

## Atmospheric Chemistry and Structure

### Outline:

- Components of a biogeochemical cycle
  - The concept of mass-balance budgets
- The Atmosphere
  - Why is it important to biogeochemistry?
  - Structure and circulation
  - Atmospheric composition
  - Aerosols
- Biogeochemical Reactions in the Troposphere

Please note that the majority of the text below is taken from Chapter 3 in:  
*Schlesinger, W.H. 1997. Biogeochemistry: an analysis of global change. 2<sup>nd</sup> edition. Academic Press, California.*

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### Components of a biogeochemical cycle:

- All elements/molecules reside in **compartments** or “defined spaces” in nature
- A compartment contains a certain quantity, or **pool**, of elements/molecules.
- Compartments exchange elements/molecules. The rate of movement of elements/molecules between two compartments is called the **flux rate**.
- The average length of time an element/molecule remains in a compartment is called the **mean residence time**.
- The **flux rate** and **pools** of elements/molecules together define the **cycle** in an ecosystem.

### The concept of mass-balance budgets:

We construct **budgets** to study how element/molecules are gained and lost in ecosystems.

1. Some ecosystems are in **steady state**: this occurs when fluxes are balanced. Therefore:

$$\text{inputs} = \text{outputs}$$

2. Inputs sometimes exceed outputs, and elements/molecules accumulate in compartments of ecosystems. Therefore:

$$\text{Inputs} > \text{outputs} = \text{storage (sink)}$$

(e.g., community development following a disturbance; e.g. volcano)

3. Outputs sometimes exceed inputs of elements/molecules in communities or ecosystems

*Inputs < outputs = loss (source)*

(e.g., fire, leaching by acid deposition)

## **The Atmosphere**

*Why is it important to biogeochemistry?*

- Evolved as a result of the history of life on earth
- Controls earth's climate and determines the environment we live in
- Atmospheric circulation transports biogeochemical constituents between and amongst terrestrial and aquatic systems, resulting in a global circulation of elements.
- Atmosphere is relatively well mixed, so changes in its composition can be taken as first index of changes in biogeochemical processes at the global level (now changing rapidly due to human activities)

*Structure and circulation*

### **Figure 3.1**

The atmosphere is held on the earth's surface by the gravitational pull of the earth

- Atmospheric pressure decreases with increasing altitude because the mass of the overlying atmosphere is smaller
- Abundance of molecules in each volume of atmosphere is greater at sea level because it is compressed by the pressure of the overlying atmosphere (atmosphere is thinner at altitude)
  - The troposphere contains about 80% of the atmospheric mass

### **Figure 3.2**

Ozone absorbs about 50% of the sun's radiation

- Land and ocean surfaces reradiate long-wave (heat) radiation to the atmosphere, heating the atmosphere from the bottom up (upper troposphere (10-15 km) is only about  $-60^{\circ}\text{C}$  ensuring only small amounts of water vapour)
- Because warm air rises, the troposphere tends to be well mixed

Above troposphere is stratosphere (15 km to 50 km)

- Temperature increases with altitude in stratosphere due to absorption of UV by ozone
- Little mixing between troposphere and stratosphere
  - Materials that enter stratosphere remain there for a long time allowing for global transport.

The thermal mixing of the troposphere is largely responsible for the global circulation of the atmosphere, and local weather patterns

- CELL MOVEMENT (**Figure 3.3**)

The troposphere in each hemisphere mixes approximately every few months

- Each year there is also a complete mixing of tropospheric air between the northern and southern hemispheres (across intertropical convergence zone)
  - If concentrations of a gas are higher in one hemisphere, a large natural or human source must overwhelm the tendency for mixing to equalize concentrations (**e.g., Figure 3.4**)

Exchange between the troposphere and stratosphere is driven by:

- Hadley cells carrying tropospheric air to the stratosphere
- When height of troposphere drops due to seasonal cooling, some tropospheric gases are trapped in stratosphere and vice versa

**CONCEPT:**

Mean Residence Time (MRT)=Mass/flux

The *annual* input of tropospheric air to the stratosphere is about 75% of the stratospheric mass, leading to a MRT of 1.3 years.

*Atmospheric Composition*

**Table 3.1**

Three gases (nitrogen, oxygen and argon) make up 99% of the atmospheric mass of  $5.14 \times 10^{21}$  g

- These gases are relatively unreactive
  - Their residence times in the atmosphere are much longer than atmospheric mixing, therefore they are nearly uniform globally

Several hundred trace gases including volatile hydrocarbons are also in the atmosphere

- Most have short MRT, so are therefore minor constituents
- These gases vary in space and time
  - E.g., certain pollutants (ozone, CO) concentrated over cities
  - Winds mix these gases to lower average tropospheric background concentrations within a short distance downwind of local sources

**Figure 3.5**

Water has a MRT of 9.3 days in the atmosphere

- Average volume of water in atmosphere is  $13,000 \text{ km}^3$ , or about 25 mm above any point on earth
- Average daily precipitation flux is 2.7 mm/day

- MRT is short compared to circulation of troposphere; therefore water vapour is variable in space and time.

CO<sub>2</sub> has a MRT of 5 years – slightly longer than mixing time of atmosphere

- Because of CO<sub>2</sub> uptake by plants there is a minor seasonal and latitudinal variation of about 1% in its global concentration of 360 ppm

### Figure 3.6

The large amount of O<sub>2</sub> in the atmosphere with a MRT of 4000 years (much longer than the mixing time of the atmosphere) results in little variation in concentration.

Gases with MRT <1 year in the troposphere do not persist long enough to mix with the stratosphere

- However, chlorofluorocarbons are chemically inert in the troposphere, and therefore mix with the stratosphere where they destroy ozone in reactions with UV.

### Aerosols

In addition to gases, the atmosphere contains *particles* known as aerosols

- These arise from various sources

### Table 3.2

e.g., Soil minerals are dispersed by wind erosion (*deflation weathering*) from arid and semi-arid regions

- Particles < 1 μm diameter remain aloft by turbulent motion and are subject to long-range transport
  - Dust from Asia deserts fall into Pacific Ocean contributing iron for phytoplankton
  - Dust from Sahara supplies nutrients to Atlantic Ocean phytoplankton and phosphorus to Amazon rainforests.
- Dust in atmosphere typically warms atmosphere over land and cools atmosphere over oceans which have lower surface albedo (reflectivity)

Enormous amounts of particles enter the atmosphere in water droplets from bursting bubbles on the ocean surface

- As the water evaporates, seasalt aerosols are formed, most of which settle out of the atmosphere quickly, but some of which remain in the atmosphere for global transport

Forest fires produce charcoal carried throughout the troposphere, and small *soot* particles are produced by condensation of volatile hydrocarbons from smoke.

- Global production of fire aerosols has likely increased markedly in past century due to biomass burning in tropics (affecting regional patterns of rainfall and global climate)

- In temperate areas, forest fire controls have reduced aerosol loadings to atmosphere

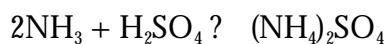
Volcanoes disperse finely divided rock materials, contributing to soil development near regions of major eruptions

- Volcanic gases and ash are transported to stratosphere by violent eruptions:
  - These undergo global transport, affecting climate for years

### Table 3.3

Small particles also produced by reactions between atmospheric gases:

- e.g.,  $\text{SO}_2$  is oxidized to  $\text{H}_2\text{SO}_4$ , which can then react with atmospheric ammonia ( $\text{NH}_3$ ):



- $\text{SO}_4$  aerosols are also produced by oxidation of dimethylsulfide released from oceans
  - $\text{SO}_4$  aerosols increase albedo of the atmosphere (therefore important in climate change models)

ALSO, variety of small particles produced through human industrial processes, especially coal combustion

- Human activities account for 10-20% of aerosol burden in today's atmosphere.
  - Recently mass of some industrial aerosols have declined in developed countries due to pollution controls (e.g., lead from auto exhaust declined in past 20 years due to decline in use of leaded gasoline)

### Fig. 3.7

Small particles much more numerous in atmosphere than large particles, but large particles contribute most to the total airborne mass.

- Mass of aerosols decreases with increasing altitude
  - Concentrations range from 1-50  $\mu\text{g}/\text{m}^3$  near unpolluted regions of earth's surface
- Inverse relationship between size of particle and persistence in atmosphere
  - Overall MRT ~5 days, and therefore not uniformly distributed in atmosphere
  - Because smaller particles have longer MRT, they have greatest influence on earth's climate and global biogeochemical transport through atmosphere
- Over land, aerosols often dominated by soil minerals and human pollutants
- Over oceans, aerosols are mixture of contributions from silicate minerals of continental origin and seasalt from the oceans

Aerosols important:

1. In reactions with atmospheric
2. As nuclei for the condensation of raindrops (cloud condensation nuclei: CCN)

- Raindrops formed when water vapor condenses on aerosols  $> 0.1 \mu\text{m}$
- As raindrops enlarge and fall to earth, they collide with other particles and absorb atmospheric gases
- Reactions of gases with aerosols or raindrops are called *heterogeneous gas reactions*
  - These reactions responsible for removal of many reactive gases from the atmosphere.

## Biogeochemical Reactions in the Troposphere

*Major Constituents –  $\text{N}_2$ ,  $\text{O}_2$  and Ar*

$\text{N}_2$ ,  $\text{O}_2$  and Ar

- All relatively unreactive
- Nearly uniform concentration
- Long mean residence time in atmosphere

$\text{N}_2$  is practically inert

- Reactive N is found only in molecules such as  $\text{NH}_3$  and NO (odd N, as opposed to molecules with even number of N atoms, e.g.,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ )
- $\text{N}_2$  is so inert that availability of odd N is one of primary factors limiting plant growth on land and in oceans

N-fixation (conversion of  $\text{N}_2$  to reactive compounds):

- Occurs in lightning bolts
- Most fixation done by bacteria that convert  $\text{N}_2$  to  $\text{NH}_3$
- Production of synthetic N fertilizer now accounting for  $\sim 1/3$  of annual global total fixation
- Denitrification returns  $\text{N}_2$  from biosphere to atmosphere

The atmosphere contains much more  $\text{O}_2$  than can be explained by storage of carbon in **land plants** today

- The accumulation of  $\text{O}_2$  is result of long-term burial of reduced carbon in ocean sediments
- This organic carbon derived from photosynthesis in the sea (transport of organic carbon from land via rivers is relatively small)
- Burial rate determined by area of ocean floor that is anoxic
  - This area is inversely proportional to  $\text{O}_2$  in atmosphere
  - Therefore balance between organic carbon burial and its oxidation maintains  $\text{O}_2$  at steady-state concentration of about 21%
  - Mean residence time of  $\text{O}_2$  in atmosphere about 4000 years