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Biosphere-Atmosphere Interactions

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2.1 Introduction

The contemporary atmosphere was created as a result of biological activity some two billion years ago. To this day, its natural composition is supported and modified, mostly through biological processes of trace gas production and destruction, while also involving physical and chemical degradation processes. The biosphere has a major influence on present environmental conditions, both on a regional and global scale. One of the best-documented and most important indicators of global change is the progressive increase of a number of trace gases in the atmosphere, among them carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), all of which are of biospheric origin. There is considerable uncertainty, however, regarding the processes that determine the concentration and distribution of trace gases and aerosols in the atmosphere and the causes and consequences of atmospheric change (Andreae and Schimel 1989). To improve our understanding IGAC created an environment for multi-disciplinary collaboration among biologists, chemists, and atmospheric scientists. This was essential to develop analytical methods, to characterise ecosystems, to investigate physiological controls, to develop and validate micrometeorological theory, and to design and develop diagnostic and predictive models (Matson and Ojima 1990).

Interactions between the biosphere and the atmosphere are part of a complex, interconnected system. The emission and uptake of atmospheric constituents by the biota influence chemical and physical climate through interactions with atmospheric photochemistry and Earth's radiation budget. Comparatively small amounts of CH₄ and N₂O present in the atmosphere make substantial contributions to the global greenhouse effect. In addition, emissions of hydrocarbons and nitrogen oxides from biomass burning in the Tropics result in the photochemical production of large amounts of ozone (O₃) and acidity in the tropical atmosphere. In turn, climate change and atmospheric pollution alter the rates and sometimes even the direction of chemical exchange between the biosphere and atmosphere through influences at both individual organism and ecosystem

levels. Recent and expected future changes in land use and land management practices provide further impetus for closely examining climate-gas flux interactions. Anthropogenic influences, e.g. tropical deforestation and the widespread implementation of agricultural technologies, have and will continue to make significant alterations in the sources and sinks for the various trace gases.

Ten years ago, at the beginning of IGAC, researchers sought to establish the source and sink strength of gases in different kinds of ecosystems, in different areas of the world. Specific goals of the programme, related to the biosphere included:

- to understand the interactions between atmospheric chemical composition and biological and climatic processes;
- to predict the impact of natural and anthropogenic forcings on the chemical composition of the atmosphere; and
- to provide the necessary knowledge for the proper maintenance of the biosphere and climate.

Earlier extrapolations of gas fluxes over space and time were often based on a single, or very small, set of measurements, and researchers sought for "representative" sites at which to make those crucial measurements. IGAC brought a new focus to the variability among ecosystems and regions of the world, in order to understand better the factors controlling fluxes (Galbally 1989). For example, studies of CH₄ flux from wetlands and rice paddies of N₂O flux from natural and managed ecosystems, and of dimethylsulphide (DMS) emissions from oceans, consciously spanned gradients of temperature, hydrological characteristics, soil types, marine systems, management regimes, and nitrogen deposition. One result of this strategy has been the recognition that the same basic processes were responsible for gas fluxes across regions, latitudinal zones, and environments. This chapter gives a general overview of the progress that has been made in the field as a whole within the last decade, with emphasis on research activities stimulated, initiated, and/or endorsed by the IGAC community. It is not our intent to provide current

assessments of all trace gas source and sink strengths, as those budgets have been compiled and published (with considerable contributions by IGAC researchers) in recent Intergovernmental Panel on Climate Change (IPCC) documents. Examples of research not conducted within the IGAC framework but relevant to the topic are CH₄ from landfills, ruminant livestock, and termites; information on these topics can be found in IPCC (1996, 1999).

Exchanges of biogenic trace gases between surfaces and the atmosphere depend on the production and consumption of gases by microbial and plant processes, on physical transport through soils, sediments, and water, and on flux across the surface-air boundaries. Thus, to understand and predict fluxes, studies of whole ecosystems are required. The goals of research over the past decade have been to develop an understanding of the factors that control flux, organise the measurements so that they are useful for regional and global scale budgets, and use the knowledge to predict how fluxes are likely to change in the future.

The IGAC Project focussed on issues of specific interest over a number of different geographical regions of Earth. A variety of projects have been conducted over the last ten years, many of which addressed issues related to exchange between the biosphere and the atmosphere. Several field campaigns, using a combination of measurement and modelling techniques, have been conducted very successfully under the IGAC umbrella, e.g. in southern Africa (SAFARI 1992 and 2000) and in various oceanic regions (ACE-1, ACE-2, and ACE-Asia) (see A.5).

Why certain trace gases were studied together and why various scientific approaches were adopted to study them is described in this chapter. Research findings specifically related to the exchange of trace gases and aerosols between the atmosphere and the terrestrial and marine biospheres will be given. In the terrestrial section, special attention is given to biomass burning and wet deposition in the Tropics, because of the significant contribution made by IGAC to these programmes. We also consider some of the anthropogenic activities that

alter biosphere-atmosphere exchange and discuss potential feedbacks related to climate change, regional level air pollution, and deposition. In the marine section, emphasis is on the biogeochemistry of DMS, given that the greatest advances were made on this topic. The chapter concludes by summarising the major accomplishments of the last decade and highlighting some of the remaining research challenges.

2.2 Key Biogenic Gases or Families and their Relevance to Atmospheric Chemistry

The study of atmospheric composition has largely focussed on trace compounds that affect either the radiative properties of the atmosphere, or the biosphere as nutrients or toxins, or play a key role in atmospheric chemistry. The trace gases that are important in this regard have been summarised in the preceding chapter. This chapter considers the role of the biosphere in emission or removal of such compounds.

Although CO₂ and water (H₂O) are both greenhouse gases which are strongly affected by the biosphere, studies of these compounds have generally been conducted in parallel scientific communities, and IGAC has maintained a focus on the chemically reactive greenhouse gases. Thus no attempt is made here to cover the large body of research on the global carbon cycle and the interactions of CO₂ with the biosphere.

2.2.1 The Carbon Family of Gases: CH₄, Volatile Organic Carbon Compounds (VOCs), and Carbon Monoxide (CO)

Methane (CH₄) is a greenhouse gas with a lifetime in the atmosphere of about nine years. Its atmospheric concentration is largely controlled by the biosphere, with 70% or more of current emissions and virtually all of pre-industrial emissions being biogenic (Fig. 2.1; Milich 1999). The dominant biogenic production process for CH₄ is microbial breakdown of organic compounds in

Fig. 2.1. Estimated annual anthropogenic and natural sources and sinks of methane (thick bars) in millions of tons, and uncertainty ranges (thin lines) (Milich 1999)

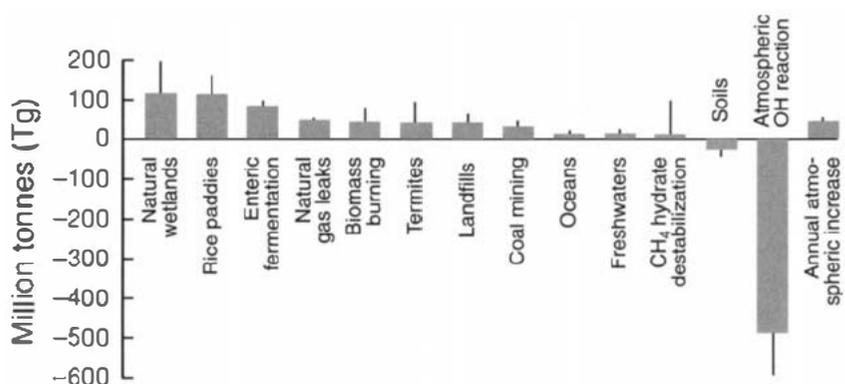
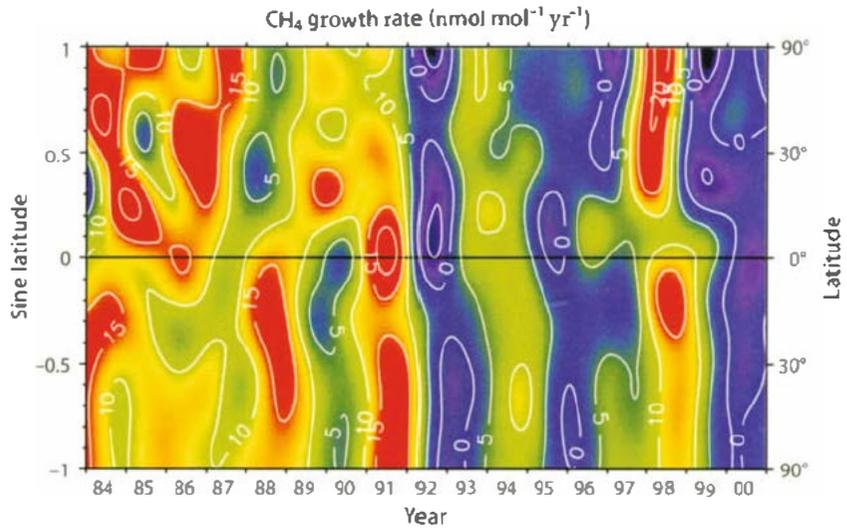


Fig. 2.2. Methane growth rates (figure courtesy of the National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL), and Carbon Cycle-Greenhouse Gases (CCGG))



anaerobic conditions. This occurs in flooded soils such as natural wetlands and rice paddies, in the rumen of animals such as cattle, in landfills, and in anoxic layers in the marine water column and sediments. Methane is also emitted directly to the atmosphere from burning vegetation as a product of pyrolytic breakdown of organic material.

Changes in land use, particularly increases in numbers of domestic ruminants, the extent of rice paddies, and biomass burning, have more than doubled biogenic CH₄ emissions since the pre-industrial era (Milich 1999; Ehhalt et al. 2001). Fossil fuel related emissions and a decrease in atmospheric oxidation rates (Thompson 1992) have further increased CH₄ concentrations but those aspects fall outside the scope of this chapter.

The atmospheric concentration of CH₄ is now about 1745 nmol mol⁻¹, compared to pre-industrial levels of about 700 nmol mol⁻¹. Growth rates have been observed directly in the atmosphere since the 1950s (Rinsland et al. 1985; Zander et al. 1989) and on an increasingly systematic basis since 1978 (Blake and Rowland 1988; Dlugokencky et al. 1994). Concentrations were increasing at about 20 nmol mol⁻¹yr⁻¹ in the 1970s, but that rate has generally declined to an average of 5 nmol mol⁻¹yr⁻¹ over the period 1992 to 1998. High growth rates of about 15 nmol mol⁻¹yr⁻¹ occurred in 1991 and 1998 (Fig. 2.2, Dlugokencky et al. 1998; Ehhalt et al. 2001) and appear to be caused by climate related increases in wetland and/or biomass burning emissions (Dlugokencky et al. 2000; Walter and Matthews 2000). IPCC (2001) estimates its rate of increase at 8.4 nmol mol⁻¹yr⁻¹.

The evolution of the CH₄ budget since the pre-industrial era provides a good example of interactions between land use and atmospheric change. A schematic of the change in total emissions from the 18th century to the present is shown in Fig. 2.3 (based on Stern and Kaufmann 1996, Lelieveld et al. 1998, and Houweling et al.

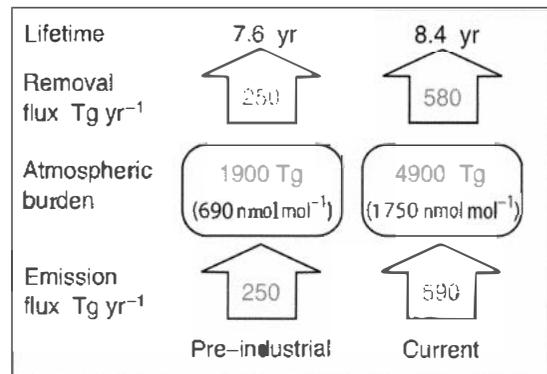


Fig. 2.3. Schematic of the pre-industrial Holocene and current (1990s) atmospheric methane budget. The mean lifetime derived from the ratio of atmospheric burden to removal rate has increased by ca. 10%, which is broadly consistent with estimates of the relative decrease in OH from atmospheric chemistry models (based on Stern and Kaufmann (1996), Lelieveld et al. (1998) and Houweling et al. (1999) (see also Fig. 7.4).

1999). The removal rates that are required to balance the source-sink budget at pre-industrial and present concentrations imply an increase in the methane lifetime. This is consistent with independent estimates of a decrease in atmospheric oxidation rates inferred from chemistry models.

Plants emit a range of volatile organic carbon (VOCs) compounds, which include hydrocarbons, alcohols, carbonyls, fatty acids, and esters, together with organic sulphur compounds, halocarbons, nitric oxide (NO), CO, and organic particles. Estimates of anthropogenic emissions for 1990 are shown in Fig. 2.4. According to current estimates plants emit up to 1200 Tg C yr⁻¹ as VOCs (Guenther et al. 1995). The amount of carbon released from the biosphere this way may be up to 30% of net ecosystem productivity (NEP), i.e. the annual accumulation of carbon in an ecosystem before taking account

NMVOC from anthropogenic sources in 1990

Sources: IEA, UN, FAO, misc.

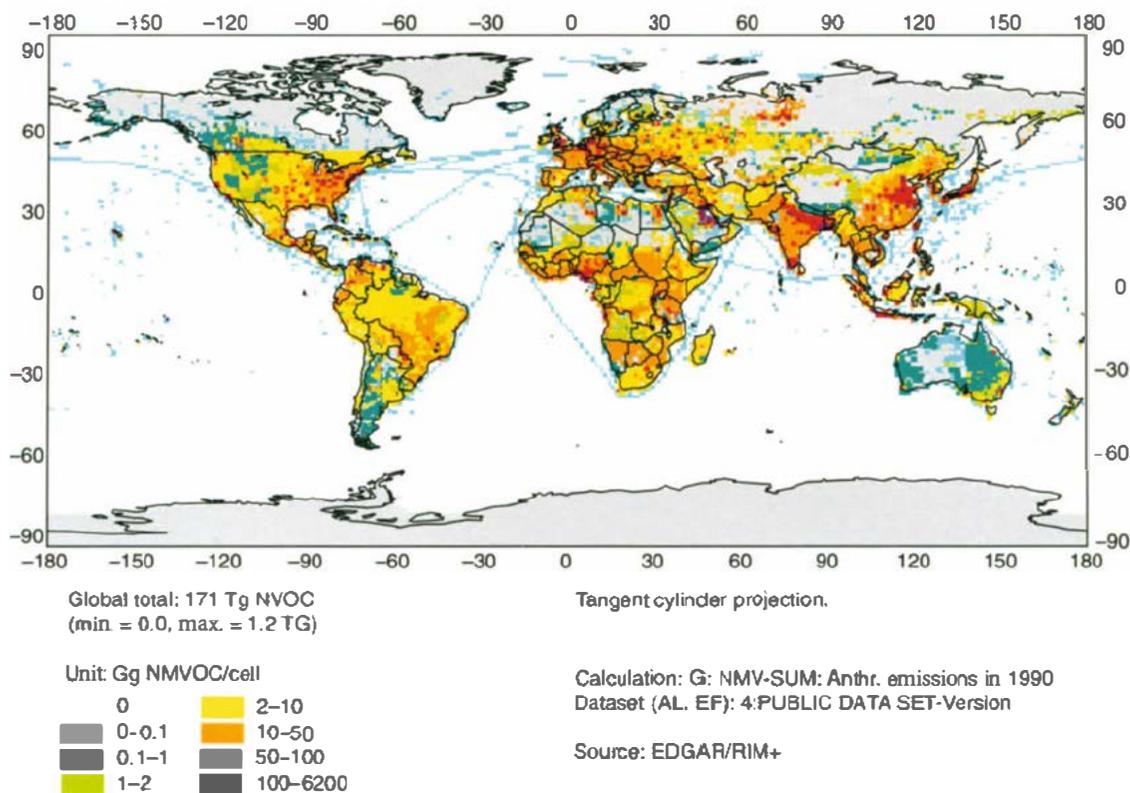


Fig. 2.4. Anthropogenic yearly non-methane VOC emissions in 1990 from the EDGAR (Emission Database for Global Atmospheric Research) database (Olivier et al. 1996)

of ecosystem disturbance (e.g. Valentini et al. 1997; Kesselmeier et al. 1998; Crutzen et al. 1999). Neglect of VOC and CO terrestrial emissions may cause significant errors in estimates of NEP and changes in carbon storage for some ecosystems.

While the oceans are supersaturated with CO and surface production of VOCs is widespread, the ocean-atmosphere fluxes are small, but less well studied, compared with terrestrial emission estimates. VOCs show a wide range of reactivities in the troposphere, with lifetimes ranging from minutes (e.g. β -caryophyllene) to two weeks (e.g. methanol) (Atkinson and Arey 1998). Many are emitted at very low rates, and in some cases are offset by plant uptake, thus having a negligible impact on atmospheric chemistry; others impact ozone production (see Chap. 3), aerosol production (see Chap. 4), and the global CO budget.

Primary pollutants emitted mainly as a result of human activity include hydrocarbons, CO, and nitrogen oxides. About half the terrestrial surface emissions of CO are due to direct emissions from vegetation and biomass burning. In addition about 45% of the total CO source to the atmosphere is due to oxidation of meth-

ane and other organics in the atmosphere, which themselves are predominantly biogenic compounds. Because CO is the end product in the methane oxidation chain the two budgets are closely linked; in addition, CO also originates from the breakdown of VOCs. The concentrations of CO are temporally and spatially highly variable due to the short lifetime of CO and the nature of its discontinuous land based sources. Estimates of anthropogenic CO emissions for 1990 are shown in Fig. 2.5.

2.2.2 The Nitrogen Family of Gases: Ammonia (NH_3), N_2O , and NO

Despite its importance for particle formation and climate, relatively little effort has been spent on understanding the sources and removal processes of NH_3 . Most work on atmospheric ammonia has been performed with respect to eutrophication and acidification close to the terrestrial sources; large scale transport and chemistry of NH_3 and ammonium (NH_4^+) have received much less attention, especially over remote marine regions. The global source strength of ammonia is about

CO from anthropogenic sources in 1990 (<1 km Alt.)

Sources: IEA, UN, FAO, misc.

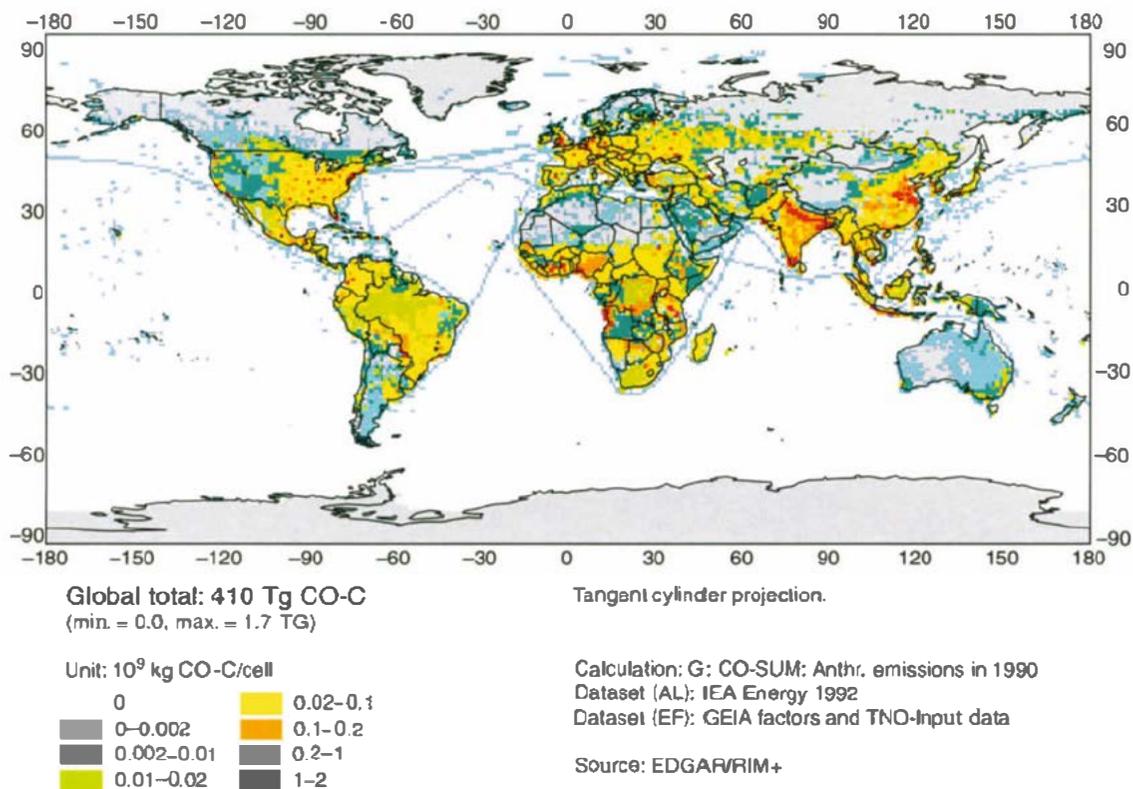


Fig. 2.5. Anthropogenic annual CO emissions in 1990 from the EDGAR database (Olivier et al. 1996)

55 Tg N yr⁻¹, which is of similar magnitude to global NO_x-N emission (Bouwman et al. 1997).

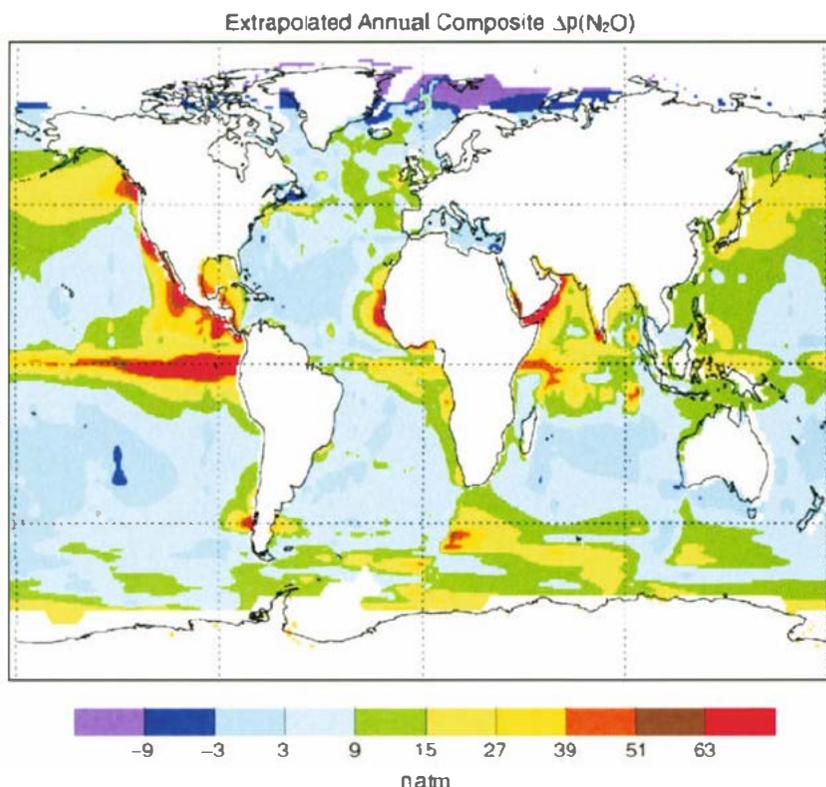
The most recent estimate for global NH₃ emissions (Bouwman et al. 1997) from animals relied on constant emission factors and amounted to 21.7 Tg N yr⁻¹, which is of similar magnitude as fossil fuel related global NO_x-N emissions. The second most important emission category is N-containing synthetic fertiliser. Again, huge differences in agricultural practice and environmental conditions cause a large variation of emissions factors. Overall global emission of ammonia derived from nitrogen fertiliser was estimated to be 9 Tg yr⁻¹, which is 10% of the amount applied. Interestingly, ammonia losses from application of urea fertiliser to rice paddies seem to contribute strongly to this. Other anthropogenic sources, such as biomass burning, cropland, and humans additionally emit about 10 Tg yr⁻¹. Natural sources, such as soils, vegetation, and oceans, emit about 10-20 Tg yr⁻¹ (Bouwman et al. 1997; Schlesinger and Hartley 1992) and are highly uncertain.

Nitrous oxide is an important greenhouse gas with a lifetime of about 120 years. The largest production process for N₂O is "leakage" during microbial nitrification

and denitrification processes in soil and aquatic systems. Significant emissions also occur from decomposition of animal waste, oxidation of ammonia (NH₃), and biomass burning. Biogenic sources of N₂O have increased with expansion of food production systems, intensification of agriculture, and anthropogenic modification of the global nitrogen cycle.

The concentration of N₂O has increased from about 270 nmol mol⁻¹ in pre-industrial times (Kroeze et al. 1999) to 314 nmol mol⁻¹ today (CMDL 2001). There is some evidence for small variations in growth rates in the early 1990s, but during the period of precise *in situ* measurements growth rates have remained near constant at around 0.8 nmol mol⁻¹ yr⁻¹ in both hemispheres (CMDL 2001). The global N₂O flux from the ocean to the atmosphere has been calculated based on more than 60 000 field measurements of the partial pressure of N₂O in surface water (Fig. 2.6). These data were extrapolated globally and coupled with air-sea gas transfer coefficients estimated on a daily basis (Nevison et al. 1995). A global ocean source of about 4 (1.2-6.8) Tg N yr⁻¹ was determined and latitudinal bands of varying emission were delimited.

Fig.2.6.
Annual composite surface
 $\Delta p(\text{N}_2\text{O})$ (10^{-9} atmospheres)
(Nevison et al. 1995)



Quantifying the wide range of N_2O sources has proved difficult and upper and lower bound estimates for specific source types can differ by a factor of ten (Ehhalt et al. 2001). However, progress has been made in balancing the source-sink budget and its recent evolution has been reviewed by Kroeze et al. (1999).

The radiative forcing of climate due to increases in CH_4 (see above) and N_2O during the industrial era is about 25% of the total due to all well mixed greenhouse gases (Ramaswamy et al. 2001). In addition both gases play a significant role in atmospheric chemistry. Increases in CH_4 tend to decrease atmospheric oxidation rates (e.g. Thompson and Cicerone 1986), but increase O_3 and stratospheric H_2O levels. The result of these indirect effects is to amplify the radiative forcing due to CH_4 emissions by around 70%. Changes in concentrations of N_2O over time have tended to decrease stratospheric O_3 (Crutzen 1979) but this effect is small (see Chap. 3).

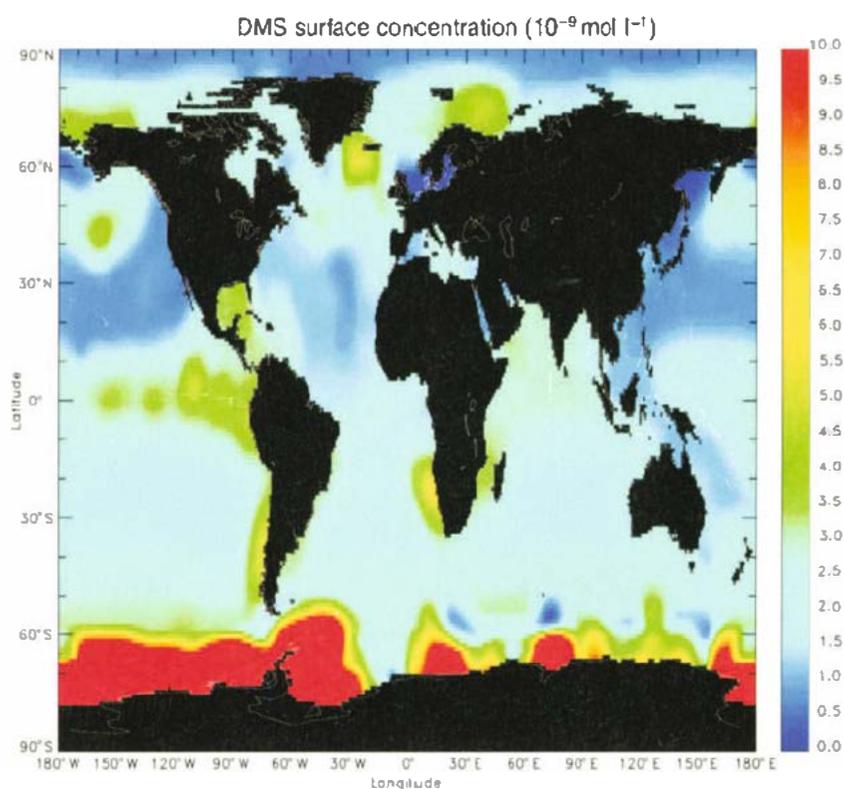
Nitric oxide has a short lifetime (approximately one day) in the atmosphere and takes part there in a complex cycle of reactions with CO and hydrocarbons to form tropospheric ozone. Total emissions, both natural and anthropogenic, range from 37 to 59 Tg N yr^{-1} (Graedel and Crutzen 1993). Estimates in the 1980s of global annual emissions of NO from soils, its largest natural source, were ca. 8 Tg N yr^{-1} ; these have been revised using an extended data set and are now estimated to be as large as 21 Tg NO-N yr^{-1} with an error term of

at least ± 4 and perhaps as large as $\pm 10 \text{ Tg N yr}^{-1}$ (see Sect. 2.7.1.3). The available data confirm that the soil source of NO is similar in magnitude to fossil fuel emissions of NO_x (Davidson and Kinglerlee 1997; Skiba et al. 1997). Minor sources include lightning, transport from the stratosphere, biomass burning, and aircraft emissions.

2.2.3 The Sulphur Family: Dimethylsulphide and Carbonyl Sulphide

Sulphur containing gases are major participants in gas to particle conversion (see Chap. 4). Anthropogenic sulphur emissions from fossil fuel oxidised to sulphate particles can act, in addition to sea salt particles, as condensation nuclei for marine clouds (see Chap. 4). Natural biological emissions of sulphur are predominantly marine in origin, with minor emissions from volcanoes. Dimethylsulphide (DMS), which is produced by microbial processes in the ocean, is emitted at the rate of 15–30 Tg S yr^{-1} (Bates et al. 1992). A recent global inventory of DMS emissions to the atmosphere has been created using the data from more than 16 000 observations of surface ocean DMS concentrations (Kettle et al. 1999) (Fig. 2.7). The estimates of DMS emitted from the ocean to the atmosphere are constrained largely due to the increased number of field observations and mass bal-

Fig. 2.7. Smoothed field of January mean DMS sea surface concentration ($10^{-9} \text{ mol l}^{-1}$). The original field was smoothed with an 11-point unweighted filter to remove discontinuities between biogeochemical provinces (Kettle et al. 1999)



ance of the sulphur budget in the marine boundary layer (Chen et al. 1999; Davis et al. 1999).

Carbonyl sulphide (COS) in the atmosphere originates predominantly from the outgassing of the upper ocean (30%), atmospheric oxidation of carbon disulphide (unknown), and biomass burning (20%), with a total emission of about 1 Tg S yr^{-1} (Andreae and Crutzen 1997; Chin and Davis 1993). With the longest tropospheric lifetime of all atmospheric sulphur compounds, COS can reach the stratosphere where it is oxidised to sulphate particles, which may impact the radiation budget of Earth's surface (Crutzen 1976) and influence the stratospheric ozone cycle.

2.3 A Paleoclimatic Perspective on CH_4 and DMS

Information on past concentrations of several trace gases is preserved in air bubbles trapped when snow is progressively buried and compacted to form ice in areas of Greenland and the Antarctic where temperatures are cold enough to prevent surface melting. The archived air preserved in this way has provided reliable estimates of changes in atmospheric CH_4 and N_2O for up to 400 000 years in the past.

Methane concentration changes are now well depicted in both hemispheres and vary from about $350 \text{ nmol mol}^{-1}$ for glacial to about $700 \text{ nmol mol}^{-1}$ for

interglacial climatic conditions (Stauffer et al. 1988; Raynaud et al. 1988; Chappellaz et al. 1990). Significant rapid CH_4 changes are associated with nearly all abrupt climatic changes that affected the northern hemisphere over the last ice age (Chappellaz et al. 1990, 1993; Brook et al. 1996), indicating a very tight response of the natural CH_4 cycle to climate fluctuations.

The Holocene record (11 500 B.P. to present) provides the natural atmospheric CH_4 variability in relatively stable climatic conditions (Blunier et al. 1995; Chappellaz et al. 1997). The early Holocene (11 500–9 000 B.P.) is a period of relatively high concentrations ($720 \text{ nmol mol}^{-1}$), with a lower mean value ($570 \text{ nmol mol}^{-1}$) centred around 5 000 B.P. and marked drops of 200-year duration around 11 300, 9 700, and 8 200 B.P. The mean inter-hemispheric difference of concentrations, which is mainly a function of the latitudinal distribution of sources and sinks, has been found to be $45 \pm 3 \text{ nmol mol}^{-1}$, i.e. markedly lower than the present-day difference of ca. $140 \text{ nmol mol}^{-1}$ (Dlugokencky et al. 1994).

A high precision record for CH_4 in the Antarctic (Etheridge et al. 1998), shows mixing ratios increasing from about $670 \text{ nmol mol}^{-1}$ 1 000 yr ago with an anthropogenic increase evident from the second half of the 18th century. Similar information is available from Greenland ice (Blunier et al. 1993). Over the pre-industrial period, natural variability is about 70 nmol mol^{-1} around the mean level.

For the last 50 years both concentration and isotopic data ($^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$) for CH_4 are now becoming available from analyses of firn air samples (e.g. Francey et al. 1999). The concentration data indicate a pause in the increase of anthropogenic emissions during the period 1920–1945, probably due to a stabilisation of fossil fuel emissions at that time, while the isotopic data have placed constraints on the relative role of natural and anthropogenic sources and sinks in the 1978 to 1995 period.

Paleo data from ice core studies have had a strong impact on our understanding of the global CH_4 cycle, in particular the latitudinal distribution of wetland emissions. Changes in monsoon patterns (Chappellaz et al. 1990) and the distribution of northern mid- and highlatitude wetlands (Chappellaz et al. 1993) have been considered. More recently Brook et al. (1996) favoured a boreal control on the CH_4 global budget. Changes in methane removal rates must also be taken into account, and model calculations (Thompson 1992; Thompson et al. 1993; Crutzen and Brühl 1993; Martinerie et al. 1995) generally, though not unanimously, suggest that hydroxyl radical (OH) concentrations were higher in glacial conditions than today. The consequent increased removal rate explains at most 30% of the reduction in concentration, implying that the larger effect is that due to lowered emissions.

Ice core data do not support a sudden release to the atmosphere of large amounts of CH_4 from clathrate (hydrate) decomposition at the last deglaciation (Thorpe et al. 1996), as proposed by several authors (e.g. Paull et al. 1991; Nisbet 1992). However, more gradual release of CH_4 from clathrates cannot be discounted as a potentially significant factor and there is some isotopic evidence for clathrate methane releases synchronous with reorganisation of ocean circulation (Kennett et al. 2000).

Global DMS emissions may be modulated by climatic conditions. Could global warming trigger a change of marine biogenic activity and consequently of DMS emissions? Human-induced atmospheric changes could also disturb the oxidation processes of DMS and modify the branching ratio between methanesulphonic acid (MSA) and non-sea salt (nss) SO_4 formation. Ice core studies may help to elucidate these questions, provided that DMS or at least a DMS-related compound is recorded in polar ice. In this regard, MSA has been considered as the most promising parameter to determine in polar ice cores. Over the last decade, a few firn and ice cores have been analysed in detail for MSA and nss SO_4 , in the hope of finding a correlation between concentrations in ice and climate fluctuations on various time scales. Some interesting results have been obtained, but glaciological phenomena have been pointed out recently that obscure the interpretation of the data.

At Antarctic locations where accumulation is relatively high ($>20 \text{ g cm}^{-1} \text{ yr}^{-1}$), MSA concentration records seem to be reliable and decadal variations can be seen

in shallow firn cores. In the Weddell Sea area, Pasteur et al. (1995) found from an ice core covering the last three centuries that MSA marine production increases at warmer temperatures, in relation probably to the amount of broken sea ice where phytoplankton can develop favourably. MSA concentration in coastal Antarctic snow seems to be linked with sea-ice extent (Welch et al. 1993). On the other hand, the validity of MSA ice records is questionable inland. A marked decreasing trend of MSA concentration was found in upper firn layers (the first 6 m) at Vostok (Wagnon et al. 1999). It is suggested that MSA scavenged in the snow crystals is progressively released from the solid phase by snow metamorphism. Part of the initially deposited MSA probably escapes back to the atmosphere. The profile obtained at Dome F (Dome-F Ice Core Research Group 1998) shows very low MSA concentrations between about 30 and 70 m depth, thereafter a rise from about 70 m up to 110 m. The effect can be attributed tentatively to the trapping of interstitial gaseous MSA in the air bubbles at the firn-ice transition (pore close-off). These observations, corroborated by MSA measurements at Byrd Station (West Antarctica) (Langway et al. 1994), lead to the conclusion that MSA concentration depth profiles from central Antarctica are most probably strongly affected by post-deposition phenomena. Sulphate records are not perturbed.

At Amundsen Scott Station (the South Pole), some decreasing trend of MSA concentrations with depth is observable in the firn layers, but it is less steep than at Vostok, probably related to the higher snow accumulation rate. Interestingly, Legrand and Feniet-Saigne (1991) detected marked spikes of MSA concentration in the upper 12 m of firn (i.e. over the last 60 years) at this site. These were attributed to the impact of El Niño events on the production rate of MSA in the sub-Antarctic marine areas or on its transport to inner Antarctica. The changes are superimposed on the general decreasing trend of MSA profiles found in the upper firn layers.

MSA records in Greenland firn cores over the last 200 years, on the other hand, show a rise starting from surface layers and lasting several decades (Whung et al. 1994; Legrand et al. 1997). This surprising trend, opposite to what is found at the South Pole, could be attributed to a change in DMS marine productivity during this period or to the marked increase of atmospheric acidity caused by anthropogenic sulphur emissions. In the latter case, the amount of MSA remaining in the snow could depend on the pH of the atmosphere or of the snow.

Long-term changes in DMS-derived compounds can be seen in both Antarctica and Greenland records. The covariance of MSA and nss SO_4 concentrations observed in the Vostok core suggests that both compounds are mainly derived from marine DMS emissions. MSA and nss SO_4 concentrations are both higher in glacial condi-

tions, with higher values of the ratio $\text{MSA} / \text{nssSO}_4$ found for ice ages. An increase of marine biogenic productivity has been put forward to explain this observation (Legrand et al. 1988, 1991, 1992), but the glaciological artefacts reported above for MSA records in central Antarctic firn layers cast some doubt on the proposition. Clearly more work has to be done on the understanding of chemical composition changes of ice on the scale of several glaciations, all the more since Greenland data are contradictory to Antarctic observations. In the Renland ice core (East Greenland), MSA concentration and the $\text{MSA} / \text{nssSO}_4$ ratio are markedly lower for cold than for warm climatic stages (Hansson and Saltzman 1993). For the two deep cores recovered at Summit (GRIP and GISP 2), conclusions are similar (Saltzman et al. 1997; Legrand et al. 1997). These observations suggest that, for the sulphur cycle, the cases of the northern and the southern hemispheres have to be discussed differently. In particular, the interaction of the primary aerosol (continental dust, sea salt) with acid sulphur compounds has to be investigated.

2.4 Atmospheric Compounds as Nutrients or Toxins

Deposition of atmospheric trace compounds can act as a significant source of nutrients or toxic substances to ecosystems, and their effects on these systems may in turn affect other trace atmospheric constituents. An example is natural fertilisation of the oceans by dust deposition, which leads to increased biological productivity, hence increased uptake of atmospheric CO_2 and release of DMS. The effect of dust deposition on community structure in certain marine systems is currently a key research topic among oceanographers.

Natural biogenic aerosol particles emitted by plants play an important role in nutrient cycling in tropical ecosystems. Many tropical systems are limited by nitrogen and phosphorus and depend on atmospheric input of certain mineral nutrients to maintain productivity (Vitousek and Sanford 1986). Work conducted in the Okavango Delta in southern Africa showed that in channel fringes water is the dominant source of nutrients but that in backswamps aerosols may provide as much as 50% of the phosphorus requirement of the ecosystem (Garstang et al. 1998). Sulphur emissions have been studied since the 1970s when their role in acid rain and forest die-back became key environmental issues (see, e.g. reviews by Sehmel 1980; Hosker and Lindenberg 1982; Voldner et al. 1986). Other acids (e.g. nitric acid) or anhydrides (e.g. sulphur dioxide) can also be deposited in gaseous form.

Ozone is a significant greenhouse gas and in addition plays a major role in the atmospheric chemistry of both the troposphere and stratosphere (see Chap. 3). In

the stratosphere its role in removing biologically damaging UV radiation has received considerable attention. In the troposphere this gas is associated with negative impacts to human health and plant physiology and it can have significant negative impacts on plant productivity in polluted regions. Ozone damage occurs in most crop plants at concentrations of 0.05 to 0.3 $\mu\text{mol mol}^{-1}$, with some more sensitive plants being affected at 0.01 $\mu\text{mol mol}^{-1}$. Ozone directly affects the photosynthetic processes, which results in decreases in plant yield (Tingey and Taylor 1982). As O_3 has a short lifetime and is produced and consumed in the atmosphere, its concentration is highly variable both spatially and temporally. This makes accurate estimates of the total atmospheric burden difficult and estimates of global scale trends even more so. Surface O_3 measurements from background stations have shown both positive and negative trends of less than or about 1% yr^{-1} (e.g. Oltmans et al. 1998; Logan 1999). This complex picture may reflect real re-distribution of O_3 abundance due to changes in the emissions of precursors.

2.5 Approaches for Studying Exchange

A basic organising principle for understanding the fluxes of trace gases to and from the atmosphere is that of a source-sink budget. For each compound, there is a mass balance between the fluxes into the atmosphere (sources), removals from the atmosphere (sinks), including chemical conversions and changes in the atmospheric burden. Budgets provide the conceptual framework for bringing together a process-based understanding of surface exchange fluxes and atmospheric chemistry through demonstration of balanced source-sink budgets.

Exchanges of biogenic trace gases and particles between surfaces and the atmosphere are typically driven by the production and consumption of gases by plant, microbial, and chemical processes, and influenced by physical transport through soils, sediments, water, or across gas-liquid boundaries.

For many chemical compounds, demonstrating a balanced budget based on process models of these fluxes remains a goal rather than a reality. However, substantial progress has been made in the last decade through collaborations between a number of disciplines, including atmospheric chemistry, ecology, biogeochemistry, geochemistry, microbiology, soil science, meteorology, hydrology, and oceanography. One of the hallmarks and great successes of IGAC research has been the integration of knowledge from such relevant disciplines toward the understanding of trace gas sources and sinks.

Understanding the source-sink budget for a trace gas involves establishing and validating process models across a range of scales. Most terrestrial process stud-

ies of trace gas fluxes are carried out at small spatial scales, e.g. of the order of 1 m, in order to control the relevant environmental factors. Validation at this scale typically uses flux measurements derived from chamber studies. However, process models are also increasingly used as extrapolation tools to derive landscape, regional, and even global scale flux estimates. Most models can account for short term changes (minutes to hours) of some compounds but are limited in their ability to predict longer term (days to years) variations (Ottner et al. 1999).

This up-scaling provides flux inventories that are relevant for environmental management, but requires estimation of the key inputs to the process model such as marine plankton speciation, soil or vegetation type, land cover and management, and climatic, radiation, hydrological, and marine parameters. Validation of these scaled-up inventories requires measurement of average fluxes at the corresponding scale. These may be determined by direct flux measurements near the surface, e.g. using eddy-covariance or relaxed eddy accumulation techniques, inferred from vertical gradients in the atmospheric boundary layer, or derived from regional or global scale transport models used in an inverse mode to calculate the flux distribution that reproduces observed concentration distributions. Coupled land-ocean-atmosphere models are only available for CO₂ and H₂O with little attention being paid to other chemical compounds of biogenic origin. A few modelling studies have included the effects of anthropogenic sulphur (Erickson et al. 1995; Meehl et al. 1996; Haywood et al. 1997) for example, on climate and plant growth, but much more research is required to include a very detailed treatment of sulphur and other aerosol dynamics in on-line climate simulations. Few global climate models have examined the climate response of DMS emissions from the oceans or variability thereof (Bopp et al. 2000). Similar modelling work is required for the emissions of many other compounds as well as for deposition to the surface.

Additional validation of budgets or constraints on individual source and sink terms can be derived from dual-tracer studies. For example co-variation of ²²²Rn and CH₄ or N₂O concentrations has been used to determine regional scale terrestrial fluxes of the latter where the corresponding ²²²Rn fluxes are better known (Wilson et al. 1997; Schmidt et al. 1996). A special case of dual-tracer studies is the use of isotope ratio measurements in trace gases. Where different source types emit a trace gas with different isotopic ratios, measurement of those ratios in the atmosphere provides a means of separating the influence of each source. Typical examples of this are the use of the ¹³C fraction in methane to place constraints on the biogenic source fraction (e.g. Sugawara et al. 1996; Conny and Curie 1996; Hein et al. 1997; Bergamaschi et al. 1998; Lassey et al. 2000) and the ¹⁴C fraction to place constraints on the fossil fuel source (e.g. Lowe et al. 1988;

Wahlen et al. 1989; Manning et al. 1990; Quay et al. 1999). Isotopic studies in marine regions are currently used in the parameterisation of air-sea exchange. Methodological difficulties still prevent this approach from fully extending into marine process studies.

Process models, both diagnostic and prognostic, require large data sets for initialisation and validation. Compilation of trace gas emission inventories has been carried out by the Global Emissions Inventory Activity (GEIA) (<http://weather.engin.umich.edu/geia>). This component of IGAC was created in 1990 to develop and distribute scientifically sound and policy-relevant inventories of gases and aerosols emitted into the atmosphere from natural and anthropogenic sources. Most GEIA inventories currently available are for emissions from anthropogenic sources. Current inventories for natural sources include emissions of N₂O, NO_x, VOCs, and organic halogens. Inventories are in progress for natural sources of methane, reduced sulphur compounds, and some source-specific emissions such as biomass burning. There is still uncertainty, however, associated with all global emission inventories. The extrapolation of space- and time-limited observations to regional and global scales invites many venues for error. For example, coastal regions typically have higher concentrations than open ocean regions but the patterns are very local; in addition, marine measurements are more biased towards spring and summer than terrestrial measurements but annual scaling frequently takes place.

2.6 Terrestrial Highlights

2.6.1 Exchange of Trace Gases and Aerosols from Terrestrial Ecosystems

A Dahlem workshop was held in 1989 where the delegates focussed on research needs in the area of exchange of trace gases between terrestrial ecosystems and the atmosphere (Andreae and Schimel 1989). They focussed on five priority areas for research:

- To determine what processes are involved in production of CH₄, N₂O, and NO in different ecosystems, and if they are constant or change with time, and why different ecosystems have evolved different production pathways.
- To describe characteristics of soils that influence the area and depth distributions of production-consumption reactions modulating trace gas emissions.
- To develop mechanistic models that include microbiological and physical-chemical processes applicable at the scale of trace gas exchange experiments and to test these models with field and laboratory experiments.

- To develop ecosystem scale models for biogenic trace gas fluxes.
- To assess what quantitative changes in CH₄, N₂O, and NO fluxes can be expected in response to physical and chemical climate changes.

A large number of studies has been conducted in the last ten years attempting to address these questions. Substantial progress has been made in both expanding the databases by conducting more measurements, and improving markedly the level of sophistication with which these measurements have been carried out (see Chap. 5), together with the way they are linked to auxiliary data, e.g. isotopic data. Not only do we now have better databases but we also understand better the mechanistic processes and controlling factors regulating the fluxes. This has enabled adequate models to be formulated, although many of them are very limited in their applicability (see Chap. 6). A significant part of the effort has come via the TRAGNET trace gas network, developed in the US with strong European participation, and the BATGE trace gas exchange programme centred on the Tropics. The following section summarises the progress made in the last decade in the quantification of the terrestrial sources and sinks of methane, volatile organic carbon compounds, and nitrous and nitric oxides, and advances in the understanding of the processes controlling their fluxes. Additional sections follow on biomass burning and wet deposition in the Tropics.

2.7 Background: Emissions and Deposition

Biogenic emissions from and deposition to vegetation and soils occur in a more or less continuous way over the year with the magnitude of the exchange controlled by a complex interaction of biotic and abiotic factors. On the other hand, biomass burning releases large amounts of emissions in pulses varying in frequency depending on the geographic location, the biome, and the management. The natural biogenic aerosol comprises many different types of particles, including pollen, spores, bacteria, algae, protozoa, fungi, fragments of leaves and insects, and excrement. The mechanisms of particle emission are still not well understood, but probably include mechanical abrasion by wind, biological activity of microorganisms on plant surfaces and forest litter, and plant physiological processes such as transpiration and guttation. Vegetation has long been recognised as an important source of both primary and secondary aerosol particles. Forest vegetation is the principal global source of atmospheric organic particles (Cachier et al. 1985) and tropical forests make a major contribution to airborne particle concentrations (Andreae and Crutzen 1997). However, only a few stud-

ies of natural biogenic aerosols from vegetation in tropical rain forests have been undertaken (Artaxo et al. 1988, 1990, 1994; Echalar et al. 1998).

Gaseous or particulate matter may be removed from the atmosphere and transferred to Earth's surface by various mechanisms, known under the generic terms of "dry deposition" and "wet deposition". Research findings related to the latter in tropical systems are addressed specifically in Sect. 2.7.3. Dry deposition is the removal of particles or gases from the atmosphere through the delivery of mass to the surface by non-precipitation atmospheric processes and the subsequent chemical reaction with, or physical attachment to, vegetation, soil, or the built environment (Dolske and Gatz 1985). Dry deposition is best described by the surface flux, F , corresponding to an amount of matter crossing a unit surface area per unit time. In most modelling work, another quantity, called deposition velocity, $v_d = F/C$ (flux divided by concentration), is preferred for practical numerical reasons, because its time variations are smoother. Deposition velocities are also easier to parameterise and most data on dry deposition are actually expressed as deposition velocities, usually in cm s⁻¹. A powerful parameterisation of dry deposition is the resistance analogy (Chamberlain and Chadwick 1953), where the difference between concentrations in the air and at the surface (C_s) is equal to the product of the flux and a resistance R , an empirical quantity to be parameterised. Through parameterisation of resistances, deposition velocities are readily derived. Further, this scheme may be extended and adapted to the degree of complexity of the surface, e.g. as in the case of a forest canopy, by using a greater number of resistances, in series or in parallel, according to the rules of an electric circuit. The most powerful mechanism by which deposition occurs over a canopy is penetration into plant tissues through the stomata.

Although most pollutants undergo deposition only (downward flux), some of them show bidirectional fluxes. An illustration of such behaviour is the case of nitrogen oxides NO and NO₂, as shown by Delany et al. (1986) and Wesely et al. (1989). Nitric oxide is emitted by soils (Williams et al. 1992; Wildt et al. 1997). Once emitted, it can readily be oxidised to nitrogen dioxide, with a resulting upward flux of the latter. If the concentration of nitrogen dioxide is high, as in the case of polluted air, its flux can be directed downwards.

Contrary to nitrogen oxides, ozone undergoes deposition only, since there is no known process which could produce ozone at the surface. The deposition velocity of ozone depends mostly on the nature of the surface. If vegetation is present, ozone is deposited ("taken up" would be a more appropriate term) by penetration into plant tissues through the stomatal cavities present on leaves. This process is likely to cause damage, and, in extreme cases, decreases in crop yields. Ozone uptake

by vegetation has been put forward to explain ozone downward fluxes by Rich et al. (1970), and Turner et al. (1974), and subsequently by many other authors. Another ozone deposition mechanism occurs on bare soils, where ozone molecules are destroyed by a process similar to wall reactions observed in the laboratory, e.g. in a glass vessel. On mixed surfaces, both processes occur. Dry deposition of ozone has been extensively studied over the last forty years (Regener 1957; Galbally 1971; Galbally and Roy 1980; Wesely et al. 1978, 1982; Delany et al. 1986; Guesten and Heinrich 1996; Labatut 1997; Cieslik 1998).

Resistance analysis has been applied to the interpretation of ozone flux observations (Massman 1993; Padro 1996; Cieslik and Labatut 1996, 1997; Sun and Massman 1999), in particular to discriminate between the relative contributions of stomatal uptake and direct deposition on soil to the overall process. Most authors used an approach in which stomatal resistance for ozone uptake was deduced from stomatal resistance for evaporation, since both processes depend on stomatal aperture. Combining direct ozone deposition measurements and the inferred ozone stomatal resistance, its partial resistance for deposition on the soil was deduced as a residual.

The diurnal pattern of ozone deposition is governed by both turbulence and physiological activity of the vegetation. At night, ozone deposition is close to zero. It increases during the morning hours, both because air turbulence increases, bringing more molecules into contact with the surface, and because stomata are open for transpiration and carbon assimilation. The noon maximum value of deposition velocity ranges between 0.2 and 0.8 cm s⁻¹, depending on the intensity of turbulence and on the state of vegetation: the more active the vegetation, the more ozone is taken up. The daily variation in ozone deposition generally follows the pattern of the surface heat flux. For example, rapid deposition of ozone was observed in the lowest layers of a tropical forest canopy in Brazil, with an average flux of $-5.6 \pm 2.5 \times 10^{11}$ molecules cm⁻² s⁻¹. This co-occurred with a large NO flux of $5.2 \pm 1.7 \times 10^{10}$ molecules cm⁻² s⁻¹, which was about three times larger than the flux of N₂O. The rapid destruction of O₃ in the forest environment was also manifested by a pronounced ozone deficit in the atmospheric boundary layer. Rapid removal by the forest clearly plays a role in the regional ozone balance, and, potentially, in the global ozone balance. The location of strong NO sources and sinks in the humid Tropics makes these ecosystems pivotal in the chemistry of the atmosphere (Kaplan et al. 1988).

2.7.1 Production and Consumption of CH₄

The state of understanding of the CH₄ budget in 1990 was well summarised by Fung et al. (1991) who showed that the observed seasonal cycles at sites remote from sources could be reproduced using estimates of sources

and removal rates consistent with the literature at that time. However, large uncertainties in individual components of the budget were evident and the atmospheric global observation network did not provide sufficiently strong constraints to reduce these uncertainties.

Since 1990 considerable progress has been made, particularly through studies of CH₄ emissions from wetlands and rice paddies, but also through improved estimates of oxidation rates, better data on animal and landfill emissions, and extension of the observational network. One significant outcome of these studies has been to decrease estimates of rice emissions and increase estimates of natural wetland emissions. At the regional scale there has been a reduction in the uncertainty of some type of emissions, e.g. from ruminant animals, with some studies being prompted by requirements to report national greenhouse gas emission inventories under the United Nations Framework Convention for Climate Change (UNFCCC).

Early successes of IGAC included a systematic characterisation of CH₄ fluxes from wetlands obtained from field programs in the ABLE, BOREAS, and related projects. This area has received considerable attention by many groups during the last decade; although a comprehensive literature review is beyond the scope of this chapter, a partial summary follows. A summary of parallel studies of CH₄ from rice paddies is given separately (see Box 2.1). Dependencies of CH₄ production rates in wetlands and closely related systems on water table depth, temperature, and precipitation, were examined and used to develop regression-based explanatory models (e.g. Wahlen and Reeburgh 1992; Roulet et al. 1993; Frolking and Crill 1994). Consumption by methanotrophic communities, which may intercept a substantial fraction of below ground production, was also quantified in a variety of situations and related to environmental variables (e.g. Wahlen et al. 1992; Koschorreck and Conrad 1993; Bender and Conrad 1994).

As the available data grew, the value of organising them in terms of latitudinal transects and of using consistent methodologies and reporting formats was recognised. The US Trace Gas network (TRAGNET), a component of the IGAC BATREX project, was established to meet this need (Ojima et al. 2000) and has created a database of flux measurements covering 29 sites ranging largely, but not exclusively, from 10° N to 68° N on the American continent (see <http://www.mel.colostate.edu/projects/tragnet/>). These flux data along with site and climate characteristics are stimulating the development and validation of more sophisticated models. Recent wetland CH₄ models have improved their ability to simulate observations by explicit treatment of net primary productivity as an underlying driver of production (Cao et al. 1996; Walter and Heimann 2000). More sophisticated models of soil oxidation processes have also been developed (Del Grosso et al. 2000) and comparison of models across a

Box 2.1. Case study: Methane emissions from rice

IGAC researchers have been very active in studying methane emissions from rice paddies and considering mitigation options (RICE Activity). This is particularly relevant given projections that rice production will increase from 520 million t today up to 1 billion t during this century. Rice agriculture is subdivided into dryland, rainfed, deepwater, and wet-paddy production. The latter three categories have land continuously under water at some time of the year, creating anoxic conditions. They comprise some 50% of the rice crop area and contribute 70% of total rice production (Mnamani and Neue 1994).

Emissions from rice fields are influenced by many factors, of which the most important are water management, the amount of decomposable organic matter (e.g. rice straw) into the soil, and the cultivar of rice grown (Neue 1997). Other factors such as temperature, soil redox potential, soil pH, and the type and amount of mineral fertiliser applied also affect the emission, which reflects a net balance between gross production and microbial oxidation in the rhizosphere.

Substantial CH_4 emissions occur only during those parts of the cultivation period when rice paddies are flooded, although a delay of typically two weeks occurs after flooding. The main control of CH_4 production is the availability of degradable organic substrates (Yao and Conrad 1999). Readily mineralisable carbon, e.g. in rice straw or green manure, produces more CH_4 per unit carbon than humified substrates like compost (Van der Gon and Neue 1995). Higher soil temperature also speeds up the initiation of CH_4 formation but not necessarily the total emitted over a growing season.

Earlier estimates that up to 80–90% of the CH_4 produced in a paddy field is oxidised (e.g. Sass and Fisher 1995) may be too high. The use of a novel gaseous inhibitor, difluoromethane, which is specific for CH_4 oxidising bacteria in rice fields and which does not affect the CH_4 -producing bacteria, showed that CH_4 oxidation was important only during a rather short period of time at the beginning of the season, when ca. 40% of the CH_4 produced was oxidised before it could enter the atmosphere. This fraction then decreased rapidly and for most of the season the CH_4 oxidation was only of minor importance (Krüger et al. 2000). There is now evidence of a nitrogen limitation of the oxidation process (Bodelier et al. 2000). There is also evidence of systematic changes during the rice-growing season in the $\delta^{13}\text{C}$ value of emitted CH_4 due to changes in production, transport, and oxidation (Tyler et al. 1994; Bergamaschi 1997). This may have an impact on the $\delta^{13}\text{C}$ signal of atmospheric CH_4 , which is relevant for inverse modelling of methane sources.

range of soil sources (wetland, rice paddy, and landfills) now suggests an ability to explain variations over orders of magnitude in the net emission resulting from production and oxidation processes involving both natural and anthropogenic factors (Bogner et al. 2000).

As understanding of the CH_4 budget has improved, attention has turned to explaining interannual variability and, in particular, the high growth rates observed in 1991 and 1998, which appear to be associated with anomalous climatic conditions. A key factor in this respect has been the development of better process models for wetland emissions outlined above. An important factor in both the contemporary and pre-industrial global CH_4 budgets is the relative role of tropical vs. temperate and boreal wetlands. Recent estimates of current total wetland emissions cover a wide range from about 100 Tg yr^{-1} to over 200 Tg yr^{-1} (Hein et al. 1997; Cao et al. 1996; Houweling et al. 1999; Walter and Matthews

Up to 90% of the CH_4 emitted from rice fields passes through the rice plant. Well-developed intracellular air spaces (aerenchyma) in leaf blades, leaf sheaths, culm, and roots provide a transport system for the conduction of CH_4 from the bulk soil into the atmosphere (Mouchi et al. 1990). Modern cultivars emit generally less per plant than traditional varieties because the improved harvest index often results in less unproductive tiller, root biomass, and root exudates (Neue 1997). Work in China (Lin 1993) and the US (Huang et al. 1997) has demonstrated a two-fold difference in emission rates between rice varieties grown under similar conditions. However, under field conditions, a comparison of cultivars is more complex because farmers adjust planting densities or seed rates to achieve an optimum canopy and tiller density.

Existing model approaches are still crude, with low resolution, but they provide good regional estimates within the range of observed and extrapolated fluxes. The best estimate of the global emission of CH_4 from rice fields is likely to be in the range of 30–70 Tg (Neue 1997). Recently Matthews et al. (2000) developed a simulation model describing the main processes involved in CH_4 emission from flooded rice fields by linking an existing crop simulation model (CERES-Rice) to a model describing the steady-state concentrations of CH_4 and oxygen (O_2) in soils. Experimental field and laboratory data from five Asian countries participating in the Inter-regional Research Program were used to develop, parameterise, and test the model. Field measurements of CH_4 emissions were extrapolated to national levels for various crop management scenarios using spatial databases of required inputs on a province-district level. Lack of geographic information on required inputs at appropriate scales limits application of this model in determining current, and predicting future, source strengths.

Promising candidates for mitigation of rice emissions are changes in water management, organic amendments, fertilisation, cultural practices, and rice cultivars (Neue et al. 1998). However, while present knowledge of processes controlling fluxes allows the development of mitigation technologies, information is still lacking on trade-offs and socio-economic feasibilities. Climate change will tend to extend rice production northwards, especially in Japan and China. Elevated CO_2 concentrations will enhance the production of rice yields, but also increase carbon exudation from roots, enhancing CH_4 emissions. Breeding of new rice cultivars will be the most effective strategy for dealing with this issue (Milich 1999). However, enhanced temperatures are likely to limit the potential increases.

2000). Inversion methods tend to favour the upper half of this range and both inverse estimates and process-model estimates now suggest that tropical emissions dominate over those at higher latitudes. The best determined biogenic source of CH_4 , based on the consistency of different estimates, is that from ruminant animals. Total emissions from this source are estimated in the range 80 to 115 Tg yr^{-1} (Mosier et al. 1998; Lelieveld et al. 1998). In recent years, several studies have produced a large amount of data on emission factors per animal or per unit of production and related these to models of rumen physiology (e.g. Lassey and Ulyatt 2000). Emissions from rice paddies and biomass burning are covered separately below, and other biogenic sources such as termites and marine methanogenesis are relatively minor in significance.

Most CH_4 removal occurs through atmospheric oxidation by OH; however, consumption by methanotrophic

bacterial communities in soils is estimated to be responsible for 3 to 6% of total removals. This process is also important as it is responsible for reducing the net emissions from soils, e.g. those from rice paddies, landfills, and natural wetlands, through consumption in aerobic conditions near the surface. Thus, changes in water table can shift the balance between CH₄ production and consumption in soils.

At the outset of the IGAC programme, there were few data available on the oxidation of atmospheric CH₄ in soils and the total sink was estimated at 30 (range 15–45) Tg CH₄ yr⁻¹ (Watson et al. 1990). Now there are many more flux measurements available (including some from studies lasting more than one year), there is more information on the impact of land use change, and the relationships between oxidation rates and soil parameters have been modelled. Flux values for different ecosystems show consistent median values of 10–20 Mg CH₄ m⁻²yr⁻¹, but with skewed (log-normal) distributions (Smith et al. 2000). A major reason for the similarities between different ecosystems is that the effect of temperature on oxidation rate is small, as the organisms responsible are substrate-limited due to diffusion resistance and low atmospheric concentration. This analysis gives a global sink of 29 Tg CH₄ yr⁻¹, and a $\pm 1\sigma$ range from a 1/4 to 4 times this value (Smith et al. 2000). Thus, the best estimate is essentially unchanged but the uncertainty is increased. Global estimates from models range from 17–23 Tg CH₄ yr⁻¹ (Potter et al. 1996a) to 38 (range 20–51) Tg CH₄ yr⁻¹ (Ridgwell et al. 1999).

Changes in land use between natural grassland, pasture or arable land, and forestry can produce a large relative difference in CH₄ removal rates in soils (Smith et al. 2000; Del Grosso et al. 2000). Recent data have shown that methane-oxidising bacteria associated with the roots of rice are stimulated by fertilisation rather than inhibited, as had been generally believed; these data will make a re-evaluation of the link between fertiliser use and methane emissions necessary. The impact of disturbance on oxidation rate can be long lasting, e.g. it may take 100 years or more to recover (Priemé et al. 1997; Fig. 2.8), but nothing is known about the ecological reasons for this. There is evidence that the microorganisms principally responsible for CH₄ oxidation differ from those responsible for CH₄ oxidation in environments such as landfill cover soils, wetland hummocks, termite mounds, and oxidised zones within rice paddy soils, where much higher gas concentrations are the norm (Conrad 1996).

Ongoing climate change is expected to increase temperatures and thaw depth in tundra ecosystems, which will tend to increase methane emissions. On the other hand, increased evaporation at the surface may create an oxygenated zone, increasing methanotrophic activity. However, climate models also indicate an increase

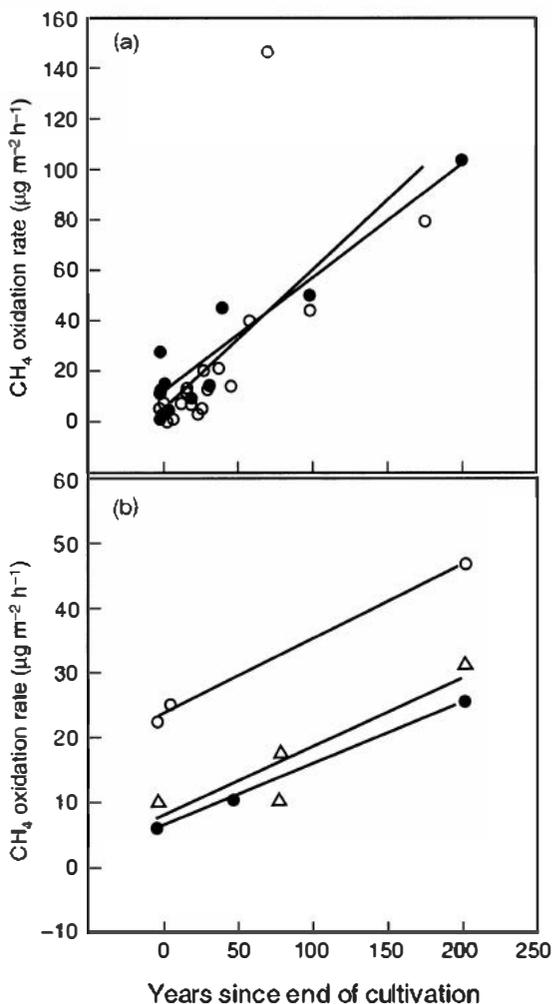


Fig. 2.8. Increase in rate of soil oxidation of atmospheric methane with time after reversion of former agricultural land to forest-woodland or to grassland. a European forest-woodland: Denmark (filled circles) and Scotland (open circles); b North American grassland (circles) and forest (triangles) (Smith et al. 2000)

in precipitation for northern latitudes (Vourlitis et al. 1993) suggesting that wet tundra soils will continue to be waterlogged and that the temperature effect will dominate.

An indication of the potential for climate feedbacks on CH₄ wetland emissions is given by recent analyses suggesting that higher CH₄ growth rate in the atmosphere during 1998 can be explained by temperature and precipitation effects on wetlands (Dlugokencky et al. 2000; Walter and Matthews 2000). Extrapolation of these results has suggested that a global mean warming of 1 °C would lead to an increase in wetland emissions of 20 to 40 Tg yr⁻¹ (B. Walter, private communication 2000).

Dlugokencky et al. (1998) showed that the overall decline in CH₄ growth rates during the 1990s was broadly consistent with a constant total emissions and

removal rate and that CH₄ concentrations would stabilise at a level 4% higher than observed in 1996 if this situation continued. Alternatively, CH₄ could be stabilised at 1996 concentrations if the total emissions were reduced by 4%. However, there is some evidence that removal rates have been increasing during the last decade (Krol et al. 1998; Karlsdottir and Isaksen 2000) at ca. 0.5% yr⁻¹. This would imply that total sources were increasing at about the same rate and is consistent with an analysis of trends in the ¹³C/¹²C ratios in CH₄ (Francey et al. 1999).

Longer term scenarios for CH₄ emissions have not been studied in as much detail as those for CO₂ emissions. One perspective is that emissions will generally follow human population because of the connection to agriculture, sewage, and landfill. However, recent trends indicate a decoupling of emissions from population (D. Etheridge, private communication 2001) and several authors have noted that anthropogenic CH₄ emissions are generally associated with inadvertent losses of energy for both animals and fossil fuel use. These lead to an alternative view that abatement of current CH₄ emissions may be possible at low or negative cost.

2.7.1.1 *Production of Volatile Organic Carbon Compounds from Vegetation*

Plant growth involves the uptake of CO₂, H₂O, and nutrients and the release of particles, water vapour, O₂, and reduced carbon compounds to the atmosphere. These reduced carbon compounds are usually described as VOCs and consist of a range of short chain organic compounds including hydrocarbons, alcohols, carbonyls, fatty acids, and esters. Recent reviews of biogenic VOC research have been published in journals of the biological (Sharkey 1996; Lerdau et al. 1997; Harley et al. 1999), chemical (Atkinson and Arey 1998), and atmospheric (Kesselmeier et al. 1998; Guenther et al. 2000) science communities as well as in a book (Helas et al. 1997) and several book chapters (e.g. Fall 1999; Guenther 1999; Steinbrecher and Ziegler 1997). The achievements of IGAC and associated research activities during the last decade on VOC emissions from plants and the currently identified research gaps are discussed in the following section.

2.7.1.2 *New Emission Measurements*

The advances in measurement techniques described in Chap. 5 have greatly increased capabilities for investigating biogenic VOC fluxes at multiple spatial and temporal scales. The resulting data have provided a more complete and accurate picture of biogenic VOC emissions. New analytical methods have extended the range

of chemical compounds that can be investigated. Enclosures coupled with environmental control systems have been used to characterise the environmental and genetic controls over emissions, while above-canopy flux measurements provide an integrated measurement of landscape-level trace gas exchange. Tower-based flux measurements are particularly useful for investigating diurnal and seasonal variations without disturbing the emission source. Aircraft and tethered balloon measurement systems can be used to characterise fluxes over scales similar to those used in regional models. These regional measurements are especially useful in tropical landscapes with high plant species diversity.

The measurement database that can be used to characterise biogenic emission processes and distributions has been greatly increased by large international field programs including EXPRESSO, LBA, SAFARI, NARSTO/SOS, EC-BEMA, EC-BIPHOREP, EC-EUSTACH (see Appendix A.3). Over a thousand plant species have been investigated, for at least a few VOCs, by these studies. Equally important has been the large number of landscapes that have been studied. IGAC-endorsed research has been particularly important for advancing measurements in tropical regions. A number of these studies have investigated emissions on multiple scales resulting in measurements that can be used to evaluate biogenic VOC emission model estimates.

Investigations of emission mechanisms, often conducted under controlled laboratory conditions, have also added to our understanding of biogenic VOC emissions. These measurements have been used to relate emissions to both environmental and genetic controls. Although these measurements have not revealed distinct taxonomic relationships, some patterns have emerged (Harley et al. 1999; Csiky and Seufert 1999).

2.7.1.3 *Newly Identified Compounds*

A substantial improvement has been achieved in the last ten years in the identification and accurate quantification of VOCs emitted by terrestrial ecosystems. The number of components reported as biogenic VOC emissions has increased from seven (ethylene, isoprene, α -pinene, β -pinene, limonene, Δ -3-carene, and *p*-cymene) to more than 50, belonging to ten different classes. The list of detected compounds is reported in Table 2.1 together with information on:

- hypothesised biological production pathways occurring inside and outside the chloroplast;
- numerical algorithms adopted for describing emission variations;
- relative abundance in vegetation emission; and
- degree of removal by OH and O₃ attack under certain atmospheric conditions.

Table 2.1. List of VOC so far identified and quantified in terrestrial vegetation emissions

VOC	a	b	c	d
a The existence of a possible biosynthetic pathway				
0	= not yet hypothesized			
1	= only hypothesized			
2	= hypothesized and partly supported by enzyme isolation or carbon labeling			
3	= hypothesized and partly supported by both enzyme isolation and carbon labeling			
b The type of algorithm followed				
1	= light and temperature dependent			
2	= temperature dependent			
c The relative abundance in the emission				
4	= high abundant			
3	= abundant			
2	= moderately abundant			
1	= present at trace level			
*	= episodic emission due to injuries			
d The production or losses occurring by within-canopy processes when levels of O₃ and OH radicals in air exceed 60 nmol mol⁻¹ and 106 molecules cm⁻³ of OH radicals, respectively				
-1	= partial losses			
-2	= complete losses			
+1	= moderate production			
+2	= strong production			
VOC	a	b	c	d
Alkanes				
n-hexane			1	
Alkenes				
Ethylene	2		2	
a C5 isoprenoids				
Isoprene	3	1	4	
b C10 isoprenoids (monoterpenes)				
Camphene	1	2	1	
p-cymene	1	1,2	2	
Δ3-carene	1	1,2	2	
Fenchene	1	1,2	1	?
d-limonene	3	1,2	3	-1
Myrcene	3	1,2	2	-1
l-β-ocimene	2	1,2	2	-1
c-β-ocimene	2	1,2	1	-1
α-phellandrene	2	1,2	1	-1
β-phellandrene	2	1,2	1	-1
α-pinene	3	1,2	3	
β-pinene	3	1,2	2	
Sabinene	3	1,2	2	
α-terpinene	2	1,2	1	-1
γ-terpinene	2	1,2	1	-1
Terpinolene	2	1,2	1	-1
Thujene	2	1,2	1	?
Tricyclene	1	1,2	1	
c C15 isoprenoids (sesquiterpenes)				
l-α-bisabolene	2	2	1	?
α-copaene	1	2	2	?
β-caryophyllene	1	2	2	-2
α-humulene	1	2	1	-2
Longifolene	1	2	1	
Valencene	1	2	1	?
Arenes				
Toluene		1	1	
Aldehydes				
Formaldehyde	1	2	2	+2
Acetaldehyde	1	2	1	+2
n-hexanal			1	
n-nonanal			1	
n-decanal			1	
l-2-hexenal	2		3*	
Benzaldehyde			1	
Ketones				
Acetone	1		2	+2
Camphor	1	1,2	2	
6-methyl-5-heptene-2-one (MHO)			1	+1,-1
Butanone			1	
2,3-butadione			1	
2-pentanone			1	
4-methyl-2-pentanone			1	
Ethers				
1,8-cineole	2	1,2	2	
Esters				
Acetyl salicylate			1	
Bornyl acetate	1	2	1	
Endobornyl acetate	1	2	1	
3-hexenyl acetate	2		3*	
Linalyl acetate	2	1,2	1	
3-methyl-3-butenyl acetate		1	1	
Alcohols				
Methanol	2		2	
2-methyl-3-buten-2-ol (MBO)	2	1	2	
3-methyl-3-buten-1-ol	2	1	1	
cis-3-hexen-1-ol	2		3*	
Linalool	3	1,2	2	
α-terpineol	2	1,2	1	?
γ-terpineol	2	1,2	1	?
Acids				
Formic acid	1	1	1	
Acetic acid	1	1	1	
Oxides				
c-linalool oxide	2	1,2	1	
l-linalool oxide	2	1,2	1	

The increased knowledge of VOC composition can be attributed to the recent measurement campaigns and analytical advances described in the previous section. Some compounds were not previously observed because of their reactivity with O₃ during sampling and analysis. The use of suitable O₃ scrubbers has reduced this problem for some compounds.

Although impressive, the list reported in Table 2.1 cannot be considered exhaustive of the potential VOCs that could be released by vegetation because of the influence that mechanical injuries, pathogen attack, ozone exposure, and natural decomposition can have on emissions. Such effects can induce the release of organic compounds that are not normally emitted by the plant. In addition, some compounds have a limited distribution within the plant kingdom and may be produced by plant species that have not yet been investigated.

2.7.1.3.1 Mechanisms and Pathways Controlling Production and Emission

At least seven different biogenic VOC production-emission categories have been identified: chloroplast, metabolic by-products, decaying and drying vegetation, specialised defence, unspecialised defence, plant growth hormones, and floral scents. Recent studies have shown that some compounds can be produced by more than one pathway (Table 2.1). There have been significant advancements in elucidating the biochemical pathways responsible for VOC production in chloroplasts. These include the identification of the enzymes associated with the synthesis of these VOCs, the chemical precursors, the production sites, and the demonstration that compounds other than isoprene (e.g. 3-methyl-3-buten-1-ol and α -pinene) are emitted in this manner (Silver and Fall 1995; Loreto et al. 1996). It has also been observed that these VOCs penetrate the intercellular space of the leaf and exit the plant via the stomata; yet emissions are not directly controlled by stomatal conductance. Instead, emissions depend on the rate of synthesis in the plant, which is coupled to the availability of precursors.

Some oxygenated VOCs (e.g. acetone, methanol, formaldehyde) could be produced as metabolic by-products and, although there has been little experimental investigation, plausible pathways have been proposed (Fall 1999). The production pathways associated with the remaining categories (floral scents, growth hormones, and specialised and unspecialised defence) have been studied primarily due to their biological importance. The production mechanisms for VOC emissions associated with these four categories have been described and are summarised by Guenther et al. (2000).

2.7.1.3.2 Environmental Influences on Emissions

A quantitative description of the environmental factors controlling biogenic emissions is needed for predicting regional emissions and how they might change. The progress made for each individual VOC is shown in Table 2.1. However, since each VOC can be emitted by more than one process, it is more convenient to discuss the environmental controls associated with the seven emission categories mentioned above.

IGAC-related research has resulted in significant advancements in descriptions of the factors controlling VOC emission, particularly isoprene, from chloroplasts. This has included the development of numerical algorithms that accurately describe short-term variations in emissions (Guenther et al. 1993). A general description of longer-term variations has been developed but

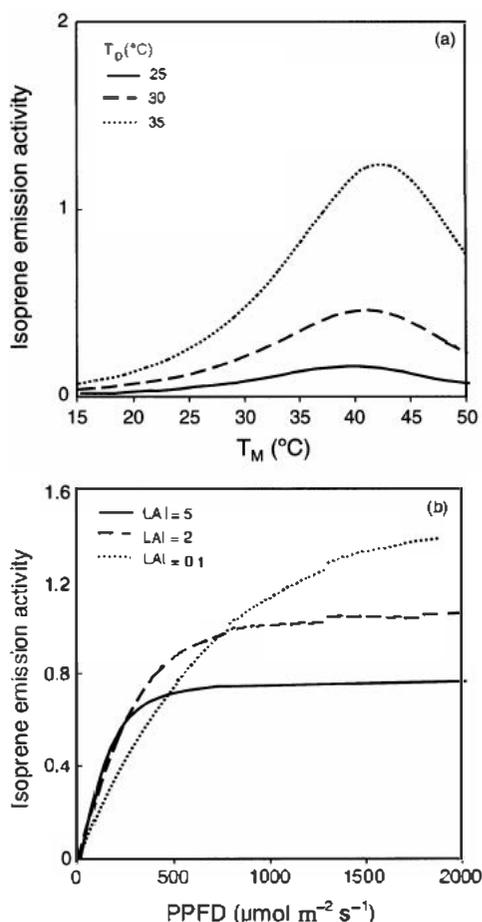


Fig. 2.9. Influence of a temperature, and b photosynthetic photon flux density (PPFD) on isoprene emission activity factors predicted by the algorithm described by Guenther et al. (2000). Temperature during the past 15 min (T_M) and temperature during the past 15 days (T_D) both influence isoprene emission. LAI is the cumulative leaf area index above a point in the canopy

an improved physiological and biochemical understanding is needed (Schnitzler et al. 1997; Guenther et al. 2000). It is known that the light response of shade leaves differs considerably from sun leaves and that the temperature that the plant has been exposed to in the past can influence its temperature dependence. This general understanding is illustrated by the response curves shown in Fig. 2.9.

Emission of stored monoterpenes from specialised defence structures results from the diffusion of compounds through the cell barrier around the resin vesicles or ducts. The amount released by this process at a given temperature is dependent on the nature of the compound, resistance properties of the cell layers, and other transport resistances within and outside of the leaf. As cell resistances and vapour pressure of the compound are temperature dependent, the emission source strength is strongly dependent on the temperature of the leaf. Recent advancements have been made in describing how the exponential increase in emissions with temperature is dependent on VOC compounds and the resistance properties of the plant.

The environmental controls over metabolic by-products, decaying and drying vegetation, plant hormones, floral scents, and unspecialised defence have not been characterised in a manner that is useful for emission modelling. Some of the primary controlling factors are known but there are no quantitative algorithms for simulating emission variations (Fall 1999; Kirstine et al. 1998; Guenther 1999). A significant obstacle to regional-scale extrapolation of these emissions is the need for databases of driving variables, e.g. temperature and irradiance intensity, which are currently unavailable.

2.7.1.3.3 *Production and Loss Mechanisms in the Plant Canopy*

Field experiments carried out within the frame of the EC-BEMA project (Valentini et al. 1997; Ciccioli et al. 1999) have shown that within-canopy losses are significant for VOCs that have atmospheric lifetimes comparable to the transport time from the canopy to the atmospheric boundary layer (ABL). Compounds with atmospheric lifetimes ranging between one and three minutes (ranked as -2 in Table 2.1) never reach the ABL whereas severe losses (>50%) are observed for compounds characterised by atmospheric lifetimes ranging between three and ten minutes (ranked as -1 in Table 2.1) (Ciccioli et al. 1999).

In addition to gas-phase reactions, adsorption and partition processes can also play an important role in removing emitted components inside the forest canopy. These effects can be particularly important in the case of polar compounds (such as alcohols and carboxylic acids) that are three orders of magnitude more soluble than isoprenoids in water droplets and stick on parti-

cles and surfaces. They have been invoked to explain the reduced flux of linalool from pine-oak forests and orange orchards.

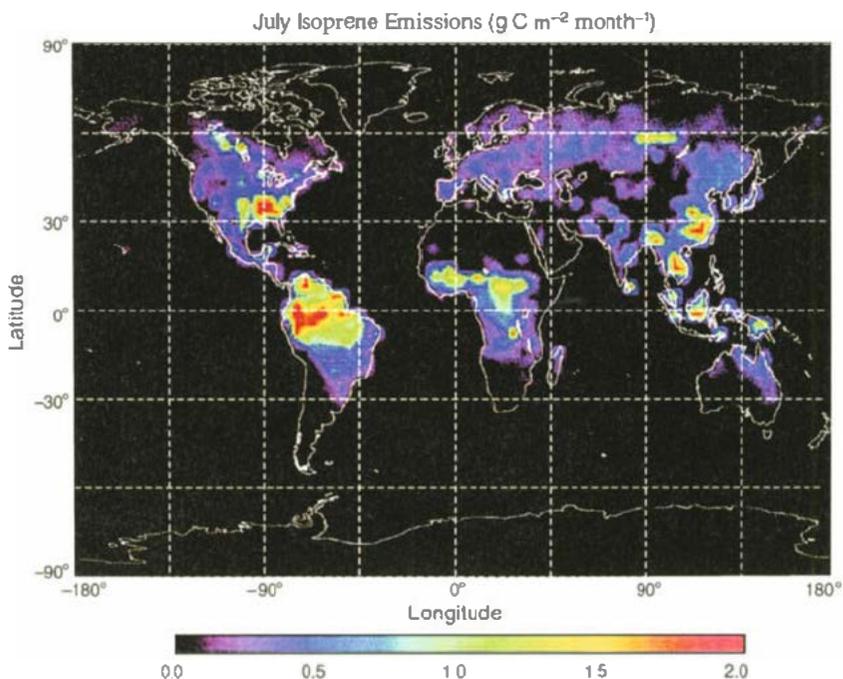
Degradation of VOCs in the canopy may lead to the formation of secondary organic aerosols (SOA), as mentioned earlier (see also Chap. 4), or gaseous products (mainly very volatile carbonyls) that can diffuse in the ABL. Photochemical degradation of VOCs has been suspected to be the main source of the huge fluxes of acetaldehyde, formaldehyde, and, partly, acetone from orange orchards. A substantial contribution to carbonyl fluxes can also arise from heterogeneous ozonolysis of lipids covering the leaf surface (Fruekilde et al. 1998), which can produce acetone, 6-methyl-5-hepten-2-one, and geranyl acetone as a function of the levels of ozone in air. Mesoscale modelling studies applied to a region north of Valencia, Spain (Thunis and Cuvelier 2000) have shown that secondary products formed by within-canopy reactions accounted for more than 70% of the ozone formed by biogenic emission from orange orchards. The complexity of within-canopy processes occurring in certain ecosystems can only be assessed by incorporating chemical processes into models describing the transport of VOCs into the ABL. At the present time, development of such models is made difficult by the fact that degradation pathways of primary products formed by photochemical reactions of mono- and sesquiterpenes are still unknown and it is not clear to what extent and in which conditions they can possibly nucleate to form SOA.

2.7.1.3.4 *Models of Emissions*

The IGAC-GEIA natural VOC project has compiled and synthesised the available information on biogenic VOC emissions and their driving variables into a global model that has been used to generate inputs for regional and global chemistry and transport models. The initial effort described by Guenther et al. (1995) provided monthly emissions of isoprene and three VOC categories (monoterpenes, other reactive VOC, less reactive VOC) with a spatial resolution of 0.5 degree of latitude/longitude. The global distribution of isoprene emissions predicted by this model for the month of July is illustrated in Fig. 2.10.

The model was constructed using the following information. Emission factors were based on the results of 20 studies that were primarily located at temperate forest field sites. Two emission types were utilised: isoprene emissions were estimated using current light and temperature conditions while all other emissions were assumed to be dependent on current temperature. Landcover characteristics were primarily based on values assigned to landscape types and a global database of current landcover distributions. Satellite (AVHRR) measurements were used to estimate monthly foliar

Fig. 2.10. Global distribution of isoprene emission rate estimates ($\text{g C m}^{-2}\text{month}^{-1}$) for July (Guenther et al. 1995)



variations. The model predicted annual emissions of about 500 Tg C of isoprene, 130 Tg C of monoterpenes, and slightly over 500 Tg C of other VOCs. These estimates are higher for isoprene and lower for monoterpenes in comparison with previous estimates. The differences are primarily due to an improved and expanded emission factor database.

Recent biogenic VOC observations have been incorporated into regional emission models for Europe (Simpson et al. 1999), Africa (Guenther et al. 1996, 1999) and North America (Guenther et al. 2000), and the IGAC-GEIA project is updating the global model. The regional totals tend to be within a factor of two of the Guenther et al. (1995) global model estimates but emissions for a particular location and time differ by more than a factor of five. Model improvements include a better chemical speciation, additional emission mechanisms, improved and expanded emission factors, better landcover characteristics and plant species distribution databases, improved canopy environment model, and higher spatial (1 km) and temporal (hourly) resolution.

2.7.1.3.5 VOCs and the Carbon Cycle

The emissions of VOCs are one pathway in the flow of carbon through plants and ecosystems. These emissions must be accounted for if the carbon balance of the system is to be accurately determined. The carbon balance of some systems is currently determined by the direct measurement of the incoming and outgoing CO_2 . For ecosystems, the balance determined by such measurements is known as the net ecosystem productivity and

reflects the change in carbon storage of the ecosystem. However this approach neglects the loss of carbon as VOCs. Estimates of the fraction that VOC emissions make up of the net carbon assimilated are 2 to 4% (Valentini et al. 1997; Kesselmeier et al. 1998; Crutzen et al. 1999). Given that the net ecosystem productivity is often only a small fraction (10%) of net carbon assimilation, the neglect of VOC emissions can cause errors of the order of 20 to 40% in the estimate of net ecosystem productivity and carbon storage. Fortunately, VOC emissions are being measured in some systems and more accurate values of net ecosystem productivity are being determined.

2.7.1.3.6 Global Change and the Ecology of Emissions

Three related aspects of global change have the potential to dramatically affect biogenic hydrocarbon emissions: increases in atmospheric levels of CO_2 , increases in surface temperatures, and changes in precipitation patterns. Increases in temperature and decreases in rainfall would both be expected to increase VOC emissions; however, there is little understanding of the magnitude of the change or whether acclimation would take place (Fuentes et al. 2000; Guenther et al. 2000). Plant species compositional change due either to climate change or land use change may result in changed VOC emissions. The direction of this change will be controlled by the phenology of the vegetation and the geographic region. Savannah areas that may undergo bush encroachment would produce higher VOC emissions with a different chemical signature.

Changes in air temperature, the length of the growing season, precipitation, and atmospheric CO₂ concentrations could lead to large changes in the VOC emissions from temperate latitude ecosystems. In tropical regions, little change may take place because plant leaves already may be near their optimal temperature for isoprene emissions. There are some suggestions that plants adapt to changing temperature regimes and that VOC emissions would also rise in the Tropics. It is also unclear if cultivating increased areas of genetically modified plants could alter the nature of VOC emissions significantly.

Changes in vegetation type can lead to large changes in VOC emissions. For instance, replacing C₃ grass species with C₄ types could change the direct emissions and emissions from the plant decay process. Current knowledge is inadequate, however, to quantify these changes. Woody plants (shrubs and sun tolerant trees) tend to have much higher isoprene and monoterpene emissions rates, compared to annual crops and grasses; therefore deforestation involving conversion of closed forest to grassland could greatly reduce biogenic VOC emissions. However, there is a tendency for higher emissions from the woody plants that replace a closed canopy forest (Klinger et al. 1998); therefore, the effect of conversion of closed forest to open woodland is unknown. Fire dominated systems in the more arid areas have suppressed woody plants and kept emissions low, but agricultural practices of grazing and fire suppression have allowed shrublands to spread with resultant increased emissions. The chestnut blight of the late nineteenth and early twentieth centuries on the US East Coast lowland forests caused massive change in forest composition with oak replacing the chestnut. Unlike oak, chestnut does not emit isoprene. The chestnut blight has thus resulted in an approximate doubling of the biomass of isoprene-emitting species (Lerdau et al. 1997).

2.7.1.4 Ammonia Emissions and Interactions with Particles

Terrestrial emissions of NH₃ are associated with animal waste, fertilisers, biomass combustion, soils, vegetation, and some other minor sources (Bouwman et al. 1997). The microbial breakdown of urea and uric acid present in animal waste produces ammonium, which subsequently partly volatilises as NH₃. The overall emission of NH₃ from waste is dependent on the specific N-excretion per animal, and the NH₃ loss during housing, storage of waste outside the stable, grazing, and application of manure on grassland or arable land. Further important properties influencing NH₃ volatilisation involve soil pH and moisture, and temperature. There is a pH-dependent equilibrium between NH₃ and NH₄⁺, with NH₃ being emitted from soils when they are alkaline.

Some northern European countries have measured and calculated country- and animal-specific emission factors. The applications of such emission factors to calculate animal related emissions elsewhere may be quite problematic, since agricultural practice and climatic factors may differ substantially from those in northern Europe. In addition, the number of animals per country may fluctuate strongly from year to year.

Dry deposition and reactions with acidic particles and particle precursor gases are the main removal mechanisms for NH₃ (see also Sect. 2.7.3). Oxidation chemistry of NH₃ is thought to play a relatively minor role (Dentener and Crutzen 1994). Because NH₃ emissions occur almost exclusively close to Earth's surface, and because plants utilise nitrogen in their metabolism, dry deposition is a very efficient process that may remove 40–60% of all emissions. Ammonia that has reacted with sulphuric or nitric acid to form NH₄⁺ is removed mainly by wet deposition and much less efficiently by dry deposition. It has an average residence time in the atmosphere of up to one week, in contrast to the much shorter residence time of gas phase ammonia, which is less than one day.

The understanding of the atmospheric NH₃ cycle is still limited, because:

- NH₃ emissions are estimated for most countries, rather than measured because of the difficulty of making such measurements (Fehsenfeld 1995).
- Emissions of NH₃ show a large spatial and temporal variability (e.g. farm-scale, winter-summer). Transport models of NH₃ and NH₄⁺ utilise larger grid scales and the temporal variability of NH₃ emissions is not accounted for in such models.
- Most models of NH₃ chemistry and transport are highly simplified and parameterised and may therefore produce results that may be spurious.
- Measurements of particulate NH₄⁺ are common, although their quality is frequently suspect; gas phase NH₃ data are scarcely available.

The comparison of models with such measurements is difficult since the measurements may not be representative for the model grid scale. This is especially the case for gas phase NH₃, which may have an atmospheric lifetime of hours. In addition, there may be substantial instrumental problems, e.g. the evaporation of ammonium nitrate from filter packs, which makes it difficult to interpret routinely performed aerosol measurements.

Wet deposition measurements of NH₄⁺ are relatively straightforward, and there are, at least in Europe and the US, substantial data sets available. However, these measurements may again not be representative for a larger model region. Also, discrepancies of model results and measurements may be due to a host of reasons, such as a poor representation of dry deposition, vertical mixing,

and in- and below-cloud scavenging or emissions. An evaluation of global model deposition with measurements in Europe and the US by Holland et al. (1999) indeed indicated substantial discrepancies but no single process could be identified as the cause of the problem.

Despite all uncertainties involved, several studies (e.g. Galloway et al. 1995) have indicated the significance of terrestrial NH_3 emissions for the global nitrogen cycle. Recent modelling studies (Adams et al. 1999; Metzger et al. 1999) indicated the potential significance of NH_4^+ and nitrate (NO_3^-) for aerosol burden and composition. These studies were performed using thermodynamic equilibrium models, developed originally for urban smog conditions. Substantial effort has been spent on extending these schemes to global modelling (e.g. Nenes et al. 1998).

A major challenge is presented by the need to increase the resolution of the models and develop sub-grid parameterisations that represent the variability of ammonia emissions and the resulting effect on particle composition. Long-term, representative, and reliable measurements of NH_3 , NH_4^+ , SO_4^{2-} , and NO_3^- are needed in conjunction with deposition measurements to constrain the NH_4^+ budget further.

2.7.1.5 Production and Consumption of N_2O and NO in Soils

Nitrogen oxides are produced in soils as obligate intermediates or by-products of the microbially mediated processes of nitrification and denitrification (Conrad 1996). The same environmental factors of soil temperature, nitrogen availability, and soil moisture affect the production of both nitrogen oxides. The pathways and enzymatic mechanisms of these processes were not well understood in the 1980s. The development of chemiluminescence instruments for NO measurement and reports in the late 1970s that increased use of nitrogen fertilisers could be one of the main causes of accumulation of nitrous oxide in the atmosphere, thus contributing to global warming, stimulated scientists to research the mechanisms involved (Firestone and Davidson 1989; Davidson and Kinglerlee 1997). The conceptual model offered by Firestone and Davidson in 1989, which has since become known as the “hole-in-the-pipe” (HIP) model, synthesised the information known at that time about the microbiological and ecological factors influencing soil emissions of NO and N_2O . The HIP model linked the two gases through their common processes of microbial production and consumption. It was a breakthrough in understanding factors controlling emissions and the model has stood the test of time. Ongoing testing of the model over the last decade with numerous data sets from temperate and tropical agroecosystems shows that it provides a sound ecological and mechanistic basis for interpreting temporal and spatial

variation at all scales of study by neatly encapsulating into two functions – nitrogen availability and soil water content – a large fraction of the variability caused by numerous environmental factors that influence the production and consumption of NO and N_2O by nitrifying and denitrifying bacteria (Davidson et al. 2000b).

Matson et al. (1989) stated that empirical models that are based on correlation analysis involving easily measured soil variables (e.g. temperature, moisture, texture, and organic carbon) often predict trace gas fluxes quite well. As data sets became more available, this set of variables has been further reduced to moisture and temperature with some corrections needed to take account of texture differences. Empirical relationships have been established for a number of different ecosystems around the world for both NO and N_2O emissions with water-filled pore space values of approximately 35% being the switch from NO to N_2O emissions. The magnitude of the emissions varies with substrate availability; the use of ^{15}N labelling techniques to measure the turnover of the soil ammonium and nitrate pools has greatly enhanced our capacity to partition nitrogen gas production among NO , N_2O , and N_2 . Trace gases are produced and consumed by defined reactions in individual microorganisms and control must be exerted at this level initially. To date, empirical models based on various physical and chemical parameters have been successful without considering the structure of the microbial community; even those models that differentiate between nitrification and denitrification neglect microbial community structure. It is still unknown whether microbial species diversity is an important factor especially if one considers changes associated with land use (Conrad 1996).

Soil mineral N, resulting from additions of synthetic N fertilisers and N from animal manure, crop residues, etc., and the mineralisation of soil organic matter and deposition from the atmosphere, is recognised as a major driver of these emissions. Much work has gone into establishing the relationships between the fluxes of N_2O and NO and the other key drivers, soil moisture and temperature. Although some questions remain to be answered, significant developments in this direction have been achieved. The logarithmic relationship between N_2O flux and soil water-filled pore space (WFPS) in a tropical forest soil is illustrated in Fig. 2.11a (Keller and Reiners 1994). A remarkably similar relationship has been found for temperate fertilised grassland, when mineral N was not limiting (Dobbie et al. 1999). These data can be contrasted with NO flux data (Fig. 2.11b) obtained from a semi-arid southern African savannah, where temperature and soil moisture are the major controlling factors on emissions. Multiple regression analyses reveal the following sequence of importance of environmental factors on NO flux: soil temperature > water-filled pore space > soil nitrate concentrations > soil ammonium concentrations (Otter et al. 1999) (see Box 2.2).

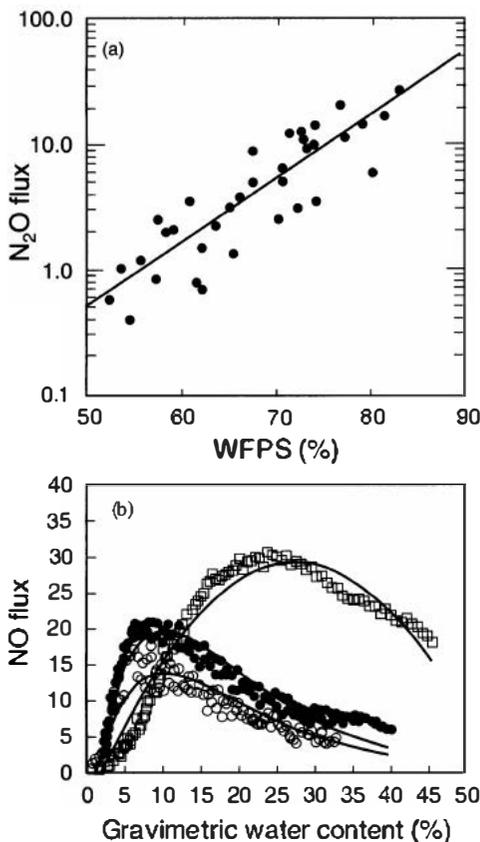


Fig. 2.11. a N₂O flux (ng N m⁻² s⁻¹) versus soil water filled pore space (WFPS), old-growth forest, Atlantic lowlands, and Costa Rica (Keller and Reiners 1994); b NO flux rate (ng N m⁻² s⁻¹) increases with gravimetric soil moisture to a maximum around field capacity (FC) for nutrient-poor (FC=7.5%) (white circles), nutrient-rich (FC=10.6%) (black circles), and floodplain (FC=27.1%) (squares) soils, and declines thereafter (Otter et al. 1999)

Continuous flux measurements are few and far between, with many more studies of N₂O than NO, mostly driven by the global warming community rather than the broader atmospheric community. Among the significant observations that have emerged from continuous N₂O flux studies over extended periods are: (a) the great variation in annual flux (from 20 to >200 Mg N₂O-N m⁻² yr⁻¹) that can occur from fertilised temperate grassland as a result of variations in the timing and amount of rainfall (Fig. 2.12); (b) the large proportion of the annual N₂O that can be derived from soil freezing/thawing events in winter, both in agricultural soils (Flessa et al. 1995; Kaiser et al. 1998) and in forest soils (Papen and Butterbach-Bahl 1999); and (c) that nitrification can be as important as denitrification in producing N₂O (Davidson et al. 1993; Panek et al. 2000). In hot dry environments, variations in the time elapsed between fertilisation, sowing, and irrigation of cereal crops have been shown to be almost as important (Matson et al. 1998).

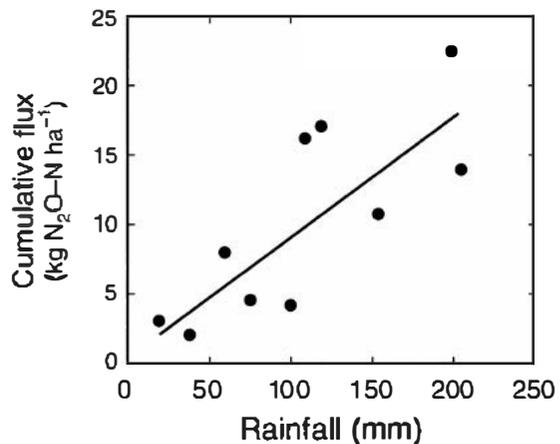


Fig. 2.12. Annual N₂O fluxes from intensively managed grassland in Scotland, UK, as a function of summer rainfall around times of N fertiliser application (Groffman et al. 2000, based on data in Dobbie et al. 1999)

Soil emissions contribute 70% and 20% of the global budgets of N₂O and NO respectively, with humid tropical forests accounting for 20–50% of all the global sources of atmospheric N₂O (Keller et al. 1986; Potter et al. 1996b; Verchot et al. 1999). Despite the different roles of N₂O and NO in the atmosphere and the many different reasons why scientists from several disciplines study one or the other gas, combining studies of the two gases and linking them mechanically in conceptual and empirical models makes good biological, ecological, and practical sense (Davidson et al. 2000b). At the outset of the IGAC project, tropical forest soils were considered to be the major contributor (3.2–7.7 Tg N yr⁻¹) of N₂O, with agricultural emissions being much smaller and more uncertain (0.03–3.0 Tg N yr⁻¹) (IPCC 1992). Rapid land use change in the Tropics was expected to result in markedly increased emissions. Early measurements of the flux of nitrous oxide from recently formed pastures in the Amazon basin showed a threefold increase relative to the flux from the original forest soil (Luizao et al. 1989). However, more recent work by Keller and Reiners (1994) shows that very large increases of soil N₂O emissions are only observed in young pastures compared with forests but that the periods of high emissions are limited to only about a decade following clearing. Thereafter, N₂O emissions from pastures fall below forest levels, probably as a result of the depletion of available nitrogen. In addition, data show that old-growth tropical forests have high fluxes, and young successional forests highly variable ones (Davidson et al. 2000b). However, Hall and Matson (1999) showed that in the presence of N deposition phosphorus-limited tropical forests exhibited enhanced emissions of N₂O; in addition, enhanced nitrogen inputs and irrigation in an intensively managed Mexican wheat system resulted in large emissions (Panek et al. 2000). There is now solid

Box 2.2. Impact of nitrogen fertiliser and deposition on nitrogen trace gas emissions

Worldwide consumption of synthetic N fertilisers has increased 20-fold since 1950 to about 82 Tg N yr⁻¹ in 1996 (Bouwman 1998). About 40% of current consumption is in the Tropics and subtropics, particularly in Asia, and is expected to rise to 60% by 2020 (Hall and Matson 1999). Animal wastes used as fertiliser supplied an estimated additional 65 Tg N yr⁻¹ in 1996, compared with 37 Tg N yr⁻¹ in 1950 (Mosier and Kroeze 1999), and this input is likely to increase in the future. The expected effect of the additional N use is a further major increase in N₂O from agricultural sources. These increases in N fertiliser use are also expected to raise the agricultural contribution to soil NO emissions to over 50% (Yienger and Levy 1995). In the IPCC (1999) assessment, direct emissions of N₂O from agricultural soils were taken to be 1.25 ± 1% of the N applied (Bouwman 1996), but a re-evaluation indicates that the observed emission factors are strongly skewed, giving an uncertainty range from one-fifth to five times the mean value, i.e., from 0.25% to about 6% of the N applied, and suggesting that the mean flux from this source may be even higher or lower than presently accepted. Recent data (Fig. 2.13) on N₂O and NO emissions from N fertilised and N-saturated systems in temperate regions give indications as to how global change and changing land management practices may be enhancing emissions. However, Hall and Matson (1999), raise the possibility that increasing nitrogen deposition in tropical regions is likely to have very different effects than nitrogen deposition in the temperate zone, with much greater feedbacks to the atmosphere (see Sect. 2.7.3).

Figure 2.13a and b show a remarkable similarity in graphs of N₂O emission vs. deposition and N₂O emission (nmol mol⁻¹) vs. fertiliser application for sites in Scotland. In a three-year continuous record study of nitrogen trace gas fluxes from untreated and limed soils of a N-saturated spruce and beech forest ecosystem in Germany (Fig. 2.13c and d) there was a significant positive correlation between the amount of *in situ* N input by wet deposition and magnitude of *in situ* N₂O and NO emissions (Papen and Butterbach-Bahl 1999; Gasche and Papen 1999). At the beech site, 10% of the actual N input was released from the soil in the form of N₂O whereas at the spruce site the fraction was 0.5%, indicating that forest type itself is an important modulator of N₂O release from soil. However, there is a marked similarity in the N₂O data obtained from Scotland and from Germany. Approximately 15% and 7% of the actual N input was lost as NO from the German soils stocked with spruce and beech, respectively. Liming resulted in 49% reduction of NO emissions as compared to an unlimed spruce control site. The results indicate that the reduction in NO emission was due to an increase in NO consumption within the limed soil. Liming of a spruce site resulted in a significant increase in ammonification, nitrification, and N₂O emissions as compared with an untreated spruce control site. On the basis of these results it was concluded that the importance of temperate and boreal forests for the global N₂O source strength may have been significantly underestimated in the past and that these forests, in which N deposition is high, most likely contribute in excess of 1.0 Tg N₂O-N and 0.3 Tg NO_x-N yr⁻¹ (Papen and Butterbach-Bahl 1999; Gasche and Papen 1999).

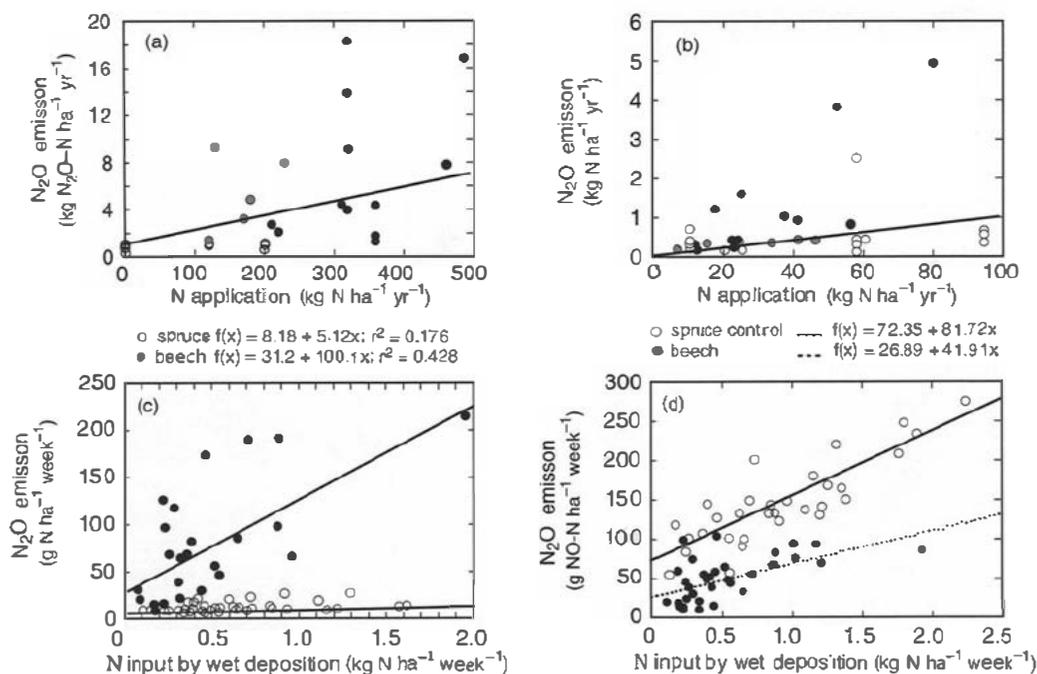


Fig. 2.13. Deviations of N-induced emissions of N₂O in Scotland from the IPCC "default" values. a Mineral N-induced emissions from grass (solid black circles), arable land with cereal crops (open circles), and arable land with non-cereal crops (grey-shaded circles), together with the IPCC default emission factor (1.25% of the N applied) (solid line) (Dobbie et al. 1999; Skiba and Smith 2000); b N deposition-induced emissions from forest and moorland soils downwind of poultry and pig farms (solid black circles), in large-scale acid mist experiments (open circles) and in upland areas (grey-shaded circles), together with the IPCC default emission factor (1% of the N applied) (solid line) (Skiba and Smith 1999); c linear regression analysis between *in situ* N input by wet deposition and *in situ* N₂O emission rates from soil of spruce and beech control sites. For correlation analysis, data for mean weekly N₂O emission rates and mean weekly N input (data from Huber 1997) by wet deposition measured in the throughfall were used (1994–1995) (Papen and Butterbach-Bahl 1999); and, d linear regression analysis between weekly mean NO emission rates and weekly amounts of N input (sum of ammonium and nitrate) by wet deposition (measured in the throughfall) (Huber 1997) at the spruce control and beech sites of the Högwald forest; data obtained in the time period January 1994 to December 1994 (spruce sites) and September 1994 to June 1995 (beech sites), respectively, were used for correlation analysis (Gasche and Papen 1999)

evidence that agricultural emissions of N_2O exceed those from the tropical forests (2.1 ± 1 Tg N yr^{-1} directly from agricultural soils, plus another 4.2 ± 2.1 Tg from animal production and from N leached from agricultural soils into surface and ground waters (Mosier et al. 1998)). However, management and environmental conditions play a major role in determining emissions from tropical and temperate systems. For example, in tropical pastures with a fertile loamy soil developed from volcanic ash, the fraction of fertiliser nitrogen lost as N_2O (6.8%) and NO (1.3%) was much higher than the loss percentages generally observed in temperate agricultural lands (about 1% and 0.5% for N_2O and NO respectively). On a banana plantation with similar soil, the loss percentages for N_2O and NO were 1.3–2.9% and 5.1–5.7%, respectively. In a fertilised sugar cane field in Hawaii and fertilised pastures with well-aerated soils in Puerto Rico, however, the percentage (1.1–2.5%) of fertiliser lost as N_2O came close to the loss rates generally observed in temperate regions (Bouwman 1996; Matson et al. 1996). There is still no clear cut answer; while some evidence indicates that emissions from land use change in the Tropics may be lower than originally expected, but increased fertiliser usage and nitrogen deposition may, yet again, lead to expectations of increased emissions.

Nitric oxide emissions are greatest from savannah areas of the world (Table 2.2). The greatest uncertainties lie with tropical grasslands and agricultural systems due to the difficulty in estimating land area and the extent of land use change. Emissions in sub-tropical regions are pulsed by rainfall, making annual integrations difficult. Data sets from natural regions converted to a variety of agro-ecosystems are few and there are indications that as data become available emission estimates will increase as shown in Table 2.2 when estimates pub-

lished in 1995 and 1997 are compared (Davidson and Kinglerlee 1997).

Adsorption of NO_x onto plant canopy surfaces may reduce emissions to the atmosphere to as low as 13 Tg N yr^{-1} , although the absorption effect is probably smaller than this. Measurements of NO_x exchange are complicated by the partial oxidation of NO to NO_2 , the presence of NO_2 as an atmospheric pollutant from other sources, and the deposition of NO_2 onto plant leaf and soil surfaces. Nitric oxide undergoes oxidation, mostly by reactions with ozone, to form NO_2 . This process begins immediately following NO emission from the soil. During upward transport through the plant canopy the NO_2 product may be partly deposited, resulting in a reduced NO_2 flux from the canopy. The presence of NO_2 from other sources can result in a net deposition, rather than emission, of this compound; this makes field flux measurements hard to interpret (e.g. Delany et al. 1986). Several attempts have been made to resolve this problem by modelling (Kramm et al. 1991; Vila-Gereau et al. 1995; Galmarini et al. 1997; Kirstensen et al. 1997), in particular by parameterising the vertical transfer of NO in terms of resistances (Chamberlain and Chadwick 1953) (see Sect. 2.6.1).

Several process-oriented models have been developed over recent years that simulate N trace gas emissions as part of more general simulations of C and N biogeochemical transformations in terrestrial ecosystems. Key examples are: DNDC (Li et al. 1992); CenturyNGAS (Parton et al. 1996); ExpertN (Engel and Priesack 1993); NLOSS (Riley and Matson 2000); CASA (Potter et al. 1996b); and DAYCENT (Parton et al. 2001). These and other models have been applied with varying degrees of success to the simulation of N_2O and NO emission data from contrasting temperate and tropical re-

Table 2.2. Comparison of NO estimates by biome (Tg NO-N yr^{-1}) (Davidson and Kinglerlee 1997)

Biome	Y and L ^a (no canopy)	D and K ^b (no canopy)	Y and L (W/canopy effect)	D and K (w/Y and L's canopy effect)
Tundra	0.02	0.1	0.02	0.0
Temperate grassland	0.52	1.1	0.34	0.7
Temperate woodland	0.09	4.7	0.05	2.9
Temperate forest	0.07	4.0	0.04	0.2
Temperate agriculture	1.82	1.8	1.33	1.0
Tropical grassland	2.50	7.4	1.60	4.3
Tropical woodland	0.39	5.0	0.22	0.3
Tropical dry forest	0.11	2.0	0.06	1.0
Tropical rainforest	3.4	1.1	0.85	0.3
Tropical agriculture	1.16	3.6	0.92	2.9
Deserts and semi-deserts	–	5.0	–	0.5
Total	10.2	21.0	5.45	13

^a Yienger and Levy.

^b Davidson and Kinglerlee.

gions. Uptake and emissions may occur simultaneously and models using unidirectional fluxes are no longer appropriate, yet they are still used widely. A modification of one of the models (Century), using a different trace gas production module, has also been used to simulate the important changes in N_2O and NO emissions that are associated with conversion of tropical rain forests to pastures. Modelled net increases in gas fluxes over the first 15 years after conversion were over 5 Gg N m^{-2} (a mean of $340 \text{ Gg N m}^{-2} \text{ yr}^{-1}$), of which N_2O accounted for 90% (Liu et al. 1999). The DNDC model has been applied in a modified form to N-limited pastures in Australia (Wang et al. 1997). The model estimates of annual N_2O emissions and N transformations agreed well with observations, for conditions where the N flows are an order of magnitude smaller than those in Northern Hemisphere midlatitude systems already modelled by DNDC (Li et al. 1992; Frolking et al. 1998). N_2O fluxes from N fertilised grassland in the UK (and those for cereal-growing sites in the same region) have been successfully predicted by a summary model based on relationships between flux and soil water-filled pore space, mineral N content, and temperature (Conen et al. 2000). The NLOSS model has been used to simulate nitrification and denitrification sources of N gases and has been tested against ^{15}N data from irrigated wheat systems in Mexico (Riley and Matson 2000). At the global scale, the CASA model uses satellite estimates of absorbed infrared radiation in combination with soils and climate databases to estimate N_2O fluxes as a proportion of N mineralisation in the soil (Potter et al. 1996b).

Groffman et al. (2000) have explored the relationships between annual, rather than hourly or daily, fluxes and ecosystem-scale variables such as plant community and soil type, and annual climate rather than field-scale variables such as soil moisture and temperature. They concluded that there are indeed coherent patterns in annual N_2O flux at the ecosystem scale in forest, cropland, and rangeland ecosystems, although these patterns vary by region and only emerge with continuous (daily or weekly) flux measurements over several years. An ecosystem approach to evaluating N_2O fluxes is useful for regional and global modelling and for computation of national N_2O flux inventories for regulatory purposes, but only if measurement programmes are comprehensive and continuous.

2.7.2 Biomass Burning

2.7.2.1 Introduction and History

Fire and its impact on Earth's atmosphere have been present ever since the evolution of land plants, some 350 to 400 million years ago. Before the advent of humans, fires were ignited naturally by lightning strikes, espe-

cially during dry periods. Today, however, fire is almost exclusively the result of human activities, such as the burning of forested areas for land clearing, of natural grasslands and savannas to sustain nomadic agriculture, of agricultural residues, and of biomass as fuel for cooking and heating. Even wildfires are frequently caused by human activities, e.g. camp fires, cigarettes, or sparks from engines. Natural wildfires play a significant role only in the boreal and savannah regions of the world. The return frequency of wildfires varies widely across the biomes of the world; for example, in savannas it is typically three to five years, whereas in boreal regions fire may recur only once every 500 years.

As a result of the increasing human impact on our planet, it is likely that the amount of biomass burned annually has strongly increased (by some 30–50%) over the past century, especially because of increasing tropical deforestation and domestic biofuel use. In some regions, such as Southeast Asia and Brazil, smoke from deforestation fires has been so intense in recent years as to cause serious health concerns. In principle, the fact that at present most vegetation fires are the result of human activities would imply the capacity to control and manage emissions from biomass burning better. Unfortunately, this has seldom been translated into government policy and even less often implemented effectively.

The first pioneering papers on the impact of biomass burning on the chemistry of the atmosphere were published in the late 1970s and early 1980s (e.g. Radke et al. 1978; Crutzen et al. 1979). Scientific interest in this topic grew when early estimates suggested that pyrogenic (i.e. fire-related) emissions of some atmospheric pollutants could rival or exceed those from fossil fuel burning (Crutzen and Andreae 1990). Further impetus to study biomass burning came from the discovery that pollution from pyrogenic emissions could affect large areas of the world as a consequence of long-range transport (Andreae 1983; Fishman et al. 1990; Reiche et al. 1986). The investigation of the role of biomass burning in atmospheric chemistry was therefore seen as a high priority when the objectives of IGAC were formulated in 1988.

Since the IGAC Biomass Burning Experiment (BIBEX) became active in 1990, research activity in this field has increased rapidly, and, over the last decade, fire has been recognised widely as a major source of important trace gases and aerosol particles to the global atmosphere. Following well-publicised large fire catastrophes in recent years and intensive scientific efforts over the last decade, the general public as well as the scientific community is now aware that emissions from biomass burning represent a large perturbation to global atmospheric chemistry, especially in the Tropics. Satellite and airborne observations have shown elevated levels of O_3 , CO , and other trace gases over vast areas of Africa, South America, the tropical Atlantic, the Indian Ocean, and the

Pacific Ocean. There is now also strong evidence that smoke aerosols perturb climate by scattering and absorbing sunlight and by influencing cloud microphysical processes.

We have also learned that the effects of burning are not limited to the emissions from the fires themselves, but that vegetation fires have pronounced effects on trace gas emissions from plants and soils. In the case of CO₂, NO, and N₂O, post-fire emissions may be more significant than the immediate pyrogenic release. Fire also alters the long-term dynamics of the cycling and storage of elements within terrestrial ecosystems, thereby changing their potential as sources or sinks of various trace gases. Finally, deposition of pyrogenic compounds onto tropical ecosystems may affect their composition and dynamics. In the following sections, we review some of the results and attempt to put them into the larger context of global change research.

2.7.2.2 Scientific Approach

Since the early 1990s, BIBEX has designed and carried out a number of biomass burning experiments in various ecosystems throughout the world, often in collaboration with other international programmes, particularly with other IGBP Core Projects. These experiments have produced extensive local-scale data on vegetation fire characteristics, emissions, and ecology, while simultaneous regional-scale measurements, using remote sensing and aircraft sampling platforms, have provided a capability to scale results up. Typically, these experiments have involved ground measurements on individual fires, airborne sampling and analysis of smoke plumes, and remote sensing of regional and global fire activity. Emphasis to date has been placed on tropical ecosystems, but an increasing number of experiments are now being organised in the boreal zone in response to climate change concerns.

STARE (Southern Tropical Atlantic Regional Experiment), with its two components SAFARI (Southern Africa Fire-Atmosphere Research Initiative) (see Box 2.3), and TRACE-A (Transport and Chemistry near the Equator) was the first large experiment coordinated by BIBEX. Conducted in 1992, STARE brought together scientists from many countries to investigate the chemical composition, transport, and fate of fire emissions originating from South America and southern Africa.

2.7.2.3 Land-Use Fires, Wildfires, and Domestic Biomass Burning: General Trends, Uncertainties, and Possible Changes

In the regional and global research activities on fire ecology and atmospheric chemistry, key questions have been

addressed: What is the current state of vegetation fires at the global scale? Are there quantitative and qualitative changes of vegetation fires compared to historic times? The baseload of natural fires and anthropogenic fires during evolutionary time scales has been determined by several factors: climate and vegetation changes, changes of land occupation, and cultural practices. The magnitude of historic and prehistoric vegetation burning remains largely unknown, however, because only fragmentary data obtained by case studies are available (summarised in Clark et al. (1997)). BIBEX research and other observations reveal uncertainties, recent changes, and new insights of fire occurrence in the following main vegetation zones.

Tropical evergreen forest. Deforestation statistics by the FAO and others in many studies have provided the baseline data for calculation of pyrogenic emissions due to land use change. While these numbers are useful for estimating the net release of carbon to the atmosphere, they do not reflect the entire spectrum of fire activities. Recurrent fires following the initial deforestation burns not only present additional emission pulses but also lead to impoverishment of forest ecosystems resulting in reduced above- and below-ground phytomass (Goldammer 1999a; Nepstad et al. 1999). Extreme climate variability such as the ENSO-related droughts of 1982–1983 and 1997–1998 favour the application of fire for land use change and maintenance of agricultural systems and facilitate the spread of uncontrolled fires (wildfires) in humid tropical ecosystems that under average climate conditions are subjected to less fire. The area burned by wildfire in the Indonesian and Malaysian provinces on Borneo Island in 1982–1983 covered ca. 5×10^6 ha, and in 1997–1998 land use fires and wildfires combined burned ca. $8\text{--}9 \times 10^6$ ha in Indonesia alone.

Tropical savannas and open seasonal forests. Assessments made in the early 1990s on the average annual amount of savannah phytomass burned were in the range of $3\text{--}4 \text{ Pg yr}^{-1}$ (Andreae 1993). Model predictions on the savannah area annually burned ranged between $750 \times 10^{10} \text{ m}^{-2} \text{ yr}^{-1}$ (Hao et al. 1990) and $1500 \times 10^{10} \text{ m}^{-2} \text{ yr}^{-1}$ (Goldammer 1993). More detailed studies on fire regimes and fuel loads in Africa point towards lesser amounts of regional and global combustion of savannah phytomass (Menaut et al. 1991; Scholes et al. 1996). Recent and ongoing growth of rural populations and intensity of land use involves landscape fragmentation and competitive utilisation of phytomass for grazing and domestic burning (biofuel use) and may represent a reason for a decrease of fire activities in tropical savannas and open forests; desertification in the sub-Saharan Sahel zone of Africa and other regions leads to a reduction and discontinuity of fuel loads and wildfire occurrence.

Box 2.3. Case study: SAFARI-92

The following example from the SAFARI-92 campaign (Lindesay et al. 1996) highlights the scientific approaches used to test hypotheses and validate models related to biogenic and biomass burning emissions and depositions. It is approaches like these that have allowed for an integrated understanding of the magnitude and controllers of sources, sinks, and exchange processes. During SAFARI-92, experimental vegetation fires were set and studied in the Kruger National Park, South Africa, and at some sites in Zambia and Swaziland. These experiments provided a broad set of data on trace gases and aerosol emissions, from which emission factors for fires in dry savannas and related biomes could be derived. The relationships between fuel characteristics, burning conditions, and fire behaviour were elucidated.

Regional studies on atmospheric chemistry and air mass transport showed that savannah fires in southern Africa account for a substantial amount of photochemical oxidants and haze over the subcontinent. These studies also showed that the export of smoke-laden air masses contributes strongly to the burden of ozone and other trace gases and aerosols over the tropical ocean surrounding Africa. However, results also showed that biogenic soil emissions severely impacted atmospheric chemistry. Investigations on the relationships among fire, soil moisture status, and soil trace gas emissions showed that soil moisture played a crucial role but that fire history also had an important influence on the emission of several trace gases. Figure 2.14a shows the relationship among daily NO emissions and nitrate concentrations plotted against water-filled pore space. Figure 2.14b describes the relationship between NO emission rate and nitrification rate in areas where fire has been excluded and in areas where the vegetation has been burned every two years (Parsons et al. 1996). These relationships were later incorporated into a simulation model to predict NO emissions from semi-arid savannas thereby reducing the large uncertainty associated with the magnitude of previous savannah measurements (Otter et al. 1999).

Remote sensing studies confirmed that Advanced Very High Resolution Radiometry/Land Aerial Cover (AVHRR/LAC, 1 km) imagery was a useful tool for fire monitoring in the region. In combination with biomass models, the remote sensing data could be used for the estimation of the seasonal and geographical distribution of pyrogenic emissions. The results from SAFARI-92 confirmed that it is justified to consider biomass burning as a significant contributor to the overall increase in greenhouse gases that has occurred over the last 150 years, accounting for some 10–25% of current estimates (Andreae 1993).

In order to establish accurately the global budgets of trace gases, reliable source strength and distribution estimates are needed. At present, the uncertainties associated with budget calculations are necessarily large, owing to the often-inadequate quantification of individual sources and the problems associated with extrapolating from a number of poorly known sources to achieve a global estimate. The contribution of vegetation fires in the savannah regions of southern Africa has been such a poorly quantified source, despite the fact that savannas are recognised as one of the most significant biomes in terms of global biomass burning emissions (Andreae 1993) and that a large portion of the savannah burns each year. It will now be possible to refine these estimates on the basis of results obtained from SAFARI-92. Modelling studies incorporating the emission data, meteorological information, and the chemical measurement data obtained during these campaigns indicate that the fires on the African and South American continents are indeed a major source of the gas-

eous and particulate pollutants, particularly ozone, found in the troposphere over the study regions (Thompson et al. 1996a). Data from airborne observations (Fig. 2.15) aboard a DC-3 using a combination of spectrometers and chemiluminescence instruments, showed that episodic pyrogenic emissions were not adequate to account for the buildup of tropospheric ozone in the region but that the continuous production of biogenic NO_x emissions and especially the amounts produced at the start of the rainy seasons have important consequences for regional scale ozone formation (Harris et al. 1996). The vertical distribution of NO₂ and NO as well as that of CO₂ showed markedly different characteristics. All three compounds have a strong gradient toward higher values near the ground, and the CO₂ and NO_x mixing ratios correlated linearly. The anticorrelation of the profiles of these compounds with that of CO rules out biomass burning as a source of the observed NO_x and CO₂ near the ground, supporting the field evidence of no active fires in the region. It was concluded that the source of the elevated NO_x mixing ratios near the surface was biogenic emission from the soil (Harris et al. 1996).

SAFARI-92 was an innovative project in many ways. In addition to being the largest international, interdisciplinary investigation of biomass burning and its atmospheric emissions, it also represented the first time that a large-scale fire emission measurement campaign included, as integral components: the characteristics of the biomass, the fire ecology, the fire dynamics in the area, the biogenic emissions, and the long-range transport of the aerosols and particulates.

As a follow-up to SAFARI-92, a much smaller experiment, SAFARI-94, was organised by BIBEX to investigate the composition of trace gases in the troposphere over Africa outside the burning season. EXPRESSO (Experiment for Regional Sources and Sinks of Oxidants), designed primarily to investigate the exchange fluxes of trace gases between the tropical biosphere and atmosphere, took place in the Congo Basin in 1996–1997 (Delmas et al. 1999). In 1997, AFARI-97 (African Fire-Atmosphere Research Initiative) was carried out in Kenya, investigating the atmospheric effects of fires occurring in the fertile savannas of East Africa. At the same time, an experiment designed to quantify aerosol and trace gas fluxes from the Miombo woodlands of southern Africa was initiated. ZIBBEE (The Zambian International Biomass Burning Emissions Experiment) began in 1997 and is ongoing. At the present time, BIBEX is heavily involved in the planning of two large tropical fire-atmosphere experiments: SAFARI-2000 is studying the transport and climatic effect of biogenic, pyrogenic, and anthropogenic emissions in southern Africa, while IBA (The Large Scale Biosphere-Atmosphere Experiment in Amazonia) is investigating the climatological, ecological, biogeochemical, and hydrological functioning of Amazonia, and the sustainability of development in this region.

In the boreal zone, BIBEX has been involved in the development of research programs addressing the role of fire in boreal ecosystems and its consequences for the global atmosphere and climate. FIRESCAN (Fire Research Campaign Asia-North) conducted the first joint Russian-western experimental fire in central Siberia in 1993, and continues with the planning of further such under the auspices of the IGBP Northern Eurasia Study (FIRESCAN Science Team 1996). In addition, BIBEX is active in ICFMB (The International Crown Fire Modeling Experiment), a series of high-intensity experimental crown fires carried out in the Canadian Northwest Territories during the 1997–2000 period for the purpose of developing a physical model of crown fire initiation and propagation.

Areas of Mediterranean and temperate vegetation. Mediterranean forest and shrub vegetation, including Californian chaparral and South African fynbos, are increasingly converted to suburban residential use. The consequent suppression of natural and human-caused wildfires results in a buildup of fuels that often cannot

be burned by prescribed fires. High-intensity wildfires are an inevitable consequence of fire suppression in these ecosystems. However, there is no indication of change in the average area burned in the recent decade. In the industrial countries of the temperate region the application of fire in non-forest land use systems has

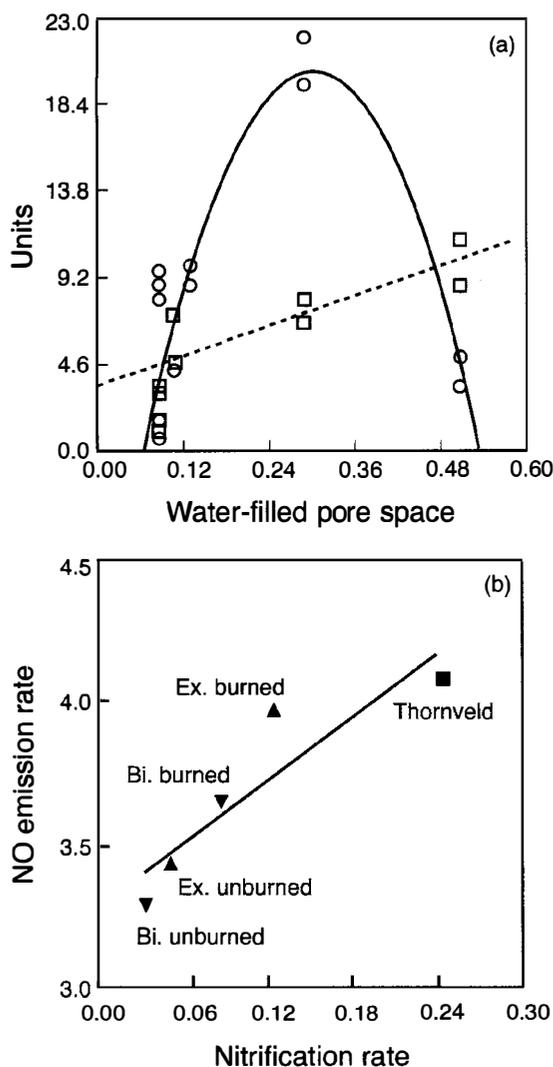


Fig. 2.14. a Mean daily NO emissions ($\text{ng N-NO m}^{-2} \text{s}^{-1}$, circles) and NO_3 concentrations ($\mu\text{g N-NO}_3 \text{g}^{-1}$ dry soil, squares) in the fire exclusion plots, plotted against water-filled pore space simulated using the HotWet model. Solid and dashed lines represent fitted functions to the NO emissions and NO_3 concentrations, respectively; b Mean NO emissions ($\text{ng N-NO m}^{-2} \text{s}^{-1}$) measured by Parsons et al. (1996) and Levine et al. (1996) plotted against mean nitrification rate (mg N kg^{-1} dry soil) measured in the corresponding plots. Linear function: $\text{NO emission rate} = 0.04 (\text{nitrification rate}) + 0.003$, $r^2 = 0.911$, $P < 0.030$, $n = 5$

been eliminated (e.g. in Europe) or is subject to legal restrictions due to air pollution and traffic risks (e.g. in North America). Natural and human-caused wildfires in temperate forests are usually suppressed. Prescribed burning in forestry has been receiving more attention in the US where it is envisaged to expand the prescribed burned area under the jurisdiction of the USDA Forest Service to $1.2 \times 10^{10} \text{ m}^{-2}$ by 2010 (Haines et al. 1998).

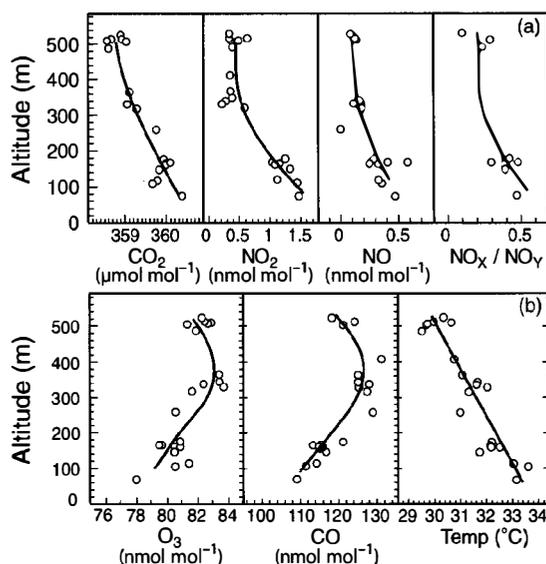


Fig. 2.15. a Vertical profiles of CO_2 , NO_2 , and NO and the ratio $\text{NO}_x / \text{NO}_y$ measured in the SAF11 profile during SAFARI 92 (Harris et al. 1996); b Vertical profiles of ozone, CO, and temperature measured during SAFARI on September 28, 1992 (Harris et al. 1996)

Temperate-boreal steppe-forest ecotones. A typical region representing the steppe-forest fire environment is central Asia. Recent remotely sensed data from Mongolia indicate that in the past years political and socio-economic changes in the country were responsible for a sharp increase in the area burned by wildfires. In 1996 and 1997 more than $10 \times 10^{10} \text{ m}^{-2}$ and $12 \times 10^{10} \text{ m}^{-2}$ burned in the grass steppes and adjoining coniferous forests (Goldammer 1999b).

Boreal forest. More than 70% of the global boreal forest area is located in Russia. Fire statistics published after the dissolution of the USSR indicate that more than 650 000 ha of forests were burned annually. This number most likely is still an underestimation. In the period 1990–1996, burn areas totalling more than $1.12 \times 10^{10} \text{ m}^{-2} \text{ yr}^{-1}$ were recorded (Stocks et al. 1999, 2000). Satellite imagery revealed that a large area was burning in central Siberia during the 1987 fire season, totalling ca. $10 \times 10^{10} \text{ m}^{-2}$ (Cahoon et al. 1994). While the fire exclusion policy of the USSR reduced the area burned by natural fires, the scale of human-caused fires increased over the same period. Current economic problems resulting in a weakening of the fire control system in Russia are responsible for a recent increase in area burned.

In Canada, detailed forest fire statistics have been archived since 1920 and, within limits, this extensive record permits a general analysis of trends in this country (Stocks et al. 1999). Fire occurrence has increased rather steadily from approximately 6 000 fires annually in the 1930–1960 period, to almost 10 000 fires during

the 1980s and 1990s. This is due to a growing population and increased forest use, but also reflects an expanded fire detection capability. During the 1981–1996 period an average of 9 246 fires annually burned over an average of $2.5 \times 10^{10} \text{ m}^{-2}$ in Canada, with the annual area burned fluctuating by an order of magnitude ($0.76\text{--}7.28 \times 10^{10} \text{ m}^{-2}$). Lightning accounts for 35% of Canada's fires, yet these fires result in 85% of the total area burned, due to the fact that lightning fires occur randomly and therefore present access problems usually not associated with human-caused fires, with the end result that lightning fires generally grow larger, and detection and control efforts are often delayed. In addition, the practice of "modified" or "selective" protection in remote regions of Canada results in many large fires in low-priority areas being allowed to perform their natural function.

Domestic biofuel use. Plant biomass provides about 14% of the world's demand of primary energy. Half of the global population meets an average of 35% of its energy needs by domestic biomass burning. In Africa, for example, the biomass contribution to the total energy use typically ranges from 90–100% in poor, 55–65% in middle, and 30–40% in high income groups. Unlike free-burning vegetation fires, which are usually restricted to a few months during the dry season, domestic biofuel combustion takes place during the whole year (Marufu et al. 2000).

Summary assessment of trends in global vegetation fire occurrence. The trends of changing fire occurrence and fire regimes are not uniform. Qualitative and quantitative data on fire occurrence and fire effects are still insufficient to determine reliably the amount of phytomass burned in all eco- and land-use systems worldwide. However, improved remote sensing capabilities and rigorous fire detection algorithms now provide regional fuel load and burning estimates within a much narrower range of uncertainty. Fire in boreal and tropical forests and the resulting ecological effects play a potentially critical role in determining the rate of global climate change (Goldammer and Price 1998; Stocks et al. 2000; Nepstad et al. 1999). Changes in the carbon balance of these two forest biomes could strongly influence global warming through impacts on atmospheric CO_2 . The implications of regional circumpolar changes of climate and fire regimes on boreal ecosystem properties, permafrost changes, and the release of gas and carbon stored in organic terrain and ice must be further addressed by research.

2.7.2.4 Characterisation of Emissions

A central objective of BIBEX was to characterise and quantify the production of chemically and radiatively

important gases and aerosol compounds from biomass burning. To meet this goal, the BIBEX scientific community has produced a large set of measurements that describe qualitatively and quantitatively the pyrogenic emission of gases and aerosols. The results show that the composition of fire emissions is mainly determined by two factors: the elemental composition (carbon, nitrogen, sulphur, halogen, minerals, etc.) of the biomass fuel, and the relative contribution of flaming and smouldering combustion in the vegetation fires.

Heating of vegetation fuels produces combustible gases by pyrolysis and volatilisation of waxes, oils, etc. Sustained flaming conditions are obtained when the vegetation reaches a temperature of about 600 K. Smouldering combustion involves heterogeneous reactions of atmospheric oxygen with solid fuel. The combustion type dominating in a given fire is influenced by the water content, the density and structure of the fuel, the oxygen availability in intense flaming, and the meteorological conditions prevailing during the fire.

Generally, emissions from fires occurring in natural vegetation are a mixture of compounds from flaming and smouldering combustion, with different proportions being typical of the various types of fires. The major part of savannah and domestic fuels is consumed in the flaming stage, while charcoal making is a purely smouldering process; forest biomass is combusted about equally by both processes. Lobert et al. (1991) summarised the composition of emissions released during the different burning stages. Relatively oxidised compounds, such as CO_2 , NO , NO_2 , SO_2 , N_2O , as well as N_2 and elemental carbon particles are emitted during the flaming stage of a fire. The emission of more reduced compounds (CO , CH_4 , nonmethane hydrocarbons, PAH, NH_3 , HCN, CH_3CN , amines, CH_3Cl , H_2S , COS, DMS, and organic particles) occurs during the smouldering stage (e.g. Lobert et al. 1991; Yokelson et al. 1997).

2.7.2.5 Emission Ratios and Emission Factors for Different Chemical Compounds from Fires in Various Ecological Systems or Vegetation Types

To express the emission of trace gases and aerosols from fires quantitatively, we use the concept of emission ratios and emission factors. These parameters relate the emission of a particular compound of interest to that of a reference compound, such as CO_2 or CO (emission ratio), or to the amount of fuel burned (emission factor). Emission ratios are obtained by dividing the excess trace compound concentrations measured in a fire plume by the excess concentration of a simultaneously measured reference gas, such as CO_2 or CO. To obtain "excess" concentrations, the ambient background concentrations must be subtracted from the values meas-

ured in the smoke. For example the emission ratio of methyl chloride, CH₃Cl, relative to CO is:

$$ER_{\text{CH}_3\text{Cl}/\text{CO}} = \frac{\Delta\text{CH}_3\text{Cl}}{\Delta\text{CO}} = \frac{(\text{CH}_3\text{Cl})_{\text{Smoke}} - (\text{CH}_3\text{Cl})_{\text{Ambient}}}{(\text{CO})_{\text{Smoke}} - (\text{CO})_{\text{Ambient}}}$$

The various techniques for these calculations and the associated errors are discussed in Le Canut et al. (1996). For gases, the results are expressed in terms of molar ratios. For aerosols, emission ratios are usually given in units of mass of aerosol per kg carbon in the form of CO₂ (g kg⁻¹ C(CO₂)). In this chapter, all results will be presented after conversion to emission factors (see below).

The selection of CO or CO₂ as reference gas is determined by the ultimate objective of the analysis and on the fire phase (flaming or smouldering) during which the compound is preferentially released. For compounds emitted predominantly in the smouldering stage of fires, CO is a suitable reference gas as it is also emitted predominantly during this stage. Close correlations between derived-derived gases and CO can usually be obtained, which allows fairly accurate estimation of trace gas emissions from fires for which the CO emission is known. For compounds containing nitrogen or halogen elements, the emission ratio relative to CO is also dependent on fuel composition, i.e. the nitrogen or halogen element content of the fuel.

Flaming-derived compounds correlate well with CO₂, while correlations of derived-derived gases with CO₂ tend to be relatively poor because the variation in the relative proportion of flaming versus smouldering combustion between different fires or even different parts of the same fire results in variable trace gas to CO₂ ratios. On the other hand, the emission ratio relative to CO₂ permits the estimation of trace gas emission from fires based on the amount of biomass burned, because most of the biomass carbon is released as CO₂. Therefore this ratio is the most suitable for regional or global estimations; however, it is worth noting that when multiple ratios are used to estimate emissions, errors are propagated making overall estimates quite uncertain.

Another parameter frequently used to characterise emissions from fires is the emission factor, which is defined as the amount of a compound released per amount of fuel consumed (g kg⁻¹ dm; dm: dry matter). Calculation of this parameter requires knowledge of the carbon content of the biomass burned and the carbon budget of the fire (usually expressed as combustion efficiency, see Ward et al. 1996); both parameters are difficult to establish in the field as opposed to laboratory experiments where they are readily determined. Where fuel and residue data at the ground are not available, a fuel carbon content of 45% is usually assumed in order to derive emission factors from emission ratios.

During the various BIBEX field experiments, and in other studies over the last decade, a large number of

emission ratios/factors have been determined. Recently, these data have been compiled into a coherent set of recommended emission factors (Andreae and Merlet 2001). In Table 2.3 we present emission data from this compilation for selected gaseous and particulate emission products and for the most important types of fire regimes (savannas and grasslands, tropical forest, ex-tropical forest, domestic biofuel burning, charcoal combustion, and agricultural waste burning). These emission factors are based on an analysis of some 130 publications, a large fraction of which were produced as a result of BIBEX campaigns. The values given are means and standard deviations wherever possible; when only two values for an emission factor are available in the literature, these two values are given as a range, and where only a single measurement is available, it is given without an uncertainty estimate. It is evident from this compilation that only for savannah fires do we have adequate data for most compounds, whereas for other fire types only the emissions of some key compounds have been satisfactorily determined. The release of compounds for which data are missing for a given type of fire can, however, be estimated by scaling emissions to CO or CO₂.

2.7.2.6 Emissions from Global Biomass Burning

Estimation of the amounts of trace substances emitted from biomass burning requires knowledge of both the emission factors (i.e. the amount of trace substance per amount of fuel combusted) and the actual amount of fuel burned. We have shown above that the emission factors for many important compounds, such as CO and CH₄, are now fairly well known, with a typical uncertainty of about 20–30%. In spite of this progress, large uncertainties persist for regional and global fire emissions because of the difficulties inherent in estimating the amount of biomass burned. In particular, there are differences of as much as an order of magnitude in regional estimates based on estimates of typical fire frequencies in the various vegetation types, and those based on actual fire counts obtained from remote sensing. These issues will be discussed in more detail in Sect. 2.6.2.7. Table 2.4 provides a summary of estimates made over the last decade using the former approach. In the following paragraphs, we discuss global emissions for key compounds based on the emissions factors in Table 2.3 and the biomass burning estimates of Logan and Yevich (R. Yevich, personal communication 2001) given in Table 2.4 (also see Andreae and Merlet (2001) for further information).

Carbon compounds. CO₂ is the major carbon compound emitted and accounts on average for about 80–90% of the mass of carbon burned, ca. 3 650 Tg C(CO₂) yr⁻¹. CO represents around five to eight percent of the carbon burned, ca. 300 Tg C(CO) yr⁻¹. Hydrocarbon (methane

Table 2.3. Emission factors for selected gases and aerosols for different forms of biomass burning (in g species per kg dry fuel burned)

Species	Savanna and grassland	Tropical forest	Extratropical forest	Biofuel burning	Charcoal burning	Agricultural residues
CO ₂	1613 ±95	1580 ±90	1569 ±131	1550 ±95	2611 ±241	1515 ±177
CO	65 ±20	104 ±20	107 ±37	78 ±31	200 ±38	92 ±84
CH ₄	2.3 ±0.9	6.8 ±2.0	4.7 ±1.9	6.1 ±2.2	6.2 ±3.3	2.7
NMHC	3.4 ±1.0	8.1 ±3.0	5.7 ±4.6	7.3 ±4.7	2.7 ±1.9	–
C ₂ H ₂	0.29 ±0.27	0.21–0.59	0.27 ±0.09	0.51–0.90	0.05–0.13	–
C ₂ H ₄	0.79 ±0.56	1.0–2.9	1.12 ±0.55	1.8 ±0.6	0.46 ±0.33	–
C ₂ H ₆	0.32 ±0.16	0.5–1.9	0.60 ±0.15	1.2 ±0.6	0.53 ±0.48	–
C ₃ H ₄	0.022 ±0.014	0.013	0.04–0.06	–	–	–
C ₃ H ₆	0.26 ±0.14	0.55	0.59 ±0.16	0.5–1.9	0.13–0.56	–
C ₃ H ₈	0.09 ±0.03	0.15	0.25 ±0.11	0.2–0.8	0.07–0.30	–
1-butene	0.09 ±0.06	0.13	0.09–0.16	0.1–0.5	0.02–0.20	–
<i>i</i> -butene	0.030 ±0.012	0.11	0.05–0.31	0.1–0.5	0.01–0.16	–
<i>n</i> -butane	0.019 ±0.09	0.041	0.069 ±0.038	0.03–0.13	0.02–0.10	–
Isoprene	0.020 ±0.012	0.016	0.10	0.15–0.42	0.017	–
Benzene	0.23 ±0.11	0.39–0.41	0.49 ±0.08	1.9 ±1.0	0.3–1.7	0.14
Toluene	0.13 ±0.06	0.21–0.29	0.40 ±0.10	1.1 ±0.7	0.08–0.61	0.026
Methanol	–	–	2.0 ±1.4	–	–	–
Formaldehyde	0.26–0.44	–	2.2 ±0.5	0.13 ±0.05	–	–
Acetaldehyde	0.50 ±0.39	–	0.48–0.52	0.14 ±0.05	–	–
Acetone	0.25–0.62	–	0.52–0.59	0.01–0.04	–	–
Benzaldehyde	0.029	0.027	–	0.02–0.03	–	0.009
Furan	0.095	–	0.40–0.45	–	–	–
2-methyl-furan	0.044–0.048	0.17	0.47	–	–	0.012
Furfural	–	–	0.29–0.63	0.22	–	–
Acetonitrile	0.11	–	0.19	–	–	–
Formic acid	–	–	2.9 ±2.4	0.13	–	0.22
Acetic acid	–	–	3.8 ±1.8	0.4–1.4	–	0.8
H ₂	0.97 ±0.38	3.6–4.0	1.8 ±0.5	–	–	–
NO _x (asNO)	3.9 ±2.4	1.6 ±0.7	3.0 ±1.4	1.1 ±0.6	3.9	2.5 ±1.0
N ₂ O	0.21 ±0.10	–	0.26 ±0.07	0.06	–	0.07
NH ₃	0.6–1.5	–	1.4 ±0.8	–	–	–
HCN	0.025–0.031	–	–	–	–	–
SO ₂	0.35 ±0.16	0.57 ±0.23	1.0	0.27 ±0.30	–	–
COS	0.015 ±0.009	–	0.030–0.036	–	–	0.065 ±0.077
CH ₃ Cl	0.075 ±0.029	0.02–0.18	0.050 ±0.032	0.04–0.07	0.012	0.24 ±0.14
CH ₃ Br	0.0021 ±0.0010	0.0078 ±0.0035	0.0032 ±0.0012	–	–	–
CH ₃ I	0.0005 ±0.0002	0.0068	0.0006	–	–	–
PM _{2.5}	5.4 ±1.5	9.1 ±1.5	13.0 ±7.0	7.2 ±2.3	–	3.9
TPM	8.3 ±3.2	6.5–10.5	17.6 ±6.4	9.4 ±6.0	–	13
TC	3.7 ±1.3	6.6 ±1.5	6.1–10.4	5.2 ±1.1	6.3	4.0
OC	3.4 ±1.4	5.2 ±1.5	8.6–9.7	4.0 ±1.2	4.8	3.3
BC	0.48 ±0.18	0.06 ±0.31	0.56 ±0.19	0.59 ±0.37	1.5	0.69 ±0.13
K	0.34 ±0.15	0.29 ±0.22	0.08–0.41	0.05 ±0.01	0.40	0.13–0.43

Table 2.4. Biomass burning estimates in Tg dry mass per year

	Crutzen and Andreae 1990	Andreae 1993	Hao and Liu 1994	Liousse et al. 1996	Logan and Yevich 2001
Tropical forest	1 560– 3800	1260	1820	1260	1330
Extratropical forest	–	1150	–	–	640
Savanna and grassland	670 – 3600	3690	2670	2680	3160
Domestic biomass fuel	670 – 1300	1960	620	1380	2900
Agricultural waste	1 100 – 1 800	850	280	300	540
Total	4000–10400	8910	5390	(5620)	8600

+ non-methane hydrocarbons) emissions range around 66 Tg C. Carbonaceous particulate matter emissions are estimated to be around 42 Tg C in organic compounds and 4.8 Tg of black carbon per year.

Nitrogen compounds. Emissions of nitrogen compounds are closely related to fuel composition and combustion type. Linear relationships have been found between the emissions of N_2O (Lobert et al. 1991) and NO_x (Lacaux et al. 1993) and the fuel nitrogen content. The release of NO , N_2O , and molecular N_2 occurs predominantly during flaming combustion, while NH_3 , amines, and nitriles are related to smouldering combustion. NO_x emissions from biomass burning are estimated at $9.7 \text{ Tg N}(\text{NO}_x) \text{ yr}^{-1}$. The emission of N_2 , which accounts for about one-third of the fuel nitrogen released, represents a conversion of fixed nitrogen to atmospheric N_2 , and consequently a loss of nitrogen available as a nutrient ("pyrodenitrification", Kuhlbusch et al. 1991). Little information is available on organic nitrogen released or the organic carbon:nitrogen ratios.

Sulphur compounds. Because of the relatively low sulphur content of biomass compared to fossil fuels, SO_2 emissions from biomass burning make only a small contribution to the atmospheric sulphur budget (ca. $1.7 \text{ Tg S}(\text{SO}_2) \text{ yr}^{-1}$). On the other hand, the COS emitted from biomass fires (ca. $0.2 \text{ Tg S}(\text{COS}) \text{ yr}^{-1}$), makes up about 20% of the source of this trace gas (Andreae and Crutzen 1997).

Emissions from domestic biofuel use. To assess the emissions from domestic biofuel use, the concentrations of CO_2 , CO , NO , and some organic compounds and aerosols have been determined in the smoke (Brocard and Lacaux 1998; Ludwig et al. 2002). The emission figures are combined with biofuel consumption rates obtained from surveys of per capita consumption and appropriate demographic information. These rates may vary considerably as they depend on many factors, among them biofuel availability, traditional habits for cooking and heating, prevailing temperatures, etc. At present, uncertainties in emissions from domestic fuel use are thought to stem mainly from insufficient knowledge of the consumption rates.

In a recent study by Marufu et al. (2000) global emissions of CO_2 from domestic biofuel use were estimated at roughly 17% of total sources (1420 of $8350 \text{ Tg C yr}^{-1}$). For CO , the contribution from biofuel combustion makes up 16% of total sources (80 of 480 Tg C yr^{-1}). For CH_4 and VOCs much of the respective two and four percent of total are derived, since biogenic sources dominate in these cases, while three and a half percent of the total (1.4 of 40 Tg N yr^{-1}) was calculated for NO_x from domestic biofuel combustion. More recent assessments indicate that emissions from biomass burning may be even higher (R. Yevich, personal communication 2001). All currently available estimates thus agree that biofuel use is a significant source for many atmospheric trace compounds, especially because the emissions occur predominantly within the chemically very active tropical atmosphere and because these gases (except CO_2) contribute to ozone formation. Recent measurements in the INDOEX campaign have confirmed the large impact of biofuel use on atmospheric chemistry and climate in the Asian region (Lelieveld et al. 2001).

The available database, in particular the biofuel consumption figures, for biofuel emissions should be improved further, even if extrapolations from spot assessments will remain necessary. Most measurements have been made in Africa. However, cooking and heating habits vary considerably between different developing regions of the world. Additionally, agricultural waste burning and, even more, smouldering dump sites are not yet characterised adequately, but are expected to contribute significantly to global emissions.

2.7.2.7 Detection of Fires and Burned Area by Remote Sensing

Reporting of national estimates of anthropogenic trace gas emissions, including those from biomass burning, are a requirement of the Framework Convention on Climate Change, and the IPCC provides guidelines for these emissions calculations (Callander 1995). For many parts of the world however, national emissions estimates from biomass burning are based largely on expert opinion or summary statistics, and the resulting accuracies are

largely unknown. Synoptic fire information derived from satellites provides a source of information for augmenting available national fire statistics. Satellite detection of active fire occurrence has been used to identify the timing and location of fires, and has been used in emission product transport studies, for example. Polar orbiting and geostationary satellite systems have been used to provide fire information (Elvidge et al. 1996; French et al. 1996; Prins et al. 1998). The first global data set of annual satellite fire distributions was developed directly as a contribution to BIBEX (Stroppiana et al. 2000).

Automated algorithms for direct estimation of burned area are currently under development with the intent of providing direct input to emissions modelling (Roy et al. 1999). Satellite based techniques for direct estimation of emitted energy, fire intensity, atmospheric aerosol loading, and vegetation recovery are also being developed. Since in most cases the data products are to be used in numerical modelling, there is a need to provide a quantitative assessment of their accuracy. For satellite products, validation using independent data sources needs to be undertaken to determine product accuracy.

New satellite systems are planned that will improve our current fire monitoring capability (e.g. Kaufman et al. 1998b). The requirements for these systems come in part from the experience gained from BIBEX. The satellite fire research community is working to secure the necessary long-term fire observations from the next generation of operational satellite systems, such as the US National Polar Orbiting Environmental Satellite System (NPOESS).

With the operational availability of satellite-derived information on the location and timing of fires and on the area burned, it will be feasible to run an improved class of models to estimate emissions on an annual basis. These improved models will require ground-based estimates of emission factors and modelled estimates of fuel load and fuel consumed for a given year, rather than representative values for a given vegetation type. As new satellite information becomes available on fire intensity, emitted energy, and fuel moisture content, these first order emissions estimates can be improved. Providing robust models that can be used for operational generation of annual emissions estimates and developing approaches to validate them provide the next challenge for the fire and global change research community.

2.7.2.8 Impacts of Burning on Trace Gas Exchange from Soils

The process of biomass burning represents a vast reallocation of nutrients in cleared tropical forest and sa-

vannah systems. Large proportions of system carbon, nitrogen, and sulphur are volatilised. Soils are affected by changes in nutrient levels, pH, and temperature, with associated changes in microbial communities. Studies conducted during the SAFARI 92 campaign showed that the mean NO emissions increased after burning, reaching $15 \text{ ng N m}^{-2} \text{ s}^{-1}$ from dry sites and exceeding $60 \text{ ng N m}^{-2} \text{ s}^{-1}$ from the wetted sites (Levine et al. 1996). The long-term effect of excluding fire from a savannah is to increase the soil nitrogen content through increased litter inputs, which in turn increases nitrification rates and soil NO emissions (Parsons et al. 1996). Soil emissions of CO_2 and CO were increased by an order of magnitude after burning, whereas exchange of CH_4 was not affected. In all cases the increases were short lived and dropped back to pre-burn levels within a few days (Zepp et al. 1996). Studies on the impact of burning on soil carbon pools showed that annual burning in a semi-arid savannah reduced the light-fraction carbon markedly but did not impact the intermediate or passive carbon pools. This has implications for the amount of soil carbon that can be readily metabolised by the soil microorganisms. Burning the savannas at longer time intervals had no effect on the pool size or the turnover rates of the various soil carbon pools (Otter 1992).

2.7.2.9 Importance to Atmospheric Chemistry and Climate

We have already pointed out that biomass burning is a significant source of several greenhouse gases, among them CO_2 , CH_4 , and, to a much lesser extent, N_2O . It also makes important contributions to the budget of several gases of stratospheric significance, such as methyl chloride and methyl bromide, N_2O , and COS. Of particular importance to the chemistry and radiative characteristics of the atmosphere are the emissions of ozone precursors, particularly NO_x , VOC, CO, and CH_4 . Because vegetation fires in tropical regions can occur only when the vegetation is dry enough to burn, fires are most abundant in the dry season, when the trade wind inversion with its large-scale subsidence and suppression of rain-forming convection prevails over the region. Because this inversion prevents convection to heights of more than a few kilometres, it was initially thought that the linkage between dry conditions and subsidence more or less precluded the transport of pyrogenic ozone precursors to the middle and upper troposphere. Recent work has shown, however, that large amounts of smoke can get swept by low-level circulation, e.g. the trade winds, towards convergent regions over the continents or the Inter-Tropical Convergence Zone, and there become subject to deep convection (Andreae et al. 2000; Chatfield et al. 1996; Thompson et al. 1996a). This transport pat-

tern can explain the abundance of fire-related O₃ and O₃-precursors in the middle and upper troposphere as observed by remote sensing and *in situ* measurements (Browell et al. 1996a; Connors et al. 1996; Olson et al. 1996).

The aerosols from biomass fires, the most obvious and visible sign of pyrogenic air pollution, may have an important impact on climate. Biomass burning is the second largest source of anthropogenic sub-micrometer aerosol (after sulphates from fossil fuel combustion), and possibly the largest source of black carbon particles. These aerosols influence climate and the hydrological cycle by scattering and absorbing solar radiation, and by changing the properties of clouds in ways that are just now being elucidated (Hobbs et al. 1997; Kaufman et al. 1998a; Ramanathan et al. 2000). Further characterisation of the radiative and cloud-nucleating properties of pyrogenic aerosols and their effect on regional and global climate remains a major challenge to the scientific community.

Whether the impact of biomass burning will grow in the future depends both on climate change and on human factors. The amount of fuel available for burning at a given place and time is a function of ecological factors, e.g. soil fertility, precipitation, and temperature. It also depends on land use, i.e. if the area has been burned previously, is used for grazing or agriculture, and so on. If climatic variations become more extreme, as climate models have suggested, we can expect a more frequent occurrence of drought years following very wet years. This would result in large amounts of fuel ready to burn in the fire season. Furthermore, in a warmer and drier climate, fire frequency is likely to increase, which would reduce biomass carbon storage by changing the age class structure of vegetation, as well as causing increased emissions of ozone precursors. To monitor the regional and global evolution of pyrogenic emissions, it would be very useful to develop unique tracers for biomass burning, and to set up continuous measurements of these tracers at selected sites.

Human activities are of central importance to the frequency and severity of biomass fires. If large parts of the humid Tropics are deforested further, they will be transformed from a biome essentially free of fires (the tropical rainforest) to biomes with much more frequent fires (grazing lands, agricultural lands, and wastelands). With a higher human population density, the frequency of ignition will go up as well. And finally, the amount of biomass burned for cooking and domestic heating, already a major source of emissions in tropical countries, will increase further. To follow these changes, we will need to develop further and validate techniques to determine the spatial and temporal distribution of biomass burning and the amounts of biomass burned in the various fire regimes.

2.7.3 Wet Deposition in the Tropics

Wet deposition plays an essential role in controlling the concentrations of trace gases and aerosol particles in the atmosphere and in providing the essential nutrients for the biological functioning of ecosystems. Wet and dry deposition affect the budgets of key nutrients and trace gases in both terrestrial and marine ecosystems, as described in other sections of this chapter.

The Tropics are a particularly important region regarding global atmospheric chemistry. Due to intense ultraviolet radiation and high water vapour concentrations, high OH concentrations oxidise inorganic and organic gases, and induce an efficient removal from the atmosphere of the oxidised products. Strong convection in the tropical regions results in huge volumes of air being drawn out of the sub-cloud layer with the resultant chemical composition of the precipitation coming from the capture of gases and small particles by the liquid phases of cloud and rain. Knowledge of the chemical composition of wet deposition allows one to track seasonal emissions from various ecosystems.

In the 1990s, due to the lack of information on wet deposition in the Tropics, a cooperative programme was undertaken, involving the Global Atmosphere Watch (GAW) of the World Meteorological Organisation and the Deposition of Biogeochemically Important Trace Species (DEBITS) Activity of IGAC (see A.5), mostly in Asia. It was followed by the Composition and Acidity of the Asian Precipitation (CAAP) programme, later expanded into Africa and South America (Lacaux 1999).

In some tropical areas, however, dry deposition is at least as important as wet deposition and must be considered in the calculation of total deposition. Dry deposition of acidic gases impacts soil and plants, as indicated in Sect. 2.4 and 2.6.1. High concentrations of sulphur and nitrogen oxides and nitric and sulphuric acids may increase acidification processes. In many arid or semi-arid regions, transport and deposition of alkaline soil particles to adjacent ecosystems are also important. The deposition of alkaline particles partly mitigates the effects of wet and dry deposition of acidic compounds.

In addition to acidity, the N content of wet deposition may strongly affect ecosystem properties such as C storage, trace gas exchange, cation leaching, biodiversity, and estuarine eutrophication. This has been shown for temperate regions with altered N inputs (e.g. Howarth et al. 1996; Mansfield et al. 1998 and papers therein). Now, however, 40% of global applications of industrial N fertiliser takes place in the Tropics and subtropics, and over two-thirds is expected to occur in now-developing regions by 2020 (Matthews 1993; Bouwman 1998). Simi-

larly, fossil fuel combustion is increasing dramatically in less economically developed regions, including much of the tropical and subtropical regions. Galloway et al. (1994) estimated that by 2020 nearly two-thirds of Earth's energy-related N inputs would take place in the Tropics and subtropics. In addition, N emissions associated with biomass burning are heavily concentrated in the Tropics, and will likely remain so for decades (Andreae 1993) (see Sect. 2.6.2).

2.7.3.1 Precipitation Chemistry in Equatorial Forests

To illustrate work undertaken by DEBITS, data for precipitation chemistry and associated wet deposition from several sampling sites located in equatorial forests are presented in Table 2.5. Hydrogen ion is abundant at all sites on an annual mean basis, indicating the generally acidic character of equatorial precipitation. This acidity is due to a mixture of mineral acids (HNO_3 , H_2SO_4 , etc.) and organic acids (formic, acetic, propionic, and others) (Andreae et al. 1990; Ayers and Gillet 1988; Galloway et al. 1982; Lacaux et al. 1991; Williams et al. 1997). In equatorial African forest precipitation, the acidity contributed by organic acids (40–60%) is equivalent to that contributed by mineral acids (ca. 40%). In Amazonia the composition of precipitation is very different, with organic acids accounting for 80–90% of the

total acidity. In the rainwater collected at several remote locations in the Northern Territory of Australia, Gillet et al. (1990) found a volume-weighted mean (vwm) pH for all samples of 4.89, with organic acids contributing about 50% of the free acidity, the remainder being H_2SO_4 and HNO_3 .

During the dry season, biomass burning has a drastic influence on rainwater composition. The chemical content of rainwater from Amazonia (ABLE-2A, wet season) and African equatorial sites (Dimonika, Congo and Zoétéfé, Cameroon) can be compared to get a rough estimate of the contribution of some of the chemical compounds from the vegetation fires (Table 2.6). In the case of Amazonia, it was assumed that the precipitation chemistry reflected the biogenic emissions of soils and vegetation, with little influence of biomass burning emissions. Therefore, the mean contribution of the vegetation-burning source in the African sites was estimated to be about 60 to 70% of the NO_3^- , NH_4^+ , and acidity contents. On the other hand, the African sites, located on opposite sides of the Equator, are alternately affected by savannah burning sources from the Southern (June to October) and Northern (November to February) Hemispheres, as shown by the ubiquitous presence of high concentrations of NO_3^- , NH_4^+ , and H^+ in rainwater samples. The gases and particles produced by savannah burning in the Northern and Southern Hemispheres are transported by the north-east and south-

Table 2.5. Weighed volume mean concentrations in $\mu\text{eq l}^{-1}$ and wet deposition in $\text{meq m}^{-2}\text{yr}^{-1}$ for precipitation collected in sites located in equatorial forests

	Location	Reference	pH	H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^-	CH_3COO^-
Africa	Dimonika (Congo)	Lacaux et al 1992	4.74	18.1	11.1	2.0	6.4	9.3	–	8.6	13.3	10.5	6.6	3.0
	Zoétéfé	Lacaux 1999	4.83	14.8 (23.7)	1.7 (2.7)	3.6 (6.5)	9.6 (15.4)	6.3 (10.2)	1.9 (3.2)	7.0 (11.6)	2.2 (3.7)	5.0 (8.4)	8.1 (13.1)	5.3 (8.4)
South America	Central Amazon	Andreae et al 1990	4.91	12.2 (29.4)	4.0 (9.5)	1.8 (4.2)	4.0 (9.6)	4.2 (10.0)	–	2.1 (5.0)	4.7 (11.3)	3.5 (8.2)	6.3 (15.1)	4.3 (10.3)
		Williams et al 1997	4.70	17.0 (46.8)	2.4 (6.7)	0.8 (2.3)	3.0 (8.2)	2.4 (6.0)	0.9 (2.3)	4.2 (11.5)	4.6 (12.6)	2.0 (5.0)	2.9 (7.5)	9.3 (25.6)

Table 2.6. Biomass burning contribution to chemical precipitation in African rainforests, assuming biogenic inputs equivalent to Amazonia

	Amazonia	Equatorial Africa			
	ABLE-2A Biogenic reference	South Equator Dimonika, Congo		North Equator Zoétéfé, Cameroon	
	$\mu\text{eq l}^{-1}$	$\mu\text{eq l}^{-1}$	Biomass burning contribution (%)	$\mu\text{eq l}^{-1}$	Biomass burning contribution (%)
H^+	5.8	18.1	68	14.8	61
pH	5.24	4.74		4.83	
NO_3^-	1.1	8.6	87	7.0	84
Organic acids	5.2	7.4	30	13.4	61
NH_4^+	1.9	6.4	70	9.6	80

east Trade Winds, respectively, to the equatorial forests and progressively scavenged by convective clouds.

The wet deposition measured in the semi-arid and humid savannas surrounding the forested ecosystems presents a source of high potential acidity, which may not result in final strong acidity of the deposition. For example, Galy and Modi (1998) have shown that the precipitation from arid savannas is characterised by a weak acidity ($H^+ = 2 \mu\text{eq l}^{-1}$) in spite of a high potential acidity (nitrate + dissociated formate + dissociated acetate = $22 \mu\text{eq l}^{-1}$). This result is explained by heterogeneous interactions occurring between alkaline soil dust particles and acidic gases. Many of these mineral dust particles are able to entirely neutralise gaseous nitric acid. These gas-particle interactions occur before the incorporation of these particles into cloud droplets or raindrops. Furthermore, high concentrations of organic aerosols (from biomass burning and condensation of biogenic hydrocarbons) and mineral dust (from deserts and arid areas) could also promote intense heterogeneous atmospheric chemistry (e.g. Dentener et al. 1996; Carmichael et al. 1996, 1997) (also see Chap. 4). These processes may affect the cycles of nitrogen, sulphur, and atmospheric oxidants significantly.

2.7.3.2 Effect of Wet Deposition on Tropical Terrestrial Ecosystems

Acidification effects are mainly due to deposition of mineral sulphur and nitrogen compounds. In tropical regions, organic acid deposition may contribute as much as 80%; however, these acids are oxidised in soils and will not participate directly in soil acidification. Soil particles exchange alkaline cations with H^+ and the concentration of alkaline ions determines the soil base saturation. When base saturation is low, acids may release aluminium ions from soil particles. In spite of its limitations, the "critical load" concept, characterising ecosystem sensitivity to acidic deposition, has been adopted as a tool for estimating potential impacts on ecosystems. In order to facilitate the development of strategies to control pollution in tropical countries, the Stockholm Environment Institute (SEI) has recently proposed a global assessment of terrestrial ecosystem sensitivity to acidic deposition that uses soil buffering capacity as a key indicator (Cinderby et al. 1998). This assessment depends on two factors: the buffering capacity of the base layer to identify soils that have high weathering rate, and the cation exchange capacity to quantify the capacity of a soil to buffer acidity.

A global map prepared by SEI (see Fig. 2.16), shows five classes of sensitivity to acidic deposition, from a critical load of $200 \text{ meq m}^{-2} \text{ yr}^{-1}$ for the insensitive class to a critical load of $25 \text{ meq m}^{-2} \text{ yr}^{-1}$ for the most sensitive class. Some selected wet deposition measurements

of non-sea salt sulphate, nitrate, and organic acids, mainly obtained by the DEBITS Activity, are also included. These combined measurements provide an overall view of tropical regions where the potential risk of acidification is important. All the equatorial rainforests of South America, Africa, and Asia are classified in the most sensitive classes. For South American soils, which have a level of mineral acidity deposition of about $10\text{--}20 \text{ meq m}^{-2} \text{ yr}^{-1}$, future acidification problems may become severe if further land use change and industrial activities occur in these regions. For tropical Africa, due to the high contribution of mineral acidity from wet deposition from biomass burning sources, the critical load is nearly exceeded in many parts of western Africa. For Asia, in some parts of China, Japan, and other industrialised and populated zones, the critical load has already been exceeded (Fig. 2.16).

Work by IGBP researchers suggests that there is substantial, although mostly indirect, evidence that the supply of N may not limit plant production in some tropical forests (Hall and Matson 1999). Thus, additions of N may have little direct effect on plant production and carbon storage, but may substantially affect rate and timing of N losses. As indicated above, tropical forest soils are highly acidic; additions of anthropogenic N may increase that acidity, leading to increased losses of cations and decreased availability of phosphorus and other nutrients, ultimately limiting plant production and other ecosystem functions. Moreover, N additions to tropical soils may result in immediate and relatively large proportional losses of N in trace gas forms, as discussed above. On-going work strives to identify the direct and indirect effects of wet deposition on tropical agro-ecosystems, and to determine its implications for ecosystem functioning and feed-backs to the atmosphere locally, regionally, and globally.

2.8 Marine Highlights

From its inception, IGAC stimulated and sponsored research on marine aerosol and gas exchange of compounds of biological origin through the Marine Aerosol and Gas Exchange (MAGE) Activity (see A.5), examples of which are given below. Similar to terrestrial biosphere-atmosphere research, integrated field campaigns in marine regions, such as the ACE-1, ACE-2 and ASGA/MAGE experiments (see A.5) have been an IGAC hallmark. These field research efforts have linked studies of emissions, transformations, and transport in the marine boundary layer. The study of pertinent marine biogeochemical cycles resulting in sea-air fluxes, however, has yet to be fully integrated into these field campaigns. While research on biosphere-atmosphere interactions in marine regions has progressed significantly in the last decade, it remains less advanced than

Wet deposition ($\text{meq m}^{-2} \text{ year}^{-1}$)

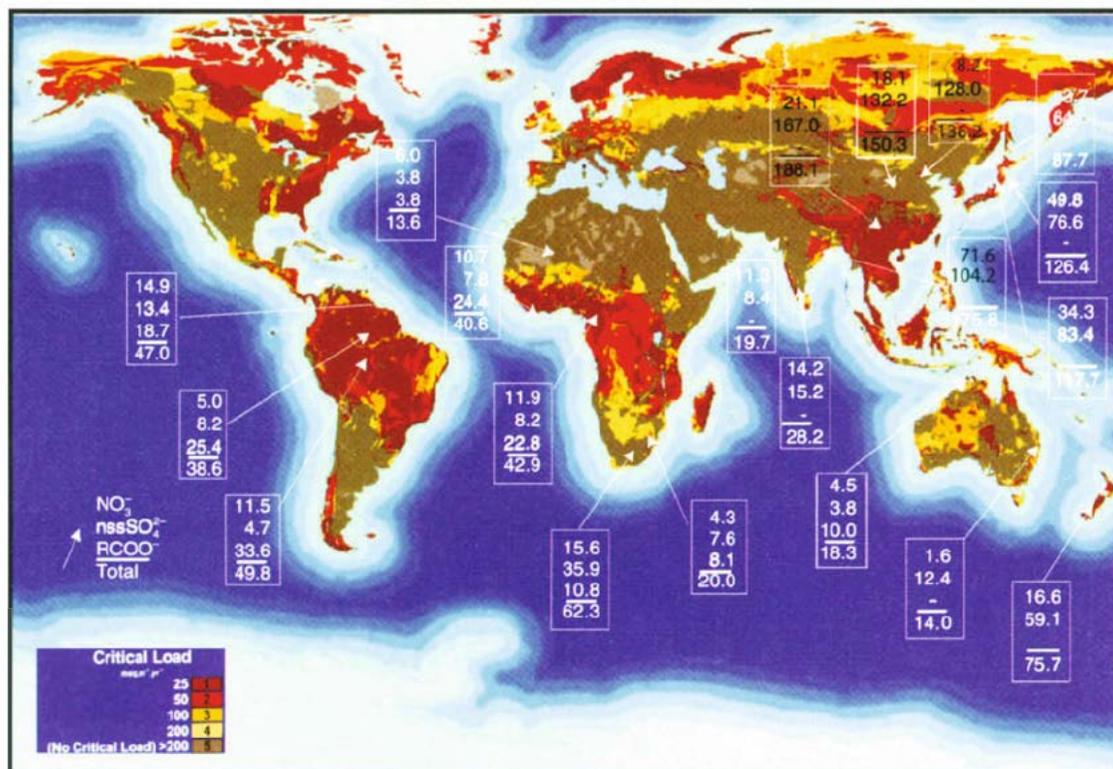


Fig. 2.16. Wet deposition ($\text{meq m}^{-2} \text{ yr}^{-1}$) of nitrate, non-sea-salt sulphate and organic acids compared with "critical load", a measure of ecosystem sensitivity to acidic deposition. Asia and Oceania (Ayers et al. 1996a); Africa (Galy and Modi 1998; Turner et al. 1996c); Amazonia (Andreae et al. 1990; Williams et al. 1997); and ecosystem sensitivity to acidic deposition (Cinderby et al. 1998)

that for terrestrial regions due to the higher demands of field logistics as well as, perhaps, a lesser recognition of the interaction by the whole of the research communities involved. In the last decade, the greatest advances occurred in DMS biogeochemistry while the marine cycling of other compounds (e.g. organohalogens) is less well, or not at all, understood. Currently, it is still necessary to estimate air-sea fluxes of most gases given existing measurements of the mixing ratios in the atmosphere and sea surface waters. The recent establishment of a new IGBP programme element, Surface Ocean – Lower Atmosphere Study (SOLAS), hopefully will inspire accelerated progress in these various research areas.

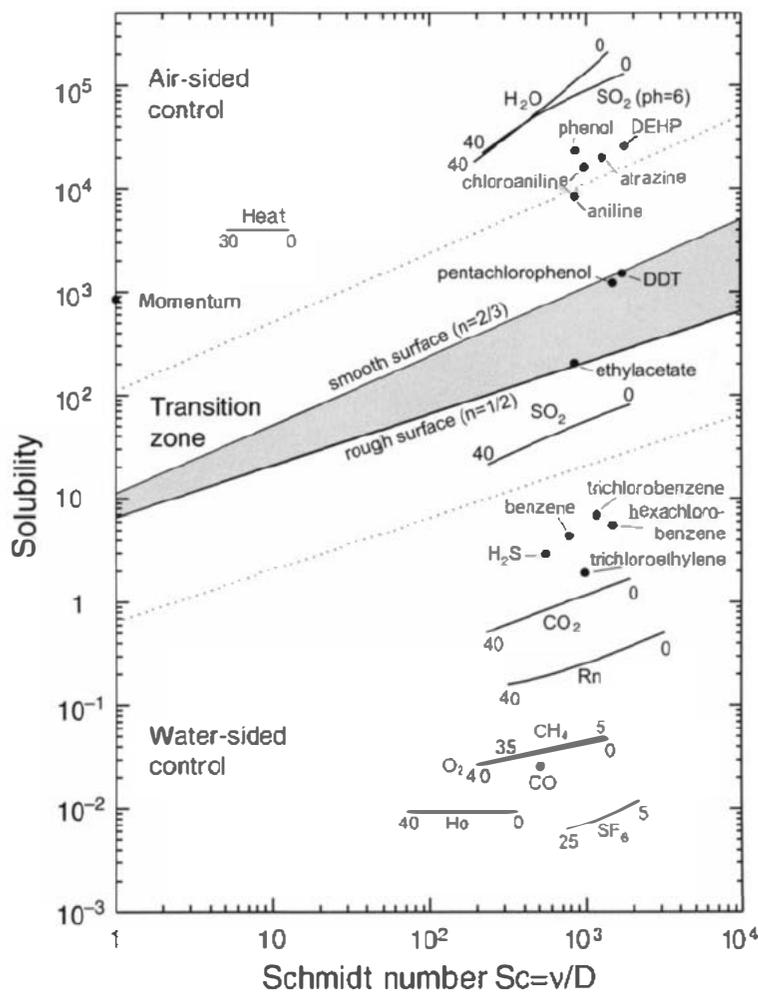
2.8.1 Air-Water Gas Exchange Parameterisation

The exchange of inert and sparingly soluble gases including CO_2 , O_2 , CH_4 , and DMS between the atmosphere and oceans is controlled by a thin (20–200 μm) boundary layer at the top of the ocean. Laboratory and field measurements show that wind waves significantly increase the gas transfer rate and that it may be significantly influenced by the presence of surfactants. The

mechanisms are still understood only marginally. Empirical gas transfer rate/wind speed relations imply an uncertainty of between 50 and 100%.

The transfer across the boundary layer at an interface shows characteristic mean properties that can be described by a transfer velocity, k , a boundary layer thickness, z , and time constant, t (Jähne and Haußecker 1998). The flux density divided by the concentration difference between the surface and the bulk at some reference level is defined as the transfer velocity, k (also known as the piston velocity transfer coefficient). The equilibrium partitioning between air and water (as measured by the Henry's law constant, H) is another key parameter of air-water gas transfer. A strong partitioning in favour of the water phase shifts control of the transfer process to the gas-phase boundary layer, and a partitioning in favour of the air phase moves control to the aqueous layer. The value of H for a transition at which the control shifts from one phase to the other depends on the ratio of the transfer velocities. For all sparingly soluble gases only the water-side controlled process is relevant (Fig. 2.17). Some environmentally important compounds (e.g. polychlorinated benzenes and some pesticides) lie in a transition zone where it is

Fig. 2.17. Schmidt number/solubility diagram including various volatile tracers, momentum, and heat for temperature ranges ($^{\circ}\text{C}$) as indicated. Filled circles refer to only a temperature of 20°C . Regions for air-sided, mixed, and water-sided control of transfer process between the gas and liquid phase are marked. At the solid lines the transfer resistance is equal in both phases. The following dimensional transfer resistances were used: $r_a = 31$, $r_w = 12Sc^{2/3}$ (smooth), $r_w = 6.5Sc^{1/2}$ (wavy surface) with $r_a = R_a u_a^*$ and $r_w = R_w u_w^*$ (after Jähne 1982, and Jähne and Haußecke 1998)



required to consider both transport processes. For reactive gases, as for SO_2 , the high transfer resistance in the water is shortcut by its very fast hydration reaction, and the transfer of SO_2 is controlled, as water vapour, on the air side (compare SO_2 only physically dissolved at a low pH with SO_2 at pH=6 in Fig. 2.17).

The intensity of turbulence determines the transfer resistance: the more intense the turbulence, the thinner the boundary layers. At the scales of the viscous boundary layer, turbulence is strongly attenuated by viscous forces. Thus, the turbulent diffusivity must decrease much faster to zero at the interface than the linear decrease found in the turbulent layer. A free water surface is, however, not solid, nor is it smooth as soon as short wind waves are generated. On a free water surface, velocity fluctuations are possible that make convergence or divergence zones at the surface possible. A film on the water surface, however, creates pressure that works against the contraction of surface elements. This is the point at which the physicochemical structure of the sur-

face influences the structure of the near-surface turbulence as well as the generation of waves. As at a rigid wall, a strong film pressure at the surface maintains two-dimensional continuity at the interface.

A significant influence of surfactants from oceanic conditions has been found by Goldman et al. (1988) and Frew et al. (1990), although contrary results have recently been presented by Nightingale et al. (2000b). The effect of surface films on the boundary layer processes is also discussed in detail in Liss and Duce (1997) and Frew (1997).

Given the lack of knowledge, all theories about the enhancement of gas transfer by waves are rather speculative (for a recent review, see Jähne and Haußecke 1998). Even worse, by just measuring the transfer rates and the wave parameters at the current state of the art it is impossible to verify one of these models conclusively. At high wind speeds, wave breaking with the entrainment of bubbles enhances gas transfer further. The uncertainties of this phenomenon are also large; less soluble gases are affected most (Keeling 1993; Woolf 1993).

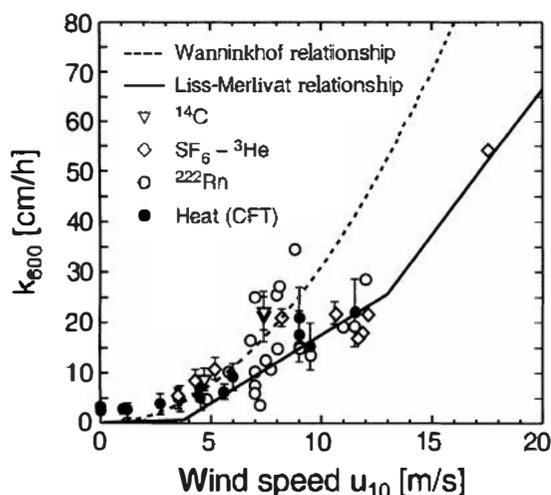


Fig. 2.18. Summary of gas exchange coefficients normalised to a Schmidt number of 600 and plotted versus wind speed (10 m above sea level), plus two empirical relationships (Jähne and Haussecker 1998)

A collection of field data is shown in Fig. 2.18. Although the data show a clear increase of the transfer velocity with wind speed, there is significant scatter in the data that can only partly be attributed to uncertainties and systematic errors in the measurements. The gas transfer velocity is not simply a function of the wind speed. The scatter mainly reflects the additional influence of the wind wave field, which may vary with all parameters that modify the microturbulence in the boundary layer such as the viscoelastic properties of the surface films present and the wind wave field.

Part of the data shown in Fig. 2.18 is based on geochemical tracers such as the ^{14}C , $^3\text{He}/\text{T}$, or $^{222}\text{Rn}/^{226}\text{Ra}$ methods. The transfer velocities obtained in this way are only mean values. Thus a parameterisation is only possible under steady state conditions over extended periods; it is questionable under changing conditions. The changes of the parameters (e.g. wind speed) are some orders of magnitude faster. Thus mass balance methods are not suitable for a study of the mechanisms of air-water gas transfer. This is also true for the tracer injection techniques pioneered by Wanninkhof et al. (1985, 1987) in lakes, and Watson et al. (1991a) and Nightingale et al. (2000a) in oceans. Progress in better understanding the mechanisms of air-water gas exchange has been hindered by inadequate measuring technology. Promising new techniques are now available (Jähne and Haußecke 1998; McGillis et al. 1999) but there are currently too few measurements using them for definite conclusions to be drawn. Thus, empirical gas exchange-wind speed relationships (see Fig. 2.17) must still be applied with caution since they have an uncertainty of up to a factor of two.

2.8.2 Marine Biogenic Emissions: A Few Examples

2.8.2.1 Methane

The ocean is a small source of methane to the atmosphere. Open Pacific Ocean saturation ratios (ratio of seawater CH_4 partial pressure to the overlying atmospheric CH_4 partial pressure) range from 0.95 to 1.17. Large areas of the Pacific Ocean are undersaturated with respect to atmospheric CH_4 partial pressures during the fall and winter. On a seasonal time scale, the driving force controlling saturation ratios outside the Tropics appears to be the change in sea surface temperature. Saturation ratios in the equatorial region have always been positive and appear to be driven by the strength of the equatorial upwelling. Extrapolating the Pacific data globally and regionally into ten zones, the calculated average flux of CH_4 to the atmosphere is 0.4 Tg yr^{-1} ($0.2\text{--}0.6 \text{ Tg yr}^{-1}$) (Bates et al. 1996). This is approximately an order of magnitude less than previous estimates, which lacked fall and winter data. Thus the open ocean is a very minor source of methane to the atmosphere ($<0.1\%$) compared with other sources (IPCC 1996). However, the coastal ocean and marginal seas appear to be a much larger source (Owens et al. 1991; Kvenvolden et al. 1993; Bange et al. 1994; Lammers et al. 1995; Scranton and McShane 1991) due to CH_4 emissions from bottom sediments; this definitely warrants further investigation.

2.8.2.2 Carbon Monoxide

The ocean is ubiquitously supersaturated with CO with respect to the atmosphere, resulting in a net flux to the atmosphere ranging seasonally and regionally from 0.25 to $13 \mu\text{mol m}^{-2}\text{d}^{-1}$. However, the total annual emission to the atmosphere (13 Tg ; see Table 3.1) is small compared to current estimates from both terrestrial natural and anthropogenic sources (1.150 Tg yr^{-1}) (Bates et al. 1995; WMO 1999). Even in the Southern Hemisphere, which accounts for two-thirds of the oceanic emissions, the ocean source is relatively small ($<1\%$), since both methane oxidation and biomass burning are large sources of CO (Bates et al. 1995).

2.8.2.3 Volatile Organic Carbon Compounds

Volatile organic carbon (VOC) compounds, or non-methane hydrocarbons, are produced in surface seawater possibly by photochemical mechanisms, phytoplankton activity, and/or microbial breakdown of organic matter (Plass-Diilmer et al. 1995; Ratte et al. 1995; Broadgate et al. 1997). Oceanic concentrations show a strong seasonal cycle (Broadgate et al. 1997). The ocean-atmosphere flux

is dominated by alkenes and is small compared to terrestrial emission estimates (<1%). However, the emissions may be significant on local scales considering the short lifetimes of the unsaturated compounds (Donahue and Prinn 1993; Pszenny et al. 1999). Additional seasonal measurements of isoprene, ethene, and propene in particular are needed in different oceanic regions.

2.8.2.4 Ammonia

Ammonia is the dominant gas phase basic compound in the marine atmosphere and, as such, has a unique influence on marine multi-phase atmospheric chemistry. Ammonia exists in seawater as both ionised ammonium, $\text{NH}_4^+(\text{s})$, and dissolved ammonia, $\text{NH}_3(\text{s})$. Dissolved ammonia makes up about ten percent of the total seawater ammonium concentration, $\text{NH}_x(\text{s})$, at a pH of 8.2 and a temperature of 25 °C (Quinn et al. 1996a) and is the compound that is emitted across the air-sea interface. $\text{NH}_x(\text{s})$ is produced in the upper ocean from the degradation of organic nitrogen-containing compounds and excretion from zooplankton. It also is released from bottom sediments to overlying waters. Loss processes for $\text{NH}_x(\text{s})$ include bacterial nitrification, uptake by phytoplankton and bacteria, and emission across the air-sea interface. There will be a net flux of ammonia from the ocean to the atmosphere if the atmospheric $\text{NH}_3(\text{g})$ concentration is less than the gas phase concentration in equilibrium with $\text{NH}_3(\text{s})$. Alternatively, there will be a net flux into the ocean if the atmospheric $\text{NH}_3(\text{g})$ concentration is greater. In either direction, the magnitude of the flux depends on the concentration difference and the transfer velocity.

Attempts to estimate the air-sea flux of ammonia have been hindered by a lack of techniques with sufficient sensitivity and by difficulties in avoiding sample contamination (Williams et al. 1992). As a result, the contribution of NH_3 to the oceanic biogeochemical cycling of N is poorly understood. The few estimates of the air-sea flux of NH_3 that have been reported and that are based on measurements of ammonia in the gas, particle, and/or seawater phases are summarised below.

The first estimates of the flux for the Pacific Ocean were based on filter collection of $\text{NH}_3(\text{g})$ and $\text{NH}_3(\text{s})$ (Quinn et al. 1988, 1990). These measurements indicated a net flux of ammonia from the ocean to the atmosphere in the northeastern and central Pacific ranging between 1.8 and 16 $\mu\text{mol m}^{-2}\text{d}^{-1}$. Clarke and Porter (1993) used measurements of aerosol volatility (which indicate the degree of neutralisation of sulphate aerosol by ammonia) to infer an efflux of ammonia from the ocean to the atmosphere of about 10 $\mu\text{mol m}^{-2}\text{d}^{-1}$ over the equatorial Pacific. Similar results have been reported for the Atlantic Ocean and the Arabian Sea. Based on aircraft measurements of aerosol ammonium during a Lagrangian experiment near the Azores, Zhuang and Huebert (1996)

estimated a flux of NH_3 from the ocean to the atmosphere of $26 \pm 20 \mu\text{mol m}^{-2}\text{d}^{-1}$. Simultaneous measurements of $\text{NH}_x(\text{s})$ and $\text{NH}_3(\text{g})$ were made in the Arabian Sea (Gibb et al. 1999). It was found that in both coastal and remote oligotrophic regions there was a flux of NH_3 from the ocean to the atmosphere. Hence, to date, measurements over portions of the Pacific and Atlantic Oceans, and the Arabian Sea indicate that the remote ocean serves as a source of NH_3 to the atmosphere even in regions of low nutrient concentrations.

Given the importance of $\text{NH}_x(\text{s})$ as an oceanic micronutrient, the loss of ammonia through venting to the atmosphere may seem surprising. However, only a small percentage of $\text{NH}_x(\text{s})$ exists as $\text{NH}_3(\text{s})$ so that this efflux most likely represents a relatively minor loss of NH_3 (Gibb et al. 1999). In addition, this loss can be episodically compensated for through the wet and dry deposition of ammonium-containing aerosol particles. For example, Quinn et al. (1988) estimated that, over the northeastern Pacific, the transfer of $\text{NH}_3(\text{g})$ from the ocean to the atmosphere was balanced by wet and dry deposition processes. In certain regions, such as the Southern Bight of the North Sea, there is a flux of ammonia from the atmosphere to the ocean due to the advection of high concentrations of ammonia from adjacent land (Asman et al. 1994). The extent and impact of the deposition of continentally derived ammonia to marine regions is unknown but may be significant. Model results suggest that about six percent of the global continental emissions of ammonia are deposited to the North Atlantic and Caribbean (Prospero et al. 1996). The deposition would be greatest in coastal waters.

It is clear that ammonia, as an oceanic micronutrient and the dominant atmospheric gas phase compound, plays a unique role in both the ocean and the atmosphere. The flux of ammonia from the ocean to the atmosphere affects aerosol chemical composition, pH, and hygroscopicity. The reverse flux, of ammonia plus ammonium in particles and rain from the atmosphere, to the ocean, may affect biological productivity. Simultaneous measurements of ammonia in the atmospheric gas and particle phases, in seawater, and in rainwater are needed to improve our understanding of the multi-phase marine ammonia system in general and the air-sea exchange of ammonia in particular. It is interesting to note that ammonia, due to its strong partitioning into the water phase, is the only gas discussed in this chapter whose transfer velocity is under the control of air-side transfer processes.

2.8.2.5 Nitrous Oxide

The world oceans represent a significant natural source of N_2O to the atmosphere (e.g. Seitzinger et al. 2000). The surface waters of many oceanic regions are supersaturated in N_2O with respect to solubility equilibrium

with the atmosphere, giving rise to a net air-sea gas exchange flux of N_2O to the atmosphere. Nitrous oxide is produced in subsurface waters both as an intermediate of denitrification, the reduction of nitrate ion (NO_3^-) to nitrogen (N_2), and as a trace by-product of nitrification, the oxidation of NH_4^+ to NO_3^- . Denitrification occurs under suboxic to anoxic conditions, and is thought to take place mainly in restricted low-oxygen regions such as the eastern tropical Pacific and the Arabian Sea, and in the sediments of continental shelves. The distribution of nitrification is thought to be more widespread, since it occurs under aerobic conditions in association with the internal recycling of fixed nitrogen.

During the past decade there have been significant improvements in our understanding of oceanic processes of N_2O production, of the distribution of N_2O in the surface and subsurface ocean, and of the magnitude of the oceanic N_2O source to the global atmosphere. The relative roles of nitrification and denitrification processes have been addressed by measuring nitrogen stable isotopes and their fractionation between N_2O and other dissolved nitrogen-bearing compounds. The interpretation of these difficult measurements is complicated by the likelihood that both nitrification and denitrification are coupled in many oceanic systems, and no clear picture has yet emerged. There have also been recent advances in the study of air-sea gas exchange processes, as indicated in Sect. 2.8.1, which will lead to improvements in the quantification of exchange coefficients as a function of wind speed.

Finally, our understanding of the large-scale distribution of N_2O in the oceans has been improved through a number of shipboard measurement programs, such as those associated with the World Ocean Circulation Experiment (WOCE) and Joint Global Ocean Flux Study (JGOFS) programs. These have generally reinforced our view that open ocean upwelling regions along eastern ocean boundaries and in equatorial and coastal regions, represent major sources of atmospheric N_2O . By contrast, the great subtropical gyres, which represent a large portion of the surface area of the oceans, are relatively close to atmospheric equilibrium for N_2O . In recent years, some extremely high N_2O concentrations have been found in the eastern Arabian Sea, in suboxic waters over the Indian Shelf (Naqvi et al. 2000). Since anthropogenic impingements on the coastal ocean may cause an increase in hypoxia, suboxia, and anoxia in some areas, these recent observations from the Arabian Sea are provocative. By modelling these distributions together with the wind field (e.g. Nevison et al. 1995), we have come to believe that the global oceans constitute a net source to the atmosphere of about 4–5 Tg of N_2O , or about one third of the global natural source strength. This value may increase as more is learned about the diverse distribution of N_2O in coastal waters (e.g. Seitzinger and Kroeze 1998).

2.8.2.6 Dimethylsulphide

2.8.2.6.1 Introduction

Dimethylsulphide was discovered in ocean waters some 30 years ago by Lovelock et al. (1972). However, it remained a compound of marginal scientific interest for about a decade, until it was established that DMS is the main volatile sulphur compound emanating from the oceans and therefore plays a major role in the atmospheric sulphur cycle (e.g. Nguyen et al. 1978; Leck and Rodhe 1991). Interest in the biogeochemical cycle of DMS increased sharply again in the late 1980s, when Charlson et al. (1987) proposed a hypothesis linking biogenic DMS emission and global climate. In short, this hypothesis states that DMS released by marine phytoplankton enters the troposphere and is oxidised there to sulphate particles, which then act as cloud condensation nuclei (CCN) for marine clouds (see Box 4.3, however, regarding the utility of the CCN concept). Changes in CCN concentration affect the cloud droplet number concentration, which influences cloud albedo and consequently climate. Large-scale climate change, in turn, affects the phytoplankton number and speciation in the oceans and thereby completes, but does not necessarily close, a feedback loop. Recent assessments of the DMS-climate link can be found in Watson and Liss (1998) and Bigg and Leck (2001) (also see Chap. 4).

In the years since publication of the DMS-CCN-climate hypothesis, almost 1 000 papers have been published discussing the distribution and biogeochemistry of DMS (and its precursors) and its link to climate. Several IGAC-inspired studies have addressed aspects of the DMS-aerosol-climate connection, most prominently among them ASTEX/MAGE (e.g. Huebert et al. 1996), ACE-1 (e.g. Bates et al. 1998), and AOE-91, 96 (e.g. Leck et al. 1996, 2001). As a result of these projects, and the large number of independently conducted studies related to the DMS-climate hypothesis, we now understand many of the details of DMS production in the oceans, its transfer to the atmosphere, and the atmospheric oxidation processes (see Chap. 3) that lead to the formation of aerosols (see Chap. 4) that can act as CCN. However, in spite of this progress, fundamental gaps remain in our understanding of key issues in this biosphere-climate interaction, in particular with regard to the processes that regulate the concentration of DMS in seawater. While the basic processes have been identified, and even quantified in specific locations (e.g. Bates et al. 1994; Simo and Pedro-Alio 1999), generally applicable models of DMS-plankton relationships are still in their infancy (e.g. Gabric et al. 1993; Jodwali et al. 2000). Therefore, we are still not able to represent the DMS-CCN-climate hypothesis in the form of a process-based, quantitative, and predictive model. Even the overall sign of the feedback cannot be deduced with certainty, since it

is not known yet if a warming climate would result in an increase or decrease of DMS emissions. Glacial-to-interglacial changes in the amounts of DMS oxidation products in polar ice cores cannot answer this question unambiguously, as they may reflect variations in atmospheric transport patterns as much as differences in DMS production (e.g. Whunget al. 1994), as is discussed in detail in Sect. 2.3.

Early, limited data sets had suggested a possible correlation between DMS and phytoplankton concentration (e.g. Andreae and Barnard 1984). This correlation is particularly evident in vertical profiles of DMS and chlorophyll *a*, which in most instances show a sharp drop of both parameters around the depth corresponding to a light penetration of one percent of the surface light flux. Close correlations between DMS and phytoplankton densities were also found in situations where a single species accounted for much of the DMS production or phytoplankton biomass (e.g. Barnard et al. 1984; Matrai and Keller 1994). These findings led to the hope that global DMS distributions could be estimated from chlorophyll concentrations obtained by remote sensing, but experimental investigations of this proposal were not encouraging (e.g. Matrai et al. 1993), except in frontal regions (e.g. Holligan et al. 1993; Belviso et al. 2000). Furthermore, a statistical analysis of almost 16 000 measurements of DMS in surface seawater failed to show any useful correlations between DMS and chlorophyll or other chemical or physical parameters (Kettle et al. 1999). One reason for the absence of a general correlation between plankton biomass and DMS is that the intracellular concentration of its metabolic precursor, dimethylsulphoniopropionate (DMSP), varies between different phytoplankton species over a range of five orders of magnitude. While it is clear that some taxonomic groups typically contain higher amounts of DMSP, these relationships are by no means clear-cut (e.g. Keller et al. 1989). At least as important, however, are the complexities of DMS cycling by biological and abiotic processes in the surface ocean, which will be addressed below.

2.8.2.6.2 *Physiological and Ecological Controls of DMS Production*

The pathways of DMSP biosynthesis in phytoplankton have been studied and have shed light on potential regulating mechanisms such as nitrogen nutrition (e.g. Gröne and Kirst 1992; Keller et al. 1999a,b), temperature (Baumann et al. 1994), and light (Vetter and Sharp 1993; Matrai et al. 1995). While DMSP, and sometimes DMS, is directly released by phytoplankton, zooplankton also play a role by grazing, or avoiding, DMSP-rich cells (e.g. Dacey and Wakeham 1986; Wolfe et al. 1997; Tang 2000).

Very high concentrations of DMS and dissolved DMSP have been reported from several coastal and/or

high latitude areas, especially where blooms of DMSP-producing phytoplankton such as the coccolithophore *Emiliania huxleyi* and the prymnesiophyte *Phaeocystis pouchetii* occur (e.g. Malin et al. 1993; Barnard et al. 1984). In this context, it is interesting to note that Kettle et al.'s (1999) DMS database revealed that high DMS regions corresponded roughly to the coccolithophorid bloom areas derived by Brown and Yoder (1994) from remotely sensed ocean colour data. Prymnesiophytes (including coccolithophores) and dinoflagellates are phytoplankton groups that tend to have high DMSP cell quotas (Keller et al. 1989) and, not surprisingly, DMS is often relatively high when these groups dominate the phytoplankton assemblage. Diatoms, on the other hand, tend to have low intracellular DMSP concentrations and it is generally observed that diatoms are less important DMSP producers in the field (e.g. Keller et al. 1989). Predicting DMS concentrations from the algal assemblage is not straightforward, however. For example, Matrai and Vernet (1997) reported that DMS concentrations were as high in diatom-dominated, Arctic waters as they were in those dominated by *Phaeocystis* sp. It is now recognised that some phytoplankton species not only produce high intracellular concentrations of DMSP, but they also have cell-surface (Stefels and Dijkhuizen 1996) and intracellular (Steinke et al. 1996) DMSP lyase enzymes that may be involved actively in DMS production, thereby contributing further to the elevated DMS concentrations associated with these organisms. The ecological roles of these lyase enzymes are not well understood but several recent studies have pointed to very interesting functions such as in grazing deterrence, carbon acquisition, and bacterial inhibition (Noordkamp et al. 1998; Wolfe and Steinke 1996; Wolfe et al. 1997).

Blooms of marine phytoplankton provide convenient natural "laboratories" for investigating the production of DMS in relation to phytoplankton community dynamics and species succession and associated processes, including grazing and bacterial turnover. However, this apparent focus on "hotspots" of DMS production in relatively nutrient rich areas can be criticised in that oligotrophic areas of the oceans, which generally have relatively low levels of DMS and DMSP throughout the year, make up a large fraction of the total ocean area and so must contribute significantly to the total global flux of DMS (Bates et al. 1992). These pioneering studies established the link between phytoplankton and DMS levels, but failed to account for a large part of the natural variability in DMS concentrations. There have been rather few actual DMS time-series studies (Leck et al. 1990; Turner et al. 1996a; Dacey et al. 1998), all of which noted seasonal periods of elevated DMS concentrations.

We now realise that bacterial processes are also very important in the overall DMS cycle. More isolates of bacteria are available with which to study biochemical pathways and physiology of DMSP and DMS metabolism

(e.g. Ledyard and Dacey 1994; Yoch et al. 1997). New methods, including use of ^{35}S tracers, improved inhibitors, and molecular genetics techniques have allowed ever more sensitive analyses of DMSP-DMS cycling rates and fates, and have permitted more detailed examination of the complex microbial communities involved (e.g. González et al. 1999; Wolfe and Kiene 1993). The potential for DMS production from dissolved DMSP is quite large (e.g. Kiene 1996b; van Duyl et al. 1998), but recent studies indicate that most of the DMSP in the sea is not converted to DMS. A demethylation-demethiolation pathway leading to production of methanethiol (MeSH) can account for 70–95% of DMSP metabolism *in situ* thereby diverting sulphur away from DMS (Kiene 1996a). The predominance of this non-DMS producing demethylation-demethiolation pathway is explained by the fact that bacteria use it to assimilate the sulphur from DMSP into protein amino acids (Kiene et al. 1999). Further understanding of this DMSP-DMS-MeSH-bacteria interaction is critical because a relatively small change in the yield of DMS from DMSP could have a major impact on the gross production of DMS, which would then be available for sea-air exchange.

Removal of DMS from the water column by biological and photochemical mechanisms also exerts a great influence on the net accumulations of DMS in surface waters. Slow biological degradation of DMS may partially explain the rise in DMS concentrations observed at the peak and initial decline phases of phytoplankton blooms (e.g. Matrai and Keller 1993; Nguyen et al. 1988). Net consumption of DMS appears to occur in the later stages of blooms after DMS-consuming bacteria have had time to develop (Kwint et al. 1996; van Duyl et al. 1998). The photochemistry of DMS in seawater remains poorly understood, despite the fact that it has been identified as a major removal mechanism under some circumstances (e.g. Kieber et al. 1996; Sakka et al. 1997; Brugger et al. 1998). DMS photooxidation appears to depend on photosensitisers in seawater, which are most likely part of the coloured dissolved organic matter (CDOM) (Dacey et al. 1998). In the open ocean CDOM originates from autochthonous primary productivity and food web processes so the interaction with DMS is probably complex. Add to this the fact that DMS producing and consuming bacterial populations are likely to be strongly influenced by UV-B in surface waters, and one can easily see the importance of understanding photophysical effects on the DMS cycle. Recently, it has been shown that viruses are significant agents in the control of bacteria and phytoplankton. Viral infections can cause a total release of intracellular DMSP (Hill et al. 1998) and viruses are known to infect DMSP-containing bloom organisms such as *Emiliania huxleyi* (Brussaard et al. 1996) and *Phaeocystis* sp. (Malin et al. 1998). It seems clear from studies such as these that the overall food web dynamics, including macro- and microzooplankton graz-

ing, bacterial, and viral activities, as well as the physico-chemical dynamics of the upper ocean (e.g. incoming solar radiation, mixing, temperature, air-sea exchange) are important factors governing DMS accumulation.

Modelling efforts have expanded our understanding of DMS production, both for field situations (e.g. Gabric et al. 1999) and laboratory systems (Laroche et al. 1999). However, our current knowledge base is not sufficient to develop and constrain predictive DMS production models for diverse biogeographic regions, in order to allow interpretation of the role of DMS in climate change, for example. Future research will need to focus on (1) gaining a full understanding of the processes that control DMS production and allow the prediction of DMS emissions, and (2) obtaining much more data concerning spatial, temporal, and interannual variation in the concentration of DMS and related compounds. Emphasis on undersampled areas and seasons would be valuable. For process studies, there is an increasing need to cross disciplinary and international boundaries to bring together experts on different aspects of DMS and related compounds for integrated field campaigns. For analysis of variability, “remote” sampling systems could be considered (such as attempted in ACE-1). It might be possible to develop a buoy-mounted monitoring system whereby samples were stored on a carousel for later analysis. Alternatively, we might follow the example of the pCO_2 measuring community, who have demonstrated that it is feasible to employ unmanned instruments on merchant ships (Cooper et al. 1998a). This would enable the collection of large data sets during long passage routes, covering diverse biogeographic areas, and different seasons, and the chance to investigate interannual variability at relatively low cost. New techniques will be needed to circumvent the present lack of a reliable storage method for DMS samples. In the first instance, it might be more realistic to concentrate on DMSP analyses.

2.8.2.7 Carbonyl Sulphide

The oceans represent approximately 30% of the total atmospheric source of COS, and much of the oceanographic work on COS over the last decade has focussed on assessing the spatial and temporal distributions of COS concentration and understanding the processes that control its temporal and spatial distribution. The photochemical source of COS was first recognised by Ferek and Andreae (1984), who demonstrated a clear diurnal cycle in the sea surface concentration of the compound. A mechanism of formation of COS was proposed by Pos et al. (1998) who suggested that the photochemical production of COS and carbon monoxide proceeds along a coupled pathway which first involves the photochemical formation of an acyl radical from coloured dissolved organic matter (CDOM). Flöck et al.

(1997) and Ulshöfer et al. (1996) suggested that cysteine is probably implicated in the reaction mechanism of COS formation as the result of its reactivity and abundance in the oceans. The photochemical COS production in natural seawater is probably not limited by the concentration of a precursor sulphur compound but rather by the concentration of CDOM represented by its ultraviolet attenuation coefficient (Ulshöfer et al. 1996; Uher and Andreae 1997). Zepp and Andreae (1994) and Weiss et al. (1995) quantified the wavelength dependence of COS photoproduction from CDOM and found that quantum efficiency of photoproduction decreases monotonically with increasing wavelength. The dark (or non-photochemical) production of COS has been proposed on the basis of the non-zero COS concentration observed at ocean depths where there is no photochemical production and where there is no mixing from the surface (Radford-Knoery and Cutter 1994; Flöck and Andreae 1996) and also on the basis of careful interpretation of sea surface COS concentration measurements using inverse models (Ulshöfer 1995). COS hydrolysis varies as a function of temperature and pH and has been evaluated several times over the last decade (Elliott et al. 1989; Radford-Knoery and Cutter 1994; Uher and Andreae 1997).

Recent models have used laboratory results for the photoproduction and hydrolysis rate constants to explain COS sea surface measurements obtained during expeditions made in the 1980s and 1990s (see Ulshöfer (1995) for a review of recent sea surface COS concentration measurements). Andreae and Ferek (1992) developed the first chemical box model to explain the diurnal variation of COS in terms of photochemical formation and hydrolysis destruction. Ulshöfer (1995) adopted an optimisation scheme based on the coupled photochemical-mixed layer used by Kettle (1994) to calculate the photoproduction and dark production constants for COS from a series of sea surface measurements made between 1992 and 1994 in the North Atlantic Ocean. von Hobe (1999) extended this work for other models and expedition measurements. Najjar et al. (1995) generalised a simplified coupled physical-chemical model on a global scale to investigate the sensitivity of COS sea surface concentration on ozone reduction and tropospheric increases of carbon dioxide. Kettle and Andreae (1998) and Preiswerk and Najjar (1998) have used existing measurements of the CDOM absorption coefficient of seawater to predict a seasonal variation in the absolute COS concentration, with maximum values at high latitudes in the summer of either hemisphere.

Future work on COS should aim to quantify more accurately the role of the oceans as a source or sink of the gas to the atmosphere. The global application of the photochemical production model for COS is currently limited by the absence of an algorithm to predict the global CDOM absorption coefficient and by the sugges-

tion that the apparent quantum yield of COS formation may vary by more than an order of magnitude in different regions of the ocean. The scarcity of profile measurements of COS concentration has been problematic for modelling efforts which have so far been developed to explain only the surface COS concentration distributions. Finally, the precise quantification of the sea-air flux of all gases produced in the upper ocean (including COS) is currently limited by the absence of an effective gas exchange parameterisation based on wind speed, average wave slope, or other measure of upper ocean turbulence, as already indicated.

2.8.2.8 *The Ocean's Role as Source and Sink of Atmospheric Methyl Bromide and other Methyl Halides*

Methyl halides are produced and consumed biologically (CH_3Br) (Moore and Webb 1996; Baker et al. 1999); (CH_3I) (Moore and Groszko 1999); photochemically (CH_3I) (Happell and Wallace 1996); and in surface ocean waters (CH_3Cl) (Moore et al. 1996). Recent measurements have shown that the flux of CH_3Cl is significantly less than early estimates (Moore et al. 1996) and that the open ocean is a net sink, rather than a source, for CH_3Br (see below).

Methyl bromide (CH_3Br) in the environment began to receive considerable attention in the early 1990s when it was being evaluated as an ozone-depleting gas, along with chlorofluorocarbons, chlorocarbons, and halons. First-order calculations indicated that methyl bromide was likely to be a significant contributor to stratospheric ozone depletion. Before then, only a few studies of CH_3Br in the ocean and atmosphere had been conducted. Lovelock (1975) detected CH_3Br in coastal waters of England and suggested that this gas could have a large natural source. Singh et al. (1983) later reported widespread supersaturations greater than 200% off the west coast of North America, lending support to the ocean as a large natural source of CH_3Br . Khalil et al. (1993) suggested that the open ocean was supersaturated in methyl bromide by 40–80%. However, prompted in part by calculations showing that the ocean simultaneously had to be a large sink for CH_3Br because of reaction with Cl^- in seawater (Elliott and Rowland 1995; Jeffers and Wolfe 1996; King and Saltzman 1997), numerous investigations, using *in situ* mass spectrometry-gas chromatography, demonstrated that the ocean on average was a net sink for atmospheric CH_3Br , with tropical and subtropical waters of the open ocean highly undersaturated and coastal waters often supersaturated in this gas (Lobert et al. 1995, 1996, 1997; Moore and Webb 1996; Groszko and Moore 1998). Certain species of phytoplankton produce CH_3Br , but apparently not at rates sufficient to explain the observed saturation levels (Saemundsdottir and Matrai 1998; Moore et al. 1995;

Scarratt and Moore 1996). Most recently, there have been suggestions that CH_3Br in temperate and coastal waters might undergo a seasonal cycle, with higher concentrations or supersaturations in the spring and early summer and undersaturations the rest of the year (Baker et al. 1999; King et al. 2000). About the same time, it also became clear that chemical and biological removal of CH_3Br in seawater constituted such a large sink for this gas that it would have a profound effect on the lifetime of CH_3Br in the atmosphere, even if the ocean were everywhere a net source (Butler 1994; Yvon et al. 1996b; Yvon-Lewis and Butler 1997). In the latest budget calculations, irreversible loss of atmospheric CH_3Br to the ocean accounts for one-quarter to one-third of the total removal (Kurylo et al. 1999).

These two findings – that the oceanic source was outweighed by its sinks and that the lifetime of atmospheric CH_3Br depended strongly upon its reaction in seawater – necessitated a re-evaluation of the global budget of this gas in the atmosphere. Once the apparently large soil sink was discovered and confirmed (Serça et al. 1998; Shorter et al. 1995; Varner et al. 1999), the calculated budget of atmospheric CH_3Br was no longer in balance. The latest calculations have sinks outweighing sources by 80 Gg yr^{-1} , out of a budget of 205 Gg yr^{-1} (Kurylo et al. 1999). It is unlikely that this

additional source will come from the ocean, as the current global coverage of surface measurements, although not complete, is representative of the various oceanic regimes, although with reduced coverage of coastal waters. Currently, a small net sink is calculated for the ocean ($3\text{--}30 \text{ Gg yr}^{-1}$) which is unlikely to change much, unless, of course, there is some significant global change driving it. Furthermore, recent studies are identifying terrestrial sources from plants and salt marshes that are making the budget gap smaller (Gan et al. 1998; Rhew et al. 2000; Dimmer et al. 1999).

Perhaps one of the most significant things to come out of these intensified studies of methyl bromide in the ocean is that other halogen gases may behave in similar, quantifiable ways. Many of these gases, which may include CH_3I , CHBr_3 , CH_2Br_2 , CH_2BrCl , and $\text{C}_2\text{H}_5\text{Br}$, among others, also have climatic implications through their chemistry or radiative effects; however, specific studies of them in the past have been limited (e.g. Sturges et al. 1992, 1993; Nightingale et al. 1995). When gases are produced and destroyed in seawater and exchanged with the atmosphere on similar time scales, their exchange with the atmosphere can be controlled in good part by their biogeochemical cycling in seawater. Recent analyses of polar firn air have provided global temporal trends for CH_3Br , while also showing *in situ*,

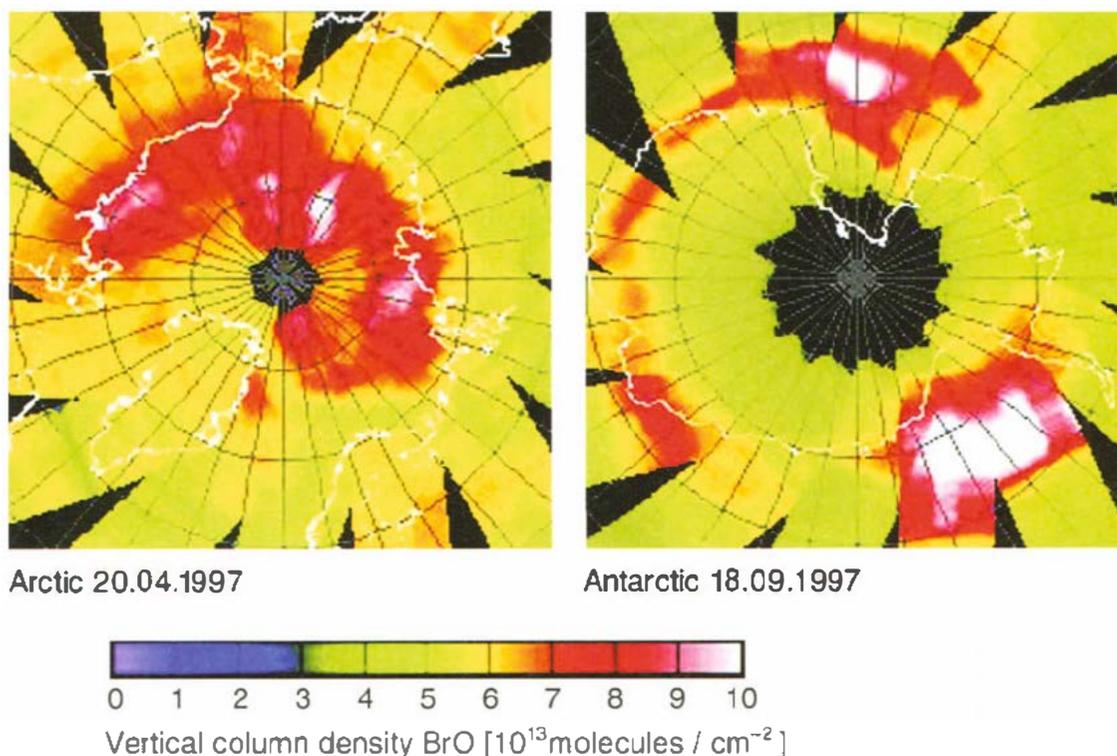


Fig. 2.19. Satellite (Global Ozone Monitoring Experiment, GOME instrument on ERS-2) observations of tropospheric BrO “clouds” in the Arctic and over Antarctica (Wagner et al. 2001). Total columns in the centre of the clouds exceed $10^{14} \text{ BrO molecules cm}^{-2}$. The clouds are visible only in springtime and have a typical lifetime of one to a few days

seasonal production for other organohalogenes (Butler et al. 1999; Sturges et al. 2001).

Large amounts of reactive bromine (and smaller amounts of chlorine) are also found in polar regions and near salt pans likely due to oxidation of halides by inorganic reactions (see also Table 3.4). However, the source of iodine compounds in the coastal marine air and of bromine in the free troposphere is much more likely to be the photochemical degradation of organohalogen compounds (like CH_2I_2 , or CH_3Br , respectively) of marine biogenic origin, as indicated above.

In field campaigns of the IGAC's Polar Air and Snow Chemistry (PASC) activity, it was discovered in the late 1980s and early 1990s (Barrie et al. 1988, 1992; Barrie and Platt 1997) that surface ozone depletion chemistry occurring in spring over the Arctic Ocean is a tropospheric analogue of stratospheric ozone chemistry, with a difference. It is driven by sea salt halogens from heterogeneous reactions occurring in sunlight on surface snow and ice, rather than by halogens from photolysis of spray can propellants. The existence of BrO and ClO as well as Cl and Br reactions with hydrocarbons was well documented in numerous measurements in air just above the surface of frozen marine areas. In spring, BrO was found in the Arctic (Hausmann and Platt 1994; Tuckermann et al. 1997) and Antarctic marine boundary layer (Kreher et al. 1997) by ground based and satellite observations (Fig. 2.19) (Wagner and Platt 1998; Richter et al. 1998; Hegels et al. 1998; Wagner et al. 2001). In addition, measurements made by chemical amplification (Perner et al. 1999), DOAS (Tuckermann et al. 1997), and by the "hydrocarbon clock" technique (Jobson et al. 1994, Solberg et al. 1996; Ramacher et al. 1999) suggest ClO levels in the pmol mol^{-1} range in the Arctic marine boundary layer. An unexpected link to the mercury cycle was discovered to result in enhanced inputs of mercury to the biosphere in these regions, when long lived elemental mercury is converted to shorter lived particulate and reactive gaseous forms of mercury (Schroeder et al. 1998). Halogen reactions are suspected to be the cause of this conversion of mercury.

As a result of these polar discoveries as well as modelling studies (e.g. Vogt et al. 1996; Sander and Crutzen 1996) (see also Chap. 3), researchers have begun to seek and confirm the occurrence of reactive halogen compounds (IO, BrO, ClO) from air-surface exchange processes in other regions (e.g. remote mid- and lowlatitude marine sites, midlatitudes coastal sites, Dead Sea basin, and the free troposphere).

2.8.2.9 Primary Marine Aerosols

Primary aerosols are also emitted directly from the oceans. The work of Blanchard and colleagues (Blanchard 1983) has shown that bubble bursting at the air-water interface injects aerosols into the atmosphere from two

sources. One is from fragments of the bubble film (film drops), the other from a jet of water that follows the bubble burst. Bubbles selectively scavenge high molecular weight surface-active compounds (Gershey 1983) and viable particulate material from the water such as bacteria and viruses (Blanchard 1983), leading to a considerable enrichment of these organic components in the aerosol relative to the water. As a result, primary particles in the marine environment will usually contain a wide range of biogenic compounds. Long-chain fatty acids, alcohols, esters, and soluble proteins have all been found in marine aerosols. Proteinaceous material and free amino acids are present in marine rain (Mopper and Zika 1987). In the atmosphere some of these compounds are degraded to form secondary aerosols, such as the fatty acids which may break down to short chain forms such as oxalic acid. Others, like the amino acid L-methionine, are oxidised. Bacteria and remains of organisms have been observed to become separated from the other aerosol components in Arctic conditions (Bigg and Leck 2001). Estimates of the organic components of marine aerosols in relatively unpolluted environments vary widely, the order of magnitude being around 10–20% by number, but this may include secondary aerosols as well as those transported from continents (Mathias-Maser 1998) (see Chap. 4).

2.8.3 Biological and Chemical Impacts of Atmospheric Deposition on Marine and Estuarine Systems

2.8.3.1 Atmospheric Iron Input to the Ocean and its Role in Marine Biogeochemistry

2.8.3.1.1 Introduction

It is now recognised that a primary transport path for iron found in the ocean is through the atmosphere. Among the first papers to address the importance of atmospherically derived iron were those of Moore et al. (1984) and Duce (1986). These authors calculated the aeolian transport of mineral matter into many areas of the ocean, and pointed out that some fraction of the iron from the mineral matter dissolved into seawater after the dust was deposited to the ocean surface. Duce and Tindale (1991) and, more recently, Jickells and Spokes (2001) have reviewed this topic.

The major reason why atmospheric dust transport has received considerable research effort over the last decade is because of the role iron has been hypothesised to play in controlling marine primary productivity over large areas of the oceans remote from land. Because of their distance from riverine and shelf inputs in these regions (e.g. Southern Oceans, North and Equatorial Pacific) one of the primary ways in which "new" iron

gets into the system is via deposition from the atmosphere of terrestrially derived material. The idea of iron being a major control on ocean production is not new. In the early decades of the 20th century it was hypothesised that the reason why large areas of the Southern Oceans contained significant amounts of residual conventional plant nutrients (nitrate and phosphate), when light and other conditions for plant growth were favourable (the HNLC, high nutrient-low chlorophyll, regions), was because of iron deficiency in the water (see, for example, Gran 1931; Harvey 1933; Hart 1934; and the recent review by DeBaar and Boyd 2000). However, it is only in the last decade that analytical techniques for iron and field-going experimental approaches have been good enough to begin to test the hypothesis critically.

2.8.3.1.2 Sources and Transport of Mineral Aerosol to the Oceans

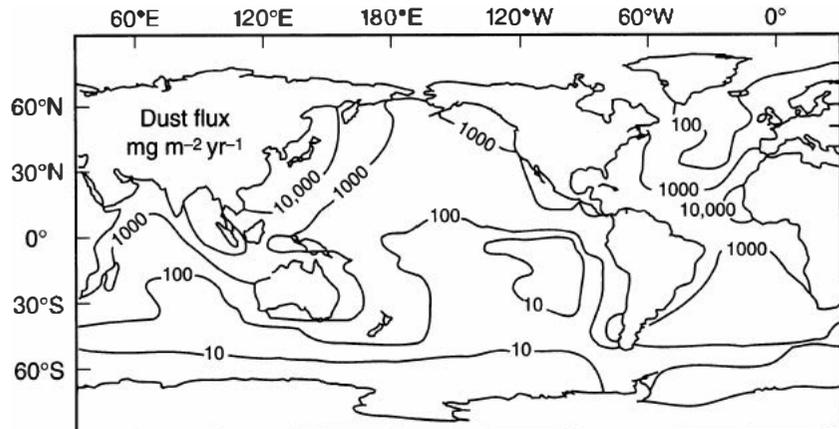
The primary sources of mineral aerosol are arid and semi-arid continental regions (e.g. Tegen and Fung 1994; Duce 1995; IPCC 1996) (see also Chap. 4). The atmospheric concentrations of dust and the deposition of dust to the ocean surface are both very episodic and are primarily associated with the transport of aerosol from dust storms or major dust outbreaks. The typical duration of such dust pulses over the ocean may range from one to four days, and the transport and deposition may also vary seasonally. Due to the episodic character of both the atmospheric dust concentrations and local rainfall, the primary removal process for dust (Duce 1995) input to the ocean in a particular region can often occur during a few events covering a relatively short period of time. For example, the results of one multi-year study showed that half of the annual deposition of dust to the ocean at Midway Island in the central Pacific occurred during only two weeks (Prospero et al. 1989). In Bermuda, Arimoto et al. (1992) found that mineral aerosol concentrations ranged over four orders of magnitude, from 0.001 to 11 $\mu\text{g m}^{-3}$.

We have very few data sets of marine surface dust concentrations collected over long periods of time. In general, the highest atmospheric concentrations of dust in marine areas are found over the North Pacific and the tropical Atlantic. Other high concentration areas are found in the Arabian Sea and the northern Indian Ocean, but there are very limited data in these regions. Accurate estimation or calculation of dust deposition is still quite difficult. An estimate of the geographical distribution of the flux of mineral matter to the global ocean is presented in Fig. 2.20 (Duce et al. 1991). Note that by far the major fraction of mineral dust is deposited in the Northern Hemisphere. The atmospheric deposition has clearly fluctuated significantly in the past, as seen in ice core and deep sea sediment samples (see, for example, Rea 1994; Andersen et al. 1998; Maher and Hounslow 1999). Numerical simulations of the mineral dust cycle are attempting to improve global data sets by linking soil types, particle emissions, gas-particle heterogeneous chemistry, and wind transport in the troposphere with aerosol satellite measurements (e.g. Marticorena and Bergametti 1995; Phadnis and Carmichael 2000) (also see Chap. 6).

2.8.3.1.3 Iron in Mineral Aerosol over the Oceans

The atmospheric deposition of iron is associated with the eroded mineral aerosol particles, and the iron is primarily bound in their aluminosilicate matrices. It is thus possible to convert mineral aerosol concentrations or fluxes to an iron concentration or flux by knowing the abundance of iron in the earth's crust. This ranges from ~3 to 5% (Taylor and McClennan 1985). Typically a value of 3.5% is used. With a mineral aerosol flux of 500–2000 Tg yr^{-1} , the input of iron would be ca. 15–100 Tg yr^{-1} . However, before the iron deposited from the atmosphere can be utilised by phytoplankton, it must be in a form that is available to these organisms. Processes that change the solubility or lability of the iron in the atmosphere will then have potential for influencing

Fig. 2.20. Calculated global fluxes of atmospheric mineral matter to the ocean (Duce et al. 1991)



the availability of the iron when the atmospheric material enters the ocean. Jickells and Spokes (2001) have carefully reviewed the information to date on the mechanisms that may control the distribution of dissolved and/or particulate iron in the material entering the ocean from the atmosphere. Some studies have observed Fe(II) in aerosol iron and its formation is postulated to occur via photochemical reduction of Fe(III) hydroxides. Certain organic compounds such as oxalate, acetate, and formate can facilitate this photoreduction. It has been suggested by several authors that the low pH (0–5) characteristic of the cloud cycling process produces acidic, hygroscopic aerosols. This combined with possible photochemical reactions results in an increase in the lability of crustally derived metals, such as iron, in the atmosphere over that seen in the parent material. In turn, this will play a role in the availability of the iron when the aerosol enters the ocean (e.g. Jickells and Spokes 2001; Zhu et al. 1992). In addition, high ionic strength solutions and alternating wet and dry cycles during cloud formation and evaporation would be common. There are likely to be many such cycles before the particles ultimately enter the ocean by dry deposition or precipitation.

Jickells and Spokes (2001, and references therein) state, in summary, that it is likely that the overall iron solubility of dry deposited mineral aerosol is <1% at a seawater pH of 8, and that a significant proportion of this iron is photoreduced to Fe(II), which is bioavailable. The solubility of iron in marine rains with a pH of 4–7 is generally 14%. Thus the input of soluble atmospheric iron to the oceans is apparently dominated by wet deposition. These estimates, based on laboratory studies, are somewhat lower than those made earlier by other authors. However, Jickells and Spokes (2001) made other oceanographic approaches to estimate the solubility of atmospheric iron. All of these approaches result in low overall iron solubility, probably less than 2%. Their final conclusion is that approximately 0.8 to 2.1% of the total iron deposited in the ocean is soluble. With a total input of 15 to 100 Tg yr⁻¹, this would result in a total soluble iron atmospheric input of from 0.12 to 2.1 Tg yr⁻¹.

2.8.3.1.4 Iron and Marine Biogeochemistry

Once the atmospheric iron has entered the oceans by either wet or dry deposition, it is hypothesised to play potentially important roles in the primary productivity of surface waters in substantial areas remote from land. These HNLC regions are estimated to cover ~20–25% of the area of the oceans. An up-to-date and detailed assessment of the chemical form of iron in seawater and how this relates to its uptake by marine organisms is to be found in several chapters in the book edited by Turner and Hunter (2001).

John Martin and his colleagues made some of the first reliable measurements of iron in the oceans and con-

ducted shipboard incubation studies in flasks and carboys of HNLC seawater that had been amended with soluble iron (Martin et al. 1994). The results were promising (e.g. Martin and Fitzwater 1988) and clearly showed that addition of iron (normally added as ferrous sulphate or other simple inorganic salts) could lead to substantial increases in plankton growth, as indicated by increasing chlorophyll concentrations with time in the experimental flasks. An interesting variant on this basic experiment, which is particularly relevant in the present context, was a study conducted in the equatorial Pacific by Johnson et al. (1994). They added the iron in a variety of inorganic and organically complexed forms, but they also used natural Asian dust aerosol particles (collected in Hawaii) and added them to one of the carboys of seawater. In this carboy the rate of plankton growth was found to be the most rapid and attained the highest chlorophyll levels, indicating that the aerosol particles were more effective at promoting growth than artificial iron supplements.

Other avenues have been explored to attack the problem in a more direct way. Young et al. (1991) monitored natural dust inputs to the North Pacific and examined any resulting change in productivity in the receiving water. Several dust deposition events appeared to be correlated with increases in primary productivity measured in on-deck incubators, but with a four day lag between the dust input and the peak in productivity. Although suggestive of a relationship, the results were too few and insufficiently clear-cut to be totally convincing. In addition, interpretation was complicated because productivity change was measured in a deck incubator, not in the ocean itself. Also, when deposition occurred, meteorological conditions changed, with greater stirring of near-surface water, which itself may have changed the productivity. However, this experiment represents a novel and potentially powerful tool since it uses the natural atmospheric input and examines the response of the real oceanic system.

A different approach to testing the iron hypothesis is that of adding inorganic iron (FeSO₄) directly to a small patch (of the order of 100 km²) of the oceans. In order to be able to track the iron enriched patch as it moves in the ocean, the gas sulphur hexafluoride is added along with the iron. Sulphur hexafluoride can be easily measured at tracer (femtomolar) concentrations in almost real time from the research vessel, enabling the enriched patch to be tracked. The principles underlying this approach are outlined in Watson et al. (1991a). It has been utilised three times to date; twice in the equatorial Pacific (IronEx I: Martin et al. (1994) and IronEx II: Coale et al. (1996)) and very recently in the southern oceans (SOIREE: Boyd et al. (2000)). On all three occasions, raising the iron level in the water by a few nanomoles per litre produced a significant enhancement in phytoplankton activity, as measured by chlorophyll concen-

Fig. 2.21. Carbon dioxide changes inside and outside the enriched patch during the course of SOIREE (Boyd et al. 2000)

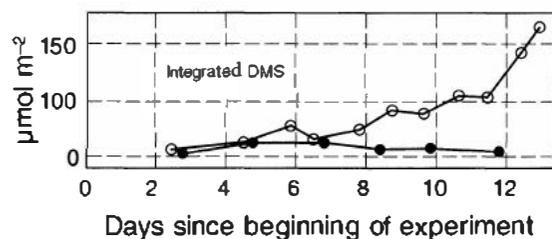
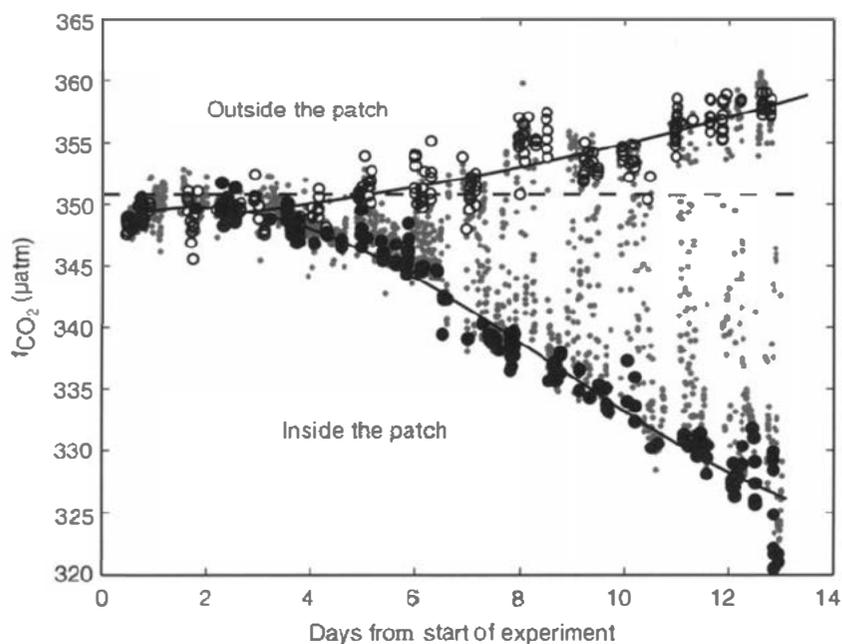


Fig. 2.22. Depth-integrated time evolution of DMS and DMSP inside (open circles) and outside (closed circles) the enriched patch during the course of SOIREE (Boyd et al. 2000)

tration increase, consistent with the iron fertilisation hypothesis. In the case of IronEx II, the increase was at least an order of magnitude. Smaller organisms were the first to utilise the iron supplement, with the larger plankton (mainly diatoms) benefitting later.

Trace gases measured in these experiments were CO₂ and DMS. The former was drawn down due the enhanced primary production. The extent of CO₂ removal roughly mirrors the increase in chlorophyll, except for IronEx I where it was very small, probably due to rapid recycling of the fixed carbon by grazers. For DMS, three- to five-fold increases occurred in all three studies, with much less variation than for CO₂. Carbon dioxide changes between inside and outside the enriched patch during the course of SOIREE are shown in Fig. 2.21, and the time evolution of DMS and its precursor DMSP integrated over a vertical column are shown in Fig. 2.22. Such a fertilisation experiment is akin to a batch culture perturbation and it is not clear whether long-term Fe enrichment and sustained higher productivity would lead to higher steady-state DMS concentrations. Given

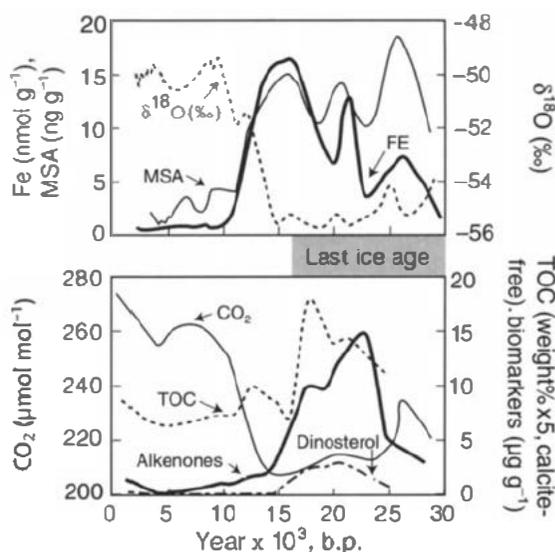


Fig. 2.23. Compendium of results from ice cores for iron, CO₂, MSA, and several other parameters (Turner et al. 1996b)

enough time, shifts in the population structure, or simply growth of the microbial populations, might re-establish low steady-state DMS concentrations with perhaps higher turnover of both DMSP and DMS. Our present understanding of the response of microbial populations to changes in DMSP and DMS supply is insufficient to make confident predictions in this regard. To put these results in a broader time context, a compendium of results from ice cores for iron, CO₂, MSA (an atmospheric oxidation product of DMS), and several other parameters is provided in Fig. 2.23. It is note-

worthy that the elevated iron and MSA and lowered CO₂ levels during the last glacial period are consistent with a scenario wherein ocean productivity was higher then due to enhanced atmospheric inputs of iron. For further discussion of the use of ice core records to examine the overall sulphur cycle see Sect. 2.3.

2.8.3.2 The Input of Atmospheric Nitrogen to the Ocean

2.8.3.2.1 Coastal Regions

There is now widespread evidence that atmospheric fixed nitrogen compounds contribute to enrichment and in some areas probably to coastal and estuarine eutrophication (Jaworski et al. 1997; Howarth et al. 1996). Current estimates of the percentage of total (natural + anthropogenic) new N loading attributed to direct atmospheric deposition at a number of North American and European locations range from 5% to over 50% (Duce 1991; Fisher and Oppenheimer 1991; Valigura et al. 1996; Dennis 1997; Holland et al. 1999). Inputs of N to estuarine systems that result from direct atmospheric deposition by-pass much of the estuarine N “filter” (Kennedy 1983; Paerl 1995, 1997). Thus, atmospheric deposition assumes an increasingly important role as a new N source in lower estuarine and coastal waters below the biological N filtering zone (Fig. 2.24).

Dry and wet atmospheric deposition introduces into estuaries a variety of biologically available inorganic (NO₃⁻, NH₄⁺, DON) compounds, most of which result from human activities (Likens et al. 1974; Galloway et al. 1994). In addition, organic nitrogen (ON) comprises a significant fraction (from 15 to over 30%) of wet and dry atmospheric deposition in coastal watersheds (Correll and Ford 1982; Scudlark and Church 1993; Peierls and

Paerl 1997). Although the composition of atmospheric ON is poorly known, recent work (Peierls and Paerl 1997; Seitzinger and Sanders 1999) indicates that constituents of this pool are biologically utilised and, hence, should be included in eutrophication assessments.

In situ bioassays and field surveys show that enrichment with the major deposition constituents NH₄⁺ and NO₃⁻ at natural dilutions and atmospherically derived dissolved organic nitrogen (DON) results in enhanced phytoplankton primary production and increased biomass (Paerl 1985; Willey and Paerl 1993; Paerl and Fogel 1994; Peierls and Paerl 1997). Atmospheric DON may selectively stimulate growth of specific types of marine phytoplankton (Neilson and Lewin 1974; Antia et al. 1991). These selective phytoplankton responses to specific nitrogen inputs, and changes in stoichiometric C:N ratios resulting from these inputs may induce changes at the zooplankton, invertebrate, herbivorous fish, and higher trophic levels.

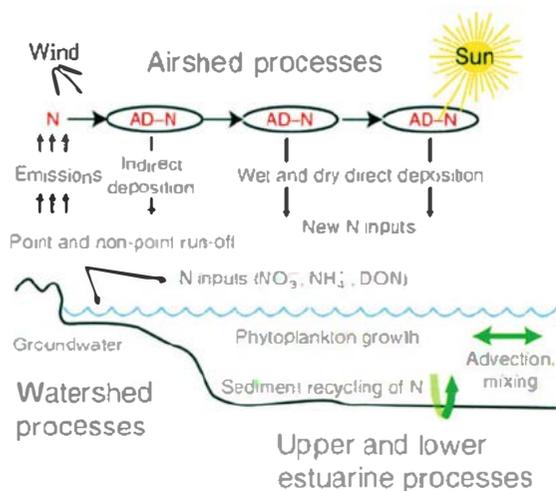


Fig. 2.24. Schematic representation of airshed, upper estuarine, and lower estuarine processes

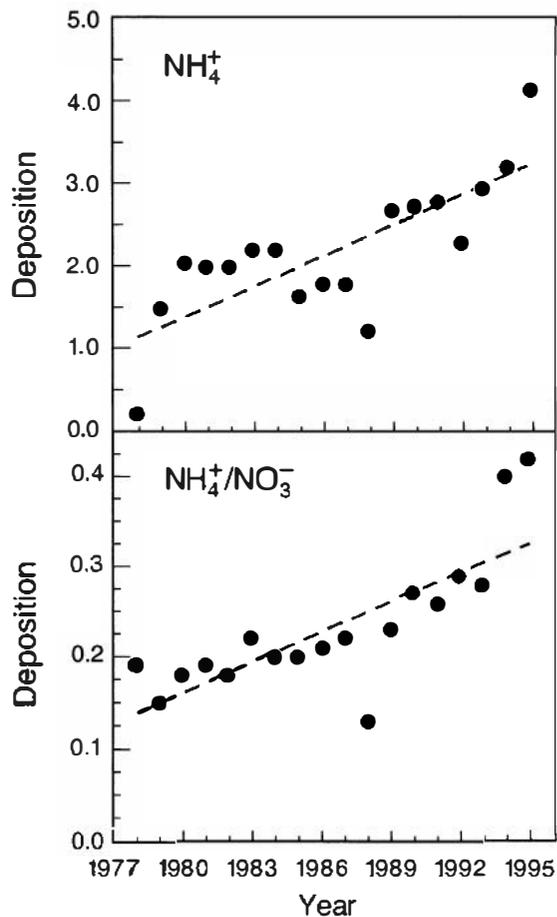


Fig. 2.25. Trends in annual atmospheric deposition (wet deposition as NH₄⁺ and NO₃⁻ expressed in kg N ha⁻¹ yr⁻¹) collected during a 20 year period at the National Atmospheric Deposition Program (NADP) site NC-35 in Sampson County, North Carolina (data re-plotted from NADP information)

Atmospheric nitrogen inputs have been examined recently in North Carolina's Albemarle-Pamlico Sound System (APSS) (Paerl 1995, 1997). Within the APSS, the Neuse River Estuary receives N inputs from a mosaic of upstream and upwind agricultural, urban, and industrial sources. Fossil fuel combustion and agricultural and industrial N emissions represent a significant and growing source of new N to this system (Paerl and Fogel 1994), reflecting a national and world-wide trend (Duce 1986; Luke and Dickerson 1987; Asman 1994; Paerl 1995; Holland et al. 1999). Depending on the relationship between watershed-estuary surface areas, degree of watershed N retention, seasonal rainfall, discharge and flow patterns, and proximity of atmospheric sources, an important fraction of nitrogen from atmospheric deposition is directly deposited on the estuary. In the case of the APSS, recent estimates are on the order of 20% (for its estuarine tributaries) to 40% (for the downstream waters of Pamlico Sound) (Paerl and Fogel 1994; Paerl 1995, 1997) of the N being directly deposited.

Atmospheric N generated from expanding intensive animal farming is of particular concern. Examination of the long-term record of atmospheric NH_4^+ and NO_3^- deposition in Sampson County, eastern North Carolina, shows a nearly three-fold increase in annual NH_4^+ deposition (also relative to NO_3^-) since 1977, with a particularly precipitous rise since the late 1980s (Fig. 2.25). The reason for this may be that unlike human waste, swine waste is stored in open lagoons and remains largely untreated, and substantial amounts (30 to >80%) of N are lost via NH_3 volatilisation alone (O'Halloran 1993).

2.8.3.2.2 *The Open Ocean*

There is also growing concern about the increasing input of human-derived nitrogen compounds to the open ocean. This is especially important in parts of the open ocean where nitrogen is the nutrient that limits biological growth. This is the case in the nutrient-poor waters of the large central oceanic gyres in the North and South Pacific and Atlantic Oceans and the southern Indian Ocean. Current estimates suggest that, at present, atmospheric nitrogen accounts for only a few percent of the total new nitrogen delivered to surface waters in these regions, with upwelling from deep waters being the primary source of new surface nitrogen. It is recognised, however, that the atmospheric input to the ocean is highly episodic, often coming in large pulses extending over a few days. At such times, atmospheric input plays a much more important role as a source for nitrogen in surface waters. A recent estimate of the current input of fixed nitrogen to the global ocean from rivers, the atmosphere, and nitrogen fixation indicates that all three sources are important (Cornell et al. 1995). Paerl and Whitall (1999) estimate that 46–57% of the total human-mobilised nitrogen entering the North Atlantic Ocean is coming via the atmosphere.

In addition, the atmospheric organic nitrogen flux may be equal to or perhaps greater than the inorganic (i.e. ammonium and nitrate) nitrogen flux in open ocean regions. The source of the organic nitrogen is not known, but a large fraction of it is likely to be human-derived. This form of atmospheric nitrogen input to the open ocean had not been considered in detail until very recently.

Not only will the input of atmospheric fixed nitrogen to the open ocean increase significantly in the future as a result of increasing human activities, but the geographical locations of much of this input will probably change as well. Galloway et al. (1994, 1995) have evaluated pre-industrial nitrogen fixation (formation of the so-called reactive nitrogen) on the continents; the near-current (1990) reactive nitrogen generated from human activities such as energy production (primarily as nitrogen oxides), fertiliser use, and legume growth; and the estimated reactive nitrogen that will be produced in 2020 as a result of human activities.

The most highly developed regions in the world are predicted to show relatively little increase in the formation of reactive nitrogen, with none of these areas contributing more than a few per cent to the overall global increase. However, other areas will contribute very significantly to increased human-derived reactive nitrogen formation in 2020. For example, it is predicted that Asia will account for ~40% of the global increase in energy-derived reactive nitrogen, while Africa will have a six-fold increase accounting for 15% of the total global increase. It is predicted that production of reactive nitrogen from the use of fertilisers in Asia will account for ~87% of the global increase from this source. Both energy sources (nitrogen oxides and ultimately nitrate) and fertiliser (ammonia, urea) result in the extensive release of reactive nitrogen to the atmosphere. Thus, these predictions indicate very significant potential increases in the atmospheric deposition of nutrient nitrogen compounds to the ocean downwind of such regions as Asia, Central and South America, Africa, and the former Soviet Union (see Fig. 2.26).

The potential problem outlined above was highlighted by a computer modelling study undertaken by Galloway et al. (1994), who generated maps of the recent (1980) and expected (2020) annual deposition of reactive nitrogen compounds from the atmosphere to the global ocean. Figure 2.26 is a map of the projected ratio of the estimated deposition of oxidised forms of nitrogen in 2020 to the values for 1980. It appears that from one and a half to three, and in some limited areas up to four, times the 1980 rate will occur over large areas of the oceans. This increased nitrogen deposition will provide new sources of nutrient nitrogen to some regions of the ocean where biological production is currently limited by nitrogen. There is thus the possibility of important impacts on regional biological production and the marine carbon cycle in these regions of the open ocean.

Increase in reactive nitrogen deposition, 1980–2020

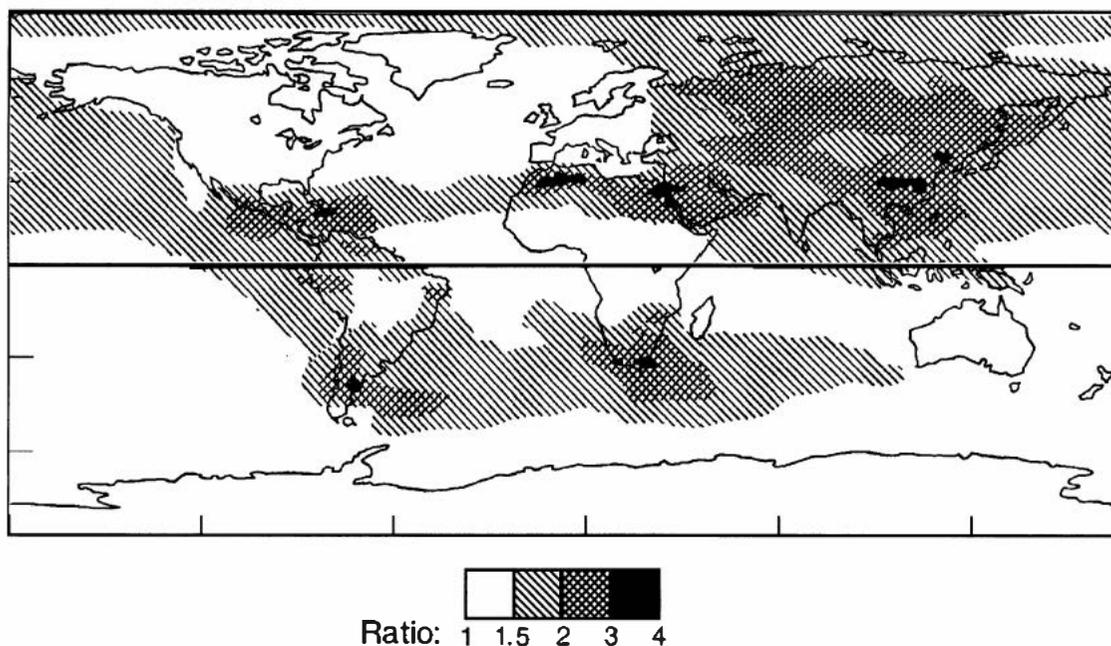


Fig. 2.26. Ratio of the estimated deposition of oxidised forms of nitrogen to ocean and land surfaces in 2020 relative to 1980 (adapted from Galloway et al. 1994, and Watson 1997)

Debate continues about the relative importance of iron, nitrogen, or other compounds as prime determinants of oceanic phytoplankton productivity and, consequently, potential controls of marine gas emissions. On geological time scales, phosphorus is accepted to be the ultimate control. Silica, another component of the same Fe and N-containing dust but with a significantly longer residence time, has also been examined as an altering agent of the species composition of marine phytoplankton in oceanic regions, favouring siliceous organisms (e.g. diatoms) (e.g. Harrison 2000; Treguer and Pondaven 2000). Such organisms would differentially affect total gas emissions but not total primary production. Such a silica hypothesis reinforces the link between marine biogeochemistry and resulting sea-air gas emissions.

2.9 Summary of Achievements and Remaining Research Challenges

Much progress has been achieved over the last decade through technological advances and appropriate scientific approaches. The advances include: remote sensing instrumentation to provide detailed spatial and temporal data; micrometeorological and isotopic techniques for estimating the flux of matter and energy within ecosystems and between ecosystems and the atmosphere, geosphere, and biosphere; techniques for manipulations

of local scale selected environmental factors; and, statistical and numerical modelling techniques capable of analysing multi-variate, nonlinear problems.

A developing system-based approach, including Lagrangian studies of air and water masses, comprising all components, e.g. soils, vegetation, and atmosphere, has led to an understanding of biogeochemical cycles of individual chemical compounds and interactions among chemical compounds. The campaign mode of carrying out field measurements has enhanced the understanding of the interconnectedness of systems and the importance of scaling issues.

Highlights of the research include:

- Reduced uncertainties in N_2O , NO , CH_4 , DMS, and certain organohalogen emissions, and a better characterisation of local and regional distribution patterns of fluxes together with a mechanistic, but not necessarily integrated, understanding of the surface factors which control these emissions and exchange.
- Effective mitigation strategies have been developed for some CH_4 emissions and a better understanding of how land management practices influence N_2O and CH_4 emissions has been gained.
- Mechanisms and pathways of production and environmental controls have been identified for a large number of VOC compounds emitted from vegetation, including canopy transfer processes. Emission models estimating global emissions have been developed.

- VOC emissions can account for a loss of two to four percent of C taken up by photosynthesis, which has implications for understanding and quantifying the C cycle.
- Improved understanding of atmospheric input of inorganic N and Fe, mainly of anthropogenic and soil origin, into coastal and open ocean environments representing 5–70% of total input in the case of nitrogen and the subsequent impacts on the C uptake of the oceans and the C and S cycles.
- The acidic nature of wet deposition, which differs by source and region, has been characterised.
- Improved understanding of the partitioning of dry deposition (particularly O₃ and NO₂) on leaves and soil surfaces and related physiological mechanisms has been developed.
- Emission ratios for biomass burning are well described for savannas, but less well described for humid forests and biofuels. Broad databases are available of emission factors for a large number of substances.
- To determine whether changes in the marine emissions of trace gases and particles are likely to have a significant influence on atmospheric chemistry and vice-versa, resulting from climatic (e.g. rainfall, temperature; perhaps small), elevated CO₂ (perhaps large), and/or land use changes. Key areas may include the greenhouse effect (tropospheric O₃), stratospheric ozone (CH₃Br), radiation and clouds (DMS), VOCs, tropospheric chemistry (dust-Fe-DMS-CO₂), and other unpredicted impacts (e.g. the change in marine phytoplankton communities coupled with changes in N and Fe deposition), especially in the Tropics and high latitudes.
- To understand how the hydrological cycle will be affected in various regions with climate change and the subsequent impacts on emissions.
- To improve the parameterisation of air-sea exchange and its links to biogeochemical cycling in surface waters as well as improve Lagrangian studies in water, air, and the combined ocean-atmospheric front, including international participation in order to overcome the intrinsic organisational and logistical difficulties.

To achieve more plausible and quantitatively reliable answers, several key issues remain:

- To investigate mechanisms (chemical and biological) responsible for trace gas cycling (emission and deposition) in oceans, soils, and plants, and to establish long-term sites/studies to provide that information, undertaking field experiments to determine, quantify, and discriminate among driving variables.
- To study the exchange of VOCs between vegetation, oceans, and the atmosphere along with the exchange of other trace gases.
- To understand and quantify the effect of soil-released NO and its oxidation product NO₂, under different management practices, to the atmosphere including interaction of these gases both within and above the canopy.
- To promote the establishment, wherever possible, of long-term sites for flux measurements, to investigate the magnitude of interannual variation and thus achieve more robust estimates of mean annual fluxes and global budgets.
- To design experiments that will bring synthesis from emission-type studies, regional means of fire detection and prediction, spatially and temporally resolved, and chemical transport models (see Chap. 6) in order to determine the impact of burning on atmospheric chemistry.
- To develop more realistic biological and deposition process-oriented models with interaction and feedback among process-oriented, regional models and global models in order to provide improved estimates of emission and deposition fluxes.