

establishing future climate changes or the impacts of air pollutants, and perhaps may never be able to provide more than a rough indication. To be acceptable, all models have to be tested for representativeness and accuracy. Ideally, the testing process should involve measurements in the real atmosphere, either as "hindsight", where validation of the model is attempted on a measurement data set from the past, or in parallel, where the model is developed to describe a series of present measurements. Unfortunately, some models are often used to "predict" future changes to the atmosphere and climate without being fully tested. Full acknowledgement that model results can be a coarse and often unreliable estimate of changes in a highly complex and rapidly changing medium is sometimes lacking. Students and others using models should be fully aware of their limitations.

oceans. Sulphur is the second most abundant compound in rivers (next to bicarbonate) but concentrations fluctuate highly depending on season and the frequency of drought, flood, and normal flow. A rough estimate (Figure 2.3) suggests that about 100 Tg S y^{-1} are transported to the oceans. However, only $33\text{--}42 \text{ Tg S y}^{-1}$ are weathered from rocks and sediments. The unaccounted portion is likely to be marine sulphur transported landward by the atmosphere and then deposited, but this has not been quantified. The eventual resting place of the sulphur transported to the oceans is mainly in continental shelf sediments, which, eventually on a geologic time scale, would uplift to the surface again, completing the geochemical part of the sulphur cycle.

Sulphur is of major importance as an essential nutrient in the biosphere, where it is concentrated mainly in soils. As the tenth most abundant element in the biosphere its main sources are deposition from the atmosphere, weathering of rocks, release from vegetation decay, and anthropogenic fertilisers, pesticides, and irrigation water. It is actively removed by plant uptake processes, in solution to ground water, and chemical volatilisation (for a review of these processes see Brown 1982). Sulphur is normally present in soils in an oxidised state (SO_4^{2-} for example), with concentrations varying according to the amount of organic matter. Mineral soils contain only $0.01\text{--}0.06\%$ dry weight, but rich organic soils, such as found in parts of the tropics, may contain up to 0.5% S dry weight (Brown 1982).

The biogenic cycle of sulphur use and release by plants is very complex. Sulphur in soil may be found in bound or unbound form, as organic or inorganic compounds. organic sulphur is most prevalent. Plants use sulphur to bind complex molecules, such as proteins, enzymes, and antibodies, as part of life processes. Upon the death of the plant, decomposition releases sulphur back into the soil. The action of micro-organisms is crucial to the decay process, liberating organic sulphides in two ways. Aerobic decay, occurring with free access to oxygen, allows reoxidation of organic sulphides into sulphate, to begin the uptake process all over again. Anaerobic decay, in a soil environment with limited oxygen, binds sulphur in organic form, with eventual release in part to the atmosphere as H_2S , DMS, and other organic compounds. The approximate amount of sulphur released from global soils is about 7 Tg S y^{-1} (see Figure 2.3), with considerable latitudinal variation showing a major dependence on warmer temperatures (Warneck 1988).

Sulphur in the atmosphere

The interaction of processes between the earth's surface and the atmosphere results in several sulphur compounds being released into the air. Of these, six are most important, and are presented in Table 2.5 along with some general information about sources, production, and average concentration. Secondary compounds and their related chemistry are discussed in Chapter 6.

The atmospheric sulphur cycle, incorporating aspects of Table 2.5, is shown in Figure 2.4. Many of the quantities in Figure 2.4 are speculative, particularly the transfers from land to ocean and vice-versa.

The most abundant sulphur species in the atmosphere is carbonyl sulphide (COS). Although small amounts are produced by anthropogenic combustion processes ($<25\%$), the majority of COS is naturally produced from soil decomposition, marshes and wetlands along ocean coasts, and areas of ocean upwelling that are rich in nutrients. Averaging a concentration of $500 \pm 50 \text{ pptv}$, COS shows little variation latitudinally or altitudinally, suggesting a long lifetime and no rapid sinks. The latest research (see Warneck 1988) indicates that a lifetime of 44 years is realistic, with the only sinks being stratospheric

tions, but make up an important section of the atmospheric nitrogen cycle. Nitrogen in the atmosphere is much more difficult to measure accurately than either sulphur or carbon. Following the lead of other studies (Rodhe *et al.* 1982; GTC 1984), the following discussion is divided into three parts, with a nitrogen cycle presented for each part in Figure 2.6.

Ammonia and ammonium: As the only gas soluble in water, NH_3 is a very important component of the nitrogen cycle because it can directly act as a nutrient for the biosphere. The aerosol component is ammonium (NH_4^+). The two are difficult to separate during measurement, and the results of both are often discussed together. Figure 2.6 presents the sources and sinks of NH_3 and their approximate values as Tg N y^{-1} . Of a total of 54 Tg N y^{-1} emitted to the atmosphere, NH_3 from animal urea makes up about half, mainly from cattle (51%), sheep (20%), pigs (17%), and poultry (8%) (Warneck 1988). Biomass burning inputs depend on the nitrogen content of the ecosystem. The average nitrogen content of tropical forests is about 0.45%; of tropical litter (leaves, twigs etc.), 0.85%; coniferous and deciduous forests, 0.32%; fuel wood, 0.2% and tropical grasses 0.2–0.6% (Logan 1983). Other more minor sources include coal combustion, where about 15–25% of the nitrogen released is NH_3 (Smil 1985), human excreta, and fertilisers.

As with other active nitrogen gases in the atmosphere, it is difficult to establish globally representative background concentrations. NH_3 is lowest over remote oceans, on the order of 0.1 ppbv (Table 2.8) with concentrations in continental background air 6–10 ppbv (Logan 1983). Due to higher temperatures influencing soil-based sources, NH_3 concentrations are higher in summer than winter, and higher during the day than at night. With only about 6 days of lifetime, NH_3 rapidly converts to NH_4^+ . NH_4^+ is a major component of the two most prevalent aerosols in the atmosphere, ammonium sulphate and ammonium nitrate. Both aerosol and gas decrease in concentration exponentially with height (Warneck 1988). The major sink is wet and dry deposition, which removes about 49 Tg N y^{-1} from the atmosphere. NH_3 is also removed by direct uptake upon contact with plants and soil surfaces.

Nitrous oxide: Nitrous oxide (N_2O) is the other nitrogen gas compound apart from N_2 that is inert in the troposphere. With a lifetime of about 170 years (Table 2.8), its major sink is photochemistry in the stratosphere, where it may interfere with the ozone layer (see Chapter 3). N_2O is also a greenhouse gas (Chapter 5). Figure 2.6 establishes that the major source of N_2O is emissions from soil and oceans through microbial processes. In the ocean, highest concentrations and emissions to the atmosphere occur in areas where strong upwelling brings deep-water nutrients to the surface. Anthropogenic inputs are only about 8% of natural emissions, but are considered important because they are increasing over time. N_2O emissions increase with higher temperature and moisture. Emissions reach a daily maximum around noon, and seasonally the maximum occurs in summer. Emissions can be considerably enhanced on a local scale by irrigation practices. With its long lifetime and major natural sources, N_2O shows very little variation in global distribution, and decreases slightly with height in the troposphere, depending on the availability of photochemical activity.

Nitrogen oxide species: The nitrogen compounds that are most strongly influenced by anthropogenic emissions are nitric oxide (NO) and nitrogen dioxide (NO_2). These are often considered in combination as NO_x , and are the major part of a series of highly active primary and secondary compounds (including HCN and N_2O_5) which are together termed NO_y . Of the two gases, the main primary emission is NO, but this rapidly oxidises to NO_2 , leaving the latter dominant in the atmosphere. NO_x is short lived (Table 2.8) and oxidises rapidly into NO_3^- aerosol or HNO_3 (nitric acid). It is crucial to the formation of

Chapter 3

Tropospheric and Stratospheric Ozone

Recent developments in the field of global atmospheric chemistry have established that ozone (O_3) plays a crucial role in both the troposphere and stratosphere. The relationship between stratospheric ozone and climate has been under study for two decades, particularly in association with ozone depletion and ultraviolet radiation. It has only been since the late 1970s that the importance of tropospheric ozone chemistry has become extensively apparent. Tropospheric and stratospheric ozone are often considered together as total ozone in the atmospheric column, and both can have important impacts on the climate system. Both areas of ozone are influenced by the four major processes that dominate the geochemical and biogeochemical cycles in the atmosphere: emissions from natural and anthropogenic processes and resultant in-situ secondary formations; chemical transformations and reactions; atmospheric transport through circulation; and removal mechanisms (GTC 1984). Tropospheric ozone concentrations make up only 10% of the total ozone column, yet may have major impacts on climatic change through global warming (see Chapter 5).

The production and loss of ozone in both the troposphere and stratosphere are strongly linked to atmospheric chemistry at both levels. Excellent reviews can be found in Rodhe *et al* (1982); GTC (1984); WMO (1986); and Crutzen (1988). For the troposphere, this discussion will concentrate on basic gas-phase reactions which involve a few critical species: nitrogen oxides (NO , NO_2 , NO_x); free hydrogen/oxygen radicals (OH , HO_2 in particular); hydrocarbons (both methane, CH_4 , and non-methane, NMHC); and carbon monoxide (CO). For the stratosphere, processes involving nitrous oxide (N_2O) and chlorofluorocarbons are added.

Tropospheric Ozone

Background concentrations of tropospheric ozone can be found in rural and remote atmospheres. Concentrations created from anthropogenically dominated emissions occur in areas influenced by urban centres. Ozone in urban dominated atmospheres is discussed in Chapter 9. For purposes of this discussion, global background ozone and the associated chemistry are considered. In the unperturbed troposphere ozone formation and destruction are part of a dynamic balance controlled mainly by emissions from marine and terrestrial biospheres, and sinks through atmospheric photochemistry and surface deposition. As anthropogenic emissions enter the system, changes in the balance can occur,