

GASEOUS GEOCHEMICAL CYCLES

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Keywords: carbon, earth's atmosphere, nitrogen, oxygen, sulfur, isotopes, compounds.

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Summary

Human ability to produce gaseous compounds at levels exceeding those of natural sources has led to numerous investigations of the biogeochemical cycling of major atmospheric gases. The term cycle provides a description of material and energy flow, and does not imply that only a closed and “steady state” system is considered. Description of the processes is given at different levels, with interactions of elemental particles, elements, and compounds, followed by interactions between global reservoirs. Carbon (C), oxygen (O), nitrogen (N), and sulfur (S) are important elements at both global and regional scales.

The rapid growth of the world population is discussed in the context of:

- food production;

- world climate;
- acid deposition;
- stratospheric ozone destruction; and
- trace substances pathways and cycling.

The scientific understanding of carbon, oxygen, nitrogen, and sulfur cycling is assessed on the basis of major chemical reactions and physical processes.

1. Introduction

The term *gaseous cycle* refers to the transfer and transformation of gasses between various biogeochemical reservoirs, lithosphere, hydrosphere, atmosphere, and biosphere. An understanding of the interactions between the reservoirs is essential to any assessment of gaseous geochemical cycles.

2. Earth's Atmosphere

The main biogeochemical reservoir of gases is Earth's atmosphere. It consists of a mixture of gases, water droplets, ice particles, and aerosols that form a thin layer that surrounds the planet. The main constituents are the light, reactive elements nitrogen, oxygen, hydrogen, carbon, sulfur, and the halogens, together with the non-reactive noble gases. They are present as compounds, molecules, atoms, ions, and radicals, with the main constituents "average concentrations" in a dry atmosphere as set out in Table 1.

Constituent	Average concentration (ppmv ¹)	Residence time
N ₂	780 840	10 ⁶ years
O ₂	209 460	5000 years
Ar	9 340	10 ⁹ years
Ne	18	10 ⁹ years
Kr	1.1	10 ⁹ years
Xe	0.09	10 ⁹ years
CO ₂	356	15 years
CO	0.1	65 days
CH ₄	1.65	7 years
H ₂	0.58	10 years
N ₂ O	0.33	20 years
O ₃	0.01–0.1	100 days
NO/NO ₂	10 ⁻⁶ –10 ⁻²	1 day
NH ₃	10 ⁻⁴ –10 ⁻³	5 days
SO ₂	10 ⁻⁵ –10 ⁻⁴	10 days
HNO ₃	10 ⁻⁵ –10 ⁻³	1 day

¹ 1 ppmv = 1 part per million by volume

Table 1. Average composition and residence time in a dry atmosphere

In this context the residence (meaning the life- or turnover) time, τ (measured in years, or days), is defined as:

$$\tau = \frac{M}{S} = \frac{M}{Q} \tag{1}$$

where M represents the total mass of a compound in the reservoir (g, or tons), while S and Q represent the total input and removal rates respectively (g y^{-1} , or tons y^{-1} to give τ measured in years).

The constituents of the atmosphere can be divided into two main groups:

- (a) N_2 , O_2 , Ar, and CO_2 , which are relatively non-reactive molecules with a relatively long residence time in the atmospheric gas mixture; and
- (b) components with lifetimes of a few days that are, chemically speaking, impurities.

In addition to gaseous species present in the atmosphere in the percent, ppm, or ppb concentrations, there are also gasses present in the ppt concentration (CCl_3F , CCl_2F_2 , CF_4) or number of atoms per cm^3 (free radicals, radionuclides).

Concentrations of trace gases vary in space and time, and the recorded variations may arise from:

- (a) analytical procedures used for estimating some atmospheric components;
- (b) increases with time in the concentration of some components (CH_4 , N_2O) as the result of anthropogenic activities; and
- (c) fluctuations in response to industrial emissions of pollutants, source strength, and sink mechanism.

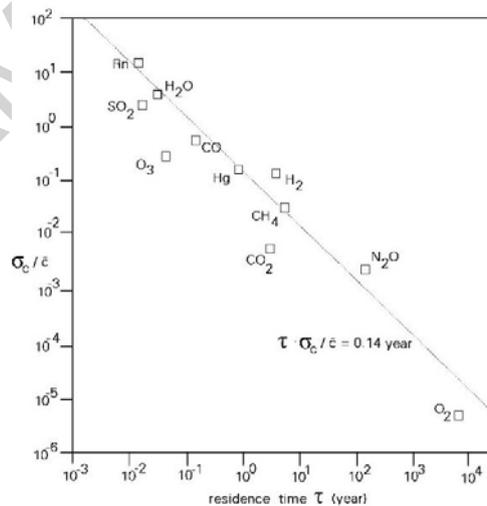


Figure 1. The relationship between coefficient of variation (relative standard deviation of concentration) and residence time τ

The spatial variability between relative standard deviation of concentration (σ/c) and residence time is given in Figure 1. Gases with a long residence time, comparable with the time-scale of mixing of atmospheric masses (years), have a low variability (low σ/c), while atmospheric transport cannot prevent trace impurities with a high variability in the air.

Earth's atmosphere is vertically divided into a number of layers according to temperature distribution (see chapter *Aeronomic Phenomena*), as shown in Figure 2.

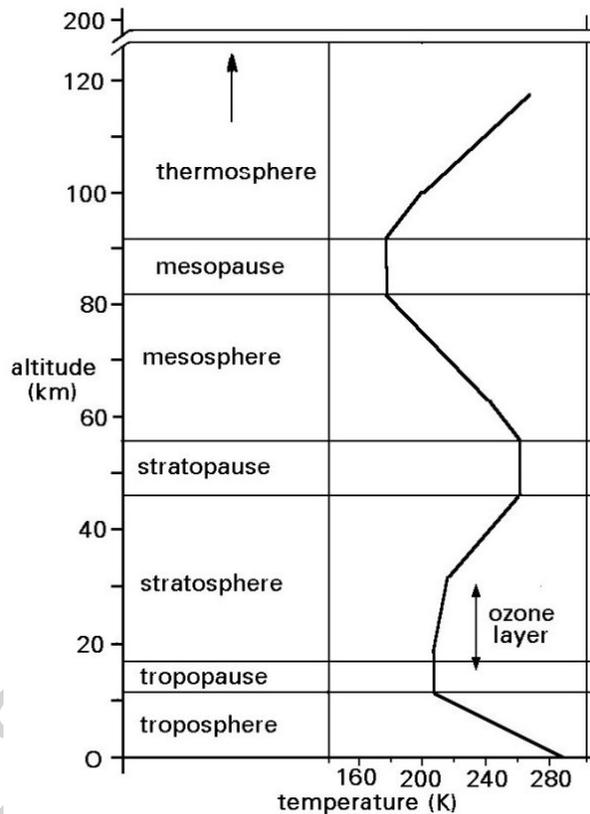


Figure 2. The vertical temperature structure of the atmosphere

In the lowest part, the troposphere, the temperature decreases with height, clouds form, precipitation takes place, and heating takes place as the result of radiation absorbed by the earth surface and less dense air.

The boundary layer (tropopause) has an altitude of 7 km to 18 km. The next layer, the stratosphere, is characterized by:

- temperature inversion;
- heating from above by absorption of ultraviolet radiation by the ozone layer;
- lower mixing of pollutants; and
- a longer lifetime of pollutants removed by transport or precipitation.

The stratosphere has its top near 50 km altitude. The next layer, the mesosphere, exhibits a sharp decrease of temperature. From the temperature minimum, termed the mesopause, the temperature again raises in the thermosphere.

The atmosphere moderates radiation from the Sun. It provides thermal conditions that maintain the liquid water on Earth's surface, and supplies biological processes with CO₂, O₂, and H₂O. Cycling of one compound in the atmosphere cannot be considered in isolation from others or from the trace substances (with ppt and lower concentration, for example, O₃, hydroxyl radical OH). Most of the transformation reactions are controlled both thermodynamically and kinetically.

3. Carbon

The importance of the carbon cycle arises from the following facts:

- (a) carbon is the key element of life on Earth;
- (b) carbon significantly influences Earth's radiative balance, and therefore the surface temperature and climate;
- (c) the ratio between oxidized (CO₂, carbonates, etc.) and reduced forms (C_{org}, coal, graphite) influences the Eh of the environment; and
- (d) humans have altered the global cycle of carbon.

3.1 Isotopes

There are seven isotopes of carbon (¹⁰C, ¹¹C, ¹²C, ¹³C, ¹⁴C, ¹⁵C, and ¹⁶C), of which two (¹²C and ¹³C) are stable. ¹⁴C is the heaviest occurring carbon isotope, with a half-life (5730 ± 40) years, and is used as a chronometer and as a radiotracer for determination of the mixing and transfer rates between various carbon reservoirs. ¹⁴C originates during nuclear interaction of ¹⁴N with cosmic radiation:



Stable carbon isotopes (¹²C, ¹³C) are present in terrestrial materials in the proportion 98.89:1.11. Variation of stable isotopes' composition is linked to the PDB standard (Pee Dee belemnite from the Pee Dee formation, North Carolina) using $\delta^{13}\text{C}$ values in per mil (‰):

$$\delta^{13}\text{C} = \left(\frac{R_s - R_o}{R_o} \right) \times 1000 \quad (3)$$

where R_s is the ¹³C/¹²C ratio in the sample and R_o is the ¹³C/¹²C ratio in the standard PDB. Fractionation is controlled either by thermodynamic equilibrium reactions or by kinetic processes.

3.2 Compounds

Elemental carbon can exist in at least six crystalline forms: α-, β- graphite, diamond, lonsdaleite (hexagonal diamond), chaoite, and carbon VI. Recently described spherical

molecules of carbon containing 60 or more atoms are called fullerenes. Carbon occurs in a variety of forms that allow covalent bonding to hydrogen, oxygen, and to other carbon. The oxidation state of the carbon compounds ranges from +IV to -IV. The most common inorganic species are carbon dioxide (CO₂), carbonate ions (CO₃²⁻), bicarbonate ions (HCO₃⁻), and the carbonate minerals calcite (CaCO₃), dolomite ([Ca,Mg]CO₃), and siderite (FeCO₃). Carbonate sediments are composed of more than 50 % of carbonate minerals. Other sedimentary rocks, such as carbonaceous shales and coal, contain high proportions of organic carbon species. Photosynthesis of plants creates an important organic carbon pool (CH₂O) and a number of organic molecules on Earth. Up to the present, more than one million organic carbon compounds are known.

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Biographical Sketch

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