2.7 Trace Constituents.

Carbon dioxide. Carbon dioxide is quite uniformly mixed in the homosphere, but it exhibits interesting time variations. The CO_2 record from Moana Loa in the northern hemisphere tropics (MS fig. 1.12) exhibits an annual cycle sawtooth pattern and a long-term rise. The sawtooth pattern is due to the seasonal cycle of photosynthesis and respiration and decay of the Northern hemisphere land biosphere. Photosynthesis is dominant over respiration and decay during northern spring and summer and transfers carbon dioxide from the atmosphere to the biosphere. Respiration and decay are dominant during autumn and winter and account for the rise in atmospheric CO_2 because of its release from the land biosphere. Because Moana Loa is in the Northern hemisphere where most of the land biomass is located, it shows a strong annual cycle. Southern hemisphere stations show only a weak annual cycle composed of superposition of a weak southern seasonal cycle and an attenuated northern seasonal cycle of opposite phase.

The long-term rise in CO_2 is due to human activities: fossil fuel combustion, about $6x10^9$ metric tonnes of carbon per year (6Gt C/yr), and burning of biomass arising from clearing of tropical forests, about 2 Gt C/yr. After emission, these 8 Gt C/yr are distributed roughly as follows:

3.5 Gt C/yr stored in the atmosphere

2.5 Gt C/yr stored in the ocean

2.0 Gt C/yr stored in the Northern hemisphere land biomass, mainly as a result of regrowth of forests at middle and high latitudes.

Although the annual atmospheric storage is well measured by a global network of stations like that at Moana Loa, there is still controversy over the distribution of the remainder between the land biosphere and the ocean. Because the storage capacities of these two reservoirs will change and influence the fraction of net CO_2 emission that can be stored in the atmosphere, improved understanding of land biosphere and ocean storage mechanisms is a very important research objective.

Ice core records now provide data on atmospheric CO_2 variations over the past several hundred thousand years. MS fig. 1.13 shows a remarkable correlation between CO_2 amount and temperature derived from analyses of air bubbles trapped in an Antarctic ice core. These CO_2 variations are large enough to account for some but not all of the associated temperature variations through the greenhouse effect of CO_2. However, the cause for this close CO_2-temperature relationship is still unknown. Any graduate student that provided a convincing explanation of its cause or causes would be certain to receive a Nobel Prize in Meteorology.

Water vapor. Water vapor abundance declines rapidly upward and poleward from the lower tropical troposphere because condensation and precipitation at low temperature limit its concentration (MS Fig. 1.14). The average scale height of water vapor is

approximately $\left(\frac{d\ln e}{dz}\right)^{-1} \approx 2\text{km}$. The total amount of water vapor per unit area in a vertical column, called the precipitable water, is measured in units of length of the corresponding liquid column, consistent with rain gauge measurements:

$$\text{Precipitable water} = \frac{1}{\rho_l}\int_0^\infty \rho_v dz \approx \frac{1}{\rho_l}\int_0^\infty q_v \rho dz$$

where ρ_l = density of liquid water = 10^3kgm^{-3}. The global average precipitable water is about 2cm and the global average annual precipitation is believed to be about 1m, so the mean atmospheric residence time of water vapor is about $0.02\text{m} \div 1\text{m} \approx 0.02\text{yr} \approx 7\text{dy}$.

Ozone. MS Fig. 1.17 shows that the ozone mixing ratio reaches a maximum of about 10 parts per million by volume (ppmv) over the equator slightly above the 10hPa level (about 30-35km). This location reflects the ozone production mechanism. Maximum absorption of solar ultraviolet radiation (wavelength < 250nm) occurs in the upper tropical stratosphere. The maximum ozone partial density is at much lower height, about 30hPa (20-25km). The ozone column, or total ozone, is analogous to precipitable water but is measured in different units, Dobson units (DU), after G. M. B. Dobson who pioneered the development of total ozone measurement techniques. In DU,

$$\text{Total ozone} = \frac{10^5}{L_0}\int_0^\infty n(O_3) dz,$$

where the factor L_0=2.69x10^{22}molecules per cubic meter is Losschmidt's Number, the number of molecules per cubic meter of an ideal gas under STP conditions. Column amounts of other trace gases are measured in similar units, cm (STP), with the same formula except that the factor 10^2 replaces the conversion factor 10^5 (1DU=1000cm (STP)). Under "normal" conditions, total ozone ranges between about 0.2 and 0.5DU, with the largest amounts found at high latitudes because ozone produced in the tropical stratosphere is transported downward and poleward into the lower high latitude stratosphere as shown in Fig. 1.17 and discussed in the accompanying text.

The ozone hole is due to catalytic destruction of ozone by industrially produced halogenated hydrocarbons, mainly chloroflourocarbons (CFCs) in the presence of thin polar stratospheric clouds. During Antarctic spring, total ozone has fallen from a "pre-hole" value of about 240DU in the early 1970s to as low as 100DU in recent years. In the 1990s, a weaker ozone hole has been observed in the Northern hemisphere stratosphere during winter. There is no doubt that the cause of the ozone hole is industrially generated halogenated hydrocarbons.

Methane (CH_4), CFCs, nitrous oxide (N_2O). The mean residence time of each of these gases is long enough to ensure nearly uniform tropospheric mixing, but each is destroyed in the stratosphere as a result of photodissociation and active chemical processes initiated by photodissociation. Consequently their concentrations decrease upward in the

stratosphere (MS Fig. 1.20). The methane amount has approximately doubled and the nitrous oxide concentration has risen by about 40% over the past century mainly as a result of land use changes due to agriculture and other human activities. CFCs are manufactured substances and none were present in the atmosphere before the 1930s (MS fig. 1.21). Very recently, the concentration of CFC-12 has begun to decline as a result of the worldwide production ban on ozone-depleting compounds.