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4 Biogeochemical cycles

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The elements carbon (C), nitrogen (N), sulphur (S), hydrogen (H), oxygen (O) and the halogens (X = F, Cl, Br, I) play key roles in the maintenance of life on the Earth. Quite apart from being essential components of the fundamental building blocks of life, such as proteins, these elements perform vital regulatory functions in the Earth system. For example, carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are naturally occurring greenhouse gases, trapping heat in the form of infrared radiation that otherwise would escape to space and thus ensures that the surface temperature of the Earth is habitable for life. Elements travel or cycle through the whole Earth system, i.e. the oceans, the atmosphere, the land, etc., and may be transformed from one compound to another as they do so. This is the basis of the study of biogeochemical cycles. In this chapter we will consider how these elements cycle through the atmosphere and how and why they are partitioned into the various compounds observed.

A fundamental concept is the budget of a compound: put simply we consider the sources (direct emissions and/or photochemical productions) of the compound and the sinks (loss processes chemically and/or physical) for the compound. If the sources and sinks balance this will lead to a constant concentration of the compound being observed in the atmosphere (Fig. 4.1a), if sources are greater than sinks the concentration of that compound in the atmosphere will increase with time (Fig. 4.1b), and if sources are less than sinks the concentration of that compound in the atmosphere will decrease with time (Fig. 4.1c). However, can we be more quantitative? If the budget is balanced what will the constant concentration be and what controls this parameter? It turns out (see the derivation of this equation which follows) that the concentration of a compound *A* at time *t*, $[A]_t$, is

$$[A]_t = E/R(1 - \exp(-Rt)) \quad (I)$$

where *E* is the source or emission rate and *R* is the loss rate. When sufficient time has elapsed, a constant concentration of *A*, $[A]_{\text{constant}}$ is reached and is equal to *E*/*R*. If the emission rate *E* increases, a new $[A]_{\text{constant}}$ is established which is bigger than before, and if the emission rate decreases the new $[A]_{\text{constant}}$ is smaller than before. If the loss rate *R* increases, $[A]_{\text{constant}}$ decreases and if the loss rate decreases, $[A]_{\text{constant}}$ increases. Hence, the concentration of any compound in the atmosphere is determined rather simply by *E* and *R*.

DERIVATION OF EQUATION (I)

Imagine compound *A* has a total source or total emission rate *E* (having units of mass emitted per unit time) and is

removed from the atmosphere at a rate R (having units of per unit time). We can write the rate of change of the concentration of A , $(d[A]/dt)$ as

$$d[A]/dt = E - R[A] \quad (\text{i})$$

When the emission and removal rates are equal, the concentration of A is constant with time (i.e. $d[A]/dt = 0$), hence

$$E - R[A]_{\text{constant}} = 0 \quad (\text{ii})$$

$$[A]_{\text{constant}} = E/R \quad (\text{iii})$$

What about the time scale required for this constant concentration to establish? Let

$$y = E - R[A] \quad (\text{iv})$$

$$\Rightarrow dy = -Rd[A] \quad (\text{v})$$

$$\Rightarrow -dy/R = d[A] \quad (\text{vi})$$

Substituting (iv) and (vi) into (i) we obtain

$$dy/dt \cdot (-1/R) = y \quad (\text{vii})$$

or

$$dy/y = -Rdt \quad (\text{viii})$$

Integrating leads to

$$\ln y = -Rt + C \quad (\text{ix})$$

where C is a constant of integration and substituting for y we obtain

$$\ln \{E - R[A]\} = -Rt + C \quad (\text{x})$$

Finally, assuming that $[A] = 0$ at $t = 0$

$$[A]_t = E/R(1 - \exp(-Rt)) \quad (\text{I})$$

Thus A will reach its steady state or constant value E/R with an e-folding time of $1/R$

Example

Given the following data calculate the steady-state concentration or constant concentration of A and plot the change in

concentration with time in each case:

$$1 \quad E = 10^{12} \text{ kg year}^{-1} \quad R = 10^{-6} \text{ s}^{-1}$$

$$2 \quad E = 10^{12} \text{ kg year}^{-1} \quad R = 10^{-4} \text{ s}^{-1}$$

$$3 \quad E = 10^{10} \text{ kg year}^{-1} \quad R = 10^{-6} \text{ s}^{-1}$$

Answer

Let t be the number of seconds in a year = $60 \times 60 \times 24 \times 365 = 3.1536 \times 10^7 \text{ s}$

$$1 \quad E/R = 10^{12}/(10^{-6} \times t) = 3.2 \times 10^{10} \text{ kg}$$

$$2 \quad E/R = 10^{12}/(10^{-4} \times t) = 3.2 \times 10^8 \text{ kg}$$

$$3 \quad E/R = 10^{10}/(10^{-6} \times t) = 3.2 \times 10^8 \text{ kg}$$

Notes

With a much shorter lifetime, scenario **2** reaches the steady-state concentration much more quickly than **1** or **3**. Scenarios **1** and **3** take the same time to reach steady-state because they have the same lifetime, but because the emission rate is greater for **1** than **3** the steady-state concentration is much larger.

4.1 Sources

Sources (sometimes referred to as emissions) of compounds in the atmosphere can be divided into primary and secondary sources. A primary source is one where the compound is released directly into the atmosphere, whereas a secondary source is one where the compound is generated *in situ* in the atmosphere. An example is carbon monoxide (CO) that has both primary and secondary sources in the atmosphere. Carbon monoxide is emitted directly into the atmosphere by a number of sources, such as from the exhaust of road vehicles during high temperature incomplete combustion of fossil fuels. It is also produced in the atmosphere from the photooxidation of hydrocarbons that are themselves emitted into the atmosphere (see Chapter 5). In addition there are two major primary sources, anthropogenic (from human activity) and biogenic (from natural sources). Typical anthropogenic sources include: mobile sources such as vehicles, railways, vessels and aircraft, and stationary sources such as manufacturing industries, power plants, waste incineration, buildings and homes. Biogenic sources include all living systems such as plants, trees, animals, insects and microbes. However, there are non-living natural sources of compounds in the atmosphere: for example dust in the atmosphere can come from wind-blown soil, and lightning is an important source of nitric oxide (NO) in the atmosphere. Biomass burning can be both anthropogenic (deliberate or accidental burning of vegetation by humans) and biogenic (e.g. natural forest fires) and are an important source of a number of compounds. In general, anthropogenic source strengths can be quite constant (e.g. power plant emissions) or at least tend to follow a regular pattern (vehicle emissions follow a regular diurnal pattern). Hence it is possible to determine the overall anthropogenic source strength of a particular compound by constructing an emission inventory (several examples follow in this chapter), but such inventories are still an approximation. Biogenic source strengths are often determined by levels of sunlight, temperature and nutrients, and can therefore be highly seasonal in nature. Therefore, it is much harder to estimate the biogenic source strength of a particular compound.

4.2 Sinks

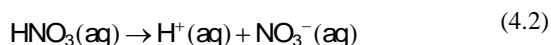
There are two main sink or loss processes for compounds in the atmosphere, namely depositional (sometimes referred to as physical) loss processes and photochemical loss processes.

Depositional loss processes

There are two types of depositional loss, wet deposition and dry deposition. Wet deposition involves the uptake of soluble compounds into aqueous media, e.g. aerosols, fogs, clouds and during rainfall. Therefore, the more soluble a species is the faster the uptake and therefore the greater the loss rate (see Chapter 6 for more details). A measure of the solubility of a species is the Henry's Law coefficient K_H ($\text{mol L}^{-1} \text{atm}^{-1}$) and the fraction of compound C remaining in the gas-phase after dissolution can be expressed as

$$C/C_0 = 1/(1 + 10^{-6} K_H RT (L/\rho_w)) \quad (\text{II})$$

where C/C_0 is the fraction of species C remaining in the gas-phase, R is the gas constant ($0.08205 \text{ l atm mol}^{-1} \text{K}^{-1}$), T is the temperature in Kelvin, L (g m^{-3}) is the liquid water content and ρ_w is the density of water (1 g cm^{-3}). Solubility increases as the relative amount of oxygen in the compound increases, so methane (CH_4) is rather insoluble, whereas methanoic acid (HCOOH) is moderately soluble. Compounds such as hydrogen peroxide (H_2O_2) are highly soluble and wet deposition is an appreciable loss process in this case. Strong acids such as nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will not only dissolve in aqueous media but will undergo rapid dissociation once in the aqueous phase, e.g.



Such strong acids undergo near total uptake into the aqueous phase.

Dry deposition occurs when a compound can be adsorbed or react on surfaces at the ground and removed from the atmosphere. There are several factors that determine the dry deposition loss rate. The first is the characteristics of the gas. The more polar the gas the more likely it is to have a significant dry deposition rate (polarity arises when there is an uneven distribution of charge about a chemical bond and is particularly associated with compounds that contain elements such as F, O, Cl). Second, the surface type is of course important the rate of dry deposition to an ice surface is likely to be very different to that to a surface covered with vegetation. It is usual to relate the flux F ($\text{mol m}^{-2} \text{s}^{-1}$) to the surface to the gas concentration C (mol m^{-3}) at a reference height, where the constant of proportionality is the dry deposition velocity (V_d). Hence

$$F = -V_d C \quad (\text{III})$$

Dry deposition velocity is normally associated with a reference height of 10 m and will be positive for a depositing species. The V_d will vary with gas and surface type and is typically $0.1\text{--}1 \text{ cm s}^{-1}$ for gases. The simple concept of deposition velocity (V_d) is useful for incorporation into complex atmospheric models, but this hides the complexity of the deposition process. In reality the dry deposition process consists of three distinct phases. First, turbulent transfer from the bulk atmosphere transports material to a thin layer of stagnant air adjacent to the surface. Second, molecular diffusion transports material across this layer to the surface. Third, material can now be taken up by the surface. It is usual to model each of these processes by a concentration difference and an associated resistance to transfer. The total resistance R_t can be related back to the deposition velocity via

$$R_t = R_a + R_b + R_c = V_d^{-1} \quad (\text{IV})$$

where R_a is aerodynamic resistance, R_b is the quasi-laminar resistance and R_c is the surface resistance. Such a model of dry deposition is known as the bulk resistance model.

Photochemical loss processes

Compounds can also be converted to another compound in the atmosphere via photochemical processes. The simplest photochemical loss process is photolysis itself, where a compound absorbs a photon of sunlight and this energy leads to

dissociation of that molecule or isomerization, where the new molecule has the same composition but is structurally different from its parent compound. In the lowest 10 km of the atmosphere, the troposphere, the wavelengths of solar energy available are those longer than 300 nm. Aldehydes and ketones and iodocarbons in particular can be dissociated by solar photons in this region. At higher altitudes in the atmosphere, in the stratosphere (between around 10 and 50 km) higher energy photons as short as around 200 nm are available. Here, many molecules such as H₂O₂, HNO₃, methyl chloride (CH₃Cl), methyl bromide (CH₃Br) and the chlorofluorocarbons (CFCs) can be dissociated. The rate of photolysis J is given by

$$J = \int \Phi \Psi \sigma d\lambda \quad (V)$$

where Φ is the quantum yield, i.e. the number of molecules dissociated per photon (usually Φ is 1), Ψ is the photon flux, i.e. the number of photons at a particular wavelength per unit area per second, and σ is the absorption cross-section, which is a measure of how likely the molecule will absorb a photon at a particular wavelength.

WORKED EXAMPLE 4.1

Calculate the photolysis rate of nitrogen dioxide (NO₂) given the following data averaged over the wavelength range 300–400 nm:

$$\Phi = 1.0; \Psi = 5 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}; \sigma = 2 \times 10^{-19} \text{ cm}^2$$

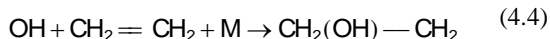
$$\begin{aligned} J(\text{NO}_2) &= \int \Phi \Psi \sigma d\lambda = 1.0 \times 5 \times 10^{15} \times 2 \times 10^{-19} \\ &= 1 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

Chemical reaction can be initiated by free radicals such as hydroxyl (OH), chlorine (Cl) and nitrate (NO₃) or by reaction with ozone (O₃) (see Chapter 5) and stabilized Criegee intermediates (sCI). Throughout the daytime atmosphere the OH radical is an important oxidant, whereas the NO₃ radical is important only at night. In the marine environment and in polar regions Cl atoms can be an important oxidant in the troposphere; their role in the stratosphere is discussed in Chapter 8. Ozone can react with unsaturated species such as alkenes. The primary ozonide formed from the reaction of ozone with an alkene dissociates into a vibrationally excited Criegee intermediate which can then either undergo unimolecular decomposition or form a sCI. Stabilized Criegee intermediates can be an important oxidant over the regions of high emissions of the precursors (e.g. unsaturated hydrocarbons). Table 4.1 shows how the rate coefficients of the reactions of OH with some hydrocarbons vary and their corresponding lifetimes (see an example of lifetime determination that follows). If one considers the alkanes, e.g. CH₄, ethane (C₂H₆) and propane (C₃H₈), the reaction with OH proceeds via abstraction of a hydrogen atom:



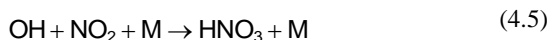
Therefore, it is possible to explain the increase in rate coefficient from CH₄ to C₃H₈ by the fact that there are progressively more H atoms available. Therefore, one would conclude that very large alkanes react very quickly and have short lifetimes; this is indeed the case. If one compares CH₄ with CH₃Cl, by our previous argument, we would assume that CH₃Cl would react more slowly than CH₄, with 3 H atoms as opposed to 4. However, this is not the case. Now we must consider the effect of the C—Cl bond. We know that Cl is electronegative and will draw electron density away from C and leave the 3 H atoms with a slight positive charge. This induced dipole increases the reaction between the H and OH. If we replace all the H atoms in CH₄ with Cl, i.e. CCl₄, we reach a situation where OH cannot react with the compound; it is an endothermic process. Hence, CCl₄ can accumulate in the troposphere and will reach the stratosphere where it is

broken down by ultraviolet light, releasing chlorine (Chapter 8). Once again, if we consider the alkene, e.g. ethene (C₂H₄), by considering the number of H atoms, we would conclude that OH should react more quickly with C₂H₆ and at about the same rate as CH₄. Inspection of Table 4.1 shows that OH reacts 10 000 times faster with C₂H₄ than it does with CH₄. The reason is that a different mechanism, addition, is occurring:



The OH radical adds to one end of the double bond rapidly, forming a radical. Isoprene (C₅H₈) contains two double bonds and is therefore even more reactive.

Whereas deposition usually leads to the permanent removal of that compound from the atmosphere, it is possible in some cases for the compound to be reformed if the photochemical reaction converts the compound into a temporary reservoir, which can then be decomposed into its component parts, e.g.



In reaction (4.5) OH radicals and NO₂ combine to form nitric acid (HNO₃) but in the stratosphere this can be photolysed (reaction 4.6) to release back OH and NO₂. Note that hν represents a photon of light. Therefore, the full equation that describes the budget of a compound *x* can be written:

$$dX/dt = E_P + P_{PC} - V_d[X]/h - k_w[X] - L_{PC}[X] \quad (\text{VI})$$

where *E_P* is the emission rate from primary sources, *P_{PC}* is the production rate from *in situ* photochemistry, *V_d/h* is the dry deposition loss rate, *k_w* is the wet deposition loss rate and *L_{PC}* is the loss rate from *in situ* photochemistry (chemical reactions and photolysis).

LIFETIMES

A simple way to determine the lifetime of compound *x* is to consider the following example of species *x*, which is removed primarily by reaction with OH, photolysis, dry deposition and wet deposition:

$$-d[X]/dt = k_r[\text{OH}][X] + J[X] + V_d[X]/h + k_w[X] \quad (\text{i})$$

$$\begin{aligned} \Rightarrow -d[X]/[X] &= (k_r[\text{OH}] + J + V_d/h + k_w) dt \\ \Rightarrow \int d[X]/[X] &= \int -(k_r[\text{OH}] + J + V_d/h + k_w) dt \\ \Rightarrow \ln \{[X]/[X]_0\} &= -(k_r[\text{OH}] + J + V_d/h + k_w)t \end{aligned}$$

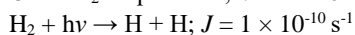
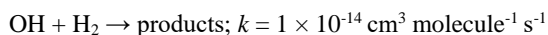
(ii)

where [X]₀ is the initial concentration and [X] the concentration after time *t*. Therefore, the time scale for the decay is given by the term (k_r[OH] + J + V_d/h + k_w), and the lifetime is 1/{k_r[OH] + J + V_d/h + k_w}, i.e. the lifetime is the

reciprocal of the sum of the loss rates. The larger the loss rate the shorter the lifetime.

WORKED EXAMPLE 4.2

Calculate the lifetime of hydrogen (H_2) at the Earth's surface given the following information:



$$k_w(\text{H}_2) = 1 \times 10^{-9} \text{ s}^{-1}$$

$$V_d(\text{H}_2) = 1 \times 10^{-9} \text{ ms}^{-1}$$

Assume that $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$ and $h = 0.1 \text{ m}$.

Answer

$$\begin{aligned} \text{Lifetime of } \text{H}_2 &= 1 / \{k_t[\text{OH}] + J + V_d/h + k_w\} \\ &= 1 / (1 \times 10^{-14} \times 1 \times 10^6 + 1 \times 10^{-10} + 1 \times 10^{-9} + 1 \times 10^{-9}/0.1) \\ &= 47\,393\,365 \text{ s} \\ &= 1.5 \text{ years} \end{aligned}$$

4.3 Carbon

All living matter is carbon based and the element is an essential part of life on Earth. The major reservoirs of carbon in the atmosphere are CO_2 (~400 ppmv), CH_4 (~1.8 ppmv) and CO (~0.1 ppmv), but, myriad other volatile organic compounds (VOCs) are emitted into the Earth's atmosphere from a variety of sources and constitute a large pool of atmospheric carbon.

Carbon dioxide

Measurements of levels of CO_2 over the past 50 years or so (Fig. 4.2) show a dramatic rise from around 315 ppmv in the late 1950s to the present day value of over 400 ppmv. Analysis of ice cores has facilitated an assessment of the changes to atmospheric levels of CO_2 (Barnola *et al.*, 1987). The analysis shows that up until 1800, levels of CO_2 were pretty constant at 280 ppmv, but have risen dramatically since the onset of the Industrial Revolution. The cause of this rapid change is a combination of the burning of fossil fuel, deforestation and changes in land use. Carbon dioxide is the major contributor (~60%) to the total radiative forcing of the long-lived greenhouse gases, trapping outgoing terrestrial radiation in the infrared region of the spectrum, and an increase in its atmospheric mixing ratio is expected to lead to a warming of the Earth's surface. The extent of the warming predicted is currently of considerable debate, but estimates based on future global population and land use suggest that levels of CO_2 may double from pre-industrial levels to around 700 ppmv, and that global surface temperatures may increase by around 2–4.5°C over the next 100 years (IPCC, 2013). Current estimates for the 'budget' of CO_2 (see Table 4.2), based on measurements over the period 2002–2011, show that for a perturbation of 8.3 Gt C year⁻¹, approximately half is retained in the atmosphere, with major known sinks being the ocean (~ 2.1 Gt C year⁻¹) and uptake by land (~ 1.6 Gt C year⁻¹). If CO_2 levels rise as expected and the associated warming of the surface is realized, this will have potential consequences for the CO_2 sink terms. Carbon dioxide is less soluble in warmer water and global warming will lead to a gradual rise in sea-surface temperatures, hence reducing the effectiveness of the ocean as a sink for CO_2 . In addition, as the amount of dissolved inorganic carbon in the ocean increases, a decrease in ocean buffering is expected, again reducing the effectiveness of the ocean to take up CO_2 . Nevertheless, biological processes in the ocean may themselves counteract these physical changes. For example,

favourable changes in the external supply of biologically limiting nutrients such as iron (Fe), silicon (Si), phosphorous (P) and nitrogen (N), could increase the strength of biological production within the ocean surface and assimilate more CO₂ dissolved in the ocean.

It is readily apparent that the climate system is extremely complex. The exchange of CO₂ with terrestrial plants is another important sink. Plants assimilate CO₂ in the process of photosynthesis, releasing O₂, where the gain in carbon is known as the gross primary production (GPP). However, plants also release CO₂ through respiration processes (taking up O₂) and so the difference between assimilation and release of CO₂ gives the net primary production (NPP), i.e. the net amount of new stored carbon. The largest land NPP is found in tropical forests (33%), tropical savannas and grasslands (22%) with cultivated land (6%), temperate forests (12%), wetlands (6%), temperate grassland and shrubland (10%), boreal forests (4%) and deserts and semi-deserts (4%) all making significant contributions to CO₂ uptake (Ajtay *et al.*, 1979; IPCC, 2013). Assessing the response of plants to increasing CO₂ levels is far from simple. It has been shown that growth promotion occurs under elevated CO₂ levels, and studies suggest that an increase in growth of more than 30% is typical for a doubling of CO₂ concentration. However, growth temperature is very important, and it has been observed that simultaneous increases in air temperature and CO₂ concentration offset the stimulation of biomass and grain yield in rice compared with increases in CO₂ alone. Elevated CO₂ does seem to raise the maximum temperature at which plants can survive, but for any plant, exceeding their optimal growing temperature will have serious consequences on their growth. Therefore, the response of a particular species to changes in CO₂ levels will depend on how far away from its optimal growing temperature it is. Again in studies on rice, it was found that season-long enrichments of CO₂ from 300 to 700 ppmv resulted in a 21–27% increase in net canopy photosynthesis and a 10% reduction in total evapotranspiration. Higher levels of CO₂ lead to partial closure of stomata, reducing the stomatal conductance and leading to increasing water-use efficiency. Therefore, increasing CO₂ levels may have an overall positive effect on terrestrial plant growth, but there are caveats, which will be discussed in a later section. The overall lifetime of CO₂ is around 120 years, and it is therefore well mixed in the atmosphere.

Methane

Methane (CH₄) is the most abundant organic species in the atmosphere and contributes ~18% to the radiative forcing attributed to long-lived greenhouse gases. On a molecule per molecule basis, CH₄ is a far more effective greenhouse gas (factor of 20 based on a 100 year time horizon) than CO₂ and therefore understanding its budget is of great importance. In a similar way to CO₂, levels of methane have risen dramatically over the past 200 years. Pre-industrial levels were around 750 ppbv, but now stand at ~1800 ppbv in the Northern Hemisphere and ~1700 ppbv in the Southern Hemisphere. Methane increased at around 1.3% per year for most of the twentieth century until the early 1990s (Blake & Rowland, 1988), when the rate of growth slowed to 0.6% per year (Steele *et al.*, 1992) and a near zero growth rate was observed between 1999–2006 (IPCC, 2013). It is not known with certainty why there has been a slowdown: reduction in sources or an increase in the concentration of the OH radical, the major sink for CH₄, are possibilities. Since 2007 CH₄ levels have risen again by approximately 1%. The current estimated budget for CH₄ is shown in Table 4.3, where it is apparent that both natural and anthropogenic sources are equally important. The anthropogenic sources are evenly spread between fossil-fuel-related release (30% of the total anthropogenic source), waste management (22%), enteric fermentation of cattle (27%), biomass burning (10%) and rice paddies (11%). Natural sources of CH₄ are dominated by wetland emissions, particularly in the tropics. The decomposition of organic matter under oxygen-deficient conditions leads to the production of CH₄ and it is no surprise that where temperature is highest and microbial activity most intense, the largest natural source of CH₄ is found. Termites also produce a non-negligible quantity of CH₄, and other insects may well do the same. The dominant loss process for CH₄ in the atmosphere is via reaction with the hydroxyl radical, OH, $k_{298} = 6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (DeMore *et al.*, 1997), with minor contributions from stratospheric removal and consumption of methane in soils by methanotrophic bacteria. The global residence time of CH₄ in the atmosphere is approximately 10 years, leading to a slight interhemispheric gradient.

Carbon monoxide

The budget of CO is dominated by the atmospheric oxidation of methane and other VOCs (see next section), initiated by the OH radical (see Chapter 5) and from incomplete combustion associated with biomass burning and fossil fuels. Vegetation and oceans are also a non-negligible source of CO. Hence, anthropogenic sources dominate, although it

should be noted that the oxidation of natural VOCs released from vegetation provides over half the source from VOC oxidation. Despite having no significant direct impact on global warming, CO is an extremely important atmospheric species, whose major loss process is reaction with OH ($k_{298} = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997) giving the atmospheric residence time of *ca.* two months.



In fact, reaction with CO constitutes ~70% of the total sink for OH, hence the importance of CO in the Earth's atmosphere. A strong gradient exists between Northern Hemisphere and Southern Hemisphere CO levels e.g., current background levels of CO are 60–70 ppbv in the Southern Hemisphere and 120–180 ppbv in the Northern Hemisphere, with extremely high levels experienced in urban and industrialized areas (as high as ppm levels). The strong gradient exists because the Northern Hemisphere has much larger anthropogenic sources than does the Southern Hemisphere. Furthermore, the abundance of the OH radicals within the tropics prevents large scale inter-hemispheric transport. A summary of the global atmospheric budget is given in Table 4.4.

Volatile organic compounds

Myriad volatile organic compounds (VOCs) are emitted into the atmosphere by both biogenic and anthropogenic sources. These VOCs have varying lifetimes depending on their structure, with the vast majority undergoing photooxidation initiated by the OH radical (Chapter 5), ultimately leading to the production of CO₂ and H₂O. Photooxidation may lead to the production of intermediate compounds such as carboxylic acids and nitrates, which are soluble and therefore can be removed by wet deposition. In general, the biogenic VOCs are more reactive in the atmosphere than the anthropogenic VOCs, thus the biogenic VOCs play a significant role in photochemical oxidation cycles even when their concentrations are lower. Natural sources of VOCs are believed to dominate (Singh & Zimmerman, 1992) constituting around 90% of the carbon flux. Apart from methane and dimethyl sulphide, the major source of biogenic VOCs is terrestrial plants (Fall, 1999). In some cases the reason why plants manufacture certain VOCs is well known. For example, ethene plays a key role in growth and development and its production is greatly enhanced following plant wounding, exposure to chemicals and infection (Fall, 1999). However, for other VOCs such as isoprene (2-methyl 1,3-butadiene, C₅H₈) the reason for its production is less clear.

Emission of isoprene is in fact the single largest source of carbon to the atmosphere after methane. In general, deciduous trees and most woody plants emit isoprene, although ferns, vines and some herbaceous plants are also emitters. Emission of isoprene is light dependent, dropping to zero in the dark, and is also temperature dependent, with the flux increasing rapidly with temperature. Figure 4.3 shows the distribution of isoprene emissions derived from a land-surface vegetation model (Wang & Shallcross, 2000). Singaas *et al.* (1997) have suggested that isoprene acts as a thermal protectant, which is consistent with the observation that emissions are elevated as temperature increases. However, there are problems with this explanation in that many species in hot desert environments do not emit isoprene at all, whereas plants of the same genus in more temperate climates do (Fall, 1999). Another possible explanation includes neutralization of free radicals within the plant. Isoprene is extremely short-lived, whose rate coefficient for reaction with OH is near the gas-collision limit ($k_{298} = 1.01 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, DeMore *et al.*, 1997), giving rise to a lifetime of a few hours. Consequently, levels of isoprene in the atmosphere are very variable and display a strong diurnal (day–night) cycle, peaking in mid-afternoon and rapidly decaying at night, as well as a strong seasonal cycle, peaking in late spring. In forests, levels of isoprene can reach 15 ppbv, although pptv levels are more typical elsewhere.

In Chapter 5 a detailed discussion is presented of the role played by VOCs in the presence of NO_x (NO and NO₂) in the production of tropospheric ozone. At the Earth's surface ozone is deleterious to plants, entering the stomata and destroying cell lining, while being itself a greenhouse gas. As levels of CO₂ increase it is anticipated that global emissions of isoprene will also increase, driven mainly by increasing surface temperature. It has been noted that isoprene may be responsible for a significant proportion of ozone production in the troposphere, and it is possible that isoprene emissions will change in the future, changing tropospheric ozone. Once again, natural biogeochemical cycles are intricately coupled with the climate system.

Monoterpenes (C₁₀H₁₆) are another major class of VOC manufactured by plants. A selection of the most common monoterpenes is shown in Fig. 4.4, whose ecological role includes herbivore defense, attraction of pollinators and

allelopathic effects on competing plants. Monoterpene emissions are dependent on temperature rather than light and therefore emissions continue into the night. Monoterpenes rapidly react with the OH radical, and also with the NO₃ radical and like isoprene have short lifetimes of a few hours to days. Plants also emit C₆ aldehydes and alcohols known as the hexenal family, which have antibiotic properties (Hatanaka, 1993).

Anthropogenic emissions of VOCs are dominated by combustion of fossil fuel, with alkanes, aromatics and alkenes being the major VOC classes. In urban areas, emissions of VOCs follow a typical diurnal cycle, tracking rush hour traffic flow. Photochemical smog formation in the summer months is driven by the emission of these VOCs, in the presence of NO_x and sunlight (Chapter 5). In urban areas, individual VOC levels can be of the order of some ppbv, whereas in background air levels of the more reactive species can be in the pptv range or less.

WORKED EXAMPLE 4.3

Carbon cycle

Given the concentration of CO₂ (400 ppmv), CH₄ (1.8 ppmv) and CO (0.1 ppmv) what is the fraction of carbon in each reservoir?

Simple answer:

$$\text{CO}_2 = 400/401.9 = 0.9953$$

$$\text{CH}_4 = 1.8/401.9 = 0.0045$$

$$\text{CO} = 0.1/401.9 = 0.0003$$

Not all the compound is carbon though

$$\begin{aligned} \text{CO}_2 \text{ fraction of carbon} &= 12/44 \\ &= \text{molar mass of carbon/molar mass of CO}_2 \end{aligned}$$

$$\begin{aligned} \text{CH}_4 \text{ fraction of carbon} &= 12/16 \\ &= \text{molar mass of carbon/molar mass of CH}_4 \end{aligned}$$

$$\begin{aligned} \text{CO fraction of carbon} \\ &= 12/28 \text{ molar mass of carbon/molar mass of CO} \end{aligned}$$

Revised answer:

$$\text{CO}_2 = 109.1/110.5 = 0.9874$$

$$\text{CH}_4 = 1.35/110.5 = 0.01222$$

$$\text{CO} = 0.04/110.5 = 0.0004$$

Not a large difference but the importance of CH₄ has doubled!

4.4 Nitrogen

Nitrogen (N₂) represents nearly 80% of the Earth's atmosphere and is chemically inert throughout the lower atmosphere. Only in the upper atmosphere, where significant fluxes of very short wavelength radiation can be found, N₂ can be broken down by photolysis. Despite their small and highly variable sources, the other nitrogen-containing species present in the atmosphere at significant levels, ammonia (NH₃), NO and NO₂ play a disproportionately large role in determining atmospheric composition. Ammonia for example is the only alkaline gas in the atmosphere and is important in the neutralization of acid aerosols. Nitrogen oxides, NO and NO₂, play a vital role in the production and destruction of ozone in both the troposphere (Chapter 5) and the stratosphere (Chapter 8) and therefore affect the radiative budget of the Earth and the oxidizing capacity of the atmosphere.

Nitrous oxide

Nitrous oxide (N₂O) is one of the most important greenhouse gases, whose current atmospheric mixing ratio is about 330 ppbv, compared with an estimated pre-industrial level of around 285 ppbv with a mean growth rate of ~0.9 ppb yr⁻¹ over the past 10 years. N₂O has a Global Warming Potential (GWP) which is ~300 times higher than that of CO₂ for a time horizon of 100 years. Nitrous oxide has an extremely long lifetime (~150 years) and is virtually inert in the troposphere, being destroyed in the stratosphere by direct photolysis and reaction with O(¹D) atoms



Nitrous oxide is released to the atmosphere from both soils and aquatic systems with soils under natural vegetation (undisturbed soils) (37%), cultivated soils (agriculture) (23%) and oceans (21%) making up the bulk of the known sources. The fossil fuel combustion and various industrial processes can also make a non-negligible contribution to the sources of N₂O. Overall the contribution of anthropogenic sources is about the same as natural terrestrial sources (IPCC, 2013). Denitrifying bacteria transform nitrate to N₂ and some N₂O under anaerobic conditions, which can then evade to the surface and enter the atmosphere. The major uses of nitrogen fertilizers in the Northern Hemisphere make a small Northern to Southern gradient of ~1.2 ppbv. A budget for N₂O is presented in Table 4.5 based on the IPCC (2013) assessment. There are many uncertainties including the estimation of the ocean source, since N₂O is both lost to and emitted from the oceans. Since it delivers NO_x to the stratosphere, N₂O plays an important role in controlling the abundance of stratospheric ozone.

Ammonia

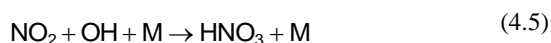
Ammonia has a short lifetime in the atmosphere of approximately 1-2 days and is removed mainly by both wet and dry deposition processes, with some additional small loss processes via reaction with OH and NO₃ radicals. The main sources arise from biological activity, such as the decomposition of urea in animal urine by enzymes, the decomposition of excrement and the release from soils and the ocean following mineralization of organic material. Anthropogenic sources are ~4-fold higher than natural sources which centre around its use in fertilizers and as a byproduct of waste production. Since deposition processes dominate its loss and sources are diverse, levels of ammonia are highly variable, ranging from 0.1 to 10 ppbv over continental regions. It has already been noted that ammonia is the only alkaline gas in the atmosphere and neutralizes H₂SO₄, HNO₃ and HCl to form ammonium salts leading to aerosols. Deposition of ammonium salts to the soil decreases its pH, leading to a decline in growth and the aerosols from these salts can deteriorate regional air quality and atmospheric visibility and influence global radiation budgets (see Chapter 2).

Nitrogen oxides

In the atmosphere, NO and NO₂ (NO_x) are extremely tightly coupled during sunlit hours and rapidly interconvert with one another in the presence of ozone (see Chapter 5):



Individually, NO and NO₂ have extremely short lifetimes of the order of seconds, but, by considering the two compounds together as NO_x, the lifetime is lengthened to many hours. Hence, NO and NO₂ display strong diurnal cycles and their concentrations will display a seasonal cycle. In urban areas, NO_x can reach hundreds of ppbv, and in particularly polluted environments ppmv levels, whereas clean maritime air will have levels of only 5–10 pptv. The major loss processes for NO_x are conversion to HNO₃ via reaction with OH



and dry deposition of NO_x. Nitric acid can be removed by wet and dry deposition, constituting a loss of NO_x from the atmosphere. In the troposphere, in the presence of VOCs, NO_x can promote the formation of ozone (Chapter 5) and can also be sequestered to form temporary nitrate reservoirs such as peroxyacetylnitrate (PAN), which is an acyl nitrate (CH₃C(O)O₂NO₂). PAN is an excellent indicator of the photochemical processing of an air mass, which can allow NO_x to be transported away from source regions and influence chemistry on regional and global scales.

For most sources, NO_x is emitted in the form of NO. Natural sources of NO are from soil processes and lightning discharge, while an ever increasing source is that from the high-temperature combustion of fossil fuels. At the high temperatures inside an internal combustion engine



leads to the formation of NO. There are considerable uncertainties within the budget for NO_x, such as the soil and lightning source strengths, however, the burden from fossil fuels is reasonably well defined and set to increase globally, despite the growing use of three-way catalysts in vehicles and is summarized in Table 4.6.

4.5 Sulphur

Sulphur is incorporated into the amino acid residue cysteine and methionine and is vital for the structural integrity of proteins; therefore it is an essential element for living organisms on Earth. Cross-linking in proteins via sulphur–sulphur bonds is of great importance; intermolecular ‘disulphide’ linkages can lead to large-scale structures such as nails, while intramolecular linkages allow the protein to adopt specific configurations as in the case of an enzyme. On decomposition by bacteria, organic sulphur compounds usually release hydrogen sulphide (H₂S). However, H₂S is but one of many sulphur compounds released into the atmosphere, which include sulphur dioxide (SO₂), carbonyl sulphide (OCS), carbon disulphide (CS₂) and dimethyl sulphide (CH₃SCH₃, also known simply as DMS).

Since the onset of the industrial revolution the sulphur burden in the atmosphere has increased dramatically due to the burning of fossil fuels that inevitably contain some sulphur. Hence the anthropogenic contribution to the total sulphur

emission budget, mainly in the form of SO₂, approaches 75%, with the bulk of these emissions (around 90%) emanating from the Northern Hemisphere. Natural emission sources, which make up the remaining 25%, are pretty evenly distributed over the two hemispheres, with a slight bias towards the Northern Hemisphere (Brasseur *et al.*, 1999). It should be noted that a very large amount of sulphate is released into the atmosphere from the oceans in the form of sea salt. However, these very coarse particles are rapidly deposited back to the ocean and play no further role in the global sulphur cycle. In addition, sulphur-containing minerals are transported around the globe during wind-driven erosion of soils.

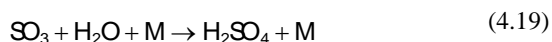
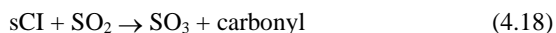
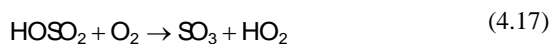
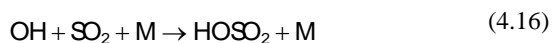
A summary of the most recent estimates of the global budgets for each of the five main sulphur species is presented in Table 4.7. It is apparent that each of these budgets has a large error associated with it, despite intensive research over the past 25 years. The diverse range of sources and their often inaccessibility to study means that the sulphur budget is still only known approximately and new sources and sinks for each compound may well emerge in the future.

Sulphur dioxide

The burning of fossil fuels is the major source of SO₂ in the atmosphere, with volcanoes, smelting of metal sulfides and oil refineries being other significant sources. The contribution to the SO₂ budget from the oxidation of natural reduced sulphur compounds (see later) is quite minor by comparison. The sinks of SO₂ are dry and wet deposition, and oxidation by OH and stabilized Criegee Intermediates (sCI) in the gas phase or by O₃ and H₂O₂ in the aqueous phase which make its lifetime from few hours to several days. Sulphur dioxide emissions are strongly linked with acid rain formation which can damage plant and animal life as well as damage buildings and monuments and are also known to lead to respiratory problems in humans and animals.

The presence of aerosols in the atmosphere has an influence on the Earth's climate, resulting from both direct and indirect effects on the radiation budget (see Chapter 2). The direct effect arises because aerosols scatter and absorb incoming solar radiation, thereby reducing the energy reaching ground level. The indirect effect results from the role of aerosols in cloud formation, since clouds reflect incoming radiation. Both effects are influenced by the number, size distribution and chemical composition of the aerosol, and are currently believed to lead to atmospheric cooling, which offsets the warming influence of radiatively active greenhouse gases such as CO₂.

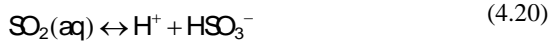
The majority of aerosols in the atmosphere are generated as a result of gas-to-particle conversion processes, although there are substantial contributions from other sources, such as resuspended mineral dust and sea-salt aerosols. An essential prerequisite for gas-to-particle conversions to occur is the presence of a species in the gas phase at a partial pressure in excess of its saturation vapour pressure with respect to the condensed phase (i.e. condensable material). It is generally accepted that the most significant condensable molecule formed in the troposphere is sulphuric acid (H₂SO₄), which has also been long recognized as the most important from the point of view of the nucleation of new particles. The major source of H₂SO₄ results from the oxidation of anthropogenically derived SO₂, for which the predominant gas phase oxidation pathway is initiated by reaction with the OH radical and sCIs:



In recent years, the role of sCI has become important in sulfur chemistry due to the rapid oxidation of SO₂ which accounts for significant production of SO₃ (and ultimately H₂SO₄). The oxidation of SO₂ by sCIs can rival the OH oxidation pathway especially in high alkenes emission terrestrial regions (e.g. rainforest, boreal forest, heavily polluted urban environments). Given the typical rate coefficients for $k_{4.18} \sim 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{4.16} \sim 9.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a daytime [OH] $\sim 1.0 \times 10^6 \text{ molecule cm}^{-3}$ results in a [sCI] $\sim 2.3 \times 10^4 \text{ molecule cm}^{-3}$ being required

for the two SO₂ oxidation rates to be equal. A variety of model-measurement studies have estimated surface level of sCI in the range of 1 × 10⁴ molecule cm⁻³ to 1 × 10⁵ molecule cm⁻³ (Khan *et al.*, 2018), thus sCI can make a significant contribution to H₂SO₄ formation in the terrestrial boundary layer.

Once formed, sulphuric acid will either be taken up by existing aerosols or will create new ones. Sulphur dioxide is sufficiently soluble for aqueous phase oxidation to be another important route for its conversion to sulphuric acid ($K_H \sim 1.23 \text{ mol L}^{-1} \text{ atm}^{-1}$ at 25° C). Once taken up into the aqueous phase, SO₂ establishes an equilibrium with the bisulphite ion and the sulphite ion



where K_1 is the equilibrium constant for reaction (4.20) and K_2 is the equilibrium constant for reaction (4.21). The Henry's Law coefficient for SO₂, $K_H(\text{SO}_2)$, can be expressed as

$$K_H(\text{SO}_2) = [\text{SO}_2(\text{aq})]/P(\text{SO}_2) \quad (4.22a)$$

where [SO₂(aq)] is the aqueous concentration of SO₂ and $P(\text{SO}_2)$ is the partial pressure of SO₂ in the gas-phase, but, because of the formation of bisulphite (the dominant species in HSO₃⁻ in aqueous media) and sulphite ions, it is more common to use an effective Henry's Law coefficient, termed $k_{\text{Heff}}(\text{SO}_2)$ and defined as

$$k_{\text{Heff}}(\text{SO}_2) = \frac{([\text{SO}_2(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}])}{P(\text{SO}_2)} \quad (4.22b)$$

Equation (4.22) can then be rearranged in the form

$$K_{\text{Heff}}(\text{SO}_2) = k_H(\text{SO}_2) \left(1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2 \right) \quad (4.23)$$

Inspection of equation (4.23) shows that solubility of SO₂ is dependent on pH, decreasing at low solution pH, where the $k_{\text{Heff}}(\text{SO}_2)$ then approaches the value of $k_H(\text{SO}_2)$. The aqueous-phase oxidation of the bisulphite ion to the sulphate ion is dominated by H₂O₂ for pH < 5, with oxidation by dissolved ozone becoming the main contributor for pH > 4.5. Other mechanisms for aqueous-phase oxidation exist (see Jacob & Hoffmann, 1983) but are generally less important. Depending on the amount of moisture in the atmosphere, 20–80% of the SO₂ emitted is oxidized to sulphate, with the remainder being removed by dry deposition. The mixture of SO₂ and sulphate (i.e., sulfur tropospheric aerosol) has a lifetime of between 2 and 6 days before being lost via wet or dry deposition. Because of the short-lived nature of sulfur tropospheric aerosols, the cooling effect is very localized and short-lived compared with the warming effects of greenhouse gases.

Highest SO₂ mixing ratios are found over the major industrial regions of the world, the eastern USA, Europe and the far east, where levels are as high as a few ppb. Reliable measurements of SO₂ in remote regions are problematic due to loss of SO₂ on moist surfaces, such as instrument inlets, but, mixing ratios drop to below 100 pptv.

Carbonyl sulphide

There are a large variety of carbonyl sulphide (OCS) sources, both natural and anthropogenic. Coastal regions of oceans and areas of high biological activity are found to have higher fluxes of OCS than open waters, yet overall the oceans are a significant source. Biomass burning accounts for almost 10% of the global OCS emissions yet there is no clear distinction as to what percentage is natural (from forest fires) or man-made (from burning agricultural waste, deforestation, firewood burning). Soils, wetlands and volcanoes are other sources of OCS, but their impact is far less important than the other sources. The two other important sources of OCS are the oxidation of CS₂ and DMS. Carbonyl sulphide is relatively insoluble ($K_H \sim 2.2 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 25° C) and the major loss processes are uptake by oxic soils (such as aridsols) and vegetation. The reaction of OCS with the OH radical is slow ($k_{298} = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; Atkinson *et al.*, 2004), and therefore gas-phase removal in the troposphere is a minor loss process. Plants are found to be able to take up OCS by the enzyme carbonic anhydrase under dark conditions as long as the plant was able to take up OCS through the leaf stomata or the leaf cuticle. Soils have a temperature optimum for OCS uptake, which is likely to be due to the dependence on enzyme catalyzed processes, where the enzymes amplify the trace gas exchange up to a certain threshold. The vegetation and soil uptake fluxes of OCS are still sparse and underestimated which can reflect its global budget shown in Table 4.7. The lifetime of OCS in the atmosphere is very large (approximately 18 months) with respect to all loss processes, making it the most long-lived of the sulphur species considered. Since OCS is so long lived it can be transported up to the stratosphere, where it is photolysed by UV radiation, or reacts with O atoms to subsequently act as a source of SO₂ and ultimately sulphate particles (stratospheric sulfate aerosol known as the Junge layer). The Junge layer is formed of a mixture of 25% H₂O and 75% H₂SO₄ which occurs at an altitude of approximately 20 km during volcanically quiescent periods. Due to the longer residence time of the stratospheric aerosol compared with the tropospheric aerosol (which are rapidly scavenged in the atmosphere) and because of their cooling effects, stratospheric aerosols can minimize the warming due to increasing green house gas levels in the atmosphere.

Typical mixing ratios of OCS in the troposphere are around 500 pptv, and do not vary dramatically with altitude. The combination of low solubility, low reactivity with OH and somewhat diffuse sources would be concomitant with these observations. Latitudinal measurements differ somewhat, but more recent studies suggest that a gradient does exist across the hemispheres which changes with season: higher concentrations in the summer in the Southern Hemisphere perhaps reflecting the dependence of production from the ocean and from the oxidation of DMS on the availability of sunlight and lower concentrations in the summer in the Northern Hemisphere likely to follow that of vegetation, which is the dominant sink of OCS.

Carbon disulphide

Carbon disulfide (CS₂) is naturally produced from rotting organic material in oceanic, coastal and marshlands, but spatial analysis indicates large concentrations over continental masses, suggesting the main sources of CS₂ are anthropogenic (Watts, 2000). Anthropogenic sources such as chemical processing dominate, being over 50% of the estimated source, most notably in the production of cellulose. Soils and wetlands are thought to be the other natural sources, but the emission fluxes of CS₂ from these sources are sparse (Watts, 2000) which make them extremely hard to estimate. The significantly shorter lifetime for CS₂, compared with OCS, results in a highly non-uniform distribution in the troposphere, with very little penetration into the stratosphere expected. Observed levels range from 2 pptv under clean marine conditions up to approximately 300 pptv in areas heavily influenced by anthropogenic emissions.

The lifetime of CS₂ is of the order of a week: the major loss process is reaction with the OH radical ($k_{298} = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson *et al.*, 2004), with SO₂ and OCS as major products. These oxidation products can increase the formation of the global atmospheric sulphate aerosol. The dry deposition through vegetation is also a significant loss process of CS₂. Carbon disulphide is another relatively insoluble species ($K_H = 5.5 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 25° C) and therefore wet deposition is unlikely to be important.

Hydrogen sulphide

The budget of H₂S is the least well characterized of all the sulphur compounds considered here. However, it is widely agreed that H₂S is the major reduced sulphur compound released from soils and vegetation and is also a significant component of the marine budget (Möller, 1984). Like the other sulphur compounds considered thus far it is quite

insoluble ($K_H \sim 9.5 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 25°C) and in conjunction with available seawater measurements it would appear that H_2S is supersaturated in seawater.

Hydrolysis of OCS and reduction of sulphates appear to be the main source of H_2S in seawater, although there is evidence suggesting that H_2S formation is related to primary production in the oceans. Hydrolysis of OCS is a chemical process that occurs in the oxic water column to maintain H_2S concentrations. Bacteria in anoxic environments can reduce sulphate to respire, producing H_2S as a by-product. The H_2S can then be transported up the water column towards the surface where it can escape to the atmosphere. The shallow water environments such as estuaries, mudflats, salt marshes and swamps are all active H_2S emission regions for this reason. In soils, H_2S is produced by the degradation and mineralization of sulphur containing organic matter by bacteria. Another major natural source of H_2S is volcanoes. Like CS_2 , anthropogenic sources of H_2S , such as the combustion of fossil fuel, dominate, contributing nearly half the total burden.

The main sink of H_2S is the reaction with OH radical ($k_{298} = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson *et al.*, 2004) to form the HS radical giving rise to a lifetime of just 2–3 days. The HS radical is in turn rapidly oxidized in the atmosphere to SO_2 , although the precise details of the mechanism are uncertain. The short lifetime of H_2S means that its distribution in the troposphere is highly variable, and marine levels can vary between 5 and 100 pptv, rising to as high as many hundreds of pptv in wetland regions (Brasseur *et al.*, 1999).

Dimethyl sulphide

Dimethyl sulphide (CH_3SCH_3) commonly known as DMS, is the most abundant natural sulphur compound emitted into the atmosphere. Haas first discovered the release of DMS from phytoplankton in 1935 and in 1948 Challenger and Simpson showed that DMS was generated from the Zwitter ion, dimethyl-sulphone-propionate (DMSP), also known as dimethyl- β -propiothetin. It is commonly believed that DMSP is produced by phytoplankton as an osmoregulating substance, which is released by grazing from zooplankton, cell leakage, senescence or viral infection (Watts, 2000). Once in the water, DMSP can be metabolized by the enzyme DMSP-ase, found intracellularly and in DMS-producing bacteria leading to DMS production.

Dimethyl sulphide is largely insoluble ($K_H \sim 4.74 \times 10^{-1} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 25°C and 32.5 salinity units) and therefore degasses from the water column. Although other sources of DMS have been identified, such as from vegetation, soils, wetlands, anthropogenic sources, production from the oceans is believed to dominate (Table 4.7). However, it should be noted that estimates of the oceanic are wide ranging, from around 10 Tg year⁻¹ up to 110 Tg year⁻¹ (Watts, 2000) (1 Tg = 1×10^{12} g).

Two approaches have been used to estimate the oceanic flux, one using seawater measurements and a mass transfer coefficient from sea to air (Liss & Slater, 1974; Lana *et al.*, 2011), the other using air concentrations of DMS and its lifetime (Watts, 2000). Both methods have their flaws, for the former the actual mass transfer coefficient used will depend on which tracer, such as CO_2 or Rn , the measurement is based on (e.g. Liss & Merlivat, 1986) and will vary with wind-speed, for which several parameterizations exist (e.g. Wanninkhof, 1992). Air-sea transfer is also affected by the composition of the microlayer at the interface, which is poorly understood. For the latter approach a sure knowledge of the lifetime for DMS is required, thus if additional loss processes do exist then this estimate will of course be a lower limit. Both methods require a compilation of many seawater and atmospheric observations over the whole globe throughout the year which can improve the estimation of DMS oceanic flux.

The residence time of DMS is assumed to be very short, of the order of a day as it is rapidly removed by reaction with both OH ($k_{298} = 6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson *et al.*, 2006) and the NO_3 radical ($k_{298} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, Atkinson *et al.*, 2006). Removal of DMS via reaction with halogen radicals such as Cl or BrO has been speculated and may well be significant additional loss processes in the marine environment (e.g. James *et al.*, 2000; Khan *et al.*, 2016).

The oxidation mechanism for DMS is extremely complex and has been the focus of numerous studies. Reaction of DMS with OH is thought to proceed via two channels, abstraction (reaction 4.23a) and addition (reaction 4.23b)



The subsequent fate of the CH_3SCH_2 radical and the $\text{CH}_3\text{S(OH)CH}_3$ adduct in the atmosphere is an area of considerable debate, with new laboratory studies constantly refining the assumed mechanism, but subsequent reactions in this complex scheme lead to the formation of either SO_2 or $\text{CH}_3\text{SO(O)OH}$, known as methanesulphonic acid (MSA). In doing so, NO may be oxidized to NO_2 , giving rise to the possibility that ozone may be formed.

The importance of the oxidation of SO_2 to H_2SO_4 has been discussed in detail, as H_2SO_4 can act as a condensation nuclei and lead to the formation of new particles. In contrast, MSA tends to stick to existing aerosol surfaces and does not lead to the formation of new particles (Brasseur *et al.*, 1999).

The distribution of DMS reflects the fact that it is so short lived and has a strong biological source from the oceans. Therefore DMS concentrations are highest around high-productivity coastal and open-ocean regions, and display a strong seasonal cycle, reflecting the seasonal pattern of phytoplankton growth and decay. Since DMS is also so short lived, it also displays a very strong diurnal cycle.

The CLAW hypothesis

In 1987 a link between phytoplankton and cloud albedo was proposed. In their seminal paper, Charlson, Lovelock, Andreae and Warren suggested that phytoplankton are able to modify Earth's climate through the generation of clouds by producing DMS, which is oxidized to give non-sea-salt sulphate (NSSS), leading to increased cloud formation and number density of cloud droplets, which in turn increases the cloud albedo counteracting global warming (negative feedback). There is evidence to suggest that the individual steps in the CLAW hypothesis are correct, but there is great uncertainty in the subsequent effect that the increased cloud albedo will have on the production of DMS. This hypothesis has been highly contentious over the years and adversaries to the CLAW hypothesis suggest that increased CO_2 levels in the atmosphere decrease the pH of the oceans and could lead to reduction in production of DMS from phytoplankton, which would intensify warming (positive feedback) due to increased green house gas levels in the atmosphere (Six *et al.*, 2013). Despite the CLAW hypothesis opening the door to a new area of interest and research, the scientific community is still yet to reach a conclusive answer to its validity.

4.6 Halogens

The halogens, chlorine, bromine and iodine, are present in the Earth's atmosphere in both inorganic and organic forms. Natural ecosystems use halogen-containing compounds for myriad purposes (Gribble, 1994), while the use of halogen-containing species, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs) and halons (containing bromine as well as fluorine and possibly chlorine) in a variety of industrial applications has led to a dramatic increase in the halogen burden in the atmosphere. In Chapter 8, the impact of the CFCs and their replacement compounds on stratospheric ozone is discussed in more detail and will only be briefly mentioned here. Recently the anthropogenic halogen load has become more controlled due to legislation. Thus, biogenic halogen emissions begin to play a more important role as they make up an increasing part of the total halogen load. The total atmospheric budget for the halogens is far from complete: however, in this section, the sources, sinks and lifetimes of the major known species will be presented.

Organohalogens

Both monohalomethanes and polyhalomethanes may be formed by enzyme-catalysed reactions naturally. A variety of studies have begun to elucidate the potential roles of organohalogens in natural ecosystems. Nightingale *et al.* (1995) showed that levels of CH_3I , CH_2Br_2 , CHBr_3 , CHBr_2Cl , CHBrCl_2 and CHCl_3 were elevated in beds of the marine macroalgae *Laminaria digitata*. Release rates were influenced by partial desiccation, light availability, tissue age, tissue wounding and grazing. These compounds may act as antimicrobial agents or grazing deterrents, since herbivory of marine macroalgae is intense and often the primary factor affecting their distribution and abundance. The simpler organohalogens may act as intermediates in the synthesis of more complex halogenated antigrazing compounds, or could result from the breakdown of such compounds following plant death.

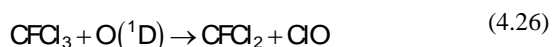
In soils very high haloperoxidase activity has been reported in the surface organic layer, where high microbial activity (e.g. fungi and bacteria) is known to be involved in the degradation of organic matter. The function of haloperoxidase activity in soil can be intra- or extra-cellular formation of organohalogenes for the chemical defence of the producing microorganisms. Alternatively, haloperoxidases could be released by microorganisms in order to produce hypohalites. Formation of hypohalites *in situ* in the soil will cause oxidation of the refractory organic matter in the organic layer to produce more soluble and accessible organic compounds, but also organohalogenes such as chloroform (CHCl₃).

Methyl halide formation occurs in fungi. Methyl chloride is an effective precursor to the biosynthesis of veratryl alcohol (3,4-dimethoxybenzyl alcohol). Veratryl alcohol is a secondary metabolite, which is biosynthesized by many white rot fungi and plays a central role in lignin degradation. A further possibility for the role of CH₃Cl is associated with the high methoxyl content of lignin, which can be as much as 20%. The diversion of excess one-carbon fragments from this source into volatile CH₃Cl, which will rapidly diffuse from the cell, may represent a means of overcoming the biochemical handicap likely to be imposed by a very large one-carbon pool in the cell. The sources, sinks and residence times of a range of organohalogenes will now be discussed.

Chlorofluorocarbons

Table 4.8 shows the uses of the major CFCs and other chlorinated halocarbons prior to controls on their use introduced by the Montreal Protocol. Originally thought to be inert in the atmosphere, it has been known for over 30 years that CFCs lead to the destruction of stratospheric ozone. Provided the implementation of the Montreal Protocol and subsequent legislation is adhered to, the stratospheric abundance of halogenated ozone-depleting substances is expected to return to the pre-1980 level of 2 ppbv chlorine equivalent by about 2050. Based on AGAGE (Advanced Global Atmospheric Gases Experiment) measurements, the three most abundant CFCs are CFC-12, CFC-11 and CFC-113 with mixing ratios of 516.2, 230.1 and 71.5 pptv in 2016 which declined by 21.8, 13.8 and 5.1 pptv from 2008, respectively.

The CFCs are destroyed by photolysis in the stratosphere or via reaction with O(¹D) atoms, e.g. for CFC-11



The effectiveness of the halogen species in destroying ozone, i.e. their ozone depletion potentials, is discussed in Chapter 8. Lifetimes for these compounds are long, 45 years for CFC-11, 100 years for CFC-12 and 85 years for CFC-113 (IPCC, 2013). CFCs account for ~70% of the total halocarbon radiative forcing, with CFC-11, CFC-12 and CFC-113 contributing 0.062, 0.17 and 0.022 Wm⁻², respectively.

Replacement compounds – hydrochlorofluorocarbons, hydrofluorocarbons and hydrofluoroolefins

The phase-out of CFC production generated an immediate need to find replacements to meet the continued industrial demand. However, scope for direct substitution is limited, and some historical CFC requirements are being superseded by alternative technology, such as the use of pump-action aerosols or the use of hydrocarbons as refrigeration (McCulloch, 1994). Alternative replacement compounds must not only match the properties needed to provide the specific effect desired but must also fulfil other criteria such as energy efficiency, safety (non-toxic and non-flammable) and environmental acceptability.

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were introduced as an interim CFC replacement, since the presence of a labile C–H bond allows the compound to be oxidized via reaction with the OH in the troposphere. Tropospheric removal via reaction with OH considerably shortens the atmospheric residence time of the HCFC and HFC compared with the CFC it replaces. HFCs have effectively zero ozone depleting potential (ODP) as they contain no chlorine. HCFCs do contain chlorine, but they deplete stratospheric ozone to a much lesser extent than CFCs. HCFCs and HFCs have global warming potential (GWP) that is smaller than the compound they replace, CFCs, but that are larger than CO₂, thus they contribute to climate change directly through radiative forcing by absorption of infra-red radiation. The reaction with OH in the troposphere does not eliminate the possibility of the HCFCs contributing to stratospheric ozone depletion, and for HCFCs and HFCs contributing to global warming or other adverse effects as there is still the

possibility the compound, or its oxidation products, will reach the stratosphere.

The most popular HCFCs used in the refrigeration sector as a replacement of CFCs are HCFC-22, HCFC-141b, HCFC-142b whose global productions have not been phased out completely under the Montreal Protocol Agreement especially in south and Southeast Asia which is reflected in their increased AGAGE measured average mixing ratios from 2010 to 2016 by 30.1, 4.0 and 1.7 pptv, respectively. Three HCFCs (HCFC-22, HCFC-141b and HCFC-142b) account for ~15% of the total halocarbon radiative forcing, whereas six HFCs (HFC-23, HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-152) contribute only ~5% of the total halocarbon radiative forcing. The most commonly used is HFC-134a as a replacement for CFC-12 which has a history of use in automobile air conditioners and foam blowing applications. The AGAGE measured mixing ratios of HFC-134a reached 60.7 ppt in 2016, with an increase of 31.8 ppt since 2010. The largest emissions of HFC-134a found in North America, Europe and East Asia. The worldwide use of HFCs increased their concentrations significantly in the last decade which is alarming in respect of global climate because of their high GWPs. Under an amendment to the Montreal Protocol (Kigali amendment, 2016), a global agreement was reached to limit the future use of HFCs: developed countries reduce HFCs use by 2019 and two groups of developing countries freeze HFCs use by 2024 and 2028, respectively.

As an alternative of HFCs (i.e. fourth generation refrigerant), hydrofluoroolefins (HFOs), the unsaturated hydrofluorocarbons have emerged which have no ODP and very low GWP. HFOs can react with OH, Cl, O₃ and NO₃ making their lifetimes very short, *ca.* a few days. One of the main oxidation products from these reactions is trifluoroacetic acid (TFA) which can be washed out of the atmosphere into the aqueous environmental compartment or can react with *s*CI to form highly oxygenated species with low vapour pressures that can lead to secondary organic aerosol formation.

Methyl chloroform

Methyl chloroform (CH₃CCl₃) was used primarily as a cleaning solvent. Industrial sales have declined rapidly in recent years as control measures have become effective, thus the global emissions of CH₃CCl₃ amounted to ~2 Gg in 2012 and have decreased by around 80% since 2005 (WMO, 2014). The only natural source of CH₃CCl₃ is biomass burning which can be important, but Simpson *et al.* (2007) found it as a negligible source with the emission flux of 0.014 Gg year⁻¹. The seasonal variations of methyl chloroform are found for AGAGE measurement sites with summer minimum which is driven by increased scavenging by OH. The residence time of CH₃CCl₃ is 5 years due to reaction with OH, although uptake by the oceans may also be a non-negligible loss.

Carbon tetrachloride

In 1931, carbon tetrachloride (CCl₄) began to be used as a chemical intermediate in the production of CFCs and also as a solvent, with usage increasing rapidly from the 1950s to the 1980s. Since the introduction of the Montreal Protocol, which listed CCl₄ as a controlled substance, large-scale production has declined rapidly, and been accelerated by the global phase-out of CFC production, which consumed 80–90% of the total CCl₄ production. The decrease in AGAGE measured mixing ratios of CCl₄ from 2008 to 2016 is 8.9 ppt, with an atmospheric mixing ratio of 80.1 pptv in 2016. The North-South interhemispheric gradient of about 1.3 ppt since 2006 shows that there are some emissions sources of CCl₄ in the Northern Hemisphere (WMO, 2014). The possible emission sources can be fugitive emissions from industries, productions during bleaching or emissions from old landfills.

Carbon tetrachloride is removed by photodissociation in the stratosphere, where it eventually yields phosgene (COCl₂). The ocean is also a sizeable sink for CCl₄ with approximately 20% of atmospheric CCl₄ being consumed by ocean mixing and hydrolysis. The soil can also act as a sink of CCl₄. The combined loss processes lead to a residence time for CCl₄ of 26-35 years.

Dichloromethane

Dichloromethane (CH₂Cl₂) is a man-made solvent that is used in a wide range of applications, such as the decaffeination of coffee, metal degreasing, drug preparation and paint stripping. It is also used as a blowing agent in the foam plastics industries. The surface mixing ratios of CH₂Cl₂ (2000-2012) increased at a global mean rate of ~8% per year, with the largest growth observed in the Northern Hemisphere (a factor of 3 greater than in the Southern Hemisphere) due to the

increased anthropogenic emissions. The continuous increase in growth of CH_2Cl_2 could significantly offset a portion of the decline in anthropogenic chlorine provided by the Montreal Protocol which can delay ozone hole recovery (Hossaini *et al.*, 2017). Ambient mixing ratios of 40–60 pptv and 15–20 pptv have been observed in the Northern and Southern Hemispheres respectively. There is no direct evidence for substantial natural sources, although atmospheric measurements of background concentrations in the Southern Hemisphere are double those that have been calculated using known emission fields. Gribble (1994) notes that CH_2Cl_2 has been observed in the oceans and marine algae and may well have a seasonal maritime source. Biomass burning is also a significant source especially in the Southern Hemisphere (Lobert *et al.*, 1999). The tropospheric lifetime for CH_2Cl_2 is around 0.4 years, with reaction with OH being the dominant loss process ($k_{298} = 1.15 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997) and photolysis as a minor loss process.

Chloroform

Chloroform (CHCl_3) is known to have both anthropogenic and natural atmospheric sources, which are approximately of equal magnitude. Anthropogenic emissions arise from the use of CHCl_3 as a chemical intermediate in industrial processes, as a solvent, as a secondary product during chlorination processes, and from coal combustion and waste incineration. Chlorination processes that lead to the production of chloroform include sewage treatment, paper pulp bleaching, the chlorination of drinking water. However, paper manufacture is no longer an important source because of the phase out of chlorine in the paper processing industries.

Natural production of chloroform appears to be very widespread among different biota, and known sources include rice fields, soil ecosystems, termites, fungi and moss, although marine algae are believed to represent the dominant natural source. Biomass burning is another significant source of chloroform. Anthropogenic sources are better constrained, but natural emissions have not been fully explored or quantified and so no significant trends of AGAGE observations are apparent since the beginning of the record in 1994. Reaction with the OH radical is the dominant loss process ($k_{298} = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997) giving a lifetime for chloroform of about 0.5 years.

Perchloroethene and trichloroethene

Perchloroethene (PCE) and trichloroethene (TCE) are used as industrial solvents and degreasers. Industrial emission estimates suggest that source regions are broadly similar to those of CH_2Cl_2 . There has been a suggestion that certain types of macroalgae in the subtropical oceans may be capable of synthesizing chlorinated alkenes such as TCE and PCE, with the dominant source regions being located within the Northern Hemisphere.

Consumption of PCE has been declining steadily since the 1970s with the introduction of more efficient cleaning equipment, which has enabled a greater proportion of solvent to be recovered and recycled rather than be released into the environment. The primary loss process for both species in the atmosphere is reaction with the OH radical, with residence times of 96 days for PCE ($k_{298} = 1.72 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997) and 5 days for TCE ($k_{298} = 2.2 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997).

Chloromethane or methyl chloride

Chloromethane or methyl chloride is by far the most abundant organohalogen in the atmosphere, with man-made emissions being negligible in comparison with natural ones. CH_3Cl currently contributes around 17% of tropospheric chlorine which concentration (~540 pptv) has remained fairly constant over the last few years (WMO, 2014). A short residence time (1–1.5 year) following reaction with OH ($k_{298} = 3.76 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997) and loss to soil and oceans. The absence of an interhemispheric gradient is consistent with widespread natural sources, not concentrated within the industrialized Northern Hemisphere.

A global source strength of $0.75 \text{ Tg year}^{-1}$ is required to balance the global budget of CH_3Cl (Table 4.9). The known natural sources of CH_3Cl include the ocean, tropical forests, fungi, salt marshes, wetlands, rice paddies and mangroves from where the ocean (~700 Gg year^{-1}) and tropical forests (~2050 Gg year^{-1}) contribute most of its global sources. Anthropogenic sources identified include biomass burning and other combustion processes and mixing ratios as high as 2 ppbv have been observed in forest fire smoke. Biomass burning is estimated to produce ~500 Gg year^{-1} . Current evidence would tend to indicate that the overwhelming proportion of the atmospheric CH_3Cl burden is of direct

biological origin, and biosynthesis has been demonstrated in a wide variety of organisms, such as polypore fungi, macroalgae and higher plants. Studies have concluded that higher tropospheric boundary layer mixing ratios of CH₃Cl in air masses of marine origin are consistent with a widespread natural flux from the oceans.

Methyl bromide and other organobromo compounds

Atmospheric methyl bromide (CH₃Br) is derived from both anthropogenic and biogenic sources. The budget of CH₃Br (Table 4.9) has been the subject of recent debate and it is still not fully resolved. The phase out of controlled emissions of CH₃Br doesn't decrease its global burden as expected, suggesting that the balance of emissions is now overwhelmingly of natural origin. Methyl bromide is believed to be the main carrier of bromine to the stratosphere, where bromine is extremely efficient at promoting ozone destruction (see Chapter 8). The mean AGAGE measured tropospheric concentration is 7.0 pptv in 2016, which is a reduction of 2.2 pptv from peak levels measured during 1996-1998. A strong North-South interhemispheric gradient is seen suggesting that either there are greater sources in the Northern Hemisphere or greater sinks in the Southern Hemisphere. The oceans are now believed to be a net sink for tropospheric CH₃Br, although parts may act as a source. CH₃Br is also used as a pesticide in the cultivation of high-value agricultural produce, although its use is being phased out as part of the Montreal Protocol, and about 40% of the applied compound may reach the atmosphere. Soils themselves are a sink for CH₃Br, with a total sink of around 30 Gg year⁻¹. On the other hand, vegetation (mangroves, rapeseed), fungus, saltmarsh, shrublands, rice paddies and wetlands are the other sources of CH₃Br. Around 3 Gg of CH₃Br is generated from vehicle emissions. Biomass burning is another potentially large source of CH₃Br (~23 Gg year⁻¹), but current uncertainties in emission rates are large. The combined residence time of CH₃Br, allowing for loss to the oceans, soils and by reaction with the OH radical ($k_{298} = 2.98 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; DeMore *et al.*, 1997), is currently estimated to be 0.8 years.

The short-lived brominated species (e.g. CHBr₃, CH₂Br₂, CHBr₂Cl and CHBrCl₂) can be a significant source of stratospheric bromine with a contribution of up to 5 pptv, representing 25% of total inorganic stratospheric bromine (WMO, 2014). Bromoform (CHBr₃) and dibromomethane (CH₂Br₂) are the most abundant short-lived brominated species accounting for ~75% of the short-lived bromocarbons in the marine environment. The emissions of CHBr₃, CH₂Br₂ are predominantly from marine macro-algae and phytoplankton, displaying large emission variabilities. The abiotic substitution of bromine in CHBr₃ with chlorine is supposed to be the main source for bromochloromethanes (e.g. CHBr₂Cl and CHBrCl₂). The other minor sources of bromocarbons are from water treatment and disinfection; they are formed as byproducts when chlorine is added to water to kill bacteria. The long-term *in situ* measurement data of CHBr₃ and CH₂Br₂ at Mace Head gives a seasonal trend with maximum concentrations during summer months and minimum concentrations during winter months. An excellent correlation between CHBr₃ and CH₂Br₂ suggesting a common marine source presumably originating from macroalgae in coastal region (Carpenter *et al.*, 2003). The combined loss by OH and photolysis give the residence times of CHBr₃, CH₂Br₂, CHBr₂Cl and CHBrCl₂ of 24, 123, 137 and 78 days, respectively (WMO, 2014).

Methyl iodide

Methyl iodide (CH₃I) is believed to be the main gaseous iodine species in the troposphere usually with a concentration of 0.1-5 pptv which plays an important role in the natural iodine cycle. The time series of atmospheric CH₃I show an increasing trend from 2003/2004 to 2009/2010 by several tens of percent in the marine environment (WMO, 2014). The C-I bond is easily cleaved and CH₃I has the longest residence time of any organoiodine compound. Methyl iodide is photolysed, giving rise to a residence time of between 2 and 10 days depending on location and season. Methyl iodide is almost exclusively of marine origin, with some minor contribution from biomass burning, rice paddies, fungi, volcanoes, peatland ecosystems and wetlands. The oceanic productions include photochemical degradation of organic matter in seawater and biogenic activities of phytoplankton and macroalgae. There have been no enhanced levels of CH₃I observed in urban areas, suggesting no emissions due to fossil fuel combustion, industrial emissions. The levels of CH₃I exhibit a seasonal cycle, with highest levels in summer and early autumn and has been found to be more abundant in the tropics and over oceanic regions of high biomass productivity. In the warm tropical surface waters, subject to high solar irradiance, photochemical production of CH₃I is significant. This contrasts with negative saturation anomalies (-0.65 pmol kg⁻¹) measured in cold surface waters of the open ocean around Greenland, subject to low light levels. Therefore high-latitude oceans may be a sink during autumn and winter. Photochemical production of CH₃I would go

some way to explaining the lack of correlation between CH₃I and CH₃Cl, CH₃Br, CH₂Br₂, CHBr₃, CHBr₂Cl and chlorophyll. Kelp, bacteria, phytoplankton and macroalgae are all believed to be small but significant sources of oceanic CH₃I.

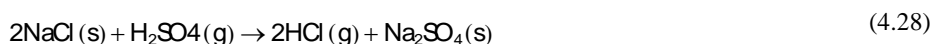
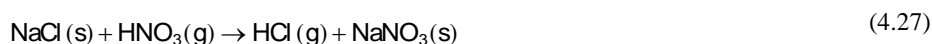
Other organoiodine compounds

There is much uncertainty about the contribution of individual organic iodine compounds to the global iodine budget and a small number of short-lived organoiodine species have been observed, including C₂H₅I, CH₂ICl, CH₂I₂ and CH₂I₂, whose residence times are approximately 4 days, a day, an hour and a few minutes, respectively. The total organic iodine from CH₃I, CH₂ICl, CH₂I₂ and CH₂I₂ contributes only 20% of the reactive iodine flux in the marine boundary layer (MBL), suggesting some other contributors (e.g. inorganic iodine) may be significant for the reactive iodine flux in the MBL (WMO, 2014). The atmospheric measurements of these organoiodine compounds are sparse. An extensive suite of alkyl iodides and bromides were measured at Mace Head in Ireland, Hateruma Island in the East China Sea, and Cape Ochiishi in the eastern coast of Hokkaido, Japan. Positive correlations were found between CH₂I₂/CH₂I₂, CH₂ICl/CH₂I₂ and CH₃I/C₂H₅I, which was interpreted as signifying common or linked marine sources (Carpenter *et al.*, 1999; Yokouchi *et al.*, 2011). The rapid photolysis of these compounds can lead to IO formation via the reaction of iodine radicals with ozone. Measurements of these organoiodine compounds in coastal and open oceans suggest that the organoiodine flux to the atmosphere may be considerably underestimated if CH₃I alone is considered. However, due to the short residence times, it is believed that very low levels of iodine precursors enter the stratosphere.

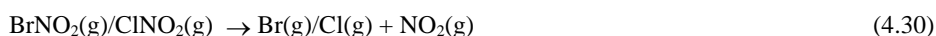
It is worth noting that several thousand naturally occurring organohalogen compounds have been identified in aquatic and terrestrial systems. The edible seaweed, *Asparagopsis taxiformis*, for example, contains over 100 such organohalogen compounds, including mixed chlorinated, brominated and iodinated ketones and alkenes. Whether there is a significant flux of these compounds to the atmosphere is still unknown.

Inorganic halogens

One of the important inorganic halogens is hydrogen chloride (HCl) which is directly emitted from volcanic eruptions, biomass burning, incineration of wastes and industrial processes e.g. semiconductor and petroleum manufacturing. Another important source results from the reaction of sea salt with gas-phase acidic compounds in the atmosphere:

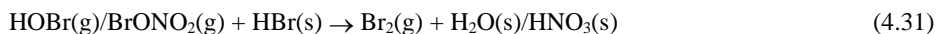


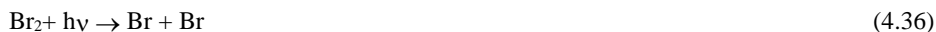
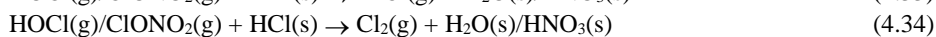
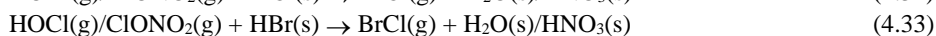
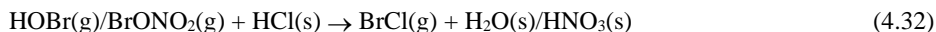
Sea salt also contains NaBr, and the reaction of sea salt with N₂O₅ can initiate the release of bromine or/and chlorine nitrite, which is itself rapidly photolysed, yielding Br or/and Cl atoms



The emission of short-lived organohalogens can produce inorganic halogen compounds (e.g. BrCl, I₂, HOCl, HOBr) in the atmosphere, and these may in turn generate free halogen atoms.

HCl and HBr adsorbed on ice can participate heterogeneous reactions with hypohalous acids (HOX) or halogen nitrates (XONO₂) in the dark winter of the polar region and convert photochemically inactive chlorine and bromine reservoir compounds (e.g. Br₂, BrCl and /or Cl₂). During spring these compounds release halogen atoms through photolysis.





In general, once released, halogen atoms may react with O_3 (X is Cl, Br and I)



forming XO. Both IO and BrO can either react with themselves or each other, in either case regenerating the free halogen which can again remove an ozone molecule or producing other halogen products.



The molecule OIO can also be formed by cross reaction between IO and BrO (DeMore *et al.*, 1997). Considerable interest surrounds OIO, which has been observed in the marine boundary layer, although its chemistry is uncertain at this time. XO can also form temporary reservoir species, HOX and XONO₂, via reaction with HO₂ and NO₂:



For Br and particularly I, these reservoirs are quite short-lived in the troposphere, being either taken up into aerosol, or destroyed by photolysis in the case of IONO₂. The role of halogen reservoirs in the stratosphere is discussed in Chapter 8. XO can also react with NO to regenerate X



Chlorine atoms can also react with hydrocarbons (RH) to form HCl, which limits its effectiveness in destroying ozone in the troposphere. However, Br can only abstract hydrogen from labile species such as aldehydes and HO₂, although addition to unsaturated species is also possible. Iodine atoms are unable to react with any hydrocarbons and reaction with ozone is by far the dominant channel in the troposphere. Iodine chemistry is therefore the most likely to lead to significant ozone destruction in the troposphere, although, under special circumstances, such as in the boundary layer in the Arctic spring, bromine chemistry can initiate rapid surface ozone destruction.

It is worth noting that, once released, fluorine atoms can react with O₃, but on reaction with RH forms the very stable HF. Since release of fluorine from its major reservoir compounds, such as the CFCs, HCFCs, HFCs and the PFCs (perfluorocarbons), occurs in the stratosphere, HF is transported back down to the troposphere where it is removed by wet deposition. The lifetime of inorganic halogens and their reservoirs is highly variable and will depend strongly on the aerosol loading present.

4.7 Hydrogen

Hydrogen (H_2) is the second most abundant oxidizable trace gas in the atmosphere which has a globally averaged tropospheric mixing ratio of around 530 ppbv with a lifetime of ~ 2 years. Figure 4.5 shows how the concentration of H_2 varies with time at the Earth's surface in both the Northern and Southern Hemispheres. Although the levels are very similar, the trends and depth of the seasonal cycle are not, i.e. H_2 levels are $\sim 3\%$ higher in the Southern Hemisphere compared with that in the Northern Hemisphere and the seasonal variation in the Northern Hemisphere is around 50 ppbv, whereas it is only 25 ppbv in the Southern Hemisphere. Hydrogen is produced by the photolysis of HCHO



where HCHO is itself produced from the oxidation of methane and other VOCs in the atmosphere. Hydrogen is also emitted during incomplete combustion of fossil fuel and biomass burning and from nitrogen fixation in the continental and marine biosphere, therefore it is surprising that its levels are higher in the Southern Hemisphere than the Northern Hemisphere. It is destroyed by reaction with OH and by dry deposition to soils. The uptake by soil is the most dominating loss process of H_2 which is associated with enzymatic and microbial activities linked to H_2 diffusivity. Thus, the soil-loss process gives rise not only to the smaller levels H_2 in the Northern Hemisphere but also the stronger seasonal cycle.

4.8 Summary

Budget. For each element and each compound containing that element a budget can be constructed where the known sources and sinks are compiled. If the sources outweigh the sinks then the concentration of that compound will increase with time in the atmosphere, if the sinks outweigh the sources then the concentration will decrease with time.

Sources. There are primary sources, where the compound is released directly to the atmosphere and secondary sources where the compound is formed in the atmosphere. Of the primary sources there are anthropogenic sources (arising from human activity) and biogenic sources (natural).

Sinks. There are two depositional sinks, wet and dry deposition, where compounds are physically removed by incorporation into aqueous media or destruction at a surface. There are also photochemical sinks, photolysis is where the compound is broken apart by sunlight and chemical loss via reaction with oxidants such as the OH radical and O_3 .

Carbon. The major form of carbon in the atmosphere is CO_2 , with CH_4 and CO the next two most important forms. There are myriad VOCs emitted into the atmosphere that are oxidized to CO_2 and CO. CO_2 and CH_4 are very important greenhouse gases in the atmosphere.

Nitrogen. The major form of nitrogen in the atmosphere is N_2 itself and with N_2O this constitutes 99.99% of the total N. However, NO_x and NH_3 are present in trace levels and have a profound impact on the composition of the atmosphere, particularly photochemical smog.

Sulphur. The major emission of sulphur into the atmosphere is in the form of SO_2 , but the longest lived reservoir is OCS. DMS is the largest biogenic emission of S into the atmosphere. Sulphur is important in the atmosphere because it can lead to aerosol formation and clouds and therefore cool the planet (negative greenhouse effect).

Halogens. The major natural sources of Cl, Br and I in the atmosphere are CH_3Cl , CH_3Br and CH_3I . Many chlorine containing compounds have been made for industrial applications and in particular the CFCs, chlorofluorocarbons, have become the dominant source of chlorine in the atmosphere. Recent legislation has banned the use of CFCs.

Hydrogen. Hydrogen has a strong soil loss process and this gives rise to very different seasonal cycles in the Northern and Southern Hemispheres.

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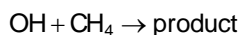
Further reading

- Brasseur, G.P., Orlando, J.J. and Tyndall, G.S. (1999) *Atmospheric Chemistry and Global Change*. Oxford University Press, New York.

Questions

1 Discuss the main removal mechanisms (sinks) for pollutants in the troposphere.

Methane, an important greenhouse gas, is emitted into the Earth's atmosphere at a rate of $500 \times 10^9 \text{ kg year}^{-1}$. The principal atmospheric removal mechanism for methane is reaction with the OH radical:



$$k_1 = 6.3 \times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Given an average OH concentration of $5 \times 10^5 \text{ molecule cm}^{-3}$:

- calculate the steady-state mass (referred to as $[A]_{\text{constant}}$) of methane in the atmosphere
 - the lifetime for methane.
- 2 Relative measurements were made of ethane (triangles) and isoprene (squares) at a rural site in the Northern Hemisphere, the monthly average levels are shown below
What are the major sources and sinks for each of these compounds? Hence or otherwise explain why the seasonal cycles vary in the way that they do.
- 3 The concentration of NO on a weekday in Bristol, a small city in the UK, is shown in the figure below. Why are there peaks at around 9 am and 5 pm and why are the two peaks not the same size?
- 4 What is the CLAW hypothesis and why is sulphur chemistry so important in the atmosphere?
- 5 The concentration of halogenated compounds, CFC11 (CFCl_3), CFC12 (CF_2Cl_2), CCl_4 and CH_3CCl_3 from 1994 to 2016 are shown in the figure below. All these compounds are banned and their production and subsequent emission should have ceased since the mid-1990s. Explain why the concentration-time profiles have the form they do. (Data courtesy of Dr. S.J. O'Doherty.)

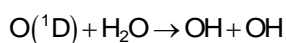
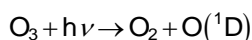
Answers

1 Physical removal

- *Wet deposition*. Incorporation of soluble species into aqueous media such as rain drops, fog, aerosols. Species removed efficiently by this mechanism include; HNO_3 , HCl , NH_3 , SO_2 .
- *Dry deposition*. Polar species can be irreversibly adsorbed and then broken down on a variety of surfaces. Species which are efficiently dry deposited include; O_3 , NO_2 , HNO_3 , HCl .

Chemical removal

- *Photolysis*. Some species absorb solar radiation in the UV or visible region, which leads to bond cleavage, e.g. O_3 , NO_2 , CFCs.
- *Removal by reaction with OH*. All VOCs react with the OH radical and in most cases, reaction with OH is the major removal mechanism. Once reaction has taken place, VOCs are transformed into soluble species that can be efficiently removed. OH is formed from O_3 photolysis in the troposphere (see Chapter 5)



$d[\text{CH}_4]/dt = \text{emission rate} - \text{loss rate at steady state or equilibrium}$
 $d[\text{CH}_4]/dt = 0$

$d[\text{CH}_4]/dt = \text{emission rate} - k_1[\text{OH}][\text{CH}_4]$

$d[\text{CH}_4]/dt = 500 \times 10^9 - k_1[\text{OH}][\text{CH}_4] = 0$

$d[\text{CH}_4] = 500 \times 10^9 - k_1[\text{OH}][\text{CH}_4] \Delta t = 0$

In one year 500×10^9 kg CH_4 removed, where $\Delta t = 1$ year in seconds

$[\text{CH}_4] = 500 \times 10^9 / \{k_1[\text{OH}] \Delta t\} = 5 \times 10^{12}$ kg

Lifetime(CH_4) = $1/(k_1[\text{OH}])$
= 3.18×10^8 s = 10.1 years

- 2 Sources of ethane are largely anthropogenic, natural gas and biomass burning with much smaller natural sources, i.e. oceans and vegetation. The major loss process is reaction with OH. Therefore the emissions are pretty constant throughout the year and the seasonal cycle is driven by the change in OH during the year. Since OH is a maximum in the summer the level of ethane is lowest at this time.

Isoprene is almost totally biogenic in origin and although its major loss process is also reaction with OH, the greatest emission is in the spring and summer. Although its sink is a maximum in summer its source is also a maximum and given its very short lifetime one only sees high concentrations in the spring and summer.

- 3 The peaks are due to rush hour traffic in the morning and evening. The structure in the NO concentration during the day may be due to local emissions on that day or due to local meteorology (see Chapters 9 and 10). However, it is odd that the peak in NO is smaller in the evening than the morning, does this mean that less cars leave the city than enter it? The reason is because the boundary layer (see Chapter 9) increases in size during the day and so the emission of NO has a larger volume to expand into and therefore its relative concentration (ppbv) is smaller for the same emission.

- 4 See text.

- 5 Without any prior knowledge of the lifetimes of these species equation I shows that the decay rate will be dependent only on the loss rate. CH_3CCl_3 has decayed away to about a quarter of its original level (representing two half-lives) and we could guess that the lifetime was about 5 years. It has C–H bonds and therefore reacts with OH radicals in the troposphere. The other species are all fully halogenated species that do not react with OH, therefore they are destroyed in the stratosphere by photolysis. CF_2Cl_2 has decayed away slightly more rapidly than CCl_4 , but they both have similar lifetimes. CFCl_3 continued to rise and is only now beginning to decay, suggesting that it was still emitted (albeit in small amounts) during this period.

Fig. 4.1 (a) Source and sink terms are equal, the concentration remains constant with time, e.g. N_2 and O_2 . (b) Source is greater than the sink, the concentration increases with time, e.g. hydrochlorofluorocarbons (HCFCs) and CO_2 (currently). (c) Source is smaller than the sink, the concentration decreases with time, e.g. CH_3CCl_3 and chlorofluorocarbons (CFCs).

Fig. 4.2 Schematic of the rise in atmospheric CO_2 over the past 50 years recorded at Mauna Lao, Hawaii, USA. Location 19° N, 155° W; sample height 3397 m a.s.l. (Adapted from Earth System Research Laboratory, National Oceanic and Atmospheric Administration, <https://www.esrl.noaa.gov/gmd/ccgg/trends/full.html>).

Fig. 4.3 Distribution of isoprene emissions derived from a land-surface model (see Wang & Shallcross, 2000) using emission algorithms from Guenther *et al.* (1995).

Fig. 4.4 A selection of the most common monoterpenes found in the atmosphere.

Fig. 4.5 Hydrogen (H_2) measured at the surface in the Northern Hemisphere (NH) and Southern Hemisphere (SH). (Data courtesy of Dr S.J. O'Doherty, School of Chemistry, University of Bristol.)

Table 4.1 Examples of rate coefficients for the reaction of hydrocarbons with OH, and their corresponding lifetimes assuming an $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$, kinetic data taken from Atkinson *et al.* (2006) and DeMore *et al.* (1997).

Hydrocarbon	Rate coefficient at 298 K ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Lifetime
CH ₄	7×10^{-15}	10 years
C ₂ H ₆	3×10^{-13}	4 months
C ₃ H ₈	1×10^{-12}	1 month
C ₂ H ₄	1×10^{-11}	3 days
C ₅ H ₈	1×10^{-10}	1/2 day
CH ₃ Cl	1×10^{-13}	1 year
CO	2×10^{-13}	6 months
CCl ₄	*	50 years*

* Is destroyed in the upper atmosphere, and the lifetime is determined by transport.

Table 4.2 Global budget for an anthropogenic perturbation of CO₂

	1750-2011 Cumulative PgC	1980-1989 PgC year ⁻¹	1990-1999 PgC year ⁻¹	2000-2009 PgC year ⁻¹	2002-2011 PgC year ⁻¹
Atmospheric increase	240 ± 10	3.4 ± 0.2	3.1 ± 0.2	4.0 ± 0.2	4.3 ± 0.2
Fossil fuel combustion and cement production	375 ± 30	5.5 ± 0.4	6.4 ± 0.5	7.8 ± 0.6	8.3 ± 0.7
Ocean-to-atmosphere flux	-155 ± 30	-2.0 ± 0.7	-2.2 ± 0.7	-2.3 ± 0.7	-2.4 ± 0.7
Land-to-atmosphere flux	30 ± 45	-0.1 ± 0.8	-1.1 ± 0.9	-1.5 ± 0.9	-1.6 ± 1.0
Land-to-atmosphere flux partitioned as					
Net land use change	180 ± 80	1.4 ± 0.8	1.5 ± 0.8	1.1 ± 0.8	0.9 ± 0.8
Residual land sink	-160 ± 90	-1.5 ± 1.1	-2.6 ± 1.2	-2.6 ± 1.2	-2.5 ± 1.3

Source: Based on IPCC (2013).

Table 4.3 Sources and sinks for methane in the atmosphere expressed as Tg CH₄ per year

Tg (CH ₄) yr ⁻¹	1980-1989		1990-1999		2000-2009	
	Top-Down	Bottom-Up	Top-Down	Bottom-Up	Top-Down	Bottom-Up
Natural Sources	193 (150-267)	355 (244-466)	182 (167-197)	336 (230-465)	218 (179-273)	347 (238-484)
Natural Wetlands	157 (115-231)	225 (183-266)	150 (144-160)	206 (169-265)	175 (142-208)	217 (177-284)
Other sources	36 (35-36)	130 (61-200)	32 (23-37)	130 (61-200)	43 (37-65)	130 (61-200)
Freshwater (lakes and rivers)		40 (8-73)		40 (8-73)		40 (8-73)
Wild animals		15 (15-15)		15 (15-15)		15 (15-15)
Wildfires		3 (1-5)		3 (1-5)		3 (1-5)
Termites		11 (2-22)		11 (2-22)		11 (2-22)
Geological (incl. oceans)		54 (33-75)		54 (33-75)		54 (33-75)
Hydrates		6 (2-9)		6 (2-9)		6 (2-9)
Permafrost (excl. lakes and wetlands)		1 (0-1)		1 (0-1)		1 (0-1)
Anthropogenic Sources	348 (305-383)	308 (292-323)	372 (290-453)	313 (281-347)	335 (273-409)	331 (304-368)
Agricultural and waste	208 (187-220)	185 (172-197)	239 (180-301)	187 (177-196)	209 (180-241)	200 (187-224)
Rice		45 (41-47)		35 (32-37)		36 (33-40)
Ruminants		85 (81-90)		87 (82-91)		89 (87-94)
Landfills and waste		55 (50-60)		65 (63-68)		75 (67-90)
Biomass Burning (incl. biofuels)	46 (43-55)	34 (31-37)	38 (26-45)	42 (38-45)	30 (24-45)	35 (32-39)
Fossil fuels	94 (75-108)	89 (89-89)	95 (84-107)	84 (66-96)	96 (77-123)	96 (85-105)
Sinks						
Total chemical loss	490 (450-533)	539 (411-671)	515 (491-554)	571 (521-621)	518 (510-538)	604 (483-738)
Tropospheric OH		468 (383-567)		479 (457-501)		528 (454-617)
Stratospheric OH		46 (16-67)		67 (51-83)		51 (16-84)
Tropospheric Cl		25 (13-37)		25 (13-37)		25 (13-37)
Soils	21 (10-27)	28 (9-47)	27 (27-27)	28 (9-47)	32 (26-42)	28 (9-47)
Global						
Sum of sources	541 (500-592)	663 (536-789)	554 (529-596)	649 (511-812)	553 (526-569)	678 (542-852)
Sum of sinks	511 (460-559)	567 (420-718)	542 (518-579)	599 (530-668)	550 (514-560)	632 (592-785)
Imbalance (sources minus sinks)	30 (16-40)		12(7-17)		3 (-4-19)	
Atmospheric growth rate	34		17		6	

Note: The values in brackets represents minimum and maximum values.

Source: Data taken from IPCC (2013).

Table 4.4 Global budget for carbon monoxide in the atmosphere

Sources (Tg CO per year)				Sinks (Tg CO per year)	
<i>In situ</i>		Direct			
Oxidation of CH ₄	800	Biomass burning	700	Reaction with OH	2100 ± 600
Oxidation of isoprene	270	Vegetation	150	Uptake by soils	400 ± 100
Oxidation of industrial NMHC	110	Ocean	50	Flux into stratosphere	110 ± 30
Oxidation of biomass NMHC	30	Fossil and domestic fuel	650		
Oxidation of acetone	20				
Subtotal	1230		1550		
Total sources			2780 ± 1000	Total sinks	2600 ± 780

NMHC, non-methane hydrocarbons.

Sources: Data taken from Graedel and Crutzen (1993), IPCC (2001) and IPCC (2013).

Table 4.5 Estimates of the global sources and sinks for N₂O in Tg N per year

Anthropogenic sources	IPCC estimate 2006-2011
Fossil fuel combustion and industrial processes	0.7 (0.2-1.8)
Agriculture	4.1 (1.7-4.8)
Biomass and biofuel burning	0.7 (0.2-1.0)
Human excreta	0.2 (0.1-0.3)
Rivers, estuaries, coastal zones	0.6 (0.1-2.9)
Atmospheric deposition on land	0.4 (0.3-0.9)
Atmospheric deposition on ocean	0.2 (0.1-0.4)
Surface sink	-0.01 (0 - .1)
Total anthropogenic sources	6.9 (2.7-11.1)
Natural Sources	IPCC estimate 2006-2011
Soils under natural vegetation	6.6 (3.3-9.0)
Oceans	3.8 (1.8-9.4)
Lightning	-
Atmospheric chemistry	0.6 (0.3-1.2)
Total natural sources	11.0 (5.4-19.6)
Total natural + anthropogenic sources	17.9 (8.1-30.7)
Stratospheric sink	14.3 (4.3-27.2)
Observed growth rate	3.61 (3.5-3.8)

Source: Data taken from IPCC (2013). Note: The values in brackets represents minimum and maximum values.

Table 4.6 Atmospheric budget for NO_x and NH₃ (TgN yr⁻¹).

Anthropogenic	NO _x	NH ₃
Fossil fuel combustion and industrial processes	28.3	0.5
Agriculture	3.7	30.4
Biomass and biofuel burning	5.5	9.2
Total	37.5	40.1
Natural sources		
Soils under natural vegetation	7.3 (5-8)	2.4 (1-10)
Oceans	-	8.2 (3.6)
Lightning	4 (3-5)	-
Total	11.3	10.6
Total Anthropogenic + natural	48.8	50.7
Deposition from the atmosphere		
Continents	27.1	36.1
Oceans	19.8	17.0
Total	46.9	53.1

Sources: Data from IPCC (2013).

Note: The values in brackets represents minimum and maximum values.

Table 4.7 Global annual sources and sinks of OCS, CS₂, H₂S, DMS and SO₂ in Tg per year

		OCS	CS ₂	H ₂ S	DMS	SO ₂
Source	Open ocean	0.10 ± 0.15* 0.89 ^r	0.11 ± 0.04* [¶] 0.24 ^r	1.50 ± 0.60*	20.70 ± 5.20* 28.1 (17.6-34.4) † †	
	Coastal ocean	0.10 ± 0.05*	0.04 ± 0.02* [¶]	0.30 ± 0.10*		
	Salt marshes	0.10 ± 0.05*	0.03 ± 0.02*	0.50 ± 0.35*	0.07 ± 0.06*	
	Anoxic soils	0.02 ± 0.01*	0.07 ± 0.06*			
	Vegetation	0.37 ± 0.07*			1.58 ± 0.86*	
	Tropical forests	0.42 ± 0.12*			1.60 ± 0.50*	
	Soils	0.29 ± 0.17*			0.29 ± 0.17*	
	Wetlands	0.03 ± 0.03*	0.02 ± 0.02*	0.20 ± 0.21*	0.12 ± 0.07*	
	Volcanism	0.05 ± 0.04† 0.01 ^r	0.05 ± 0.04† 0.02 ^r	1.05 ± 0.94**	20§§	
	Precipitation	0.13 ± 0.08*				
	OCS + OH	0.08 ± 0.07†				
	DMS oxidation	0.17 ± 0.04‡				
	CS ₂ oxidation	0.42 ± 0.12†				
	Biomass burning	0.07 ± 0.05§ 0.04 ^r	1.8§§			
	Anthropogenic	0.12 ± 0.06* 0.38 ^r	0.34 ± 0.17† 0.70 ^r	3.30 ± 0.33‡‡	0.13 ± 0.04* 1.50 ^r	176§§
Total		1.31 ± 0.68*	0.66 ± 0.37*	7.72 ± 2.79*	24.49 ± 5.30*	200
Sink	Oxic soil	0.92 ± 0.78*	0.44 ± 0.38*			
	Vegetation	0.56 ± 0.10*				
	Reaction with OH	0.13 ± 0.10†	0.57 ± 0.25†	8.50 ± 2.80*	25.00 ± 1.30*	20§§
	Reaction with O	0.02 ± 0.01†				
	Photolysis	0.03 ± 0.01†				
	Cloud scavenging	180§§				
Total		1.66 ± 1.00	1.01 ± 0.63	8.50 ± 2.80	25.00 ± 1.30*	200
Total imbalance		0.35 ± 1.68	0.35 ± 1.00	0.78 ± 5.59	0.51 ± 6.60	–

Sources: *Watts (2000); †Chin and Davis (1993); ‡Barnes *et al.* (1994); §Nguyen *et al.* (1995); ¶Xie *et al.* (1997); **Andreae (1990); ††Fried *et al.* (1992); ‡‡Watts and Roberts (1999); §§Möller (1984); †††Lana *et al.* (2011); ^rLee and Brimblecombe (2016).

Table 4.8 Historical applications (prior to controls over use) of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and current applications of hydrofluorocarbons (HFCs)

Sector	Compound	Application
Aerosols	CFC-11 (CFCl ₃) CFC-12 (CF ₂ Cl ₂) CFC-114 (CClF ₂ CClF ₂) HCFC-22 (CHF ₂ Cl) HCFC-142b (C ₂ H ₃ ClF ₂) HFC-134a (CH ₂ FCF ₃) HFC-152a (CH ₃ CHF ₂)	Used as pure fluids or mixtures for aerosol propellants
Foam blowing	CFC-11 CFC-12 HCFC-22 HCFC-141b(C ₂ H ₃ Cl ₂ F) HFC-134a HFC-152a HFC-245fa (CF ₃ CH ₂ CHF ₂) HFC-365mfc (CF ₃ CH ₂ CF ₂ CH ₃) HFC-227ea (CF ₃ CHF ₂ CF ₃) E-HFC-1234ze (E-CHF=CHCF ₃)	Used as foam blowing agent
Solvents	CFC-113 (CCl ₂ FCClF ₂) CH ₃ CCl ₃ CFC-11 CCl ₄	Solvents used for electronics, precision cleaning and dry cleaning
Refrigeration and air-conditioning	CFC-11 CFC-12 HCFC-22 HFC-134a HFC-152a HFC-143a (CH ₃ CF ₃) HFC-32 (CH ₂ F ₂) HFC-125 HFC-227ea HFC-1234yf (CH ₂ =CF ₂ CF ₃)	Used for wide range of refrigeration and air conditioning applications

Table 4.9 Atmospheric budget for CH₃Cl and CH₃Br

	CH ₃ Cl (Gg year ⁻¹)	CH ₃ Br (Gg year ⁻¹)
Anthropogenic Sources		
Leaded Gasoline	N.Q.	0-3
Coal Combustion	162 (29-295)	9.2
Fumigation	N.Q.	9.9 (8.6-11.3)
Biomass Burning	468 (198-738)	23 (10-36)
Oceanic Source	700 (510-910)	32 (22-44)
Terrestrial Sources		
Tropical and subtropical plants	2040 (1430-2650)	N.Q.
Mangroves	12 (11-12)	1.3 (1.2-1.3)
Rapeseed	N.Q.	5.1 (4.0-6.1)
Fungus	145 (128-162)	2.2 (1.0-5.7)
Salt Marshes	85 (1.1-170)	7.0 (0.6-14.0)
Wetland	27 (5.5-48)	0.6 (-0.1-1.3)
Rice Paddies	3.7 (2.7-4.9)	0.7 (0.1-1.7)
Shrublands	15.0(9.0-21.0)	0.7 (0.5-0.9)
Total Sources	3658	84
Sinks		
Reaction with OH	2832 (2470-3420)	56 (48-63)
Loss in Soil	1058 (664-1482)	30 (19-41)
Loss in Ocean	370 (296-445)	33 (20-44)
Loss in Stratosphere	146	4
Total Sinks	4406	123
Net (Sources-Sinks)	-748	-39

Sources: Data from WMO (2014).

Note: The values in brackets represents minimum and maximum values. N.Q. means not quantified. Biomass burning includes both indoor biofuel use and open field burning.