frac{\text{total stock of students}}{\text{residence time of students}} \\ &= \frac{14,000}{4 \text{ yr}} \\ &= \underline{3,500 \text{ /yr}} \end{aligned}$$

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## 2. The Water Above

**What is the residence time of H<sub>2</sub>O in Earth's atmosphere?**

- Assume the atmospheric H<sub>2</sub>O is in steady state

$$\therefore F_{\text{w}} = F_{\text{out}}$$

$F_{\text{w}}$ : flow of H<sub>2</sub>O into the atmosphere

$F_{\text{out}}$ : the flow out = the global precipitation rate

- From the Appendix,  $F_{\text{w}} = 5.18 \times 10^{14} \text{ m}^3/\text{yr}$   
 $M_{\text{w}} = 1.3 \times 10^{13} \text{ m}^3$  (the stock of H<sub>2</sub>O)
- The residence time  $T_{\text{w}} = M_{\text{w}}/F_{\text{w}} = 0.025 \text{ yr} = \underline{9.1 \text{ days}}$

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### 3. Carbon in the Biosphere

**What are the residence times of carbon in continental and marine vegetation?**

➤ From the Appendix,

Stock of living continental biomass  $M_t = 5.6 \times 10^{15} \text{ g(C)}$

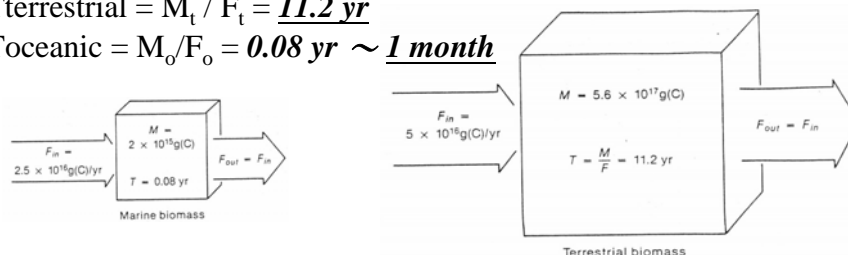
Continental net primary productivity  $F_t = 5 \times 10^{16} \text{ g(C)/yr}$

Stock of living marine plants  $M_o = 2 \times 10^{15} \text{ g(C)}$

Marine net primary productivity  $F_o = 2.5 \times 10^{16} \text{ g(C)/yr}$

➤ Terrestrial =  $M_t / F_t = 11.2 \text{ yr}$

➤ Toceanic =  $M_o / F_o = 0.08 \text{ yr} \sim 1 \text{ month}$



### 4. Natural $\text{SO}_2$ (1/2)

**Natural sources add sulfur dioxide ( $\text{SO}_2$ ) to the atmosphere at a rate of about  $10^8$  tonnes(S)/yr. The background concentration of atmospheric  $\text{SO}_2$ , measured in remote areas where anthropogenic sources are not likely to have much influence, is about 0.2 parts per billion, by volume [ppb(v)]. What is the residence time of atmospheric  $\text{SO}_2$  in the remote regions ?**

➤ Known:

Flow of  $\text{SO}_2$  to the atmosphere:  $F = 10^8$  tonnes/yr

The concentration of atmospheric  $\text{SO}_2$ :  $0.2 \times 10^{-9}$

## 4. Natural SO<sub>2</sub> (2/2)

- Let's determine how many moles of air Earth's atmosphere contains.

$$N_{\text{air}} = \frac{m}{M} = \frac{5.14 \times 10^{21} \text{ g}}{28.85 \text{ g/mol}} = 1.8 \times 10^{20} \text{ moles of air}$$

- Moles of SO<sub>2</sub> is the product of moles of air times molar fraction of SO<sub>2</sub>.

$$N_{\text{SO}_2} = (1.8 \times 10^{20}) \times (0.2 \times 10^{-9}) = 3.6 \times 10^{10} \text{ mols of SO}_2$$

- Next, we must calculate the mass of SO<sub>2</sub>

$$m_{\text{SO}_2} = 32 \times (3.6 \times 10^{10}) = 1.15 \times 10^{12} \text{ g(S)} = 1.15 \times 10^6 \text{ tonnes(S)}$$

- The residence time

$$T = \frac{m_{\text{SO}_2}}{F} = \frac{1.15 \times 10^6 \text{ tonnes(S)}}{10^8 \text{ tonnes(S)/yr}} = 0.0115 \text{ yr} = \underline{4.2 \text{ days}}$$

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## 5. Anthropogenic SO<sub>2</sub> (1/2)

**With anthropogenic sources included, what is the globally averaged SO<sub>2</sub> concentration in the atmosphere? What is the SO<sub>2</sub> concentration in industrialized regions like the northeastern United States?**

- Referring to the Appendix, anthropogenic sulfur emissions to the atmosphere were about  $8.5 \times 10^7$  tonnes(S)/yr.
- Therefore, the globally averaged total SO<sub>2</sub> concentration will be about 85% of the natural background concentration, or  $0.85 \times 0.20 \text{ ppb(v)} = \underline{0.17 \text{ ppb(v)}}$ .

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## 5. Anthropogenic SO<sub>2</sub> (2/2)

➤ Approximate regional concentration of SO<sub>2</sub> is obtained,

$$\begin{aligned}\text{Regional concentration of SO}_2 &= \frac{\text{SO}_2 \text{ concentration in the region} \times \text{The fraction of anthropogenic SO}_2 \text{ produced in the Northeast}}{\text{The fraction of Earth's area occupied by this air shed}} \\ &= \frac{0.17 \times 0.12}{0.002} = \underline{10.2 \text{ ppb(v)}}$$

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## 6. A Polluted Lake (1/2)

**A stable and highly soluble pollutant is dumped into a lake at the rate of 0.16 tonnes per day. The lake volume is  $4 \times 10^7 \text{ m}^3$  and the average water flow-through rate is  $8 \times 10^4 \text{ m}^3/\text{day}$ . Ignore evaporation from the lake surface and assume the pollutant is uniformly mixed in the lake. What eventual steady-state concentration will the pollutant reach?**

➤ Known:

The stock of water  $M_w = 4 \times 10^7 \text{ m}^3$

The rate of water flow-through  $F_w = 8 \times 10^4 \text{ m}^3/\text{day}$

The pollution input rate  $F_p = 0.16 \text{ tonnes/day}$

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## 6. A Polluted Lake (2/2)

- The residence time of water in the lake

$$T_w = \frac{M_w}{F_w} = \frac{4 \times 10^7 \text{ m}^3}{8 \times 10^4 \text{ m}^3/\text{day}} = 500 \text{ days}$$

- $\therefore T_p = T_w$  (Because the pollutant is uniformly mixed in the lake)

$$\therefore M_p = F_p T_p = 0.16 \text{ tonnes/day} \times 500 \text{ days} = 80 \text{ tonnes}$$

- If we multiply the volume of a cubic meter of water by the density of water, we discover that a cubic meter of water weighs exactly one metric ton.

$$\therefore m_w = V_w \times D_w = 4 \times 10^7 \times 1 = 4 \times 10^7 \text{ tonnes (water)}$$

- The steady-state concentration of pollutant:

$$\frac{80 \text{ tonnes pollution}}{4 \times 10^7 \text{ tonnes water}} = 2.0 \times 10^{-6} = 2 \text{ ppb(w)}$$

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## 7. The Flow of Atmospheric Pollutants between Hemisphere (1/6)

Ethane ( $\text{C}_2\text{H}_6$ ) is a constituent of natural gas. It is emitted to the atmosphere whenever natural gas escapes unburned at wells and other sources, a process that constitutes the only major source of ethane in the troposphere of the northern hemisphere,  $C_N$ , is roughly 1.0 ppb(v), and the average concentration in the southern hemisphere,  $C_S$ , is roughly 0.5 ppb(v). Ethane can exit from the troposphere by any of three mechanisms: passage to the stratosphere; chemical reaction resulting in transformation to other chemical species; and deposition to Earth's surface (for example, by washout from the atmosphere in rain or snow). It can also leave one hemisphere's troposphere by flowing to the other's.

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## 7. The Flow of Atmospheric Pollutants between Hemisphere (2/6)

Assuming that the total exit rate from each hemisphere's troposphere is proportional to the concentration in the respective troposphere, and knowing that 3% as much natural gas escapes to the atmosphere unburned as is burned, estimate net rate of ethane flow cross the equator.

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## 7. The Flow of Atmospheric Pollutants between Hemisphere (3/6)

- According to the Appendix, natural gas was burned at a rate of  $6 \times 10^{19}$  J/yr, and the energy content of natural gas is  $4 \times 10^7$  J/m<sup>3</sup>(STP). Because one mole of any gas (STP) occupied 22.4 liters, there are 44.6 moles of gas in a cubic meter. Therefore, natural gas was burned at a rate

$$R = \frac{6 \times 10^{19} \text{ J/yr}}{4 \times 10^7 \text{ J/m}^3} \times 44.6 \text{ moles/m}^3 = 6.7 \times 10^{13} \text{ moles/yr}$$

- Since natural gas escapes to the atmosphere at a rate equal to 3% of R, and since 6% (on a mole-per-mole basis) of natural gas is ethane.

$$E_N + E_S = (0.03)(0.06)(6.7 \times 10^{13} \text{ moles/yr}) = 1.2 \times 10^{11} \text{ moles/yr} \quad (1)$$

- Because nearly all natural gas is mined and vented in the northern hemisphere, we'll assume that  $E_S = 0$  (2)

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## 7. The Flow of Atmospheric Pollutants between Hemisphere (4/6)

- The **steady-state** conditions on  $X_N$  and  $X_S$  are, respectively:

$$E_N + \alpha X_S = \alpha X_N + \beta X_N \quad (3)$$

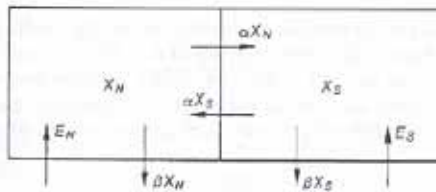
$$E_S + \alpha X_N = \alpha X_S + \beta X_S \quad (4) \quad (\text{inflow} = \text{outflow})$$

- Add the equations together:

$$E_N + E_S = \beta (X_N + X_S)$$

$$\Rightarrow \beta = \frac{E_N + E_S}{X_N + X_S} \quad (5)$$

- Substitute Eq.(5) to Eq.(3)



$X_N$ 、 $X_S$ : the amounts of ethane in the two boxes (hemispheres)

$E_N$ 、 $E_S$ : sources term (emissions to the boxes from the ground)

$\alpha X_N$ 、 $\alpha X_S$ : flow across the equator

$\beta X_N$ 、 $\beta X_S$ : sinks within each box

## 7. The Flow of Atmospheric Pollutants between Hemisphere (5/6)

- Yield the interhemispheric flow rate,

$$\begin{aligned} \alpha(X_N - X_S) &= E_N - \frac{(E_N + E_S) X_N}{X_N + X_S} \\ &= \frac{E_N X_S - E_S X_N}{X_N + X_S} \end{aligned} \quad (6)$$

- From the Appendix we learn that the number of moles in the atmosphere is  $1.8 \times 10^{20}$ , so

$$X_N = \frac{1.8 \times 10^{20} \text{ moles(air)}}{2 \text{ hemispheres}} \times 1 \times 10^{-9} \frac{\text{moles(ethane)}}{\text{moles(air)}} = 0.9 \times 10^{11} \text{ moles(ethane)} \quad (7)$$

Similarly,  $X_S = 0.45 \times 10^{11} \text{ moles(ethane)} \quad (8)$

## 7. The Flow of Atmospheric Pollutants between Hemisphere (6/6)

- Substituting Equ.(1), (2), (7) and (8) into Equ.(6), we determine the net rate of flow of ethane across the equator:

$$\begin{aligned}\alpha(X_N - X_S) &= \frac{(1.2 \times 10^{11})(0.45 \times 10^{11}) - 0}{0.9 \times 10^{11} + 0.45 \times 10^{11}} \\ &= 0.40 \times 10^{11} \text{ moles/yr}\end{aligned}$$

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## 8. A Perturbed Phosphorus Cycle (I) (1/6)

The box model shown in Figure II-8 can be used to study phosphorus cycling in a lake. In the model,  $X_1$  represents the amount of phosphorus (P) in living biomass,  $X_2$  represents the amount of phosphorus in inorganic form, and  $X_3$  represents the amount of phosphorus in dead organic material. Each  $X_i$  is in units of micromoles of phosphorus per liter of lake water.  $F_{ij}$  is the flow of phosphorus from stock  $i$  to stock  $j$ .

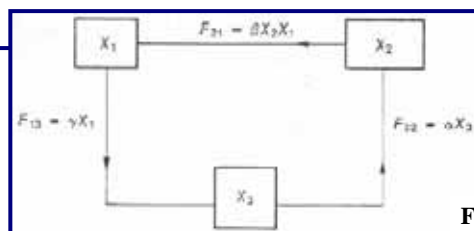


Figure II-8

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## 8. A Perturbed Phosphorus Cycle (I) (2/6)

In the steady state,  $X_1=0.2$  micromoles(P)/liter,  $X_2=0.1$  micromoles(P)/liter, and the residence time of phosphorus in living biomass is 4 days. Assume that at time  $t=0$ , the system is perturbed by the sudden addition of 0.02 micromoles(P)/liter to the inorganic phosphorus compartment, but the rate constants  $\alpha$ ,  $\beta$ , and  $\gamma$  remain unchanged. When a new steady state is reached, how much phosphorus will be in each compartment?

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## 8. A Perturbed Phosphorus Cycle (I) (3/6)

- The first step is to determine the numerical values of the rate constants  $\alpha$ ,  $\beta$ , and  $\gamma$ .

- Let the initial steady state be characterized by values of the  $X_i$  denoted  $\bar{X}_i$ .

- The steady-state conditions are derived by setting the inflow to each box equal to the outflow from that same box:

$$\beta\bar{X}_2\bar{X}_1 = \gamma\bar{X}_1 \quad (a) \quad \alpha\bar{X}_3 = \beta\bar{X}_2\bar{X}_1 \quad (b) \quad \gamma\bar{X}_1 = \alpha\bar{X}_3 \quad (c)$$

- With numerical values for the  $\bar{X}_i$  substituted in, we get

$$0.02\beta = 0.2\gamma \quad (1) \quad \alpha = 0.02\beta \quad (2) \quad 0.2\gamma = \alpha \quad (3)$$

The Eq.(3) can be derived from Eqs.(1) and (2), so this redundancy means that we don't have enough constraints to determine the three rate constants.

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## 8. A Perturbed Phosphorus Cycle (I) (4/6)

- We have to use one other piece of information — **the residence time of P in living biomass is 4 days.**

$$\frac{\bar{X}_1}{\gamma \bar{X}_1} = 4 \text{ days} \quad (4) \quad \left( \begin{array}{l} \text{The stock of P in living biomass is divided} \\ \text{by the flow of P in or out in steady-state.} \end{array} \right)$$

- Combining Eq.(4) with Eqs.(1) and (2), it follows that

$$\begin{aligned} \gamma &= (4 \text{ days})^{-1} \\ \beta &= (0.4 \text{ days})^{-1} [\text{micromoles(P)/liter}]^{-1} \\ \alpha &= (20 \text{ days})^{-1} \end{aligned}$$

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## 8. A Perturbed Phosphorus Cycle (I) (5/6)

- **Now we can solve the problem easily.**
- Call the new values of the  $X_i$ , after the perturbation and after a new steady state is reached,  $\bar{X}'_i$ .
- The  $\bar{X}'_i$  must satisfy the same steady-state equations (Eqs.1-3) satisfied by the  $\bar{X}_i$ , because the rate constants have not changed.
- The new steady-state conditions are

$$\frac{\bar{X}'_1 \bar{X}'_2}{0.4} = \frac{\bar{X}'_1}{4}, \quad \frac{\bar{X}'_3}{20} = \frac{\bar{X}'_1 \bar{X}'_2}{0.4}.$$

$\Rightarrow$

$$\bar{X}'_2 = 0.1 \text{ micromoles(P)/liter} \quad (5)$$

$$\bar{X}'_3 = 5\bar{X}'_1. \quad (6)$$

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## 8. A Perturbed Phosphorus Cycle (I) (6/6)

- Finally, we can make use of the fact that the addition of phosphorus was 0.02 micromoles(P)/liter.

- Because phosphorus flows in a closed cycle, the total amount present initially plus the amount added to the system at  $t=0$  must equal the total amount present for all times subsequent to  $t=0$ . Hence,

$$\begin{aligned}\bar{X}'_1 + \bar{X}'_2 + \bar{X}'_3 &= 0.02 + \bar{X}_1 + \bar{X}_2 + \bar{X}_3 \\ &= 0.02 + 0.2 + 0.1 + 1 \\ &= 1.320\end{aligned}\quad (7)$$

- Substituting Eqs.(5) and (6) into Eq.(7), and by Eq.(7),

$$\begin{aligned}\bar{X}'_1 + 0.1 + 5\bar{X}'_1 &= 1.320 \quad \Rightarrow \quad \bar{X}'_1 = \underline{0.203 \text{ micromoles(P)/liter}} \\ \bar{X}'_3 &= \underline{1.017 \text{ micromoles(P)/liter}}\end{aligned}$$

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## 9. Where Would All the Water Go? (1/6)

**If evapotranspiration from Earth's land area were to diminish by 20% uniformly over the land area, as might result from widespread removal of vegetation, what changes would occur in the globally averaged precipitation on the land surface and in the globally averaged runoff from the land to the sea?**

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## 9. Where Would All the Water Go? (2/6)

- To solve the problem, a systematic look at the global water budget is helpful. The following water flow rates can be defined:

$E_{LL}$ : rate of evapotranspiration from the land that falls as precipitation on the land

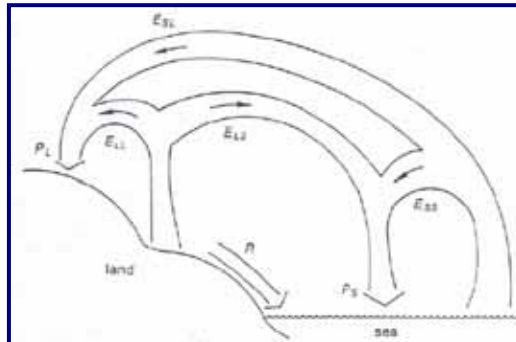
$E_{SS}$ : rate of evaporation from the sea that falls as precipitation on the sea

$E_{SL}$ : rate of evaporation from the land that falls as precipitation on the land

$P_L$ : rate of precipitation on the land

$P_S$ : rate of precipitation on the sea

$R$ : rate of runoff from the land to the sea



## 9. Where Would All the Water Go? (3/6)

- Our problem can now be restated in terms of these definitions:  
*How will  $R$  and  $R_L$  change if  $E_{LL}$  and  $E_{LS}$  both diminish by 20%?*

- There are 3 water-conservation relations among the 7 quantities we have defined.

$$P_S + R = E_{SS} + E_{SL} \quad (1) \quad \text{➤ Water is conserved in the sea.}$$

$$P_L = R + E_{LL} + E_{LS} \quad (2) \quad \text{➤ Water is conserved on land.}$$

$$R + E_{LS} = E_{SL} \quad (3) \quad \text{➤ Rate of water flow from land to sea equals the rate from sea to land.}$$

- Any two of these can be derived from the third plus the two identities that follow from the definitions:

$$P_L = E_{LL} + E_{SL} \quad (4)$$

$$P_S = E_{SS} + E_{LS} \quad (5)$$



## 9. Where Would All the Water Go? (4/6)

- All told, there are 3 independent relations among the 7 quantities. Thus, 4 independent empirical values are needed to determine all 7 quantities.

- From the Appendix, values for  $P_L$ ,  $P_S$ , and  $R$  are given.

$$P_L = 108 \times 10^3 \text{ km}^3/\text{yr}, \quad P_S = 410 \times 10^3 \text{ km}^3/\text{yr}, \quad R = 46 \times 10^3 \text{ km}^3/\text{yr}.$$

- The 4<sup>th</sup> piece of information is that **approximately 25% of the evapotranspiration from the land precipitates on the sea, while 75% or 3 times as much, precipitates on the land.**

$$E_{LL} = 3E_{LS}$$

- With the 4<sup>th</sup> information and the Eqs.(1)(2)(3), we obtained:

$$\begin{aligned} E_{LL} &= 46.5 \times 10^3 \text{ km}^3/\text{yr}, & E_{LS} &= 15.5 \times 10^3 \text{ km}^3/\text{yr} \\ E_{SS} &= 394.5 \times 10^3 \text{ km}^3/\text{yr}, & E_{SL} &= 61.5 \times 10^3 \text{ km}^3/\text{yr} \end{aligned}$$

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## 9. Where Would All the Water Go? (5/6)

- If the reduction in evapotranspiration is uniformly distributed over the land, it's reasonable to assume that  $E_{LL}$  and  $E_{LS}$  each decrease by 20%.
- Using primed quantities ( $P'_L$ ,  $P'_S$ ,  $R'$ , etc.) to denote the rates subsequent to the 20% decrease in evapotranspiration, we can write

$$\begin{aligned} E'_{SS} &= E_{SS}, & E'_{SL} &= E_{SL} \\ E'_{LL} &= 0.8E_{LL}, & E'_{LS} &= 0.8E_{LS} \end{aligned} \quad (6)$$

- Then, setting up new conservation equations and identities for the primed quantities, the primed versions of Eqs.(3) and (4) become:

$$R' = E'_{SL} - E'_{LS} \quad (3')$$

$$P'_L = E'_{LL} + E'_{SL} \quad (4')$$

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## 9. Where Would All the Water Go? (6/6)

- Use Eq.(6) then leads to

$$R' = E'_{SL} - E'_{LS}$$

$$P'_L = E'_{LL} + E'_{SL}$$

- Use Eqs. (3) and (4), these can be written as

$$R' = R + 0.2E_{LS}$$

$$P'_L = 0.8E_{LL} + E_{SL}$$

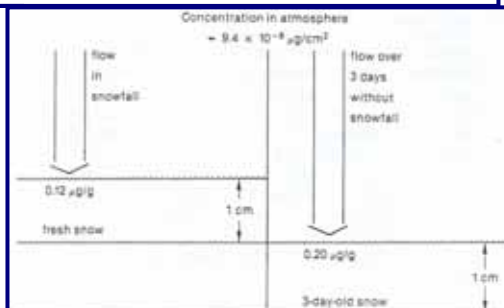
- Numerically,  $R' = (46.0 + 3.10) \times 10^3 \text{ km}^3/\text{yr}$ , which is about 7% increase over  $R$ ; and  $P'_L = (108 - 9.30) \times 10^3 \text{ km}^3/\text{yr}$ , which is about a 9% decrease from  $P_L$ .

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## 10. Aluminum in the Himalaya (1/5)

In a remote area in Nepal, the concentration of aluminum (Al) in outdoor air at ground level averages  $9.4 \times 10^{-8} \mu\text{g}/\text{cm}^3$ . (It is much higher inside the Sherpa dwellings because of wood and yak dung burning). At the same site, the Al concentration in the top 1 cm of fresh snow averages  $0.12 \mu\text{g}/\text{g}$ , while in the top 1 cm of three-day-old snow it averages  $0.20 \mu\text{g}/\text{g}$ .

- (a) Calculate the average deposition velocity of the Al falling to the ground when it is not snowing.
- (b) How large are the particles to which the falling aluminum is attached?



## 10. Aluminum in the Himalaya (a) (2/5)

- The flow is  $0.20 - 0.12 = 0.08 \mu\text{g(Al)}/3 \text{ days}$ . This is the rate of increase of aluminum concentration in the top centimeter of snow.

- Since  $\rho_{\text{fresh snow}} = 0.1 \text{ g/cm}^3$ , and the aluminum was measured in  $0.1 \text{ g (snow)}/\text{cm}^2$  of surface. Hence, the flow can be expressed as

$$F = \frac{0.08 \frac{\mu\text{g(Al)}}{\text{g(snow)}} \times 0.1 \frac{\text{g(snow)}}{\text{cm}^2}}{3 \text{ days}} = 0.0027 \mu\text{g(Al)}/\text{cm}^2\text{day}$$

- The stock in the atmosphere is  $M = 9.4 \times 10^{-8} \mu\text{g}/\text{cm}^3$ .

- The deposition velocity is  $\frac{F}{M} = 2.9 \times 10^4 \text{ cm/day} = 0.34 \text{ cm/sec}$ .

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## 10. Aluminum in the Himalaya (b) (3/5)

- To calculate the size of the particles falling at this speed, a digression is needed. **Stokes Law** describes the rate at which objects fall through a medium like air or water, provided the velocity of the object is small enough to create no turbulence. The law states that the frictional drag force on a spherical object is  $F = 6\pi\eta vr$ .

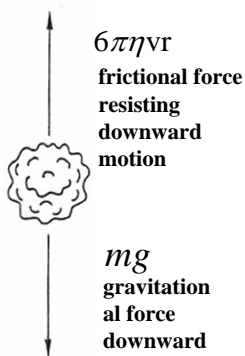
- Stokes Law is applicable provided a certain quantity called the Reynolds number,  $R$ , defined by  $R = \rho_m vr/\eta$  is less than about 0.5.

$\eta$ : viscosity of the medium $v$ : velocity $r$ : the object's radius $\rho_m$ : density of the medium
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## 10. Aluminum in the Himalaya (b) (4/5)

- A falling object soon reach a terminal velocity in which the frictional force retarding its motion equals the gravitational-minus-buoyancy force pulling it downward.



- For a particle falling through air the buoyancy is negligible and so the downward force is the product of  $mg$ .
- Hence the terminal velocity can be calculated by setting  $6\pi\eta vr = mg$  . (1)
- We know the values of everything in Eq.(1) except  $r$  (所求) and  $m$ . Next, we'll find the value of  $m$ .

Fig. II-11

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## 10. Aluminum in the Himalaya (b) (5/5)

- Assuming the particles to which aluminum is attached are spherical,  $r$  is their average radius.
- It's very reasonable assumption that the density of the particle,  $\rho_p$ , is very roughly equal to  $1 \text{ g/cm}^3$ , the density of water. This is because small particles falling from the atmosphere are often actually aerosols. Aerosols may contain water; but even if dry, they are comprised of fluffy solids – irregular hollow structures less dense than typical solid materials forming Earth's crust. Thus, we find

$$m = \frac{4}{3} \pi r^3 \rho_p.$$

- Rewriting Eq.(1) yields

$$6\pi\eta vr = \frac{4}{3} \pi r^3 \rho_p g \Rightarrow r = \left( \frac{4.5\eta v}{\rho_p g} \right)^{1/2} = \left( \frac{4.5 \times 1.72 \times 0.34 \times 10^{-2}}{1 \times 9.8} \right)^{1/2} = 0.05 \text{ m} = 0.0005 \text{ cm} = \underline{5 \text{ microns.}}$$

## 11. An Indoor Risk (1/7)

Radioactive radon gas ( $\text{Rn}^{222}$ ) enters an average building at the rate of one picocurie per second per square meter of foundation area. Consider a house with a foundation area of  $200 \text{ m}^2$  and an air volume of  $1000 \text{ m}^3$ . Assume that the house is well designed for energy conservation so that the ventilation rate is low and only one tenth of the air in the house is exchanged with outdoor air every hour.

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## 11. An Indoor Risk (2/7)

- (a) What will be the average steady-state concentration of  $\text{Rn}^{222}$  in the house?
- (b) In the steady state, what whole-body radiation dose, in rads/yr, will an adult male receive directly from  $\text{Rn}^{222}$  decay 12 hr a day in the house? (rad: 「輻射劑量」的單位)

➤ The rate of decay is called the activity and it can be written  
 $\text{activity}(t) = \lambda N(t)$  (1) (Unit: number of decaying atoms/time)

➤ Here,  $\lambda$  is a rate constant related to the half-life by

$$\lambda = \frac{\ln 2}{T_{1/2}} = \frac{0.693}{T_{1/2}} \quad (2)$$

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## 11. An Indoor Risk (a) (3/7)

- The equilibrium value of N is determined by setting the rate of inflow of  $Rn^{222}$  atoms equal to the rate of outflow (see Fig. II-11).
- The rate of inflow of  $Rn^{222}$  is determined by the source term, 1 pCi/m<sup>2</sup>sec. For a house with a foundation area of 200 m<sup>2</sup>, this is

$$200 \text{ pCi/sec} \quad \text{or} \quad 200 \times 0.037 = 7.4 \text{ decays/sec}^2 \quad (1 \text{ pCi/m}^2\text{sec} = 0.037 \text{ decays/sec}^2)$$

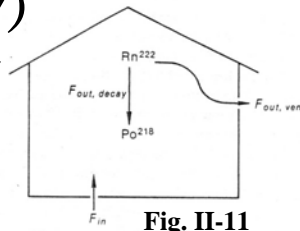


Fig. II-11

**That is,  $Rn^{222}$  activity enters the house at a rate of 7.4 decays/sec<sup>2</sup>.**

- Eq.(1) tells us that the number of atoms of an isotope equals  $\lambda^{-1}$  times the activity of that isotope.

$$N(t) = \frac{\text{activity}(t)}{\lambda}$$

Therefore,  $F_{in}$  (The rate at which atoms of  $Rn^{222}$  enter the house)

$$= \frac{\text{the rate at which activity due to } Rn^{222} \text{ enters the house}}{\lambda \text{ (the rate related to the half - life)}}$$

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## 11. An Indoor Risk (a) (4/7)

- Using the value of  $T_{1/2}$  for  $Rn^{222}$  of 3.8 days, or  $3.3 \times 10^5$  sec, we obtain

$$\lambda = \frac{0.693}{3.3 \times 10^5} = 2.1 \times 10^{-6} / \text{sec}.$$

- Therefore, we determined that  $F_{in} = \frac{7.4}{\lambda} = 3.5 \times 10^6$  atoms/sec.

- The outflow rate consists of two terms:

1. loss of  $Rn^{222}$  by radioactive decay in the house ( $F_{out, decay}$ ).

This decay rate is simply the activity  $\lambda N = 2.1 \times 10^{-6} N / \text{sec}.$

2. outflow resulting from ventilation ( $F_{out, vent}$ ). The ventilation rate is 0.1 air exchanges per hour, then 1/10 of the  $Rn^{222}$  in houses is removed every hour as well. Hence, the 2<sup>nd</sup> term in the outflow rate is  $0.1N / \text{hr}$  or  $2.8 \times 10^{-5} N / \text{sec}.$

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## 11. An Indoor Risk (a) (5/7)

- Combining two outflow terms, we find

$$\begin{aligned} F_{\text{out}} &= F_{\text{out,decay}} + F_{\text{out,vent}} \\ &= (2.1 \times 10^{-6} + 2.8 \times 10^{-5})N \\ &= 3.0 \times 10^{-5} \text{ N/sec} \end{aligned}$$

- The steady-state value of N now can be calculate by

$$\begin{aligned} F_{\text{in}} &= F_{\text{out}} \\ 3.5 \times 10^6 \text{ /sec} &= 3.0 \times 10^{-5} \text{ N/sec} \end{aligned}$$

Hence,  $N = 1.17 \times 10^{11}$  atoms

- The steady-state concentration, C, will be  $C = \frac{N}{V}$ .

$$\Rightarrow C = \frac{1.17 \times 10^{11}}{1000} = 1.17 \times 10^8 \text{ atoms/m}^3.$$

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## 11. An Indoor Risk (b) (6/7)

- Assume that during the 12 hr indoors, the adult male typically has at any time about 1.2 liters of freshly breathed air in his lungs. The concentration tells us that this much air will contain

$$(1.2 \times 10^{-3}) \times (1.17 \times 10^8) = 1.4 \times 10^5 \text{ atoms of Rn}^{222}.$$

- The activity of the lung air is  $\lambda N = (2.1 \times 10^{-6}) \times (1.4 \times 10^5)$   
 $= 0.29 \text{ decays/sec}$

- Thus during a typical year of 12-hr days in the home, our subject's lungs will endure  $365 \times 12 \times 3600 \times 0.29 = 4.6 \times 10^6 \text{ Rn}^{222} \text{ decays}$ .
- To estimate the whole-body dose, we must determine the number of ergs deposited in the body and divided by the number of grams of body weight.

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## 11. An Indoor Risk (b) (7/7)

- The Appendix tells us that each  $\text{Rn}^{222}$  decay produces an  $\alpha$ -particle with 5.5 MeV of energy.

- 1 MeV =  $1.6 \times 10^{-6}$  ergs, so  $4.6 \times 10^6$  decays/yr deposits

$$4.6 \times 10^6 \times 5.5 \times 1.6 \times 10^{-6} = 40.5 \text{ ergs/yr.}$$

- A typical adult male has a mass of  $7 \times 10^4$  g, so the whole-body dose, in rads, is

$$\frac{40.5}{100 \times 7 \times 10^4} = 5.8 \times 10^{-6} \text{ rads/yr}$$

每克物質吸收100 erg的能量稱為1 rad