

Chapter 1:

Changes in the Chemical Composition of the Atmosphere and Potential Impacts

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1. Introduction

Direct measurements of the chemical composition of the atmosphere during the past 30-50 years have clearly demonstrated that the concentration of several key components exhibit systematic trends. Indirect information—from ice cores, lake sediments, etc.—has shown that large changes also have occurred during the agro-industrial era, i.e., the past 200 years. There are several fundamental questions related to these observed changes:

- How large are changes due to man-made impacts compared to natural fluctuations?
- What is the nature of the most important man-made processes that have contributed to the observed changes?
- What are the potential impacts of the changes in atmospheric composition?
- Are the changes likely to continue into the future?
- What are the major uncertainties or gaps in knowledge that limit our understanding of the present situation and prevent us from predicting future developments?

We begin this chapter by introducing a number of key environmental issues related to the observed changes in atmospheric composition and their impact on ecosystems and human society. These issues have been a major driving force in atmospheric chemistry research during the past few decades.

1.1 Greenhouse gases and climate

Increasing concentrations of CO₂, CH₄, N₂O and several other gases with absorption bands in the infrared part of the spectrum contribute to the so called greenhouse effect leading to a warming of the Earth's surface and the troposphere (and a cooling of the stratosphere and mesosphere). This process, first quantitatively studied by Arrhenius (1896), has provided an additional radiative energy input into the troposphere/surface part of the climate system of about 2.4 W/m² since the beginning of the agro-industrial era (IPCC, 1996; see [Figure 1.1](#)).

1 **1.2 Aerosols and climate**

2 An increasing load of aerosol particles in the troposphere (sulfates,
3 organics, black carbon etc.) caused by emission from both industrial processes
4 and biomass burning, has decreased the amount of incoming solar radiation
5 reaching the Earth's surface by 0.5 to 2 W/m². This cooling can have
6 counteracted a substantial part of the warming due to greenhouse gases. The
7 main reason for the large uncertainty in this quantitative estimate is our poor
8 understanding and lack of data on how the increasing aerosol mass
9 concentration has affected the number concentration of cloud condensation
10 nuclei (CCN) and thereby the reflectivity of the clouds (IPCC, 1996; see
11 Figure 1.2).

12 **1.3 Acidification and eutrophication**

13 Increasing deposition of acidifying sulfur and nitrogen compounds has
14 led to widespread damage to terrestrial and limnic ecosystems in some parts of
15 the world—e.g. northern Europe and northeastern North America—near and
16 downwind of large industrial emission regions, following deposition on poorly
17 buffered soils (refs.)

18 Whereas sulfur emissions are now declining in these particular regions,
19 emissions are increasing at a rapid rate in some other regions (China, India,
20 Southeast Asia) raising concern about more widespread acidification problems
21 in the future.

22 Fixed nitrogen (NO₃⁻, NH₄⁺) is a limiting nutrient in many ecosystems.
23 As a consequence, the increased nitrogen deposition in and around many
24 industrial parts of the world has caused eutrophication of both terrestrial and
25 marine ecosystems with consequences for plant and animal species
26 composition and also for the atmospheric carbon balance (see Figure 1.3).
27 (ref.)

28 **1.4 Enhanced tropospheric ozone**

29 Observations at the Earth's surface and at mountain sites in Europe
30 suggest that tropospheric ozone (O₃) has increased by a factor 4 or more

1 during the past century. This increase is believed to be mainly due to man-
2 made emissions of NO_x, hydrocarbons and CO, which interact with solar
3 radiation to produce O₃. The elevated concentration of ozone causes concern
4 because of its impact on climate (O₃ is a greenhouse gas!) and its adverse
5 effects on plants and human health (ref.).

6 Photolysis of tropospheric O₃ is the primary source of the hydroxyl
7 radical (OH), an extremely strong oxidant. Oxidation by OH is the main sink
8 for a large number of environmentally important atmospheric species
9 including toxic gases such as CO, greenhouse gases such as CH₄, and gases
10 responsible for stratospheric O₃ depletion such as CH₃Br. In this manner,
11 tropospheric O₃ plays a critical role in determining the oxidizing and cleansing
12 efficiency of the atmosphere. The rise in O₃ and NO_x since pre-industrial
13 times has increased the source of OH, but this increase has been compensated
14 by more rapid removal of OH due to the rise in reduced gases (particularly CO
15 and CH₄). Atmospheric models predict little change in the global mean OH
16 concentration since pre-industrial times (less than 10% in most models),
17 reflecting these compensating factors. The 1978–1994 record of the
18 methylchloroform proxy shows no significant trend in global mean OH
19 concentrations during that period ($0.0 \pm 0.2\% \text{ yr}^{-1}$) (Prinn *et al.*, 1995).

20 **1.5 Depletion of stratospheric ozone**

21 One of the most dramatic changes in atmospheric composition observed
22 during the past decades is the depletion of ozone in the stratosphere. This
23 global (extra-tropical) phenomenon is most pronounced at high southern
24 latitudes during the spring months. There is now a general consensus that the
25 ozone depletion is caused by chlorine- and bromine-containing gases of
26 industrial origin. This leads to an increasing flux of UV radiation into the
27 troposphere with potential impacts on human health, ecosystems and the
28 photochemistry of the troposphere (see **Figure 1.5**). Furthermore, stratospheric
29 ozone depletion provides a negative net contribution to the tropospheric
30 energy balance (x W/m²).

1 **1.6 Transport of toxic substances (metals, organic compounds,** 2 **radionuclides)**

3 Elevated levels of toxic substances (gaseous or bound to particles) in the
4 atmosphere represent an issue of a different character than the previous five
5 questions. These toxic compounds—for example, Hg, Cd, PAH, PCB, Cs-
6 137—occur in very low concentrations and are not believed to be of any
7 importance for the balance of the major atmospheric components. The
8 atmosphere serves, however, as the major transport medium for these types of
9 toxic compounds and an estimate of their effects on human health and
10 ecosystem requires that processes of emission, transport, transformation and
11 deposition be understood (see Figure 1.6).

12 **1.7 Transport of nutrients**

13 [To be completed]

14 These issues have received growing attention not only from the members
15 of the scientific community, but also from decision makers in the government
16 and industry. With the change in society's attitude regarding the environment,
17 the relation between atmospheric chemistry research and environmental policy
18 design has been growing substantially over the last decades and actions to
19 protect the global environment have been taken. Major challenges, however,
20 remain. Although substantial advances have been made in understanding
21 fundamental processes in the chemical system of the atmosphere, our
22 predictive capability remains limited in spite of its importance for informed
23 decision making. New and challenging problems at the chemistry-climate and
24 chemistry-biology interfaces are emerging and will require much attention in
25 the future. The availability of space instrumentation in the near future to
26 observe chemical species in the troposphere will provide unprecedented
27 information on the global distribution and on the evolution of key biogenic
28 and anthropogenic compounds.

29

2. Atmospheric Chemistry and the Earth System

The most abundant gases in the Earth's atmosphere are molecular nitrogen (N_2) and oxygen (O_2), in contrast to what is observed in the atmosphere of our neighboring planets Mars and Venus. A particular property of the Earth's atmosphere is that many of its chemical compounds, including 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 oxidized 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. For example, nitrous oxide (N_2O), which is a product of nitrification/denitrification processes in soils and waters, is destroyed primarily by photolysis in the stratosphere and is oxidized to produce nitric oxide (NO). NO and its oxidation product NO_2 are converted into nitric acid (HNO_3) which is removed from the atmosphere by precipitation or deposited on the surface. Methane (CH_4), produced in oxygen-deficient environments, is oxidized in the atmosphere to water vapor and carbon monoxide (CO) and further into carbon dioxide (CO_2). Similar degradation mechanisms affect nonmethane hydrocarbons, including those (such as isoprene and monoterpenes) which are produced by vegetation. Atmospheric CO_2 is constantly exchanged with the ocean and continental ecosystems at rates that depend on the water temperature and on the seasonal evolution of the terrestrial biosphere, respectively. Sulfur, when produced naturally, is released from the ocean to the atmosphere, primarily as dimethyl sulfide ($(CH_3)_2S$ (or DMS)). These compounds are photolyzed or oxidized into sulfur dioxide (SO_2) which is further converted into sulfuric acid (H_2SO_4) and sulfate aerosol particles. Water (H_2O) is an important greenhouse gas and also plays a key role in the Earth system since it circulates between the ocean, the atmosphere and the biosphere and is constantly switching between the vapor, the liquid and the solid phases. It is also an important chemical compound of the atmosphere, since it is the major source of hydroxyl (OH) and

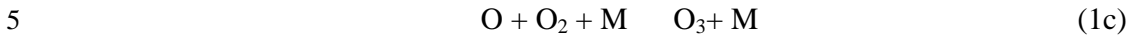
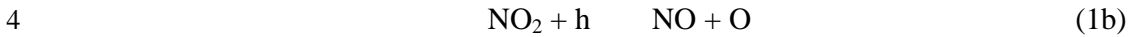
1 hydroperoxy (HO₂) radicals, and provides sites (droplets and ice particles) for
2 chemical processes (that are not possible in the gas phase) to occur in the
3 condensed phase or at the interface.

4 The circulation of chemical elements in the Earth system is often
5 described in terms of global biogeochemical cycles, and one of the challenges
6 for the scientific community is to quantify the global budget (burden and
7 residence time in each component of the geosphere and transfer rates between
8 them) of key chemical elements or compounds. These cycles produce
9 important feedback mechanisms in the Earth system. They have often been
10 dramatically perturbed by human activities including agricultural practices,
11 industrialization and urbanization. Changes in land-use including massive
12 biomass burning, particularly in the tropics, and energy consumption, mostly
13 fossil fuel burning, have been the sources of substantial changes in the
14 chemical composition of the atmosphere and in the deposition rate of acids
15 and other toxic products on the Earth's surface. An important task for the
16 scientific community is to "close" the biogeochemical cycles and to "balance"
17 the chemical budgets in the Earth system.

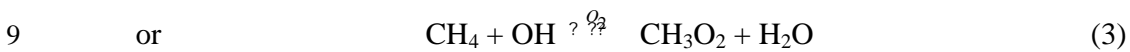
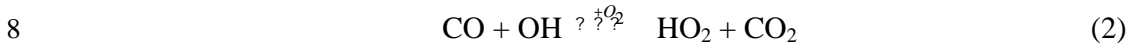
18 The global distribution of chemical compounds in the atmosphere
19 depends not only on the exchange rates between the surface and the
20 atmospheric boundary layer. It is also determined by the rate at which
21 chemical compounds are injected from the boundary layer to the free-
22 troposphere and are transported by the large-scale atmospheric circulation.
23 Transport by deep convective cells and frontal systems as well as exchanges
24 through the tropopause are important processes that are not well understood.
25 Chemical transformations through gas-phase reactions or multi-phase
26 processes proceed at rates that need to be measured in the laboratory, while
27 photolysis rates are a function of the solar actinic flux that penetrates into the
28 atmosphere, and hence of absorption and scattering processes by atmospheric
29 molecules, clouds and aerosol particles.

30 Important for the chemistry of the troposphere are the chemical reactions
31 that lead to the formation of ozone. As noted by Crutzen (1972) and
32 Chameides and Walker (1973), the conversion of nitric oxide NO to nitrogen

1 dioxide (NO₂) by peroxy radicals (HO₂, CH₃O₂, etc.) leads to the formation of
2 ozone during daytime. For example,

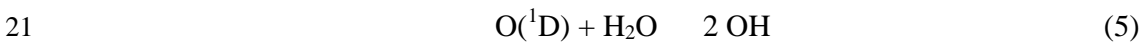
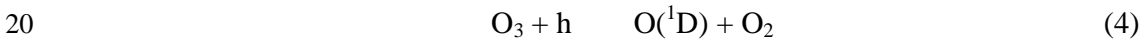


6 Peroxy radicals are provided by the oxidation of carbon monoxide,
7 methane and nonmethane hydrocarbons by OH. For example



10 Further oxidation of CH₃O₂ leads to the formation of formaldehyde
11 (H₂CO) the photolysis of which produces additional HO₂ radicals. Because of
12 the ubiquitous presence of CO, CH₄ and other hydrocarbons, and short
13 lifetime of NO_x, the production rate of ozone is "NO_x-limited" (i.e., the O₃
14 production rate varies primarily with the concentration of NO_x). An
15 understanding of the global and regional budgets of nitrogen oxides, and
16 specifically of the anthropogenic versus natural sources of atmospheric NO is
17 therefore crucial to characterize the ozone budget in the troposphere.

18 Tropospheric ozone is destroyed by photolysis in the ultraviolet when
19 the resulting electronically excited oxygen atom O(¹D) reacts with water vapor

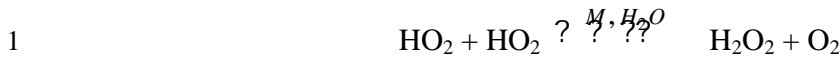


22 Hydroxyl radicals OH which are produced by reaction (5) as well as
23 hydroperoxyl radicals provide other ozone destruction mechanisms:



26 Reaction (5) provides the major source of HO_x (OH and HO₂) radicals
27 while reactions (1a), (2), (3), (6a), (6b) determine the partitioning between OH
28 and HO₂. The destruction of these radicals results from reactions involving
29 OH, HO₂, and NO₂ leading to the formation and potential wet scavenging of
30 water, hydrogen peroxide and nitric acid:

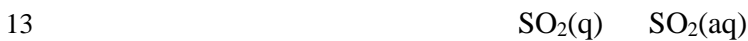




3 Of importance for the chemistry of the atmosphere are also the
 4 mechanisms that convert gas phase sulfur species into sulfate aerosol particles.
 5 Sulfur dioxide (SO₂) which is produced either by oxidation of reduced sulfur
 6 compounds (e.g., biogenic DMS) or by direct emissions (associated mainly
 7 with fossil fuel burning) is oxidized into sulfuric acid either in the gas phase



11 or in aqueous droplets through reactions involving dissolved H₂O₂, O₃,
 12 and various transition metal ions, for example



16 A key species for many processes involved in the chemistry of the
 17 troposphere is the OH radical. Because of its high reactivity with most
 18 chemical constituents including pollutants, OH is often dubbed the "detergent"
 19 of the atmosphere, because it determines the self-cleansing ability (or the
 20 oxidizing efficiency) of the troposphere. The diagram shown in **Figure 2.1**
 21 presents a schematic representation of the most important chemical processes
 22 occurring in the troposphere. It stresses the reactions that control the formation
 23 and destruction of ozone and hydroxyl. It highlights the nonlinear behavior of
 24 the tropospheric chemical system.

25 As a result, the response of the tropospheric chemical system to human-
 26 induced perturbations could be very complex, and exhibit different regimes
 27 with abrupt transitions. For example, the existence of thresholds (such as
 28 temperature threshold associated with the formation of particles) contributes
 29 to the non-linearity of the chemical system. The behavior of the atmosphere

1 and future changes in response to human-induced forcings are therefore
2 difficult to predict and could offer surprises.

3

4 **3. Observed and Expected Changes in the Chemical** 5 **Composition of the Atmosphere**

6 **3.1 Variability of atmospheric composition in the past: Evidence of** 7 **feedbacks?**

8 At locations where air is trapped in glacial ice, quantitative records of
9 atmospheric composition or deposition are available on time scales of
10 hundreds of thousands of years (i.e. multiple glacial periods) for only a few of
11 the many substances that are important on the global change scene (CO₂, CH₄,
12 N₂O, sulfate, nitrate, soil dust, sea salt). Records recovered in the southern
13 hemisphere at Vostok, Antarctica and in the northern hemisphere at Summit,
14 Greenland show a natural variability in the biosphere/atmosphere system
15 (Figure 3.1.1). This variability marks the response to major fluctuations in
16 climate seemingly correlated with the cycle of solar energy input related to the
17 orientation of the Earth to the Sun (Milankovich forcing) but also amplified by
18 physical and biogeochemical feedbacks. For example, during past glaciations
19 atmospheric CO₂ and CH₄ decreased while soil dust increased thereby
20 reinforcing what the changes apparently initiated by Milankovich forcing. The
21 nature of biogeochemical feedbacks is key to understanding global change.
22 Mankind is conducting a chemical perturbation experiment by altering many
23 biogeochemical cycles. We can ask questions, such as: How important were
24 biogeochemical cycle feedbacks in the flip from one stable climate mode to
25 another? How strong are these feedbacks relative to other purely physical
26 feedbacks such as the polar-ice albedo one? Have biological feedbacks
27 contributed to the unprecedented rate of greenhouse gas and aerosol change
28 observed today? It is interesting to note that the periodic climate variations
29 associated with Milankovich forcing are enhanced by positive feedbacks
30 through greenhouse gases and soil dust, so that climate does not seem to be
31 stabilized by biospheric responses.

1 **3.2 Recent changes in atmospheric composition**

2 Although considerable progress has been made in the past decade in
3 understanding the biogeochemical cycles of greenhouse gases, oxidants and
4 aerosols large gaps in knowledge still remain. Furthermore, uncertainties in
5 the climate feedback response of these processes are also large.

6 The concentration of greenhouse gases has increased in the atmosphere
7 since the pre-industrial period to reach levels unprecedented in the last 2
8 million years (Figure 3.2.1—CO₂, CH₄, CFCs, N₂O last 200 years). Storage in
9 the oceans and on land of anthropogenic CO₂ emissions is the he
10 concentrations are uncertain because limited knowledge about the response of
11 the terrestrial biosphere to climate changes and vice versa. The future CH₄
12 level is uncertain because of unknowns in the temperature dependence of
13 wetland sources and permafrost melting, and in atmospheric OH radical
14 concentrations (the major sink). The evolution of future N₂O levels in the
15 atmosphere are very uncertain because of poorly defined sources and sinks.
16 The inputs of large and growing amounts of nitrogen fertilizers in agriculture
17 poses the question as to where the nitrogen is going and how much N₂O may
18 be released in future from accumulation of long-lived environmental
19 subsystems (soils, waters).

20 Tropospheric ozone is an important greenhouse gas. It has a lifetime in
21 the troposphere that varies from about a week in the summer to months in the
22 dark polar winter. Increases in its occurrence in the troposphere since the pre-
23 industrial period are evident over Europe and East Asia. They are associated
24 with large increases in gaseous precursors (Figure 3.2.2). Elsewhere in the
25 remote northern troposphere decreases seem to be largely in step with recent
26 decreases in stratospheric ozone (Figure 3.2.3). The bottom line is that there
27 are not enough observations to assess present and past changes in tropospheric
28 ozone. The behavior of tropospheric ozone is complex and strongly associated
29 with our understanding of the atmospheric oxidation efficiency (OH
30 concentrations). An important question is to assess the relative contribution of
31 stratospheric and in situ photochemical sources to tropospheric ozone.

1 Historical records of the composition of reactive oxidants and their
2 precursors in the atmosphere are scarce and limited mostly to high latitude
3 regions. No instrumental record longer than 15 years exists. Long term records
4 of H₂O₂ and formaldehyde (Figure 3.2.4) in glacial ice from Summit,
5 Greenland, although promising, are of regional importance and furthermore
6 difficult to interpret because of variable atmospheric scavenging processes and
7 post- depositional chemistry taking place in the surface snowpack. The latter
8 alters the original deposition signal and can even be a source of compounds
9 such as formaldehyde (Sumner and Shepson, 1999), nitrogen oxides (Honrath
10 *et al.*, 1999) and carbon monoxide to the atmosphere. Nevertheless, these
11 records indicate an enhanced presence of these oxidants in the modern
12 northern polar middle troposphere compared to the past. The task is to
13 determine the role played by the surface snowpack in lower atmospheric
14 composition and in influencing the transfer function of a chemical constituent
15 between atmosphere and glacial firn and ice.

16 Since the pre-industrial era, sulfates from fossil fuel burning and
17 smelting as well as nitrates from fossil fuel burning (such as automotive
18 emissions) have increased in glacial snow and ice. Figure 3.2.5 compares two
19 historical records at Agassiz glacier in the winter and at Summit, Greenland
20 (~3 km altitude that sees middle and tropospheric air).

21 On a somewhat shorter time scale (two decades), instrumental records of
22 the composition of the atmosphere and precipitation exist in the acid rain
23 regions of the world, particularly, eastern North America, Europe and the
24 downwind Arctic. They show a decline in SO₂ but no significant change in
25 NO_x associated with regional pollution. It appears that the effects of the
26 introduction of catalysts by automobile engines has been largely offset by
27 increasing numbers of automobiles in these regions. In contrast, SO₂
28 emissions from the former Soviet Union which did not decrease substantively
29 in the 1980s, have fallen in the 1990s because of hard economic times rather
30 than a willful intervention by man. Sulfur emissions and attendant
31 concentrations of sulfates in the atmosphere have increased in Southeast Asia
32 and are expected to do so for the decades ahead.

4. Causes of Atmospheric Changes

The rapid changes in atmospheric composition observed over the past 100 years have been driven by emissions from fossil fuel combustion, industry, biomass burning, and agriculture. Table 1 gives present-day global inventories of anthropogenic emissions for some environmentally important gases discussed in the previous sections, and compares to the magnitudes of natural sources (biosphere, oceans, volcanoes, lightning). Anthropogenic emissions are important, and often dominant, contributors to the abundances of many atmospheric species. Also included in the Table are forecast ranges of anthropogenic emissions for Year 2100 presented by IPCC [1999] for different possible socioeconomic scenarios. These forecasts suggest that human perturbation to atmospheric composition will generally increase over the next century. In addition, future climate change may affect the natural emissions of radiatively active gases and aerosols, resulting in complicated chemistry-aerosol-climate feedbacks.

4.1 Fossil fuel combustion and industry

Our technological society is largely built on the combustion of fossil fuels and this situation is likely to persist through the end of the 21st century. Fossil fuel combustion has been the main cause for the rise of atmospheric CO₂ over the past 200 years from 280 ppmv (natural background) to 365 ppmv. In addition to CO₂, combustion emits to the atmosphere a large number of pollutants including CO, hydrocarbons, SO₂, NO_x, soot particles, trace metals, and toxic organic compounds. For many of these species, the global source from fossil fuel combustion exceeds the natural source (Table 4.1). Other emissions related to fossil fuel use include CH₄ from natural gas extraction and transport, and SO₂ from petroleum refining.

Industrial activities other than fossil fuel combustion also represent large sources of pollutants to the atmosphere. Metal smelters and the paper industry are major sulfur emitters. Carbon steel manufacturing is an important source of CO. Many organic compounds are emitted by the chemical industry and

1 their environmental impacts in terms of toxicity, climate forcing, and
2 stratospheric O₃ are often poorly understood.

3 Decadal estimates of future emissions from fossil fuel combustion and
4 industry over the next century have been presented by IPCC (1999) for four
5 different scenarios. In the most optimistic scenario (rapid technological
6 development, use of renewable energy sources, global economic convergence)
7 the fossil fuel combustion source of CO₂ will peak at 10.4 PgC yr⁻¹ in 2060
8 (70% increase over present) and then decline by 2100 to its present-day value.
9 In the worst scenario the fossil fuel source of CO₂ will gradually increase to 4
10 times its present-day value by 2100. Estimates of future emissions for NO_x
11 and CO tend to roughly follow those for CO₂. In the case of SO₂, emissions
12 are expected to decrease by 2100 (after reaching a peak in the mid-21st century
13 in two of the scenarios) due to emission controls and transition away from
14 coal.

15 **4.2 Biomass burning**

16 Biomass burning includes deforestation, agricultural fires, wood fuel
17 use, and natural fires. Most of the world's biomass burning takes place in the
18 tropics and is highly seasonal, peaking at the end of the dry season (January-
19 April in the northern tropics, August-October in the southern tropics). The
20 largest contribution to this tropical source is agricultural burning of savannas;
21 deforestation is also an important source in some regions. Natural fires are
22 important mainly in boreal forests at high northern latitudes, where they peak
23 during the summer months.

24 Biomass burning emits the same general suite of species to the
25 atmosphere as fossil fuel combustion but often in very different proportions;
26 biomass burning is less efficient than fossil fuel combustion and the
27 combustion temperatures are lower. The CO/CO₂ molar emission ratio from
28 biomass burning is 5-10%, much higher than for fossil fuel combustion, and
29 the global source of CO from biomass burning is comparable to that from
30 fossil fuel combustion. By contrast, the NO_x/CO₂ emission ratio from biomass
31 burning is less than that from fossil fuel combustion, because temperatures in

1 biomass fires are not sufficiently high for thermal NO_x formation from
2 atmospheric N_2 (they are however sufficiently high for oxidation of biomass
3 nitrogen to NO_x). The sulfur source from biomass burning is very small
4 compared to the fossil fuel source (Table 4.1) due to the low abundance of
5 sulfur in vegetation.

6 There is little knowledge of historical trends in biomass burning, and
7 IPCC (1999) does not venture to forecast trends for the next century.
8 Greenland ice core records of biomass burning tracers over the past 1000
9 years identify several historical periods of enhanced biomass burning at high
10 northern latitudes but indicate a decrease since the 1930s. Fire records
11 maintained by governmental agencies in North America and Europe over the
12 past 50 years indicate a general increase in the number of fires, due to human
13 negligence, but not much change in area burned because of improved
14 firefighting ability. In the tropics, where most of global biomass burning takes
15 place, there is essentially no information on historical trends. One would
16 expect a rise in biomass burning from increasing agriculture and deforestation
17 over the past century, but this effect could have been offset by better fire
18 control in response to the growing rural population. Reconstructed surface O_3
19 records for South America in the late 19th century do not show the
20 characteristic spring maximum seen in present-day observations, suggesting
21 that the biomass burning source might have been weaker. Satellite
22 observations of tropical tropospheric ozone since 1979 suggest a slight
23 increase in biomass burning over the past 20 years, but continuous records of
24 CO measurements at tropical sites over the past decade show no significant
25 increases.

26 **4.3 Land-use changes**

27 Major land-use changes over the past 100 years have included
28 urbanization driven by population pressure, increase in cultivated land in the
29 tropics, reforestation of formerly cultivated land in northern mid-latitudes
30 regions such as the eastern United States, and desertification in some areas
31 such as northern Africa. Tropical deforestation presently makes a significant

1 contribution to the rise in CO₂ (Table 4.1), though this contribution is
2 expected to decrease over the next century due to decimation of the primary
3 forests and may actually be overcome by the CO₂ sink from reforestation at
4 northern midlatitudes (IPCC, 1999).

5 Agriculture is thought to be the principal cause for the rises of CH₄ and
6 N₂O over the past 100 years (Table 4.1). Methane is emitted by anaerobes in
7 ruminants and rice paddies (which are effectively human-generated wetlands).
8 Nitrogen fertilizer application to crops stimulates microbial emission of N₂O;
9 it also stimulates emission of NO_x, but the resulting source is small compared
10 to that from fossil fuel combustion (Table 4.1).

11 Long-term time series of atmospheric dust over the Atlantic indicate a
12 secular increase associated presumably with desertification of northern Africa.
13 Dust is a major contributor to aerosol optical depth, scattering solar radiation
14 and absorbing terrestrial radiation. In addition, deposition of dust to the ocean
15 supplies limiting nutrients (iron and other metals) to increase the efficiency of
16 CO₂ uptake. Increasing desertification over the next 100 years is expected as a
17 result of agricultural practices and irrigation pressure in the tropics and
18 subtropics. The resulting increase in atmospheric dust could have important
19 implications for climate change, both directly by radiative forcing and
20 indirectly by fertilization of the oceans.

21 **4.4 Climate Changes**

22 Changes in the climate system could substantially affect the chemical
23 composition of the atmosphere. Such changes are related to interannual
24 variability in the dynamics of the atmosphere, to quasi-periodic oscillations in
25 the atmosphere/ocean system (such as the El Niño oscillation in the tropical
26 Pacific), and to longer timescale climatic trends. Long-term trends are
27 believed to be generated by external forcing including human-induced
28 emissions of greenhouse gases.

29 Although the mechanisms governing the Earth's climate are not fully
30 understood, the effects of climate changes on the chemical composition of the
31 atmosphere need to be identified because they provide potential positive or

1 negative feedback mechanisms in the climate system. Such feedback
2 mechanisms are illustrated below.

3 Warming of the Earth resulting from enhanced concentrations of carbon
4 dioxide, methane, and other greenhouse gases is expected to enhance surface
5 evaporation, and hence the tropospheric abundance of water vapor. Water not
6 only amplifies greenhouse warming; it also leads to the formation of the
7 hydroxyl radical (OH) and hence affects the lifetime of several chemical
8 compounds (including greenhouse gases such as methane) in the atmosphere.
9 The ozone density in the troposphere is also expected to change with potential
10 effects on the related climate forcing.

11 Climate change could also result in more intense convective activity. As
12 a consequence, the formation rate of nitrogen oxides by lightning and hence
13 the concentration of ozone in the free troposphere would probably increase,
14 producing an amplification of radiative forcing.

15 Surface emissions of several biogenic gases (including nitrogen oxides
16 by soils, isoprene and other terpenes by vegetation, dimethyl sulfide by the
17 ocean) would increase on a warmer planet. These compounds are precursors
18 of either tropospheric ozone or of aerosols, and hence could indirectly impact
19 the Earth's climate.

20 Changes in the soil moisture associated with changes in the precipitation
21 patterns would affect the intensity and the geographical locations of savanna
22 and forest fires, with significant consequences on biomass burning emissions,
23 and hence on the concentration of several chemical compounds, including
24 carbon monoxide, nitrogen oxides and ozone.

25 Finally, changes in precipitation rates associated with climate change
26 would modify the rate at which soluble gases and aerosol particles are
27 removed from the atmosphere, with consequences on the residence time of
28 several compounds (including pollutants) in the atmosphere and potential
29 feedbacks on the climate system.

30 Providing an estimate of the combined chemical effects associated with
31 climate changes on a variety of time scales is a difficult problem. Although
32 preliminary studies have suggested that such issue is potentially significant,

1 the response to this question will ultimately be provided by coupled
2 climate/chemistry/biology models.

3

4 **5. Impact of Changes**

5 In this section we focus on three major categories of impact of changes
6 in atmospheric composition: climate change, effects on ecosystems and human
7 health. Of course, these categories are not always well separated. For example,
8 a change in climate will have secondary effects on ecosystems and health.
9 Nevertheless, we believe that this structure provides a useful framework for a
10 discussion on impacts of changes in atmospheric composition.

11 Because changes in the chemical composition of the atmosphere are the
12 main drivers of anthropogenic climate change, the scientific community
13 involved in atmospheric chemistry has been much engaged in the climate
14 change issue and has established strong links with the more physically
15 oriented climate researchers. There has also been some links with ecologists
16 who study the effects on ecosystems of increased exposure to various
17 atmospheric gases and aerosol, and to UV radiation. The connection to the
18 community of scientists studying the effects of atmospheric changes on human
19 health has been considerably weaker.

20 **5.1 Climate change**

21 The issue of climate change in general, and the impact on climate of
22 human-induced processes in particular, has recently been reviewed in detail by
23 IPCC (IPCC, 1990; 1992; 1994; 1996). In our discussion we adopt the
24 terminology used by the Intergovernmental Panel on Climate Change (IPCC)
25 and use the term "climate forcing" to denote the change in the net irradiance
26 (in W/m^2) at the tropopause (after allowing for stratospheric temperatures to
27 re-adjust to radiative equilibrium, but with the surface and tropospheric
28 temperature and moisture held fixed), created by changes imposed on the
29 climate system by natural (solar radiation changes, volcanic emissions of SO_2
30 and particulate matter) or human-induced processes (greenhouse gases,
31 aerosols, changes in surface albedo). The climate forcing concept provides a

1 very useful means of comparing quantitatively the importance of the different
2 factors for change. It avoids the difficult problem of how the climate system
3 will actually respond (in terms of temperature, precipitation, winds, etc.) to the
4 imposed changes. This latter problem, which involves an intricate web of
5 interactions and feedbacks within the atmosphere and between the atmosphere
6 and the underlying surface, has to be addressed using complex models of the
7 climate system. In particular, the difficulty of assessing the climate forcing
8 and the climate response from inhomogeneous radiative agents such as
9 aerosols and ozone needs to be stressed. The climate response issue will not be
10 further addressed in the present report. For this the reader is referred to
11 reviews such as IPCC (1996) and (ref.).

12 In **Figure 5.1.1** we show a comparison of the global average climate
13 forcing during the past century due to different processes (IPCC, 1996
14 modified by Shine, 1998). Solid bars represent best estimates and vertical
15 lines uncertainty ranges. The dominant positive forcing (heating tendency)
16 results from the increased concentration of rather well-mixed greenhouse
17 gases (CO_2 , N_2O , CH_4 , CFCs, etc.). Tropospheric and stratospheric ozone
18 changes are treated separately mainly because this greenhouse gas is not well
19 mixed in the atmosphere and the observed changes have distinct spatial
20 (horizontal and vertical) patterns.

21 The largest negative forcing (cooling tendency) is due to aerosol
22 particles of human origin. Because of the limited atmospheric lifetime of
23 aerosol particles (several days) their forcing patterns are less uniform than that
24 of the greenhouse gases. As an example, **Figure 5.1.2** shows an estimate of the
25 geographical distribution of the climate forcing (both direct and indirect) due
26 to sulfate aerosols of human origin. Therefore, the global forcing estimates
27 shown in **Figure 5.1.1** are not strictly comparable to the forcings of the
28 greenhouse gases. The outstanding message of the aerosol forcing estimates is
29 the very large uncertainty associated especially with the so called indirect
30 forcing, i.e. the impact on cloud amount and cloud albedo of changes in the
31 population of aerosol particles (cf. Chapter 4). If the upper (most negative)
32 end of the uncertainty range applies, the negative forcing due to aerosols may

1 have balanced essentially all of the positive forcing due to greenhouse gases.
2 On the other hand, if the aerosol forcing is in the small end of the range,
3 greenhouse warming should have been the dominating effect during the past
4 century. It is obvious that research aiming at reducing the uncertainty of
5 aerosol forcing is of utmost importance for the climate change issue. For
6 example, it is likely, but not proven, that climate warming may have been
7 delayed by the increasing aerosol load. Because the residence time of aerosol
8 is much shorter than that of greenhouse gases (and hence aerosols will not
9 accumulate), the warming effect of the greenhouse gases may dominate (in
10 relative terms) over long periods of time.

11

12 *To be added:*

13 ** feedback of climate change on trace gas emissions, (CO₂, CH₄, NO,*
14 *isoprene and other HC....), atmospheric transport (e.g. H₂O into the*
15 *stratosphere) and transformations.*

16 ** the use of "equivalent CO₂" for other greenhouse gases vs. the difference in*
17 *forcing patterns for the different gases*

18 ** more about climate response?*

19 ** the problem of circular logic when e.g. aerosol forcing is derived as a*
20 *missing forcing by comparing climate simulations with observed trends in*
21 *global temperature and such tuned models then used to predict future climate.*

22

23 **5.2 Impacts on ecosystems**

24 Ecosystems are affected by atmospheric changes in several different
25 ways:

- 26 • direct impact of toxic gases such as O₃, SO₂ and NO₂;
- 27 • impact of increased levels of UV radiation caused by stratospheric ozone
28 depletion;
- 29 • indirect impacts caused by changes in the chemical balance of soils, lakes
30 and surface ocean water following the deposition of acidifying and
31 entrophicating substances.

1 The impacts may include anything from elimination of sensitive species
2 and altered productivity to subtle shifts in the relative abundance of plant and
3 animal species.

4 Whereas direct damage due to elevated concentrations of SO₂ and NO₂
5 has been documented mainly in or around urban areas and close to large
6 pollution sources, damage due to elevated O₃ levels is known to occur
7 regularly during the summer season in extended regions in northern Europe,
8 North America and some parts of the Middle East and Asia. The damage due
9 to O₃ cause visible leaf injury on sensitive plant species and cause a decrease
10 in the yields of important crops, in particular wheat and soy beans. In such
11 polluted regions, O₃ concentrations are also high enough to impact the growth
12 of some forest tree species (e.g., beach). These effects could have implications
13 for forest production on broad geographical and time scales. There is an
14 urgent need to increase our understanding of the current—and potential
15 future—extent of O₃ damage, especially in those parts of the world (e.g.,
16 China and India) where emissions of O₃ precursors (NO_x, HC, CO) are rising.
17 The possibility that harmful O₃ levels may occur in connection with biomass
18 burning in tropical and subtropical regions should also be investigated.

19 Increased levels of UV radiation at the Earth's surface, caused by
20 stratospheric ozone depletion, may damage terrestrial organisms including
21 plants and microbes, but these organisms also have protective and repair
22 processes. The major concern regarding effects on ecosystems seems to be
23 focused on marine phytoplankton, especially in polar areas where ozone-
24 related UV increases are the greatest. Macroalgae, seagrasses, sea urchins and
25 corals have also been found to be sensitive to UV radiation. For some of such
26 populations even current levels of UV may be a limiting factor (UNEP, 1998).

27 Large emissions of SO₂ and NO_x from industrial processes and traffic,
28 and the subsequent deposition of these compounds and their associated acids
29 have led to widespread damage to sensitive ecosystems especially in northern
30 Europe and parts of northeastern North America. This type of impact has been
31 well documented for freshwater ecosystems. Acid deposition reduces the
32 alkalinity of lakes and streams. In waters with low buffering capacity, the pH

1 can be reduced to levels that cause acute and chronic impacts associated with
2 increased aluminum levels that accompany the lowered pH. The effects of
3 acidification on soils and terrestrial ecosystems are more complex. Sulfur
4 deposition has increased concentrations of absorbed sulfate in soils and caused
5 a depletion of base cations, especially magnesium and potassium, leading to a
6 nutrient deficiency. In parts of northern Europe, the acidity of forest soils has
7 increased considerably (pH has decreased by 0.5-1.0 units) during the past 30-
8 60 years, at least partly as a result of acidification. This has led to reduced root
9 distribution of forest trees. An additional stress to forests is caused by the
10 increased mobilization of metals (e.g., Al, Cd). The combined effect of the
11 various pollutant related stresses to forest ecosystems is not yet well
12 characterized.

13 Although the sulfur emissions in Europe and North America are now
14 declining—as a result of policy actions—sulfate deposition is still well above
15 the so-called critical load above which acidification damage to sensitive
16 ecosystem will occur. This means that soils in many areas continue to
17 deteriorate as base cations are leached out of the soils.

18 In other regions of the world—e.g., southern and eastern Asia—sulfur
19 emissions are growing rapidly causing concern about future acidification
20 problems. Widespread distribution of alkaline soil dust in the atmospheres of
21 some parts of these regions—northern parts of China and a large part of
22 India—has contributed to keep rainwater pH above 5 or 6. However, this
23 buffering effect is likely to be exhausted if emissions of SO_2 and NO_x
24 continue to grow (Figure 5.1.1)

25 Deposition of nitrogen compounds (NO_3^- , NH_4^+) has led to the
26 fertilization of many terrestrial ecosystems and, following nitrification of
27 NH_4^+ , to increased nitrate leaching to groundwater and runoff. Even more
28 important may have been the use of nitrogen fertilizers. This fertilization
29 effect has caused changes in the functioning and stability of many sensitive
30 ecosystems (e.g., heathlands and bogs) in the industrialized parts of the world.
31 In very polluted areas (e.g., The Netherlands) the drinking water standard for
32 nitrate has been exceeded. On the positive side, the addition of nitrogen in

1 soils may have led to increased biomass and hence to net uptake of CO₂ from
2 the atmosphere.

3 Elevated deposition of nitrogen compounds, as well as high runoff of
4 such compounds from adjacent land areas, have contributed to eutrophication
5 of lakes and coastal waters in polluted regions. Episodes of high wet
6 deposition of nitrogen are also suspected to affect more remote marine
7 ecosystems occasionally.

8 **5.3 Corrosion**

9 Acid deposition and high concentrations of gaseous pollutant (SO₂, NO₂
10 and O₃) are known to cause damage to buildings and cultural and historical
11 monuments mainly in urban and suburban areas. The economic loss due to
12 such man-made corrosion in Europe has been estimated to be of the order of
13 10¹⁰ Euro per year (?). Mainly because of reductions in SO₂ concentrations the
14 corrosion rates are now decreasing substantially in Europe and North
15 America. However, in many other areas, especially in Eastern Europe and
16 some developing countries, corrosion problems remain severe or become more
17 acute. There are indications that in warm climates NO₂ and O₃ alone (even
18 without SO₂) may cause serious corrosion problems.

19 **5.4 Health effects**

20 Air pollutants have long been recognized as a health hazard. Well known
21 examples include the smog episodes in London - the one in December 1952 is
22 estimated to have caused 4000 excess deaths - and the photochemical
23 pollution (O₃, PAN, etc.) in Los Angeles which cause lung damage, eye
24 irritation and other effects. During recent years more subtle effects, some of
25 them believed to occur not only in urban and suburban areas but also over
26 larger regions have been identified. Here we list some of the most important
27 health issues related to man-made air pollution.

- 28 • Halogenated hydrocarbons—including the CFCs—while not harmful as
29 such, contribute to depletion of the stratospheric ozone layer. The resulting
30 *increase in UV-B radiation* at the Earth's surface is estimated to cause

1 adverse health effects including eye cancer and cataract, skin cancer (in
2 fair skinned populations) and a depression of the immune system for
3 certain tumors and infectious diseases (UNEP, 1998). **Figure 5.4.1** shows
4 an estimate of the past and future incidence of skin cancer based on
5 various scenarios related to the regulation of CFC emissions. A dramatic
6 improvement, due to the Montreal protocol and its subsequent
7 amendments, is obvious.

- 8 • *Elevated levels of O₃*, as low as 160 µg/m³, in surface air have been
9 demonstrated to have adverse health effects, even at short term exposures
10 (6 h). Today, such concentrations occur commonly during the sunny
11 seasons over large regions in Europe and North America and probably also
12 in other parts of the world where emissions of ozone precursors (NO_x,
13 hydrocarbons, CO) are large. A serious difficulty when it comes to
14 controlling O₃ pollution is the complex interactions between the various
15 precursors and the fact that they originate from both man-made and natural
16 sources (cf. Chapter 3?).
- 17 • Both direct experiments, on animals as well as humans, and
18 epidemiological studies show that *aerosols* can lead to adverse health
19 effect related to respiratory symptoms and lung functioning. Recent
20 evidence indicates that the effects are related to the mass (and number) of
21 particles less than 2.5 µm in diameter (PM 2.5) and that their chemical and
22 physical nature of the particles are less relevant. **Table 5.4.1** shows
23 concentrations of PM 10 as low as 10 µg/m³ cause a significant number of
24 cases with respiratory symptoms after a 3-day exposure.
- 25 • The *acidification of air and precipitation*, in addition to its adverse effects
26 on terrestrial and limnic ecosystems, also has consequences for human
27 health. Direct health effects of elevated levels of SO₂ and NO_x have been
28 well established (Lübker-Alcorno and Krzyzanowski, 1995). Indirect
29 health effects due to increased dissolution of metals in soils (e.g. Al, Cd)
30 and in water pipes (Cu) are also suspected. Whereas the direct effects of
31 SO₂ and NO_x are normally confined to urban areas and around industrial
32 plants, the indirect effects may occur also further away from the sources.

1 An encouraging development has taken place in many European cities
2 during the past two decades regarding SO₂ emissions. Because of emission
3 controls, concentrations have been reduced several fold, cf. **Figure 5.4.2**.

- 4 • *Mercury* is an interesting example of a contaminant that has been
5 mobilized by man and dispersed globally through the atmosphere. The
6 current deposition of mercury is estimated to exceed the pre-industrial
7 value by at least a factor of two world-wide and up to a factor of 5-10 in
8 northern Europe and North America (Bergan *et al.*, 1999). The elevated
9 deposition of mercury, over large regions, aggravated by the increased
10 leaching of mercury from acidified soils, and a subsequent
11 bioaccumulation of organic mercury in fish have resulted in toxic
12 concentration in pike in many lakes in Scandinavia and Canada (Lindqvist,
13 1991). About 10,000 lakes in Sweden are blacklisted because of this and
14 pike should not be consumed by humans.

16 **6. Methods to address scientific issues**

17 In contrast with the situation prevailing in meteorology where a
18 continuous monitoring effort provides detailed and global observations on the
19 physical state of the atmosphere, only limited observational data are available
20 on the global distribution, seasonal evolution and trends of chemical
21 compounds in the troposphere. A major effort of the atmospheric chemistry
22 community has therefore focused on the measurement of chemical compounds
23 (gases and aerosols) in the troposphere and stratosphere. Many projects, often
24 sponsored by IGAC, have used different types of instrumentation (e.g., *in situ*
25 or remote sensing techniques) on different platforms (aircraft, balloon,
26 spacecraft, ground-based). Several field campaigns performed over a limited
27 time period (see Table 1.6a) have been organized to investigate specific
28 photochemical processes at different locations. Other observational projects
29 have provided information on large-scale distributions of specific chemical
30 constituents (**Table 6b**). Periodic soundings of the atmosphere (balloon-borne,
31 lidar) have revealed the structure of the vertical distribution for a limited
32 number of atmospheric species at a few locations. Thus, in spite of efforts by

1 the international scientific community, a satisfactory global climatology of
2 tropospheric compounds is far from reality and a strategy to gather more
3 information on the spatial and temporal distribution of the major species needs
4 to be established.

5 Laboratory investigations have provided measurements of reaction rate
6 constants and absorption cross sections for several molecules and have
7 provided the fundamental knowledge for understanding atmospheric
8 photochemistry. Much progress has been made regarding gas-phase reactions;
9 a lot of uncertainties remain, however, in our understanding of multiphase
10 processes. Models have been used to assess the consequences of newly
11 measured chemical kinetics data, to analyze observations made during field
12 campaigns, to determine the sensitivity of calculated concentrations to
13 external forcings, to derive (for example, through inverse modeling) the
14 magnitude and location of the surface emissions that explain these
15 observations, and to simulate the evolution of the chemical composition in
16 response to natural or human-induced perturbations. Progress has often
17 resulted from a combined use of several of these tools.

18 The following three chapters address in a synthetic way some of the
19 important questions presented in the present chapter and discussed over the
20 last 10 years by the international atmospheric chemistry community. The foci
21 are primarily on the importance of the biosphere in the control of the chemical
22 composition of the atmosphere, the role of chemical transformations of gas-
23 phase compounds (with emphasis on tropospheric ozone and other
24 photooxidants), and the physical and chemical processes governing aerosol
25 formation and their evolution and removal from the atmosphere. The
26 questions will be addressed with a global or ubiquitous perspective, although
27 regional specificities will often be discussed. Potential impact of
28 anthropogenic perturbations on climate (radiative forcing), ecosystems
29 (deposition) and health (air quality) will also be considered.

Table 4.1 Global emission inventory estimates for some environmentally important gases mostly adapted from IPCC (1995).

	CO ₂ Pg C yr ⁻¹	CH ₄ Tg CH ₄ yr ⁻¹	N ₂ O Tg N yr ⁻¹	Sulfur Tg S yr ⁻¹	NO _x Tg N yr ⁻¹	CO Tg CO yr ⁻¹
Natural	60	160	9	18	11	200
Anthropogenic						
Fossil Fuel and Industry	6.8	100	1.3	65	22	450
Biomass burning	1.6*	40	0.5	2	12	500
Agriculture		170	3.9		1	
Landfills/sewage		65				
Total, present	7.6	375	5.7	67	35	950
Total, 2100**	8-29	300-900	5-16	27-60	34-110	950-2500

Table 5.4.1 Estimated acute health effects following exposure to a 3-day episode of PM₁₀ levels increased by 25 µg/m³ in a population of 1 million.

Table 6a

Table 6b

Figure 1.1.1

Figure 1.1.2

Figure 1.1.3

Figure 1.1.4

Figure 1.1.5

Figure 1.1.6

Figure 1.2.1

Figure 1.3.1.1

Figure 1.3.2.1

Figure 1.3.2.2

Figure 1.3.2.3

Figure 1.3.2.4

Figure 1.3.2.5

Figure 1.4.2.1

Figure 1.5.1.1

Figure 1.5.1.2

Figure 1.5.4.1 All cancer risk estimates based on various scenarios

Figure 1.5.4.2 Concentration of SO₂ during winter in Stockholm.

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