

## Atmospheric Chemistry in a Changing World

An Integration and Synthesis of a Decade of Tropospheric Chemistry Research

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# Chapter 1

## Changes in the Chemical Composition of the Atmosphere and Potential Impacts

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### 1.1 Introduction

#### 1.1.1 Atmospheric Chemistry and Life on Earth

The story of the importance of atmospheric chemistry begins with the origin and evolution of life on Earth. The accumulation of greenhouse gases in Earth's atmosphere allowed surface temperatures to be maintained above the freezing point of water. Reactions involving carbon, hydrogen, and nitrogen compounds in the primordial soup led to the formation of self-replicating molecules, and, about 500 million years ago, the rise of atmospheric oxygen led to the formation of the stratospheric ozone layer, which protects life on Earth from extremely harmful levels of solar ultraviolet radiation. Running in the shadow of these major events has been a full suite of atmospheric chemistry processes affecting and being affected by the evolving nature of both terrestrial and oceanic life. Some of these processes include biogeochemical cycling of elements, long-range transport of nutrients, regulation of temperature, and exposure to air pollution.

It is a source of wonder that the chemistry of Earth's atmosphere has been sufficiently stable to sustain some form of life on our planet for at least the past 3.5 billion years despite large changes in the physical and chemical climate. Our sister planets, Venus and Mars, show what happens when such stability does not exist. Venus's proximity to the sun has prevented the formation of an ocean and led to a runaway greenhouse effect, resulting in a very high surface temperature and a thick atmosphere consisting mainly of carbon dioxide. The Martian atmosphere is also dominated by carbon dioxide but is thin and has a very weak greenhouse effect. However, one has only to contemplate Earth's historical record to see that changes in atmospheric chemistry have played a crucial role in defining and altering the forms of sustainable life. Indirect sources of information – from ice cores and lake sediments, for example – have shown that large changes in atmospheric composition have occurred mainly during the agro-industrial era (the 'anthropocene'), i.e. the past 200 years.

Over the past century, humanity has been altering the chemical composition of the atmosphere in an un-

precedented way, over an astonishingly short time. Resulting changes in concentrations of airborne toxic gases and fine particles pose a potential threat to human health, reduce agricultural productivity, and challenge the viability of sensitive plant and animal species. The net effects of the buildup of radiatively active trace gases and the changing burden of atmospheric particles appear to be responsible for much of the climate trend observed during the 20<sup>th</sup> century, particularly the warming over the last few decades (IPCC 2001).

World-wide emissions from growing industrial and transportation activity and more intensive agriculture have caused widespread increases in concentrations of photochemical oxidants, acid gases, fine particles, and other toxic chemical species. Many of these air pollutants are known to have detrimental impacts on human health and/or natural and managed ecosystem viability.

Furthermore, higher fossil fuel consumption coupled with agriculturally driven increases in biomass burning, fertiliser usage, crop by-product decomposition, and production of animal based food and fibre have led to increasing emissions of key greenhouse gases, such as carbon dioxide, methane, and nitrous oxide. The resulting increases in absorption, and re-radiation back to Earth's surface, of infrared radiation by these gases (referred to as radiative forcing), coupled with changes in the atmospheric burden of sulphate and other components of small particles, seem to be causing significant modification of Earth's climate. Predicted impacts of climate change include disruptions of agricultural productivity, fresh water supplies, ecosystem stability, and disease patterns. Significant increases in sea level and changes in the frequency of severe weather events are also forecast. The resulting effects of all these stresses on biogeochemical cycles could exacerbate changing atmospheric composition and result in further effects on climate.

If current trends are unchecked, much more significant warming is predicted, potentially driving a wide range of perturbations in other components of the climate system. What are and will be the consequences for life on Earth? We need to understand the full range of possible effects from small perturbations lending them-

**Box 1.1. A brief look at the historical development of atmospheric chemistry<sup>1</sup>**

Although Aristotle (384–322 B.C.) recognised water vapour as a distinct component of air, it was not until the 18<sup>th</sup> century that knowledge of the composition of the atmosphere began to be known, and our understanding has evolved considerably since then. In 1750, Joseph Black discovered carbon dioxide, and a few years later Daniel Rutherford discovered molecular nitrogen. Molecular oxygen was first isolated in 1773 by Carl Wilhelm Scheele and a year later by Joseph Priestly. This gas was named oxygen by Antoine-Laurent Lavoisier in 1789.

As new observational techniques became available, less abundant chemical constituents were discovered. For example, in 1862, J. B. Boussingault discovered that methane was a component of the air. About 30 years later, Armand Gautier discovered several natural and human related sources of methane. Scientists continue to find new minor atmospheric constituents to this day, as instrument sensitivity continues to increase.

Urban air pollution connected with large cities has been known from at least the time of the Romans. Harold Des Voeux coined the term “smog” from the words smoke and fog based on his observations in London. M. Ducros introduced the term acid rain in 1845.

In 1840, Christian F. Schönbein identified ozone by its peculiar odour following electrical discharge. André Houzeau made the first measurements of ground level ozone in 1858. The measurement of the ozone absorption spectrum by Walter Noel Hartley in 1881 led him to suggest that the observed cut-off of UV radiation ( $\lambda < 300$  nm) was due to ozone. J. Chappuis, and William Huggins later, discovered additional ozone absorption bands. The first ozone column measurements, made by Charles Fabry and Henri Buisson in 1920, noted that the column was about 3 mm thick (at atmospheric pressure) with large variations. Also in the 1920s, G. M. B. Dobson developed the spectrophotometer for measuring total ozone that is still used today. Dobson made many of the first measurements showing the global variability of ozone spatially and seasonally.

In 1929, at a conference in Paris, Sidney Chapman proposed the first chemical mechanism to explain the origin of ozone, suggesting that stratospheric ozone was formed by the photolysis of molecular oxygen. It was not until the 1950s that additional reactions were added to the mechanism described by Chapman. In 1950, David Bates and Marcel Nicolet proposed the potential im-

portance of hydrogen oxides ( $\text{HO}_x$ ) chemistry in the mesosphere, while in 1965 J. Hampson highlighted the role of  $\text{HO}_x$  for the chemistry of the stratosphere. In 1970, Paul Crutzen stressed the importance of nitrogen compounds ( $\text{NO}_x$ ) in determining stratospheric ozone concentrations. In 1974, Ralph Cicerone and Richard Stolarski suggested the potential for chlorine to affect ozone catalytically.

In the early 1950s, it was established that the health symptoms and plant damage observed in the vicinity of urban centres like Los Angeles during pollution events were due to high levels of atmospheric ozone and other oxidants. Arie Jan Haagen-Smit suggested in 1951 that ozone episodes were due to solar ultraviolet light acting on hydrocarbons and nitrogen oxides emitted by motor vehicles and industry. In 1973, Paul Crutzen suggested that similar “smog reactions” involving the oxidation of methane and carbon monoxide in the presence of nitrogen oxides should lead to a substantial production of ozone in remote regions of the troposphere. A few years earlier, in 1970, Hiram Levy II had suggested that the hydroxyl ( $\text{OH}$ ) radical, which provides the dominant oxidation mechanism in the troposphere, was formed in the background atmosphere by the mechanism that had been recognised previously as occurring in polluted air, namely the reaction of water vapour with the electronically excited oxygen atom  $\text{O}(^1\text{D})$ , itself produced by the photolysis of ozone.

Halocarbons, such as CFC-11 ( $\text{CFCl}_3$ ), were first detected following the invention of the electron capture detector by James Lovelock in 1971. In 1974, a study by Mario Molina and F. Sherwood Rowland suggested that the presence of ozone-destroying chlorine in the stratosphere resulted to a large extent from the photolysis by solar ultraviolet radiation of industrially manufactured chlorofluorocarbons. The large seasonal change in ozone over Antarctica, referred to as the ozone “hole”, was discovered by Joseph Farman and colleagues in 1985. A year later, Susan Solomon and co-workers proposed a connection between chlorine chemistry and polar stratospheric clouds to explain this ozone “hole”. The fundamental photochemical mechanism leading to the ozone destruction that creates the hole was discovered by Mario and Luisa Molina in 1987. Paul Crutzen, Mario Molina, and F. Sherwood Rowland were awarded the 1995 Nobel Prize in chemistry for their accomplishments.

selves to environmental management to more ominous and more remote prospects of catastrophic and irreversible change.

It is important to understand the mechanisms and rates of emissions of trace gases and fine particles, and their subsequent transformation and dispersion; the mechanisms for their eventual removal from the atmosphere and associated deposition fluxes are of importance as well. These processes extend over a wide range of spatial scales, from the microscopic to local, regional, and global, with the global scale being affected by all others. Understanding the complicated interplay of these processes at work is an important goal of the atmospheric chemistry community.

Another key goal is to detect and track widespread and long-term changes in the chemical content and radiative properties of the atmosphere and to predict their potential impacts. The community also aspires to

address the complex challenge of identifying which atmospheric emissions need to be controlled (and to what levels) in order to prevent unacceptable atmospheric degradation, undesirable climate modification, and irreversible harm to the habitability of our planet.

The field of atmospheric chemistry and air pollution has a long history (see Box 1.1). It is only during the 20<sup>th</sup> century, however, as more sensitive instruments have been developed, that systematic progress has been made. In the last 30 years, the importance of atmospheric trace substances (e.g. ozone, greenhouse gases) in global environmental issues has been stressed. The purpose of this first chapter is to provide a framework for evaluating recent advances in our understanding of the role of atmospheric chemistry in the Earth system. It is also designed to introduce major uncertainties or gaps in our knowledge that limit our understanding of the present state of the atmosphere and prevent us from fully predicting future developments.

We begin this by outlining a number of key environmental issues related to the observed changes in atmospheric composition and their impact on ecosystems and

<sup>1</sup> Much of the content of this box is based on discussion in the 1999 book, *Atmospheric Chemistry and Global Change*, edited by G. P. Brasseur, J. J. Orlando, and G. S. Tyndall.

**Box 1.2. Definitions and units**

**Number density:** Number of particles (e.g. atoms, molecules or aerosols) of substance per unit volume of air expressed in particles  $\text{m}^{-3}$  or particles  $\text{cm}^{-3}$ .

**Mass density:** Mass of substance per unit volume of air expressed in  $\text{kg m}^{-3}$  or in  $\text{g m}^{-3}$ .

**Mole fraction:** Number density of substance divided by number density of air (dimensionless variable). Abundances expressed in  $\text{cmol mol}^{-1}$ ,  $\text{mmol mol}^{-1}$ ,  $\mu\text{mol mol}^{-1}$ ,  $\text{nmol mol}^{-1}$ , and  $\text{pmol mol}^{-1}$  correspond to volume mixing ratios of  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-6}$ ,  $10^{-9}$ , and  $10^{-12}$ , respectively. The American literature commonly adopts percent, per mille, ppmv, ppbv, and pptv for the corresponding mole fractions.

**Mass fraction:** Mass density of substance divided by mass density of air (dimensionless variable). The pertinent unit for mass mixing ratio is  $\text{kg kg}^{-1}$ , but often is expressed as  $\text{g kg}^{-1}$  or  $\text{g g}^{-1}$ . Abundances expressed in  $\mu\text{g g}^{-1}$ ,  $\text{ng g}^{-1}$ , and  $\text{pg g}^{-1}$  correspond to mass mixing ratios of  $10^{-6}$ ,  $10^{-9}$ , and  $10^{-12}$ , respectively.

**Column abundance:** Vertically integrated number density of substance (expressed in particles  $\text{m}^{-2}$  or particles  $\text{cm}^{-2}$ ). In the case of ozone, the column abundance is often expressed in Dobson units (DU). One Dobson unit corresponds to the height (in  $10^{-3}$  cm) of an ozone column if the gas were at standard temperature and pressure. It is equivalent to  $2.687 \times 10^{16}$  molecules  $\text{cm}^{-2}$ . The unit of  $\text{mmol m}^{-2}$  is the recommended unit, but is currently not widely used in the literature.

**Particle or mass flux:** Number of particles or mass of substance crossing a unit surface per unit time. Expressed in particles  $\text{cm}^{-2} \text{s}^{-1}$  or  $\text{g cm}^{-2} \text{s}^{-1}$ . Total mass flux of a substance (emitted for example at Earth's surface) is often expressed in  $\text{Tg yr}^{-1}$  ( $10^{12} \text{ g yr}^{-1}$ ).

**Atmospheric lifetime:** Average time that a substance spends in the atmosphere. Atmospheric residence time is a synonymous

concept. Expressed in days, months, or years. If the removal of a substance is directly proportional to its concentration, the lifetime is also a measure of the time that would be needed to remove  $1/e$  (63%) of its mass if its source were discontinued.

**Turnover time:** Atmospheric burden of a substance at equilibrium divided by the globally integrated removal rate. Under steady-state conditions the turnover time equals the lifetime (residence time).

**Greenhouse gases:** Gases (water vapour, carbon dioxide, methane, ozone, nitrous oxide, halocarbons) whose interactions with terrestrial radiation leads to warming of Earth's surface.

**Aerosols:** An assembly of liquid or solid particles suspended in a gaseous medium (e.g. air) long enough to enable observation or measurement. Although water droplets and ice crystals in clouds fit this definition formally, by convention they are often considered as separate categories.

**Radiative or climate forcing:** According to the IPCC terminology, the term "climate forcing" denotes the change in the net irradiance (in  $\text{W m}^{-2}$ ) at the tropopause (after allowing for stratospheric temperatures to re-adjust to radiative equilibrium, but with the surface and tropospheric temperature and moisture held fixed) created by changes imposed on the climate system by natural (solar radiation changes, volcanic emissions of  $\text{SO}_2$ , and particulate matter) or human-induced processes (greenhouse gases, aerosols, changes in surface albedo). The climate forcing concept provides a very useful means of quantitatively comparing the importance of the different factors forcing climate change. It avoids the difficult problem of how the climate system will actually respond (in terms of temperature, precipitation, winds, etc.) to the imposed changes. This latter problem, which involves an intricate web of interactions and feedbacks within the atmosphere and between the atmosphere and the underlying surface, has to be addressed using complex models of the climate system.

human society. These issues have been a motivating force for atmospheric chemistry research during the past few decades. We then examine past variations in atmospheric composition, the causes of atmospheric change, and the potential impacts resulting from atmospheric change. A few definitions of frequently used terms, which may be useful to the reader, are provided in Box 1.2.

## 1.1.2 Environmental Issues and Atmospheric Chemistry

Many major environmental issues comprise strong atmospheric chemistry components, and human activities affect the atmosphere's chemical composition in important ways. Chemical species impact climate, key ecosystems, and much of life on Earth. The concentrations of chemical compounds and their effects need to be known across a wide range of temporal (sub-second to decadal) and spatial (molecular to global) scales. The challenge to atmospheric chemists is to develop the research tools and scientific infrastructure necessary to understand and resolve the environmental issues facing humanity.

### 1.1.2.1 Greenhouse Gases, Aerosols, and Climate Forcing

As mentioned earlier, increasing concentrations of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and several other gases that absorb in the infrared part of the radiative spectrum affect the earth's climate. The man-made contribution of these gases to the so-called greenhouse effect is likely to result in a significant warming of the earth's surface and troposphere, and a cooling of the stratosphere and mesosphere. The potential for greenhouse gas effects on climate was first studied quantitatively by Arrhenius in 1896. Anthropogenic greenhouse gases have provided an additional radiative energy input to the troposphere and surface part of the climate system of about  $2.4 \text{ W m}^{-2}$  since the beginning of the agro-industrial era (IPCC 1996, 2001).

An increasing load of aerosol particles in the troposphere (sulphates, organics, black carbon, etc. – see Chap. 4) caused by both primary particle and secondary particle precursor emissions from industrial processes and from biomass burning are also contributing to climate change. IPCC (2001) estimates the direct radiative forcing due to aerosols to be  $-0.4 \text{ W m}^{-2}$  for

sulphate,  $-0.2 \text{ W m}^{-2}$  for biomass burning aerosols,  $-0.1 \text{ W m}^{-2}$  for fossil fuel organic carbon, and  $+0.2 \text{ W m}^{-2}$  for fossil fuel black carbon. Uncertainties in these numbers are large. Indirect aerosol radiative forcing, in which aerosols affect cloud reflectivity and lifetime, could cause substantial but poorly quantified additional cooling (IPCC 2001). This net cooling due to aerosols may have counteracted a substantial part of the warming expected from greenhouse gases during past decades. However, because of their relatively short atmospheric lifetimes (days to weeks), the actual cooling or warming effects from aerosols are largely regional and depend on the actual particle distributions in the given region. The large uncertainty in the quantitative estimate of aerosol effects on climate is due to the lack of data on the actual change in atmospheric composition of aerosols, and the lack of understanding of how the increasing aerosol mass concentration has affected the number concentration of cloud-forming particles and, thereby, the reflectivity and lifetime of clouds (IPCC 1996).

Estimates of the radiative forcing by different types of aerosols have been made by IPCC (2001), as noted above, although uncertainties in these estimates are also large. For example, the radiative forcing due to the direct effect of sulphate aerosols, about which relatively much is known, has been estimated to be about  $-0.2$  to  $-0.8 \text{ W m}^{-2}$ , a range of a factor of four. Looking to the future, the IPCC (2001) projects for year 2100 a radiative forcing of  $4.1$  to  $9.2 \text{ W m}^{-2}$  relative to pre-industrial times. IPCC (2001) also projects a surface temperature increase of  $1.4$  to  $5.8^\circ\text{C}$  above 1990 values: “the projected rate of warming is much larger than the observed changes during the 20<sup>th</sup> century and is very likely to be without precedent during at least the last 10 000 years, based on paleoclimate data.”

#### 1.1.2.2 Acidification and Eutrophication

Increasing deposition of acidifying sulphur and nitrogen compounds has led to widespread damage to terrestrial and limnic ecosystems in some parts of the world – e.g. northern Europe and north-eastern North America – near and downwind of large industrial emission regions, following deposition on poorly buffered soils (e.g. McNeely et al. 1995; Mannion 1992; Rodhe et al. 1995). Whereas sulphur emissions are now declining in these particular regions, emissions are increasing in some other regions (China, India, and Southeast Asia) raising concern about more widespread acidification problems in the future.

Fixed nitrogen ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) is a limiting nutrient in many ecosystems. The increased nitrogen deposition in and around many industrial parts of the world has consequently caused eutrophication (increased primary production caused by the enrichment of an ecosystem

with nutrients) of terrestrial, fresh-water and marine ecosystems with consequences for plant and animal species composition and also for the atmospheric carbon balance (e.g. McNeely et al. 1995; Mannion 1992).

#### 1.1.2.3 Enhanced Tropospheric Ozone

Observations at the earth's surface at mountain sites in Europe suggest that tropospheric ozone ( $\text{O}_3$ ) has increased by a factor of two or more during the past century (WMO 1998). Increases in ozone concentrations since the pre-industrial period are evident in Europe and East Asia, and appear to be associated with large increases in gaseous precursors, reactive oxides of nitrogen ( $\text{NO}_x$ ), hydrocarbons, and CO, which interact with solar radiation to produce  $\text{O}_3$  (see Chap. 3) (Crutzen and Zimmermann 1991). Recent measurements suggest little change in ozone in the last two decades (Logan et al. 1999), but there are not enough observations to assess thoroughly present and past changes in tropospheric ozone.

The elevated concentration of ozone causes concern because of its importance as a greenhouse gas and because of its adverse effects on plants, animals, and human health through contact exposure. Recent model studies (see, e.g. IPCC 2001) suggest that estimated increases in tropospheric ozone have produced a positive radiative forcing of approximately  $0.35 \text{ W m}^{-2}$  since pre-industrial times.

In addition, photolysis of tropospheric  $\text{O}_3$  is the primary source of the hydroxyl radical (OH), an extremely strong oxidant. Oxidation by OH is the main sink for a large number of environmentally important atmospheric chemical species including CO, greenhouse gases such as  $\text{CH}_4$ , and some gases responsible for stratospheric  $\text{O}_3$  depletion such as methyl bromide ( $\text{CH}_3\text{Br}$ ). Thus, tropospheric  $\text{O}_3$  plays a critical role in determining the oxidising and cleansing efficiency of the atmosphere. The rise in  $\text{O}_3$  and  $\text{NO}_x$  since pre-industrial times has increased the source of OH, but this increase has been compensated for by more rapid removal of OH due to the rise in other gases (particularly CO and  $\text{CH}_4$ ). Atmospheric models predict little change in the global mean OH concentration since pre-industrial times (less than 10% in most models), reflecting these compensating factors. Model studies (e.g. Krol et al. 1998; Karlsdottir and Isaksen 2000) suggest that the tropospheric OH concentration has increased in response to increasing concentrations of  $\text{CH}_4$ , CO, and other gases. Recent evaluation of the 1978–2000 record of methyl chloroform, whose primary sink is reaction with OH, shows, in comparison, that the global average concentration of OH increased between 1978 and 1988 and decreased between 1988 and 2000 (Prinn et al. 2001). Issues related to tropospheric ozone and other oxidants are addressed in Chap. 3.



#### 1.1.2.4 Depletion of Stratospheric Ozone

One of the most dramatic changes in atmospheric composition observed during the past decades is the depletion of ozone in the stratosphere. Stratospheric ozone has decreased globally by more than 5% since 1970. This change, primarily in extra-tropical regions, is most pronounced at high southern latitudes during the spring months where the ozone destruction has approached 60%, but significant decreases in ozone are also occurring in the Northern Hemisphere. There is now general consensus that the ozone depletion is largely caused by chlorine- and bromine-containing gases primarily of industrial origin. This decrease in stratospheric ozone leads to an increasing flux of UV radiation into the troposphere with potential impacts on human health, ecosystems, and tropospheric photochemistry. Since there is approximately ten times more ozone in the stratosphere than in the troposphere, the rise in tropospheric ozone has not compensated for the larger loss of stratospheric ozone. Furthermore, stratospheric ozone depletion provides a negative net contribution to the tropospheric energy balance ( $-0.15 \pm 0.1 \text{ W m}^{-2}$ ; IPCC 2001).

#### 1.1.2.5 Transport of Toxic Substances – Metals, Organic Compounds, and Radionuclides

Elevated levels of toxic substances (gaseous or bound to particles) in the atmosphere represent an issue of a different character. These toxic compounds – for example, mercury (Hg), cadmium (Cd), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), dioxins, and anthropogenic radionuclides – generally occur in very low concentrations and are not of any importance for the balance of the major atmospheric components. However, the atmosphere serves as the major transport medium for these types of toxic compounds and evaluation of their effects on human health and ecosystems requires that processes of emission, transport, transformation, and deposition be understood.

#### 1.1.2.6 Transport of Nutrients

Ecological systems, including those supporting economically important activities such as agriculture and forestry, can be profoundly impacted by the wet and dry deposition of atmospheric substances such as nitrogen- and sulphur-containing compounds. Although the coupling of the atmosphere and biosphere through the exchange of gases and aerosols occurs naturally, this coupling is being affected dramatically by human activities such as agriculture and fossil fuel burning. Forests are being damaged by the combined effects of ozone expo-

sure and pollutant deposition, i.e. nutrient overloads and acidification. Fisheries are being affected by runoff of nutrients from agricultural activities as well as toxic substances such as pesticides.

#### 1.1.2.7 Policy Considerations

The issues described above have received growing attention not only from the members of the scientific community, but also from decision-makers in governments and industries. With society's increased recognition of the importance and value of the environment, the relation between atmospheric chemistry research and environmental policy design has been growing substantially over recent decades. In some cases, international treaties to reduce emissions have been enacted and actions to protect the global environment have been taken. Major challenges remain, however. Although substantial advances have been made in understanding fundamental processes in the chemical system of the atmosphere, our predictive capability remains limited in spite of its importance for informed decision making. New and challenging problems at the chemistry-weather, chemistry-climate, and chemistry-ecology interfaces are emerging and will require much attention in the future. The availability of space instrumentation anticipated in the near future to observe chemical species in the troposphere will provide unprecedented information on the global distribution and evolution of key biogenic and anthropogenic compounds (see Chap. 5). These observations will require associated ground-based and airborne measurements to be of greatest value. Laboratory experiments and new developments in numerical modelling of associated processes will also be required (see Chap. 6).

### 1.1.3 The Atmosphere in the Earth System

The atmosphere is composed primarily (>99.999%) of molecular nitrogen ( $\text{N}_2$ ), molecular oxygen ( $\text{O}_2$ ), water ( $\text{H}_2\text{O}$ ), argon (Ar), and carbon dioxide ( $\text{CO}_2$ ). Many environmental problems are linked to changes in the atmospheric abundance of trace chemical compounds whose mole fractions vary from a few  $\mu\text{mol mol}^{-1}$  to well below a  $\text{pmol mol}^{-1}$ .

How can such seemingly small changes in the trace gas and fine particle content of Earth's atmosphere have such large effects on climate and on the biosphere? The answer lies in the complex, non-linear interconnections among the major systems that define Earth as we know her. These include the atmosphere's central role in mediating the energy flux between the sun and the planet's surface, as well as its major role in conveying fluxes of energy and materials between other components of the Earth system. A schematic view of the key processes that

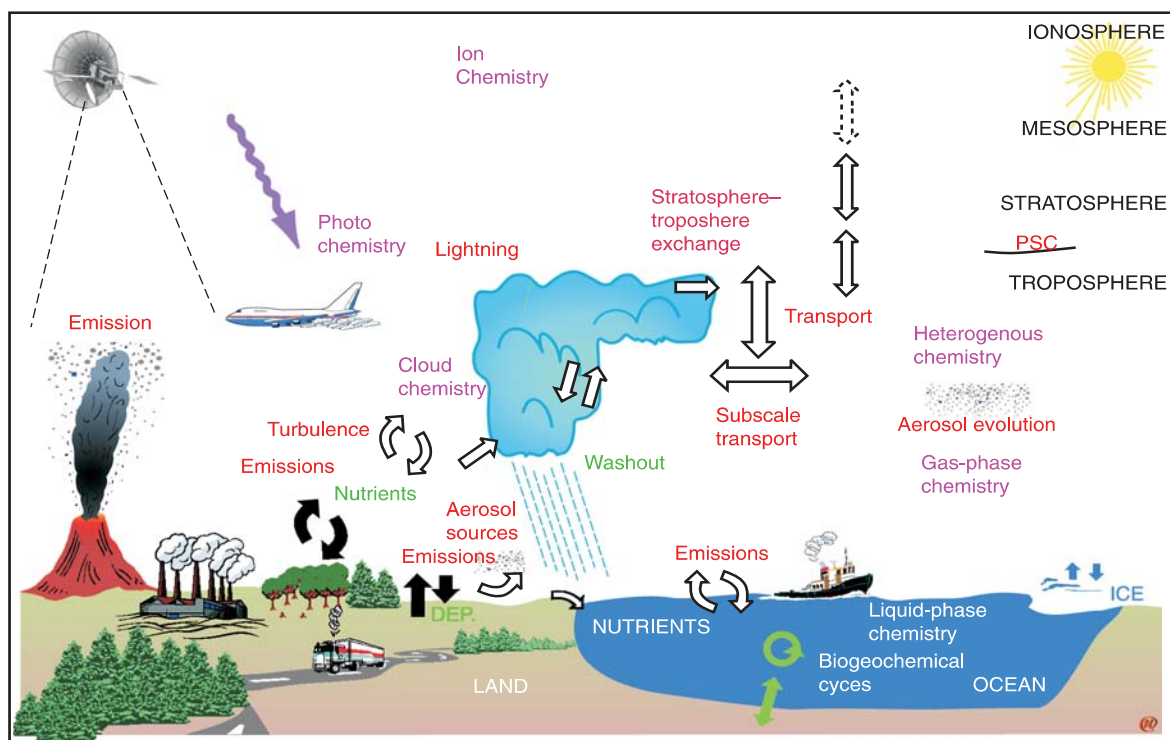


Fig. 1.1. Schematic representation of physical and chemical processes affecting chemical compounds in the atmosphere, including natural and anthropogenic emissions, large-scale transport, subscale transport including convective exchanges, gas-phase and aqueous-phase chemical and photochemical reactions, heterogeneous chemical conversion, stratosphere-troposphere exchanges, wet scavenging, and surface deposition (courtesy of M. Schultz, Max Planck Institute for Meteorology, Hamburg, Germany)

affect the formation and fate of chemical compounds in the troposphere is presented in Fig. 1.1.

A particular property of Earth's atmosphere is that many of the chemical compounds present in it, including the most abundant gases,  $N_2$  and  $O_2$ , are constantly taken up and regenerated by biological processes (microbial activity in soils, photosynthesis and respiration, foliage emissions, etc.). Reduced chemical compounds that are released to the atmosphere by terrestrial and oceanic ecosystems and as anthropogenic emissions are often oxidised in the atmosphere and the resulting products are removed by deposition to the earth's surface. Subsequent assimilation and reduction in the biosphere closes the atmosphere-biosphere cycle. The circulation of chemical elements in the Earth system is often described in terms of global biogeochemical cycles (see Chap. 2). One of the challenges for the scientific community is to quantify the global budget (burden and turnover time in each component of the geosphere and transfer rates among them) of key chemical elements or compounds. These cycles produce important feedback mechanisms for the Earth system. They have frequently and dramatically been perturbed by human activities including agricultural practices, industrialisation, and urbanisation. Changes in land use including massive biomass burning, particularly in the Tropics, and energy consumption, mostly fossil fuel burning,

have been the sources of substantial changes in the chemical composition of the atmosphere and in the deposition rate of acids and other toxic products on Earth's surface. An important task for the scientific community is to "close" the biogeochemical cycles and to "balance" the chemical budgets in the Earth system in order to understand, and eventually manage, the impact of human activities (see Box 1.3).

The global distribution of chemical compounds in the atmosphere depends on a variety of chemical, biological, and physical processes. Transport is the process by which atmospheric motions carry physical or chemical properties from one region of the atmosphere to another. It enables different chemical compounds, with different sources, to interact. Without transport, local production and destruction would tend to balance and some equilibrium concentration would be reached. It is transport that drives the atmosphere away from these equilibrium conditions and, hence, determines which regions are net sources and which are net sinks for chemical substances. Atmospheric motions are often categorised according to their spatial scales: planetary, global, synoptic (of the order of 1000 km), mesoscale (10–500 km), and small scale (below 10 km). Many compounds are released in the planetary boundary layer (PBL), where the horizontal winds are weak but often strongly turbulent. This dynamically variable layer

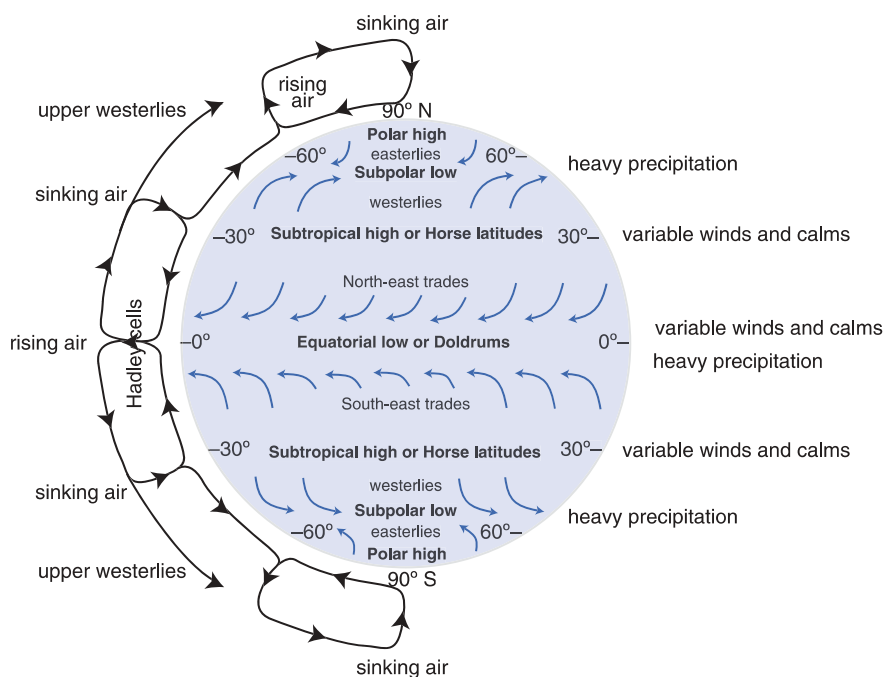
**Box 1.3. Biosphere-atmosphere interactions and human activities**

Exchange between the biosphere and the atmosphere has been modified substantially by anthropogenic activities, in particular land use changes, such as deforestation, urbanisation, and agricultural activities. These perturbations have severe ecological and socio-economic consequences that make management and mitigation strategies necessary for avoiding or limiting environmental problems. Defining efficient and cost effective management and mitigation strategies requires a detailed understanding of the actual gas exchange among terrestrial, aquatic, and atmospheric systems, and of the biological, physical, and chemical processes that control the fluxes across the biosphere-atmosphere interface. This information is also urgently needed to improve the forecasts of climate change using global climate models.

Relationships between fluxes and concentration changes derived from increasingly sophisticated models of atmospheric transport and chemistry are being employed to evaluate and interpret fluxes estimated from atmospheric observations. The increasing knowledge in this area indicates that biosphere-atmosphere interactions are more complex than thought several years ago. Continued development of numerical models and algorithms is needed to understand the non-linear behaviour of terrestrial/marine systems and the related fluxes of constituents across the biosphere-atmosphere interface. Further interdisciplinary research with an integrated approach needs to be done to cover the remaining gaps and to provide policy makers with a basis for making informed decisions on mitigation strategies on regional and global scales.

**Fig. 1.2.**

A schematic presentation of the wind system for a hypothetical water-covered earth, showing major winds and zones of low and high pressure. Vertical air movements and circulation are shown in exaggerated profile on the left of the diagram; characteristic surface conditions are given on the right. The two north-south cells on either side of the Equator make up the Hadley circulation (Brown et al. 1989)



(shallow during the night and morning, deeper during the afternoon and evening) is generally characterised by high humidity and high concentrations of compounds emitted at the surface (e.g. pollutants). In the presence of shallow or deep convection, chemical compounds are injected from the boundary layer to the free troposphere, but the rate of this boundary layer ventilation remains poorly quantified. Transport by deep convective cells and frontal systems is an important mechanism for moving air (and chemical compounds) vertically throughout the free troposphere. As air moves upward and cools, condensation takes place and precipitation can occur, which removes soluble gases and airborne particles from the atmosphere. Large-scale quasi-horizontal advection leads to intercontinental transport of relatively long lived chemical compounds. This process is responsible for trans-boundary air pollution transport. At midlatitudes, flow in the free troposphere is predominantly directed eastward in all sea-

sons, and is considerably stronger during winter. The surface winds are highly variable, with different regimes separated by fronts. Equatorward of 30°, the weather regime is characterised by fast rising motions and heavy precipitation in the Inter-Tropical Convergence Zone (ITCZ) near the equator and slow descending motions in the subtropics. Regional seasonal patterns such as the Asian monsoon or temporal variations on longer time scales, such as the El Niño phenomenon, have large impacts on the budget of chemical compounds. Mass exchanges through the tropopause also affect significantly the distribution of several chemical compounds in the troposphere. This is particularly the case for ozone, as discussed in Chap. 3. Because the air is continuously stirred by weather patterns and convective activity, long lived compounds (lifetime of several months or more) tend to be quasi-uniformly mixed in the troposphere. The complexity of the tropospheric circulation is illustrated schematically in Fig. 1.2 and 1.3.



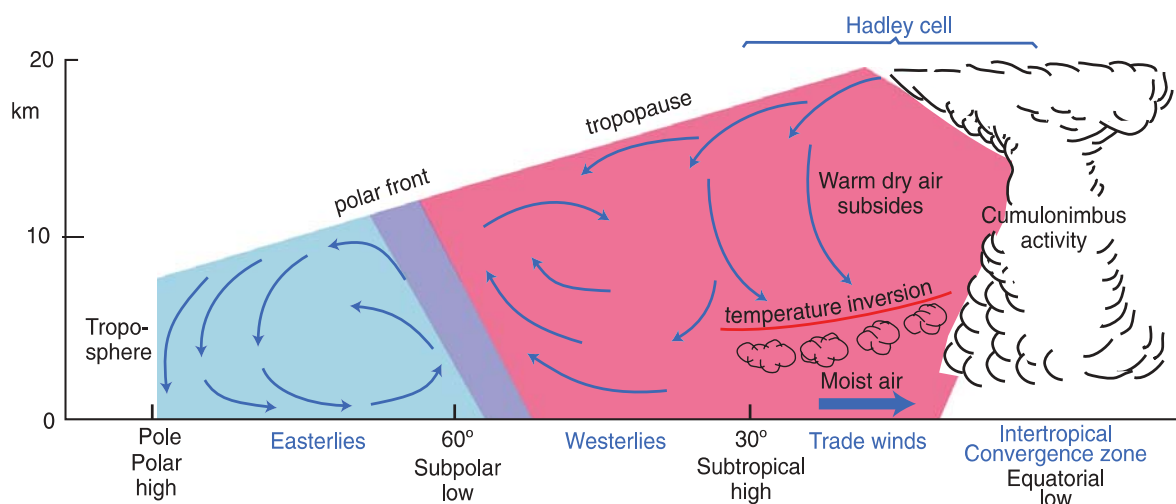


Fig. 1.3. Schematic presentation of the atmospheric circulation below 20 km altitude, from the Equator to the pole. This cross section shows the Inter-Tropical Convergence Zone (ITCZ) near the Equator, where strong upward motions take place, tropical clouds form, and intense thunderstorm activity occurs. Notice the return flow along the tropopause and the slow air subsidence in the subtropics. The polar front and the polar circulation are also shown (Brown et al. 1989)

Chemical transformations through gas-phase reactions or multi-phase processes proceed at rates that need to be measured in the laboratory, while photolysis rates are a function of the solar actinic flux that penetrates into the atmosphere, and hence of absorption and scattering processes by atmospheric molecules, clouds, and aerosol particles. A schematic representation of several of the important chemical processes occurring in the troposphere is presented in Fig. 1.4. It stresses the reactions that control the formation and destruction of ozone and hydroxyl, and that determine the oxidising efficiency of the atmosphere (see also Box 1.4). It also highlights the complexity of the tropospheric chemical system.

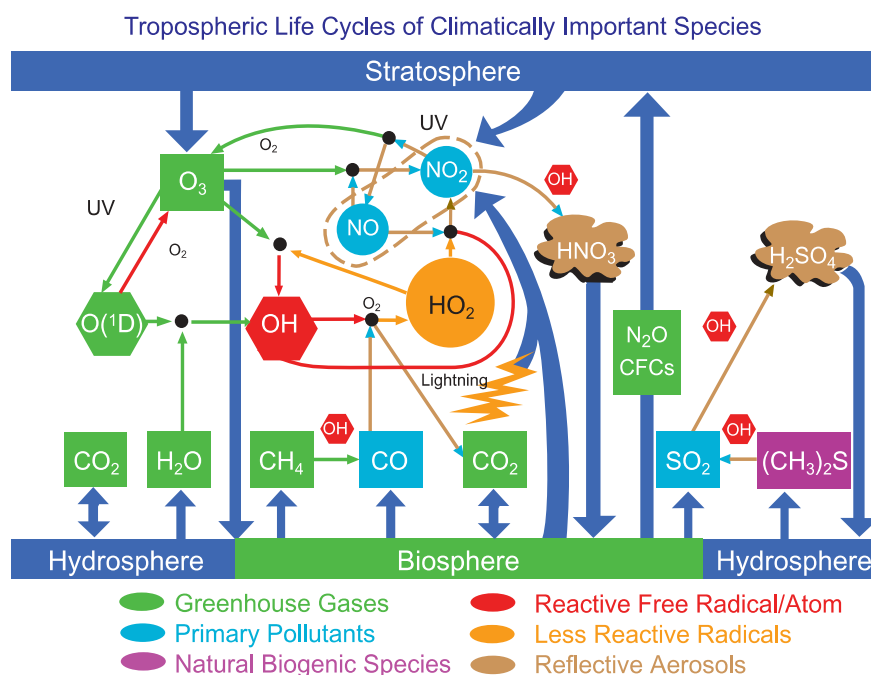
Due to the non-linearity of these processes, the response of the tropospheric chemical system to human-induced perturbations is very complex, and exhibits different regimes with abrupt transitions. For example, the existence of thresholds (such as a temperature threshold associated with the formation of particles) contributes to the non-linearity of the chemical system. As a result, the behaviour of the atmosphere in response to human-induced forcings is difficult to predict and can produce surprises.

## 1.2 Global Atmospheric Chemistry and the IGAC Project

During recent decades the field of atmospheric chemistry has evolved and grown significantly in response to the global and regional concerns discussed in this book. However, in contrast with the situation prevailing in meteorology, where continuous monitoring efforts

provide detailed global observations on the physical state of the atmosphere, only limited observational data have been available on the global distributions, seasonal evolution, and trends of chemical compounds in the atmosphere. A major effort of the atmospheric chemistry community has therefore focussed on the measurement of chemical compounds (gases and aerosols) in the troposphere and stratosphere. Many projects, often sponsored by the International Global Atmospheric Chemistry (IGAC) Project, have used different types of instrumentation (e.g. *in situ* or remote sensing techniques) on different platforms (aircraft, balloons, spacecraft, ground-based, and satellites) (see Chap. 5). Field campaigns performed over limited time periods (see Appendix A.3) have been organised to investigate specific photochemical processes at different locations. Other observational projects have provided information on large-scale distributions of specific chemical constituents (see Appendix A.3). Periodic soundings of the atmosphere (balloon-borne, lidar) have revealed the structure of the vertical distribution for a limited number of atmospheric chemical species at a few locations. Future efforts will focus on the miniaturisation of instrumentation (so that it can be used routinely on commercial aircraft, for example), and on the development of new platforms (such as unmanned aircraft). Satellite-based measurements have played an important role in determining concentrations of a variety of gases and some types of particles and in getting data sets that are truly global, particularly for the stratosphere. While relatively little information exists now, satellite measurements will become an important future source of data on the distributions of tropospheric gases and aerosols. Even with these efforts by the international scientific

**Fig. 1.4.**  
Schematic representation of  
important chemical processes  
occurring in the troposphere  
(adapted from Prinn 1994)



#### Box 1.4. Oxidising power and atmospheric lifetime

The average time for which a gas molecule or aerosol particle remains in the atmosphere is determined by a number of atmospheric chemical and physical processes. For example, many chemical compounds are destroyed by oxidation processes and the resulting products, when they are soluble in water, are scavenged in precipitation. Other compounds that are chemically stable and not very soluble in water (such as the chlorofluorocarbons) may remain in the atmosphere for years or even decades. In this case, they are transported to the middle atmosphere and may affect stratospheric chemistry.

The atmospheric lifetimes of many atmospheric gases are determined mainly by their reactions with the OH radical. Other oxidation processes include reactions with ozone ( $O_3$ ), hydrogen peroxide ( $H_2O_2$ ), the nitrogen trioxide free radical ( $NO_3$ ), and halogen species. Hydrogen peroxide, for example, converts sulphur dioxide to sulphuric acid in cloud and rain droplets, and hence contributes to the formation of acid precipitation. The  $NO_3$  radical plays a significant role at night, primarily in polluted areas. The oxidation by OH and the other gases mentioned above is referred to as the oxidising power or the oxidising efficiency of the atmosphere.

community, a satisfactory global climatology of tropospheric compounds is far from a reality. A strategy to gather more information on the spatial and temporal distributions of the major chemical species needs to be established.

Laboratory investigations have provided measurements of reaction rate constants and absorption cross sections for many trace atmospheric chemical species and have provided the fundamental knowledge necessary to understand atmospheric photochemistry. While much progress has been made regarding gas-phase reactions, significant uncertainties remain in our understanding of multi-phase processes occurring through cloud droplet, ice surface, and aerosol interactions with trace gases. Regularly updated evaluations of both gas phase and heterogeneous experimental kinetics data provide inputs for atmospheric chemistry models and highlight poorly characterised kinetic processes that require further study (e.g. NASA JPL and IUPAC compilations).

Numerical models of atmospheric chemistry and physics (see Chap. 6) have been used to assess the consequences of newly measured chemical kinetics data, to analyse observations made during field campaigns, and to determine the sensitivity of calculated concentrations to external forcings. This has made it possible to derive (for example, through inverse modelling) the magnitude and location of the surface emissions that can explain these observations and to simulate the evolution of the chemical composition in response to natural or human-induced perturbations. Progress has often resulted from a combined use of several of these tools.

As one might expect for a new field such as global atmospheric chemistry, progress has been largely *ad hoc*, so that the level of international coordination and integration that is required to address such large-scale problems is not yet adequate. By contrast, for example, the international meteorological community, which represents a far more mature and operational discipline, has achieved a state of coordination and inte-

### Box 1.5. IGAC and the atmospheric science community

Atmospheric chemistry is a central process in Earth system dynamics. Thus, research in atmospheric chemistry connects to many other efforts in global change research, assessment, and observation. Tackling global environmental problems requires a collaborative international suite of observational, research, and assessment activities.

IGAC is the leading international research project on tropospheric chemistry. It is a Core Project of the International Geosphere-Biosphere Programme (IGBP), one of a triad of international research programmes in global environmental change. The other two are the World Climate Research Programme (WCRP) and the International Human Dimensions Programme on Global Environmental Change (IHDP). IGAC interacts with many other elements of IGBP, WCRP, and IHDP, and in assessment and observation. The goals of IGAC are to develop a fundamental understanding of the processes that determine atmospheric composition, to understand the interactions among atmospheric chemical composition and physical, biospheric, and climatic processes, and to predict the impact of natural and anthropogenic forcings on the chemical composition of the atmosphere.

To achieve its goals, IGAC carries out collaborative research with other elements of IGBP:

- JGOFS, LOICZ and SOLAS (Joint Global Ocean Flux Study, Land Ocean Interactions in the Coastal Zone, and Surface Ocean Lower Atmosphere Study). These programmes study the chemical, physical, and biological processes that control the exchange of trace gases between the ocean and the atmosphere (note: SOLAS is currently in its planning stage).
- GCTE (Global Change and Terrestrial Ecosystems) studies the ecological processes that influence trace gas production from the land surface and the impacts of changes in atmospheric composition on terrestrial ecosystems.
- LUCC (Land Use and Cover Change) investigates the causes, patterns and projected rates of land-use and land-cover change, that affect rates of terrestrial emissions of trace gases.

- PAGES (Past Global Changes) investigates the composition of the atmosphere in the past, from ice core records and other paleo techniques.
- GAIM (Global Analysis, Integration and Modelling) undertakes intercomparisons and facilitates the development of atmospheric transport models and of Earth system models.
- In addition, IGAC interacts with other projects within the Programmes. Of particular relevance are:
  - SPARC (Stratospheric Processes and their Role in Climate) studies the physical and chemical dynamics of the stratosphere, especially the impact of human activities.
  - The WCRP modelling group facilitates the development of models of the physical climate system, drawing on atmospheric composition as a driver of changing climate.

IGAC also has major connection to long-term observational programs via GAW (Global Atmospheric Watch of the World Meteorological Organisation, WMO), which monitors the long-term evolution of atmospheric composition on a global and regional scale. GAW is a component of the Global Climate Observing System (GCOS). IGAC research has also contributed significantly to assessments of climate and atmospheric change. These include assessments of climate change by the Intergovernmental Panel on Climate Change (IPCC), and those on stratospheric ozone sponsored by the World Meteorological Organisation and the United Nations Environment Programme (UNEP).

As highlighted here, many organisations have strong connections to atmospheric chemistry in addition to IGAC. Because of ongoing activities within these other organisations, this document primarily focusses on chemistry in the global troposphere and provides only a cursory discussion of research activities relating to the carbon cycle, to stratospheric ozone, and to local and regional air quality.

gration which provides a sound basis for studying the physical state of the global atmosphere. Atmospheric chemistry requires a similarly sound basis for carrying out fundamental long-term studies of the chemical state of the global atmosphere. The field currently suffers from inadequate spatial and temporal observational capabilities and, especially, from the lack of sufficiently strong international efforts to verify observational methods, to improve analytical precision, and to provide the accurate calibration standards upon which any study of long-term change fundamentally depends.

IGAC, which has established strong links with other international initiatives (see Box 1.5), has sponsored a number of significant experimental and interpretative research programmes, as noted throughout this volume.

Many of the results of the IGAC efforts in the last ten years are summarised within the larger context of global and regional atmospheric chemistry in this and the following chapters of this volume. Where appropriate, research opportunities and priorities are suggested. As an introduction to the other chapters, we present in the next sections an overview of past changes in the chemical composition of the atmosphere, summarise the plausible causes of these changes, and assess possible impacts.

## 1.3 Past Changes in Atmospheric Chemical Composition

### 1.3.1 Long-term Variability: Evidence of Feedbacks

Quantitative records of past atmospheric composition are available in polar ice caps on a time scale spanning several ice ages. Gases are encapsulated in air bubbles and aerosols species are entrapped in the ice matrix. Such data allow us to deduce limits to the natural variability of atmospheric composition, document feedbacks, and offer the possibility of testing particular hypotheses and evaluating the capabilities of atmospheric models. These paleo-records clearly demonstrate that past climatic and environmental changes on Earth are highly correlated with atmospheric composition, which suggests that the nature of biogeochemical feedbacks is key to understanding global change. These data sets also suggest a number of questions, such as: How important were biogeochemical cycle feedbacks in the flip from one climate mode to another? How strong are these feedbacks on climate relative to other purely physical responses such as polar ice-albedo effects? Have biological feedbacks contributed to the unprecedented rate of greenhouse gas change observed today?

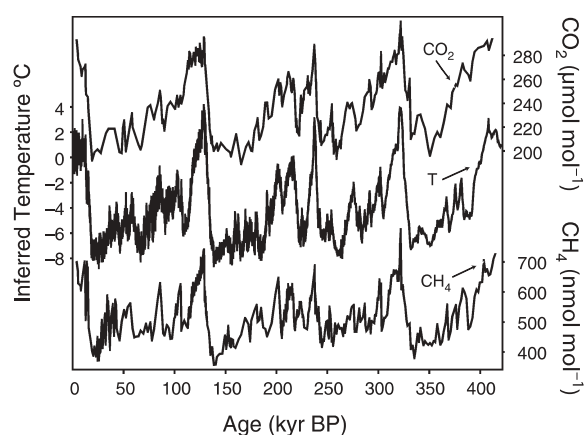


Fig. 1.5. Concentration changes of carbon dioxide, methane, and dust along the Vostok ice core (Antarctica) for the last 400 000 years. Isotopic temperature (from  $\delta^{18}\text{O}$ ) is also shown as climate proxy (data from Petit et al. 1999)

Detailed information for the past 400 000 years has been obtained from the Vostok (Antarctica) ice core for two major greenhouse gases  $\text{CO}_2$  and  $\text{CH}_4$  (Fig. 1.5). A remarkable overall correlation is found between the concentrations of these gases and temperature changes. The lowest levels of greenhouse gases are observed under full glacial conditions ( $190 \mu\text{mol mol}^{-1}$  and  $0.35 \mu\text{mol mol}^{-1}$  for  $\text{CO}_2$  and  $\text{CH}_4$ , respectively, during the last glacial maximum, 20 kyr B.P.). All the available records obtained from Antarctic and Greenland glacial ice cores show that the rises during deglaciation are about 80 and  $0.3 \mu\text{mol mol}^{-1}$  for  $\text{CO}_2$  and  $\text{CH}_4$ , respectively. While the data shown in Fig. 1.5 suggest that both greenhouse gases are strikingly in phase with the climate record, some differences emerge when the data are examined in detail. For example, as a glaciation begins,  $\text{CH}_4$  concentration decreases in phase with Antarctic cooling, whereas  $\text{CO}_2$  lags markedly behind the temperature change (Raynaud et al. 1993). Other data show that the abrupt climatic changes that affected the North Atlantic region on the decadal to centennial time scale during the last glacial-interglacial transition and during the last ice age are remarkably reflected in the  $\text{CH}_4$  records. Ice core measurements (Leuenberger and Siegenthaler 1992) also indicate a depletion of the concentrations of  $\text{N}_2\text{O}$  during ice ages in relation, probably, with reduced emissions of this greenhouse gas by soils under drier climatic conditions.

Ice core data also reveal that during ice ages the terrestrial and marine contributions to Antarctic aerosol deposition were increased significantly due to stronger winds and dryer environmental conditions. Concentrations of calcium and sodium (crustal and marine primary aerosol reference elements, respectively) in Vostok ice were higher by factors of about 30 and four, respectively, relative to Holocene (i.e. the past 10 000 years) values. Greenland ice core data suggest that the dusti-

ness of the glacial atmosphere was most likely a global phenomenon (Hammer et al. 1985; Hansson 1994).

Despite higher secondary aerosol (sulphate, nitrate, and methanesulphonate) concentrations, the atmosphere (at least as revealed by polar studies) was not more acidic during glacial periods. The present day atmosphere has become more acidic as a result of anthropogenic emissions. The cause of the higher secondary aerosol levels in the glacial Antarctic atmosphere is not fully understood.

Finally, ice cores from Greenland and Antarctica have recorded numerous large volcanic eruptions (Zielinski et al. 1996; Clausen et al. 1997). Sulphate and chloride concentrations are available for volcanic periods in numerous polar ice cores. Some of these events were powerful enough to have markedly disturbed global atmospheric composition for up to three years after eruption.

In conclusion, strong correlations have been observed between the temperature fluctuations through the glacial cycles and the concentrations of several trace gases and aerosol types. These correlations indicate strong couplings of these components through biogeochemical and physical climate processes. Elucidation of these coupling processes is one of the most exciting challenges facing global change scientists, including atmospheric chemists, during the years ahead.

### 1.3.2 Changing Atmospheric Composition During the Last Few Centuries

The concentrations of many atmospheric gases have increased since the pre-industrial period to reach levels probably unprecedented in the last 400 000 years. A combination of ice core data and direct monitoring data reveals the globally-averaged changes in atmospheric concentration for several key gases over the last few centuries (see Fig. 1.6). The gap between polar ice core data and the first direct atmospheric monitoring is now entirely filled by firn air data for the three major long lived greenhouse gases:  $\text{CO}_2$  (Etheridge et al. 1996),  $\text{CH}_4$  (Etheridge et al. 1992; Blunier et al. 1993; Etheridge et al. 1998), and  $\text{N}_2\text{O}$  (Machida et al. 1995; Battle et al. 1996). Prior to the 17<sup>th</sup> century,  $\text{CO}_2$  concentrations fluctuated naturally in the range from  $275\text{--}285 \mu\text{mol mol}^{-1}$  except during ice ages. The pre-industrial level of methane in the Antarctic was  $670 \pm 70 \text{ nmol mol}^{-1}$ . The increase in  $\text{CH}_4$  concentration started during the second half of the 18<sup>th</sup> century, reaching concentrations greater than  $1700 \text{ nmol mol}^{-1}$  in the current atmosphere. Increases in  $\text{CH}_4$  emissions appear to be the primary factor in explaining the observed changes. In addition, carbon isotope ratio ( $^{13}\text{C}/^{12}\text{C}$  and  $^{14}\text{C}/^{12}\text{C}$ ) determinations in  $\text{CH}_4$  now available for the Southern Hemisphere since 1978 from air archives and Antarctic firn air (Francey et al. 1999) constrain estimates of the natural and an-

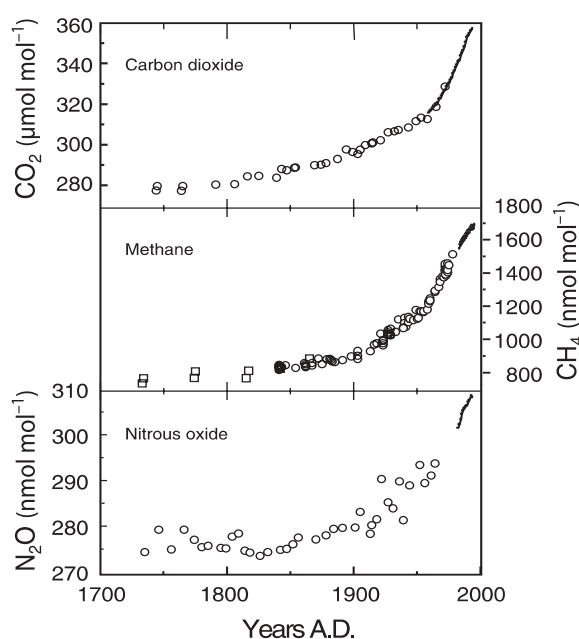


Fig. 1.6. Atmospheric concentration of major greenhouse gases  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  over the last 300 years, as reconstructed from Greenland and Antarctic ice core studies. Continuous line: atmospheric record (Etheridge et al. 1992, 1996; Blunier et al. 1993; Machida et al. 1995; see also IPCC 2001)

thropogenic global sources and sinks of methane. Nitrous oxide concentrations have increased from 285 to more than 310  $\text{nmol mol}^{-1}$  since the pre-industrial era.

Sulphates from fossil fuel burning and smelting, as well as nitrates from fossil fuel burning (including automotive emissions), have increased in polar snow and ice since the very beginning of the 20<sup>th</sup> century; however, their impacts are only noticeable in the Northern Hemisphere (Mayewski et al. 1990; Legrand et al. 1997). In comparison to a pre-industrial sulphate level of about 25  $\text{ng g}^{-1}$ , concentrations peaked at 110  $\text{ng g}^{-1}$  at the end of the 1960s. Thereafter, decreasing anthropogenic sulphur emissions in Europe and North America are clearly reflected in Greenland sulphate profiles, which exhibit a steady downward trend since about 1980.

Nitrate concentration increases in Greenland ice from a pre-industrial mean value of about 70 to 120  $\text{ng g}^{-1}$  for the period 1950–1989. This trend, valid all over Greenland, starts markedly around 1950, i.e. much later than the sulphate trend. A decline of nitrate is evident only for recent years. The nitrate trend observed in Greenland firn must be considered with some caution due to the reversibility of gaseous  $\text{HNO}_3$  deposition onto snow, even in Greenland (Fischer et al. 1998). Moreover, it must be kept in mind that the nitrogen-bearing chemical species deposited in Greenland remain unidentified. They may have been different in the pre-industrial and present atmospheres.

From pre-industrial (1755–1890) to modern times (1950–1975), carbonaceous particle concentrations at a high-Alpine glacier site have increased by factors of 3.7,

3.0, 2.5, and 2.6, for black carbon, elemental carbon, organic carbon, and total carbon, respectively (Lavanchy et al. 1999).

Only a few data are presently available on CO concentrations in the past. An increase of about 20  $\text{nmol mol}^{-1}$  is apparent between 1800 and 1950 for this compound at Summit, Greenland, where the pre-industrial level is 90  $\text{nmol mol}^{-1}$  (and 55–60  $\text{nmol mol}^{-1}$  in the Antarctic) (Haan et al. 1996). These figures need to be confirmed because glaciological artefacts in the measurements are possible (Haan and Raynaud 1998).

Formaldehyde measurements in Greenland snow are scarce and have to be viewed with caution because the deposition of this compound onto snow is reversible. At Summit, Staffelbach et al. (1991) found a doubling of pre-industrial concentration (about 2  $\text{ng g}^{-1}$ ) in recent years, with an acceleration of the increase in recent decades. Post-depositional chemical transformations taking place in the surface snow pack can even be a source of compounds such as formaldehyde (Sumner and Shepson 1999), nitrogen oxides (Honrath et al. 1999), and CO to the atmosphere. A task ahead is to determine the role played by the surface snow pack in lower atmospheric composition and in influencing the transfer function of a chemical constituent between atmosphere and glacial firn and ice.

As indicated above, changes in the tropospheric concentration of ozone and its precursors ( $\text{NO}_x$ , CO, and hydrocarbons) have been substantial since the pre-industrial era. Very few observational data are available to quantify these changes, so that estimates rely primarily on model simulations. This issue will be discussed further in Chap. 3 and 7.

### 1.3.3 Future Changes in Atmospheric Composition

Although considerable progress has been made in the past decade in understanding the biogeochemical cycles of greenhouse gases, oxidants, and aerosols, large gaps in knowledge still remain. Furthermore, uncertainties in the climate feedback response of these processes are also large. Nonetheless, many analyses suggest that concentrations of key greenhouse gases and other atmospheric constituents will continue to change in the future as a result of human activities. Concentrations of important greenhouse gases are expected to continue to increase in the coming decades. The concentration of  $\text{CO}_2$  could double or even triple its pre-industrial concentration by 2100 (IPCC 1996, 2001). On the other hand, atmospheric concentrations of CFCs and several other halocarbons should decline over the coming decades as a result of global controls to protect the stratospheric ozone layer.

Future projections of  $\text{CH}_4$  are affected by uncertainties in the temperature dependence of wetland sources



and permafrost melting, and in atmospheric OH radical concentrations (the major sink). The evolution of future  $\text{N}_2\text{O}$  levels in the atmosphere is also uncertain because of poorly constrained sources and sinks. Agricultural inputs of large and growing amounts of nitrogen fertilisers lead to questions as to where the nitrogen is going and how much  $\text{N}_2\text{O}$  may be released in the future from fixed nitrogen accumulations in environmental subsystems (soils, waters). Future emissions of  $\text{SO}_2$  and  $\text{NO}_x$  will depend mainly on the use of fossil fuels and the extent to which measures are taken to control these emissions.

## 1.4 Causes of Atmospheric Changes

The rapid changes in atmospheric composition observed over the past century have been driven largely by emissions from fossil fuel combustion, industry, biomass burning, and intensive agriculture. A sample of the many long lived gases whose atmospheric concentrations are being significantly affected by human activities is shown in Table 1.1. Estimates of the growth rates and lifetimes remain somewhat uncertain for several of the compounds listed. Current global inventories of human-related atmospheric emissions for some of the environmentally important gases discussed in previous sections are presented in Table 1.2 along with comparisons to the magnitudes of natural sources (biosphere, oceans, volcanoes, lightning). Human related emissions are important, and often dominant, contributors to the abundance of many chemical species in the current atmosphere. Also included in Table 1.2 are forecast ranges of anthropogenic emissions for 2100 presented by IPCC (2001) for different potential socio-economic scenarios. These forecasts suggest that human perturbations to atmospheric composition in general are likely to increase over the coming century. In addition, future climate change may affect the natural (and human related) emissions of radiatively active gases and aerosols, resulting in complex chemistry-aerosol-climate feedbacks.

### 1.4.1 Fossil Fuel Combustion and Industry

Our technological society is largely powered by the combustion of fossil fuels. Fossil fuel combustion has been the main cause of the rise in atmospheric  $\text{CO}_2$  over the past 200 years from  $\sim 280 \mu\text{mol mol}^{-1}$  (natural background) to  $\sim 370 \mu\text{mol mol}^{-1}$  in the year 2001. In addition to  $\text{CO}_2$ , combustion processes emit a large number of pollutants including  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{NO}_x$ , soot particles, trace metals, and hydrocarbons (including toxic organic compounds). For many of these chemical species, the global source from fossil fuel combustion exceeds natural sources (Table 1.3). Other emissions related to fossil fuel use include  $\text{CH}_4$  from natural gas, coal, and oil production and distribution, and  $\text{SO}_2$  from petroleum refining. Motor vehicle traffic is a major source of  $\text{CO}$  and  $\text{NO}_x$ .

Industrial activities other than fossil fuel combustion also represent large sources of pollutants to the atmosphere. Metal smelters and the paper industry are major sulphur emitters. Carbon steel manufacturing is an important source of  $\text{CO}$ . Many organic compounds are emitted by the chemical industry and their environmental impacts in terms of toxicity, climate forcing, and tropospheric ozone are poorly understood.

### 1.4.2 Biomass Burning

Biomass burning is associated with deforestation, agricultural fires, wood and dung fuel use, and natural fires. Most of the world's biomass burning takes place in the Tropics and is highly seasonal, peaking at the end of the dry season (January–April in the northern Tropics, August–October in the southern Tropics). The largest contribution to this tropical source is agricultural burning of savannas; deforestation is also an important source in some regions. Natural fires are important mainly in boreal forests at high northern latitudes, where their frequency and intensity peak during the summer months.

**Table 1.1.** A sample of long lived important atmospheric gases that are affected by human activities (data based on IPCC 2001)

	$\text{CO}_2$ (carbon dioxide)	$\text{CH}_4$ (methane)	$\text{N}_2\text{O}$ (nitrous oxide)	$\text{CFCl}_3$ (CFC-11)	$\text{CHF}_3$ (HFC-23)	$\text{CF}_4$ (perfluoro- methane)
Pre-industrial concentration	$\sim 280 \mu\text{mol mol}^{-1}$	$\sim 700 \text{ nmol mol}^{-1}$	$\sim 270 \text{ nmol mol}^{-1}$	0	0	40 $\text{pmol mol}^{-1}$
Concentration in 1998	365 $\mu\text{mol mol}^{-1}$	1 745 $\text{nmol mol}^{-1}$	314 $\text{nmol mol}^{-1}$	268 $\text{pmol mol}^{-1}$	14 $\text{pmol mol}^{-1}$	80 $\text{pmol mol}^{-1}$
Rate of concentration change	+1.5 $\mu\text{mol mol}^{-1} \text{ yr}^{-1}$	+8.4 $\text{nmol mol}^{-1} \text{ yr}^{-1}$	+0.8 $\text{nmol mol}^{-1} \text{ yr}^{-1}$	-1.4 $\text{pmol mol}^{-1} \text{ yr}^{-1}$	+0.55 $\text{pmol mol}^{-1} \text{ yr}^{-1}$	+1 $\text{pmol mol}^{-1} \text{ yr}^{-1}$
Atmospheric lifetime	50–200 $\text{yr}^a$	12 $\text{yr}^b$	114 $\text{yr}^b$	45 $\text{yr}$	257 $\text{yr}$	50 000 $\text{yr}$

<sup>a</sup> No single lifetime can be defined for carbon dioxide because of the different rates of uptake by different removal processes.

<sup>b</sup> This lifetime is an adjustment time that accounts for the indirect effect of the gas on its own residence time.

**Table 1.2.** Current global inventories of human related emissions for environmentally important gases compared to the magnitudes of natural sources (e.g., from the biosphere, oceans, volcanoes, and lightning) mostly adapted from IPCC (1995, 1996), with some values based on IPCC (2001). Also included are forecast ranges of anthropogenic emissions for year 2100 presented by the IPCC (2000) Special Report on Emissions Scenarios (SRES) for different possible socio-economic assumptions

	CO <sub>2</sub> Pg C yr <sup>-1</sup>	CH <sub>4</sub> Tg CH <sub>4</sub> yr <sup>-1</sup>	N <sub>2</sub> O Tg N yr <sup>-1</sup>	Sulphur Tg S yr <sup>-1</sup>	NO <sub>x</sub> Tg N yr <sup>-1</sup>	CO Tg CO yr <sup>-1</sup>
Natural	150 <sup>a</sup>	160	10.2	18	11	400
Human-related						
Fossil fuel and industry	6.8	100	1.3	65	22	400
Biomass burning	1.6 <sup>a</sup>	40	0.5	2	12	500
Agriculture		170	3.9		1	
Landfills/sewage		65				
Other						550
Human total, present	7.6	375	5.7	67	35	1 450
Human-related, 2100 <sup>b</sup>	3.3–36.8	236–1 069	4.8–19.3	11–69	16–110	363–3 766

<sup>a</sup> Annual terrestrial biosphere and ocean fluxes for carbon dioxide are generally balanced by fluxes back to biosphere and oceans.

<sup>b</sup> Based on the harmonised 26 scenarios in IPCC (2000) SRES.

**Table 1.3.**  
Combined effect estimates of daily mean particulate pollution (after American Thoracic Society)

% change in health indicator per each 10 µg m <sup>-3</sup> increase in PM <sub>10</sub>	
<b>Increase in daily mortality</b>	
Total deaths	1.0
Respiratory deaths	3.4
Cardiovascular deaths	1.4
<b>Increase in hospital usage (all respiratory diagnoses)</b>	
Admissions	1.4
Emergency department visits	0.9
<b>Exacerbation of asthma</b>	
Asthmatic attacks	3.0
Bronchodilator use	12.2
Emergency department visits <sup>a</sup>	3.4
Hospital admissions	1.9
<b>Increases in respiratory symptom reports</b>	
Lower respiratory	3.0
Upper respiratory	0.7
Cough	2.5
<b>Decrease in lung function</b>	
Forced expiratory volume	0.15
Peak expiratory flow	0.08

<sup>a</sup> One study only.

Biomass burning emits the same general suite of chemical species to the atmosphere as fossil fuel combustion (CO<sub>2</sub>, CO, VOCs, NO<sub>x</sub>, etc.), but often in very different proportions; biomass burning is less efficient than fossil fuel combustion and the combustion temperatures are lower.

There is little knowledge of historical trends in biomass burning, and IPCC (2001) does not venture to forecast trends for the next century. Greenland ice core records of biomass burning tracers over the past 1 000 years iden-

tify several historical periods of enhanced biomass burning at high northern latitudes but indicate a decrease since the 1930s. Fire records maintained by governmental agencies in North America and Europe over the past 50 years indicate a general increase in the number of fires due to human negligence, but not much change in area burned because of improved fire-fighting ability. In the Tropics, where most of global biomass burning takes place, there is essentially no information on historical trends. One would expect a rise in biomass burning from in-

creasing agriculture and deforestation over the past century, but this effect could have been offset by better fire control in response to the growing rural population. The issue of biomass burning is discussed in detail in Chap. 2.

### 1.4.3 Land-use Changes

Major land-use changes over the past 100 years have included urbanisation driven by population pressure, increase in cultivated land in the Tropics, reforestation of formerly cultivated land in northern midlatitudes regions such as the eastern United States, and desertification in some areas such as northern Africa. Tropical deforestation now makes a significant contribution to the rise in  $\text{CO}_2$  (Table 1.1). However, this contribution is expected to decrease over the next century due to decimation of primary forests and it may actually be overcome by the atmospheric  $\text{CO}_2$  sink from reforestation and fertilisation at northern midlatitudes (IPCC 2001). Agriculture is thought to be the principal cause for the rises of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  over the past 100 years (Table 1.2). Methane is emitted by anaerobes in ruminants and rice paddies (which are effectively human-generated wetlands). Nitrogen fertiliser application to crops stimulates microbial emission of  $\text{N}_2\text{O}$ ; it also stimulates emission of  $\text{NO}_x$ , but the resulting source is small compared to that from fossil fuel combustion (Table 1.3). The impact of land-use changes on the emissions of chemical compounds, as well as the question of dust (iron and other metals) emission associated with desertification and deposition to the ocean are addressed in Chap. 2.

### 1.4.4 Climate Changes

Changes in the climate system could substantially affect the chemical composition of the atmosphere. Such changes are related to interannual variability in the dynamics of the atmosphere, to quasi-periodic oscillations in the atmosphere-ocean system (such as the El Niño and La Niña phenomena in the tropical Pacific), and to longer time scale climatic trends. Long-term trends are believed to be due to external forcing including human-induced emissions of greenhouse gases.

Although the mechanisms governing Earth's climate are not fully understood, the effects of climate changes on the chemical composition of the atmosphere need to be identified because they provide potential positive or negative feedback mechanisms in the climate system. Issues to be considered are the expected warming resulting from enhanced concentrations of carbon dioxide, methane, and other greenhouse gases, possible increases in convective activity and lightning frequency, changes in precipitation rates and in soil moisture, and changes in surface emissions of temperature-sensitive biogenic compounds, among others.

## 1.5 Impacts of Changes in Atmospheric Composition

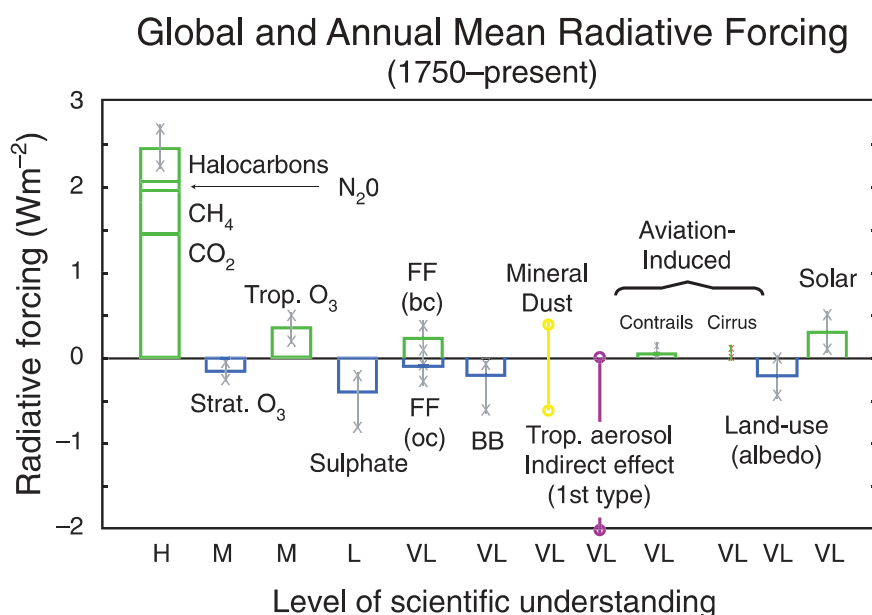
Impacts resulting from changes in atmospheric composition can be substantial. In this section, we briefly highlight three major categories of impacts associated with changes in atmospheric composition: climate change, effects on ecosystems, and effects on human health. There is also some discussion of composition change impacts on corrosion, agriculture, and water resources.

Because changes in the chemical composition of the atmosphere are expected to be the main drivers of human-induced climate change, atmospheric chemists have been deeply engaged in the climate change issue, and have established strong links with the more physically oriented climate researchers. They have also developed links with ecologists and agriculture experts who study the effects on ecosystems and crops of increased exposure to various atmospheric gases and aerosols, and to the increased levels of UV radiation associated with decreases in stratospheric ozone. Connections to the community of scientists studying the effects of atmospheric changes on human health have been considerably weaker.

### 1.5.1 Climate Change

The issue of climate change, in general, and of the impact of human activities on climate, in particular, is the subject of extensive analysis and assessment by the scientific community. At the international level, these assessments are led by the Intergovernmental Panel on Climate Change (IPCC 1990, 1992, 1995, 1996, 2001). Its recent analysis (IPCC 2001) of the global average climate forcing during the past 250 years due to recognised human-related and natural processes is shown in Fig. 1.7. The dominant positive forcing (heating tendency) results from the increased concentration of rather well mixed greenhouse gases ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , CFCs, etc.). Tropospheric and stratospheric ozone changes are treated separately mainly because this greenhouse gas is not well mixed in the atmosphere and the observed changes have distinct horizontal and vertical spatial patterns. The largest negative forcing (cooling tendency) is due to aerosol particles of human origin. Because of the limited tropospheric lifetime of aerosol particles (days to a few weeks) they are also not well mixed and their forcing patterns are less uniform than that of the greenhouse gases. As shown in Fig. 1.7, evaluation of the radiative forcing from all of the different sources since pre-industrial times indicates that the net globally-averaged radiative forcing on climate is positive.

**Fig. 1.7.** Globally-averaged climate forcing (in  $\text{W m}^{-2}$ ) during the past century due to recognized human related and natural processes (IPCC 2001). Solid bars represent best estimates and vertical lines uncertainty ranges (*H* = high, *M* = medium, *L* = low, *VL* = very low, *FF* = fossil fuel, *BB* = biomass burning, *bc* = black carbon, *oc* = organic carbon)



### 1.5.2 Impacts on Ecosystems

Ecosystems are affected by atmospheric changes in several different ways:

- Direct deposition of gases such as  $\text{O}_3$ ,  $\text{SO}_2$ , and  $\text{NO}_2$ ;
- Impact of increased levels of UV radiation caused by stratospheric ozone depletion; and
- Indirect impacts caused by changes in the chemical balance of soils, lakes, and surface ocean water following the deposition of acidifying and eutrophying substances, such as sulphates, ammonium, nitrates, etc.

The impacts may include anything from elimination of sensitive species and altered productivity to subtle shifts in the relative abundance of plant and animal species. These issues will be addressed in Chap. 2.

### 1.5.3 Corrosion

Acid deposition and high concentrations of gaseous pollutants ( $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{O}_3$ ) are known to cause damage to buildings and cultural and historical monuments mainly in urban and suburban areas. The economic loss due to such man-made corrosion in Western Europe and North America has been substantial, where, mainly because of reductions in  $\text{SO}_2$  concentrations, the corrosion rates are now decreasing significantly. However, in many other areas, especially in Eastern Europe and some developing countries, corrosion problems remain severe or are becoming more acute. There are indications that in warm climates  $\text{NO}_2$  and  $\text{O}_3$  alone (even without  $\text{SO}_2$ )

may cause serious corrosion. Modern communication and information devices are also subject to atmospherically induced corrosion. Telecommunication switching gear, magnetic recording and data storage media, and metallic connections in semiconductor structures are all susceptible to atmospheric corrosion processes.

### 1.5.4 Health Effects

Air pollutants have long been recognised as health hazards. Well known examples include smog episodes in London – the one in December 1952 is estimated to have caused 4 000 excess deaths – and the photochemical pollution ( $\text{O}_3$ , PAN, etc.) in Los Angeles, which causes lung damage and eye irritation, among other effects. During recent years more subtle effects, some of them believed to occur not only in urban and suburban areas but also over larger regions, have been identified. Here we list some of the important health issues related to specific air pollutants.

*Halogenated hydrocarbons* (including the CFCs), while not harmful as such, contribute to depletion of the stratospheric ozone layer. The resulting *increase in UV-B radiation* at the earth's surface is estimated to cause adverse health effects including higher incidences of eye cancer and cataract, skin cancer (in fair skinned populations), and a depression of the immune system for certain tumours and infectious diseases (UNEP 1998).

*Elevated levels of  $\text{O}_3$* , as low as  $75 \text{ nmol mol}^{-1}$  in surface air, have been demonstrated to have adverse health effects, even at short-term exposures. Today, such concentrations are commonly observed during the warm seasons over large regions in Europe and North America

and probably also in other parts of the world where emissions of ozone precursors ( $\text{NO}_x$ , hydrocarbons, CO) are large.

Epidemiological studies show that short-term exposure to current ambient levels of *aerosols* (i.e. 24-hour average concentrations of 30 to  $150 \mu\text{g m}^{-3}$  of particles  $<10 \mu\text{m}$  diameter ( $\text{PM}_{10}$ )) are associated with adverse health effects ranging from reduced lung function to mortality (Table 1.3).

The *acidification of air and precipitation*, in addition to its adverse effects on terrestrial and limnic ecosystems, also has consequences for human health. Direct health effects of elevated levels of  $\text{SO}_2$  and  $\text{NO}_x$  have been well established (Lübker-Alcamo and Krzyzanowski 1995). Indirect health effects due to increased dissolution of metals in soils (e.g. Al, Cd) and in water pipes (Cu) are also suspected.

*Mercury* (Hg) is an interesting example of a contaminant that has been mobilised by man and dispersed globally through the atmosphere. The current deposition of Hg is estimated to exceed the pre-industrial value by at least a factor of two world-wide and up to a factor of five to ten in northern Europe and North America (Bergan et al. 1999). The elevated deposition of Hg over large regions, aggravated by the increased leaching of Hg from acidified soils and a subsequent bioaccumulation of organic Hg in fish, has resulted in toxic concentration in pike in many lakes in Scandinavia and Canada (Lindqvist 1991).

## 1.6 Some Important Questions

The objective of this book is to synthesise and integrate the results of research conducted by the atmospheric chemistry community over the last 10 to 15 years and, specifically, to highlight key findings of projects facilitated by IGAC. This work provides the scientific basis for answering questions that are important to society:

- What determines the chemical composition of the natural atmosphere?
- How have human activities altered atmospheric composition?
- How have human activities changed the global atmospheric budgets of carbon, nitrogen, and sulphur?
- What controls tropospheric ozone?
- Is the “cleansing efficiency” of the atmosphere changing?
- How does atmospheric chemistry affect the biosphere and food production?
- How does atmospheric chemistry affect human health?
- What is the connection between atmospheric composition and climate?
- How might chemical composition evolve in the future?
- Are there risks of abrupt changes and/or irreversible changes in atmospheric composition?
- What should the research strategy be to address unresolved questions?

Although no definitive answer to some of these questions can yet be given, many of the projects completed by the scientific community in the last decade have provided information that will help address many of them. Some of the important scientific research being conducted by the international atmospheric chemistry community in order to provide the answers to these questions is summarised in Chap. 2 through 4. The importance of the biosphere in controlling the chemical composition of the atmosphere, and an assessment of the impact on the biosphere of changes in the chemical composition of the atmosphere are considered in Chap. 2. The role of chemical transformations of gas-phase compounds, with emphasis on tropospheric ozone and other photooxidants, is examined in Chap. 3. The physical and chemical processes governing the formation of aerosols, plus their evolution and removal from the atmosphere, are discussed in Chap. 4. The advances that have been made in instrumentation and modelling are described in Chap. 5 and 6, respectively. Finally, an integrated view of the causes and impacts of atmospheric chemical changes in the form of responses to the questions listed above is provided in Chap. 7.