Chapter 5:

Integration and Synthesis

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This chapter, which is intended to integrate in a coherent framework the topics presented in the previous chapters, should be regarded as a first draft. Many references are missing in different parts of the text. This document has not been reviewed and is not yet completed. Figures are not yet included. The chapter will be finalized after the Aspen meeting based on input provided at the meeting.

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1. Introduction

The previous chapters highlight some of the major findings of the last decade. They focus on the important issues related to the coupling between the biosphere and the atmosphere, photochemical processes in the atmosphere, and aerosol formation and fate. In the present chapter, we present a general overview of our understanding of the processes that determine the chemical composition of the atmosphere and emphasize several aspects of the research in which IGAC has been directly involved. We first present a synthetic view of the natural processes that determine the chemical composition of the atmosphere, and specifically summarize our understanding of the tracer emissions by the continental biosphere, the chemical couplings between the ocean and the atmosphere, and the importance of lightning for the global atmospheric composition. In a following Section, we examine the importance of human influences on the chemical composition of the atmosphere. We then examine the particular, yet important case of biomass burning, because of its importance as a source of atmospheric perturbations, specifically in the tropics. Finally, we present an overview of our understanding of global budget for chemical species and conclude by envisaging some prospects for the chemical composition in the 21st century.

2. The natural (pre-industrial) atmosphere

2.1. Introduction

Chapter 2 has highlighted the important role played by the biosphere in controlling the chemical composition of the natural atmosphere. The abundance of chemical species in the present troposphere and stratosphere has, however, been changing dramatically as a result of agricultural practices and industrial development. In order to assess the role of these human-induced perturbations, it is crucial to understand the natural processes that determine background conditions and explain the state of the atmosphere in the pre-industrial era.

It is first important to recognize that the state of the natural system is highly dynamic. Variability at a variety of temporal and spatial scales are characteristic of a nonlinear system in which chemical and biological processes are linked to the physical climate of the planet. Past changes in the air composition derived from ice core analyses are not only due to long-term periodic variations in the solar energy reaching the Earth (Milankovich cycles), but are also representative of the nonlinear response of the Earth System.

Perhaps the strongest link between the biosphere and the atmosphere is provided by the fluxes of chemical elements (e.g. carbon, nitrogen, sulfur) between these components of the Earth System. These fluxes need to be carefully estimated before global budgets of chemical compounds can be established. Different contributions have to be distinguished over the continents, including the release of molecules by plants, soils and wetlands, as well as the deposition of chemical species on the surface. In this latter case, both ′wet deposition′ of soluble species as a result of scavenging by precipitation and ′dry deposition′as a result of chemical or physical processes on the vegetation and soils must be considered. Exchanges of trace gases between the ocean and the atmosphere depend on the solubility of chemical compounds in water and on the wind speed at the surface of the ocean.

Non-biological sources are also affecting the chemical composition of the atmosphere. These include the release of material by volcanic eruptions. Such events have played a major role in determining the evolution of the atmospheric composition on geological timescales. In the contemporary atmosphere, they episodically perturb the system as observed in the last decades after the eruptions of El Chichon and Pinatubo. Finally, in situ sources and sinks of chemical compounds must be considered. This is the case for nitrogen oxides which are produced in substantial quantities by lightning flashes in thunderstorm systems or for many other species (e.g., ozone) that are produced and destroyed by in situ chemical reactions.

2.2. Surface emissions by the continental biosphere

Large amounts of oxygen, nitrogen, and carbon are exchanged between the continental biosphere and the atmosphere. As stated in Chapter 1, the presence of major atmospheric gases (N_2 and O_2) in the Earth's atmosphere results primarily from the existence of living matter and specifically from microbial processes in soils (N_2) and photosynthesis by plants (O_2). The level of atmospheric carbon dioxide is also determined in large part by photosynthesis and respiration processes in plants. The release of less abundant, but more reactive biogenic compounds plays a key role for the photochemistry of the atmosphere, since these species control to a large extent the oxidizing power of the atmosphere under non-polluted conditions and affect directly the tropospheric concentration of ozone and of the hydroxyl radical. We briefly summarize our current knowledge on the emissions of several biogenic gases.

Nitrous and Nitric oxides. Nitrous and nitric oxides are produced in soils as a result of nitrification (ammoniac converted in nitrates and nitrites) and denitrification (inverse conversion) processes. The corresponding total emission is poorly known (uncertainty of a factor 10) due to the extreme geographical variations in the observed fluxes and their strong dependence on environmental conditions. Natural fires (biomass burning) contribute to the natural emissions of nitric oxide. Nitrous oxide is very stable in the atmosphere (lifetime of 150 years) and hence penetrates into the stratosphere where it is photolyzed and oxidized. The oxidation of nitrous oxide is known to be the largest source of nitric oxide in the stratosphere. This latter compound contributes to the destruction of ozone in the stratosphere. In the troposphere, the presence of nitric oxide catalyzes the photochemical production of ozone.

Ammonia. Natural Sources of ammonia include emissions by soils, enzymatic decomposition of urea in animal urine, and emanations from decomposing excrement and biomass burning. Despite its relatively short lifetime in the atmosphere, ammonia is the third most abundant nitrogen gas (after N_2 and N_2O) in the atmosphere.

Methane. Methane is produced primarily by bacterial decomposition of organic matter in anaerobic (oxygen deficient) environments, including wetlands, lakes, etc. Substantial amounts of CH4 are released by high latitude ecosystems as well as by tropical forests. Natural sources represent only 35-40 percent of current total emissions. The contribution of wild animals is probably much smaller than that of livestock. The emission by termites is believed to be considerably smaller than in the early studies. The oxidation of methane is a major source of carbon monoxide in the natural atmosphere.

Nonmethane Hydrocarbons. Even in the present atmosphere, vegetation provides the largest source of atmospheric nonmethane hydrocarbons. The natural source of isoprene, for example, is estimated to be almost as large (in mass) as the total (natural and anthropogenic) source of methane. The emission source of terpenes and other biogenic hydrocarbons is probably as large or even larger. In recent years, much attention has been given to the biogenic emissions of acetone; this compound could provide a major source of the OH radical in the tropical upper tropophere. The lifetime of isoprene and of other primary biogenic hydrocarbons is generally short (typically less than 1 day). Their photochemical destruction occurs through reaction with the hydroxyl radical (during daytime), with ozone and NO_3 (which is most abundant during nighttime). Intermediate organic compounds are formed and can be transported away from the sources and affect photochemistry. Nonmethane hydrocarbons are a major source of carbon monoxide under natural conditions.

Detailed observations are needed to quantify the biogenic emissions of partially oxidized hydrocarbons (aldehydes, alcohols, ketones, etc.) which can be released by plants and could affect organic chemistry in the continental atmosphere.

[Need to add SO_2 by volcanoes, soil dust and perhaps insert here NO_x by lightning]

2.3. Chemical couplings between the ocean and the atmosphere

The ocean is both a source and sink for atmospheric trace gases and particles. During the past decade numerous studied have used measured seawater and atmospheric trace gas concentrations to calculate the ocean-atmosphere exchange. Aerosol concentrations in the atmospheric marine boundary layer have been used to infer a similar exchange. The following paragraphs summarize some of the recent highlights in chemical couplings between the ocean and atmosphere.

Air-sea exchange: The ocean-atmosphere flux (F) of a sparingly-soluble gas (X) can be expressed as:

$F = k\ L\ dp$

where k is the gas transfer velocity expressed in units of length/time, L is the gas solubility at the ambient surface seawater temperature expressed in units of concentration/pressure, and dp is the difference in the gas partial pressure in surface seawater and the overlying atmosphere. Factor k is parameterized using wind speed and Schmidt number which is the ratio of kinematic viscosity of seawater and the molecular diffusivity of the gas (Liss and Merlivat, 1986; Wanninkhof, 1992).

Although the calculations are straight forward, there are still large uncertainties in the resulting values of k. While the Liss and Merlivat (1986) wind speed/transfer velocity relationship has been supported by dual tracer techniques (Watson *et al.*, 1991), other studies suggest that this relationship underestimates the flux by as much as a factor of two (Smethie *et al.*, 1985; Erickson, 1989; Tans *et al.*, 1990; Wanninkhof, 1992). These differences are in part due to the wind fields used in the calculations. Since many of the wind speed/transfer velocity relationships are non-linear, transfer velocities calculated with long-term average winds will generally be lower than those obtained using short-term variable winds (Wanninkhof, 1992). The choice of wind fields depends upon the available data and the scientific objective. Studies aimed at obtaining a large scale (ocean basin or global) average gas flux by necessity use long-term average winds (Bates *et al.*, 1987; Tans *et al.*, 1990; Murphy *et al.*, 1991). The uncertainty in calculating wind speed/transfer velocity relationships remains as a major challenge to understanding the chemical coupling between the ocean and atmosphere. The major uncertainty in the air-sea exchange of the gases discussed below is due to the range of potential transfer velocities. New faster response sensors will provide additional techniques for measuring air-sea gas exchange. Reducing this uncertainty will be a major goal of SOLAS.

Dimethylsulfide: The ocean is the major natural source of sulfur to the atmosphere. Numerous studies during the past decade have helped to define regional and seasonal variations in surface seawater dimethylsulfie (DMS) concentrations. A global database of sea surface DMS measurements has been recently compiled by Kettle *et al.* (1999). The database includes over 15,000 point measurements from 23 different institutions. While this effort provides an excellent gridded data set for calculating ocean-atmosphere DMS fluxes in chemical transport models, we still lack the ability to predict how the concentrations of seawater DMS might change with a changing climate. The air-sea exchange of DMS is only a small sink in the seawater sulfur cycle and thus minor changes in surface ocean biology, chemistry, or physics could have a major effect on the surface seawater DMS concentration and flux. Future work is needed to define the processes controlling surface seawater DMS concentrations.

COS: Carbonyl sulfide (COS) is produced photochemically in the surface ocean (Zepp and Andreae, 1994; von Hobe *et al.*, 1999). Early measurements, which were generally taken in the summer season and during daytime, suggested that the open ocean was a significant source of COS to the atmosphere. However, recent measurements have shown wide regions of the open ocean, especially in the subtropical gyres and wintertime subpolar waters, to be undersaturated with respect to the overlying atmosphere (Weiss *et al.*, 1995). The revised flux calculations, taking into account the diel and seasonal variability, suggest that the open ocean is on average in equilibrium with the atmosphere (Ulshofer *et al.*, 1995; Weiss *et al.*, 1995). The coastal ocean remains a significant source or COS to the atmosphere.

Methylhalides: Methylhalides are produced and consumed biologically (CH3Br- Moore and Webb, 1996; Baker *et al.*, 1999; CH_3I – Moore and Groszko, 1999) and photochemically (CH_3I–Happell and Wallace, 1996; CH3Cl – Moore *et al.*, 1996) in surface ocean waters. Recent measurements have shown that the flux of CH3Cl (Moore *et al.*, 1996) is significantly less than early estimates and that the open ocean is a net sink rather than a source for CH3Br (Lobert *et al.*, 1997; Groszko and Moore, 1998). The oceanic source of CH3I to the atmosphere is estimated at 0.9 –2.5 Gmol/yr (Moore and Groszko, 1999). Coastal (Nightingale *et al.*, 1995; Itoh and Shinya, 1994) and high-latitude (Sturges *et al.*, 1992; 1993) production of halocarbons are a significant source of bromine to the atmosphere. In the high latitudes the resulting atmospheric bromine plays an important role in ozone loss.

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 ?moles/m2/d. However, the total annual emission to the atmosphere of 0.46 Tmoles or 13 Tg is small compared to current estimates from both terrestrial natural and anthropogenic sources of 2400 Tg(CO)/year. Even in the Southern Hemisphere, which accounts for 2/3 of the oceanic emissions, the ocean source is relatively small (< 1%) since both methane oxidation and biomass burning are large sources of CO in the southern hemisphere. (Bates *et al.*, 1995)

Methane: The ocean is a small source of CH_4 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 the saturation ratios outside the tropics appears to be the change in sea surface temperature. Saturation ratios in the equatorial region were always positive and appears to be driven by the strength of the equatorial upwelling. Extrapolating the Pacific data globally and dividing the open-ocean seasonally into two periods and regionally into 10 zones, the calculated average flux of CH_4 to the atmosphere is 25 Gmoles y^{-1} (13 to 38 Gmoles y-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, 1994). 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) due to CH4 emissions from bottom sediments and definitely warrant further investigation.

Nonmethane hydrocarbons: NMHC are produced in surface seawater possibly by photochemical mechanisms, phytoplankton activity and/or the microbial breakdown of organic matter (Plass-Dulmer *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 species (Donahue and Prinn, 1993, Broadgate *et al*., 1997; Pszenny *et al*., 1999). Additional seasonal measurements of isoprene, ethene and propene are needed in different ocean regions.

Ammonia and methylamines: Ammonia and methylamines, like other reduced biogenic gases (e.g. methane and DMS), are produced by the microbial breakdown of labile organic matter. The remote oceans are thus a small source of these compounds to the atmosphere (Quinn *et al*., 1988, 1990, 1996; Zhuang and Huebert, 1996; Gibb *et al*. 1999). The exchange of ammonia across the air-sea interface is a small sink in the seawater ammonium cycle (Gibb *et al*., 1999) and thus, like DMS, changes in ocean biology, chemistry or physics could have a major effect on the flux of ammonia to the atmosphere. Although the current ocean-atmosphere flux of ammonia is small, it plays an important role in atmospheric chemistry. Ammonia is the dominant gas phase basic species in the remote marine atmosphere, and thus can influence the formation, growth, and pH of atmospheric aerosol particles. Additional measurements of ammonia are needed in surface seawater and the overlying atmosphere.

Carbon Dioxide: The transfer of CO_2 transfer between the ocean and the atmosphere is a strong function of seawater temperature: oceans release CO_2 in regions of warm water take up CO_2 from the atmosphere in cold oceanic environments. Overall, however, the ocean represents a major sink for atmospheric CO_2, and today absorb about a third of the fossil fuel CO_2. Over the geological history, oceans have played a large role in controlling the evolution of atmospheric CO_2. A detailed discussion of the CO_2 cycle is beyond the scope of this report.

Sea-salt aerosols: Sea-salt particles are ejected into the atmosphere from the breaking of waves and can dominate the mass of both submicron and supermicron marine boundary layer (MBL) aerosol particles in the remote marine environment (Quinn *et al.*, 1998; Huebert *et al.*, 1998). Single particle analysis during ACE-1 revealed that over 90% of the aerosol particles with diameters >130 nm (Murphy *et al.*, 1998) and up to 70% of the particles with diameters >80 nm (Kreidenweis *et al.*, 1998) contained sea salt. The dominance of sea salt aerosol over the remote oceans clearly shows the need to include sea salt in climate models. In moderate to high wind speed conditions such as in the ACE 1 study area, sea salt controls the magnitude of aerosol light scattering (Quinn *et al.*, 1998; Carrico *et al.*, 1998; Murphy *et al.*, 1998) and the number of cloud condensation nuclei (Covert *et al.*, 1998; O'Dowd *et al.*, 1997). Sea-salt particles also provide reactive surfaces for the oxidation of gas phase species (e.g., SO_2, nitric acid) and thus act as a shunt in the sulfur cycle limiting new sulfur aerosol formation (Sievering *et al.*, 1999). The liberation of halogen species from sea salt contributes to the tropospheric budget of reactive chlorine (Graedel and Keene, 1995) and may affect the oxidizing capacity of the marine boundary layer (Sander and Crutzen, 1996).

The deposition of aerosol species to the surface ocean can provide nutrients to enhance biological productivity. Anthropogenic nitrogen in the form of ammonium and nitrogen oxides and iron and phosphorous associated with mineral dust all act as nutrients to plankton living in the surface ocean (Prospero *et al.*, 1996). Model results suggest that the present-day deposition rate of NO_y and NH_x over the North Atlantic Ocean are about five and ten times greater than pre-industrial times (Prospero *et al.*, 1996). Coale *et al.* (1996) demonstrated in the equatorial Pacific Ocean that iron fertilization can induce a phytoplankton bloom which in turn will affect the seawater concentration of DMS (Turner *et al.*, 1996) and CO_2 (Cooper *et al.*, 1996).

Similar experiments need to be conducted using atmospheric aerosol particles in regions downwind of mineral aerosol and anthropogenic aerosol sources.

2.4. Production of nitrogen oxides by lightning

Of the global emission rates for NO_x (= $NO+NO_2$) the thermochemical production of NO_x in lightning discharges is the least well known. Early estimates ranged from 1 TgN/yr [Levine *et al.*, 1981] to 100 TgN/yr [Franzblau and Popp, 1989]. This is a factor of 0.05 to 5 compared to the relatively well established source from fossil fuel combustion (~20 TgN/yr [Logan, 1983; Penner *et al.*, 1991; Lee *et al.*, 1997]). Even if the NOx production from lightning is only a fraction of the fossil fuel emissions, it would still be important for the ozone budget in the troposphere because of the high altitude at which it is released. According to a three-dimensional model study, tropospheric ozone increases by 12% globally if NO_x production from lightning is doubled from 5 TgN/yr to 10 TgN/yr [Brasseur *et al.*, 1996].

More recent estimates of the lightning NO_x production rate converge at a range of 2-20 Tg/yr [Lawrence *et al.*, 1995; Price *et al.*, 1997]. Yet, a large discrepancy remains between estimates obtained from laboratory studies or theoretical calculations on the one hand and extrapolation of NO_x measurements in individual thunderstorms on the other hand [Lawrence *et al.*, 1995]. Simulations with global three-dimensional chemistry transport models (CTM) place an upper limit of about 20 TgN/yr on the source strength of NO_x from lightning [Gallardo and Rodhe, 1995; Lamarque *et al.*, 1996; Levy *et al.*, 1999], arguing that higher emission rates would lead to unrealistic rates of nitrate deposition. Given the prevailing uncertainties in the upper tropospheric NO_x and HO_x chemistry and the difficulties in obtaining a reliable estimate for the nitrate deposition flux over a large region, this limit must be regarded as a weak bound.

Lightning arises from the breakdown of the charge separation in electrified convective clouds (thunderstorms). Although the details of the underlying microphysics are still poorly understood, there appears to be a consensus that electrification of a cloud above the energy threshold for lightning requires the coexistance of liquid water, ice crystals and hail or graupel in a sufficiently large regime (the charging zone) [Williams, 1985, 1994; Saunders, 1994]. A thundercloud generally represents a dipole with the positive charge on top of the negative charge, but the extent and location of the charge center can vary from cloud to cloud and within the lifetime of a thunderstorm [Solomon and Baker, 1998]. Depending on the vertical and horizontal charge distribution, lightning can occur from cloud to ground (CG), or intracloud (IC), intercloud or even from cloud to air. IC flashes are the most frequent type of flashes, yet they are far less investigated than CG flashes with their hazardous potential. The IC/CG ratio depends on the height of the cloud above freezing level and shows a latitude dependence because tropical convective clouds penetrate deeper into the troposphere than midlatitude clouds [Price and Rind, 1993]. Globally averaged ratios of 2-4 can be found in the literature [Proctor, 1991; Price *et al.*, 1997]. The total flash frequency is determined by the time it takes to rebuild a charge separation in excess of the breakdown potential which in turn depends on the updraft velocity in the charging zone and the liquid water flow into the cloud [Solomon and Baker, 1998]. The global frequency of lightning flashes was first estimated by Brooks [1925] to be on the order of 100 s^{-1} . This estimate is still widely used in the literature and has been confirmed to some degree by satellite observations [Orville and Spencer, 1979; Turman and Edgar, 1982]. More recent observations with the Optical Transient Detector [Christian *et al.*, 1996] show a global average of about 40 flashes s^{-1}. Lightning is much more frequent over land than over the oceans. The ratio is about 50:1 except for a few regions, which appear to be linked to continental outflow, where this ratio increases to about 10:1 [http://thunder.msfc.nasa.gov/data/otdbrowse.html]. There is a distinct seasonal and diurnal cycle with most flashes occurring during the northern hemisphere summer (about 1.5-2 times more than in winter [Orville and Spencer, 1979]) and during the afternoon.

A CG flash is always initiated by a relatively weak "leader" which is followed by one or several "return strokes" of about 150 microseconds and peak currents of up to 60 kA. The mean multiplicity varies from 1 to 5 strokes per flash. Storms with higher lightning frequency tend to have a mean multiplicity between 2 and 3 [Price *et al.*, 1997]. CG flashes can be negative or positive depending on the type of the storm. Intracloud flashes can occur between several charge centers simultaneously and typically show lower peak currents [Ogawa and Brook, 1964]. The production of NO in a lightning discharge is generally believed to take place according to the Zel'dovich and Raizer [1966] mechanism of N_2 and O_2 dissociation and subsequent NO formation in the hot lightning channel. Peak temperatures in a lightning flash approach 30,000K causing the air to become a completely ionized plasma. Upon cooling the atoms recombine and react with each other. In thermodynamic and chemical steady state peak NO concentrations would be reached at ~4500K [Chameides, 1979; Goldenbaum and Dickerson, 1993]. However, the lifetime of NO with respect to chemical loss reactions increases exponentially with falling temperature so that rapid cooling of air heated by lightning preserves a higher NO concentration than the steady state would predict [Hill *et al.*, 1980]. Wang *et al.* [1998] produced discharges with peak currents of 30 kA in the laboratory and found the NO production per unit length to decrease with decreasing pressure as one should expect if the cooling of the lightning channel is predominantly caused by turbulent air exchange. Field and laboratory experiments show only little direct production of NO_2 from lightning. However, in the atmosphere NO_2 will quickly form due to the fast catalytical cycle involving ozone, NO, and NO_2.

Current parameterizations of the NO production from lightning for chemical transport models typically rely on the work of Price and Rind [1992], and Price *et al.* [1997], who provide an estimate for the mean energy per flash and the average NO yield per unit energy. These values are scaled with the flash frequency in the model grid column which is parameterized as a 5th order potential function of the maximum cloud top height (used as a surrogate for the maximum updraft velocity). The effect of lightning NO_x production on tropospheric ozone concentrations also depends on the altitude at which the NO_x is released from the thunderstorm. Pickering *et al.*, [1998] define three standard vertical profiles based on several observations and results from a cloud resolving transport model. While the parameterization of Price *et al.* [1997] yields a global flash frequency distribution which is consistent with the model physics and also gives reasonable global NO_x production rates in CTM simulations, the use of average thunderstorm properties is obviously a very crude approximation. To name one very significant parameter: Lightning has been observed in storms with updraft velocities < 1 m/s (less than 1 flash per minute) to > 50 m/s (more than 50 flashes per minute) [references in William, 1995], and it is clear that these storms produce a very different energy spectrum and thus generate different amounts of NO.

Field observations of NO_x concentrations in or around active thunderstorm anvils provide another way for estimating the NO_x production rate from lightning [Noxon, 1976; Drapcho *et al.*, 1983; Ridley *et al.*, 1996; Huntrieser *et al.*, 1998 and references therein]. Although it is difficult to distinguish between the NO_x produced from lightning and the NO_x that is transported from the boundary layer in the cloud updraft, all of the measurements show typical mixing ratio enhancements between 0.4 and 2 ppbv in the thunderstorm anvil [Huntrieser *et al.*, 1998]. Assuming that their observations represent an average thunderstorm, several authors have estimated the global NO_x production from lightning by scaling the observed NO_x concentrations in the anvil with the air mass flux through the anvil or the volume of the convective cell and with an estimate for the global average lightning frequency. With 0.3-22 TgN/yr, such estimates yield similar values as the theoretical studies but do not allow for a better constraint. Clearly, more field studies are needed which must cover a broad range of thunderstorm types. Improving the simulation of NO_x production from lightning will require more explicit cloud microphysics parameterizations which are still under development [e.g. Solomon and Baker, 1998].

2.5. Chemical composition of the pre-industrial atmosphere

Very little information is available on the abundance of chemical species prior to the industrial era. Analyses of the chemical composition of air bubbles trapped in ice cores have provided estimates of the concentration for long-lived species such as carbon dioxide, methane, nitrous oxides, etc. An important finding in the last decade is that the concentration of these gases have changed sometimes dramatically in conjunction with climate fluctuations over geological timescales (typically 10,000 to 100,000 years). Transitions between glacial and interglacial periods have been accompanied by remarkable changes in the abundance of long-lived constituents. Although these fluctuations seem to be initiated by variations in the orbital parameters of the Earth (leading to changes in the intensity of incoming solar radiation), they also suggest that the Earth behaves as an integrated system in which couplings between chemistry and climate play an important role. Recent ice core analyses have also revealed significant changes in shorter-lived constituents of the atmosphere as well as in the aerosol load. Signals resulting from large volcanic explosions have been detected. **[More should be added by the IGAC specialists on ice cores]**

The level of oxidants present in the pre-industrial atmosphere is poorly known. A few observations made in Europe and elsewhere at the end of the 19th century and the beginning of the 20th century provide information about background ozone during this period. Measurements made for example at Parc Montsouris in Paris by Albert-Levy (1878) and re-analyzed by Kley (1988) and Volz *et al*. (1988) suggest that pre-industrial ozone concentrations were close to 10 ppbv in the boundary layer. Similar values are reported the Southern hemisphere, based on observations made in the late 1800’s in Argentina and Uruguay (Sandroni *et al*., 1992). These values suggest that ozone concentrations may have increased by almost a factor 2 in South America and a factor 3-4 in Europe.

Numerical chemical-transport models have been used to “predict” the pre-industrial concentration of ozone and other chemical compounds in the pre-industrial atmosphere. These models are constrained by the observed abundance of long-lived trace gases deduced from ice core analyses and are integrated after suppressing fossil fuel emissions and reducing significantly the biomass burning emissions. No reliable data exist on the level of biomass burning emissions during the 19th century, but it is generally assumed that the emissions associated with this source were 60 to 90 percent lower than the present values. NO_x sources associated with the current use of fertilizers also need to be suppressed in the model, and again the information available on this source is limited.

Figure XX shows the pre-industrial ozone concentration calculated at the surface by 2 different three-dimensional models. The comparison between these two models provides a crude indication on the range of model results. Both models, however, derive surface ozone concentrations on the continents that generally higher than suggested by available observations. It remains to be determined if this discrepancy is due to an underestimation in the observed values or an overestimation in the calculated concentrations. This issue needs to be resolved before model predictions of human-induced changes in tropospheric ozone concentrations can become reliable.

3. Human influence on atmospheric composition

3.1. Introduction

Anthropogenic sources are major contributors to the budgets of many environmentally important atmospheric species (Table 1 of chapter 1). These sources include fossil fuel combustion, industrial activities, biomass burning, and agriculture. We assess here the current understanding of anthropogenic perturbation to the abundances of different gases and discuss scenarios for the future.

Nitrogen oxides: Anthropogenic sources of NO_x include fossil fuel combustion, biomass burning, and microbial soil emission stimulated by fertilizer application. Natural sources include lightning, natural forest fires, soil emission, and transport from the stratosphere where NO_x is produced by photooxidation of biogenic N_2O. Oxidation of NH_3 provides a small additional source, in part anthropogenic (agriculture). Figure 1 shows an estimate of the present-day global distribution of NO_x emissions. Anthropogenic emissions account for about 75% of the present-day NO_x source (Table 1 of Chapter 1). As shown in Figure 1, the anthropogenic source is concentrated in the developed countries of northern midlatitudes and in biomass burning regions of the tropics. Concentrations of NO_x in the boundary layer of polluted regions are typically in excess of 1 ppbv, compared to 1-100 pptv in the remote troposphere [Carroll and Thompson, 1995; Emmons *et al.*, 1997; Thakur *et al.*, 1997]. Concentrations drop rapidly away from polluted regions because of the short lifetime of NOx against oxidation (~1 day). Human activity has increased NO_x concentrations considerably in populated regions of the world with consequences for generation of ozone smog, particulate matter (aerosol NO_3^-), and acidification and fertilization of ecosystems through HNO_3 precipitation. The degree of human influence on NOx concentrations in remote regions of the troposphere is more uncertain. The latter has important implications for the oxidizing power of the atmosphere and for the global budget of tropospheric O_3.

Figure 1. Four-panel map plot of annual mean NO_x emissions from (1) fossil fuel, (2) biomass burning, (3) soils, (4) lightning.

Observations over the past decade have demonstrated the importance of peroxyacetylnitrate (PAN) as a reservoir for the long-range transport of NO_x from polluted regions to the remote troposphere. PAN is produced during the photochemical oxidation of hydrocarbons in the presence of NO_x. It decomposes thermally back to NO_x with a lifetime of only 1 hour at room temperature but over a month at 250 K. Unlike HNO3, PAN is only sparingly soluble in water and hence not removed by wet deposition. Long-range transport of PAN at the low temperatures of the free troposphere followed by subsidence, heating, and decomposition provides a mechanism for transporting anthropogenic NO_x on a global scale [Crutzen, 1979; Singh, 1987]. Concurrent observations of PAN and NO_x from aircraft missions in remote regions of the world have now shown that decomposition of PAN is a major contributor to the NO_x budget in the lower troposphere [Singh *et al.*, 1990, 1992; Fan *et al.*, 1994; Jacob *et al.*, 1996; Schultz *et al.*, 1999]. Global 3-dimensional models are consistent with these observations [Moxim *et al.*, 1996], which imply the potential for ubiquitous anthropogenic influence on NO_x. It is thus found that fossil fuel combustion could account for over 40%

of NO_x concentrations in much of the remote northern hemisphere [Horowitz and Jacob, 1999]. In the southern hemisphere, observations from aircraft campaigns show that seasonal biomass burning influence on NO_x extends over the most remote regions of the oceans through long-range transport of PAN [Schultz *et al.*, 1999; Staudt *et al.*, 2000].

Carbon monoxide and nonmethane hydrocarbons. The main sources of CO are direct emission from fossil fuel combustion and biomass burning, and atmospheric oxidation of CH4 and nonmethane hydrocarbons (NMHCs). Figure 2 shows the global distribution of anthropogenic CO emissions, which account for about half of the global source (Table 1 of Chapter 1). Human influence on CO extends further through the oxidation of anthropogenic CH_4 and NMHCs [Granier *et al.*, 2000]. The natural background concentration of CO, based on the source from preindustrial CH_4, biogenic hydrocarbons (in particular isoprene), and natural fires, is about 30 ppbv. The present-day background is 40-50 ppbv due to ubiquitous enhancement from anthropogenic CH4, and is observed only at high southern latitudes outside of the biomass burning season. Concentrations in the boundary layer of populated continents often exceed 200 ppbv. Because of the long lifetime of CO (2 months), the influence of combustion sources can extend globally and results in background concentrations in the northern hemisphere of about 70-80 ppbv. This global enhancement of CO has important consequences for the oxidizing power of the atmosphere, as discussed in the next section.

Figure 2. Map of anthropogenic CO emissions

In contrast to CO, the anthropogenic source of NMHCs is small compared to the natural source from vegetation including in particular isoprene and terpenes (Figure 3). In most of the eastern United States, isoprene actually dominates over anthropogenic hydrocarbon emissions. Anthropogenic hydrocarbons are important in urban plumes where they promote O_3 production [Roselle *et al.*, 1991]. In winter when vegetation is dormant, they may provide the principal precursor of PAN [Bey *et al.*, 2000]. Pyrogenic NMHCs are responsible for the rapid and efficient conversion of NOx to PAN in biomass burning plumes, where the hydrocarbon/NOx emission ratio is one order of magnitude higher than in fossil fuel combustion [Jacob *et al*., 1992; Mauzerall *et al*., 1998].

Figure 2. Two-panel map plot of (a) anthropogenic and (b) biogenic NMHC emissions

Implications for tropospheric ozone and OH: Anthropogenic enhancements of NO_x, CO, and hydrocarbons in the global troposphere has implications for the global budgets of O_3 and OH. Present-day background O_3 concentrations in the lower troposphere at northern midlatitudes are 30-40 ppbv, much higher than observed in the late 19th century or in the 1950s [Marenco *et al*., 1994]. The 19th century measurements, available from a number of sites at northern midlatitudes and in the tropics, indicate values of 5-15 ppbv [Volz and Kley, 1988; Pavelin *et al*., 1999]. The data for South America and Africa do not show the springtime maximum characteristic of present-day observations and caused by biomass burning. Model simulations for the preindustrial atmosphere (shutting off all anthropogenic sources) typically overestimate the late 19th century observations by 5-10 ppbv [Wang and Jacob, 1998]. Calibration errors and interferences in the observations could explain part of the discrepancy [Marenco *et al*., 1994; Pavelin *et al*., 1999]. However, the discrepancy also lies within the uncertainty of our estimates of natural sources of NOx and hydrocarbons [Mickley *et al*., 2000].

Current model calculations suggest a 40-70% increase in the global inventory of tropospheric O_3 since preindustrial times [Lelieveld and van Dorland, 1995; Levy *et al*., 1997; Roelofs *et al*., 1997; Wang and Jacob, 1998; IPCC, 2000]. The increase could be larger, over 100%, if natural sources are overestimated [Mickley *et al*., 2000]. A sample model result for the global distribution of this increase is shown in Figure 4. The largest effect is in the northern hemisphere but increases of more than 50% are also found in much of the southern hemisphere. The increase is 20-80% in the upper troposphere, with largest relative effect in the tropics where the natural source from cross-tropopause transport makes little contribution.

Figure 2. Four-panel plot of the relative anthropogenic increases of NO_x, CO, ozone, and OH, zonally averaged and shown as a function of latitude and pressure, from Wang and Jacob [1998].

The effect of human activity on the oxidizing power of the atmosphere (OH radical concentrations) is more complicated. On the one hand, increases in NOx and O_3 boost the production and recycling of OH. On the other hand, increases in CO and hydrocarbons cause faster OH loss. The current consensus among 3-D models of tropospheric chemistry is that the global mean OH concentration has remained to within 20% of its present-day value since preindustrial times [Crutzen and Zimmermann, 1991; Lelieveld and van Dorland, 1995; Berntsen *et al*., 1997; Roelofs *et al*., 1997]. The models suggest an increase of OH in the northern hemisphere, and a decrease in the southern hemisphere, reflecting the longer lifetimes of CO and CH4 than of NO_x and O_3 (Figure 4).

Recent trends in OH concentrations have been examined from continuous records of methylchloroform (CH_3CCl_3) observations made at the ALE-GAGE network of sites since 1978 [Prinn *et al*., 1995]. Methylchloroform serves as a proxy for the global mean OH concentration. A detailed analysis of the CH3CCl3 record by Krol *et al*. [1998] indicates a 0.5% yr^{-1} increase in the global OH mean concentration from 1978 to present. This increase could be due in part to greater penetration of UV radiation in the troposphere as a result of the thinning of the stratospheric O_3 layer [Madronich and Granier, 1992]. Data from methylchloroform and other OH proxies further indicate that the interhemispheric gradient of OH concentrations is very small and certainly no more than 50% [Spivakovsky *et al*., 2000].

Sulfur: Figure 5 shows the global distribution of sulfur emissions from major anthropogenic and natural sources. Anthropogenic sulfur is emitted mainly as SO_2 from coal and oil combustion, oil refining, and metal smelting [Spiro *et al*., 1992]. It accounts globally for about 80% of sulfur emissions. Natural emissions of sulfur are principally from the oceans and from volcanoes. The lifetime of SO_2 against in-cloud oxidation to sulfate is only a few days, and sulfate is subsequently removed by precipitation on a time scale of a week [Chin *et al*., 1996]. Concentrations of SO_2 range from 1-10 ppbv over the northern midlatitude continents to 10-100 pptv in the remote troposphere. Ice core records in Greenland show a tripling of sulfate concentrations over the past century [Mayewski *et al*., 1995]

Figure 2. Global map of present-day non-seas-salt sulfur emissions.

A number of models have been applied to simulate the global distribution of atmospheric sulfate and the extent of anthropogenic influence. An evaluation and intercomparison of these models is presented by Rasch *et al*. [2000]. Figure 6, from Chin *et al*. [2000], shows the percentage anthropogenic contribution to sulfate concentrations in surface air and in the upper troposphere. Most of the sulfate over populated continents is of anthropogenic origin. Unlike for NO_x, there is no long-lived reservoir that can transport anthropogenic sulfur on global scales. As a result, biogenic sources dominate the supply of sulfate over most of the oceans; this result is well established by observations from island sites and ship cruises, as well as isotopic studies. More uncertain is the origin of sulfate in the upper troposphere, where it plays a key role in the formation of new aerosol particles. A critical question is the degree to which SO2 and sulfate are scavenged during deep convective transport from the lower to the upper troposphere. Several observational and model studies suggest that a significant fraction escapes scavenging [Chatfield and Crutzen, 1984; Wang *et al*., 1998; Dibb *et al*., 1999; Cohan *et al*., 1999; Mari *et al*., 2000]. However, the paucity of measurements remains a key hurdle for assessing our understanding of the sources of sulfate in the free troposphere.

Figure 2. Two-panel map plot showing the percentage anthropogenic contribution to sulfate aerosol concentrations in surface air and in the upper troposphere, as computed with a global 3-D model.

Chlorine A large number of inert halocarbon compounds are produced by the chemical industry for use in a variety of applications. These compounds are eventually released to the atmosphere where they have relatively long lifetimes against oxidation and photolysis, and may thus penetrate in the stratosphere with consequences for the O_3 layer. Figure 7 shows the temporal evolution of total halocarbon chlorine in the atmosphere. Methyl chloride contributes a natural background of 0.5 ppbv. Anthropogenic compounds, principally CFCs, dominate. Total chlorine rose to a maximum of 3.5 ppbv in the mid 1990s, Phasing out of the CFCs began with the Montreal protocol in 1986, resulting by 1996 in a worldwide ban on production of CFCs and some other halocarbons such as CH3CCl3. Recent observations show that atmospheric concentrations of CFCs have leveled off, conforming to the Montreal protocol, and that CH_3CC_{l3} concentrations have been dropping rapidly reflecting its short lifetime (4-5 years) [WMO, 1999]. Concentrations of HCFCs, used as temporary replacement products for CFCs, have been rising rapidly in recent years [WMO, 1999]. However, their lifetime is relatively short and hence they will not accumulate in the atmosphere to the same degree as CFCs. The HCFCs are scheduled for phase-out by 2020. Because of the long lifetimes of CFCs, total chlorine concentrations by the middle of the 21st century will still be over half of values in the mid 1990s (Figure 7).

Figure Temporal trend of halocarbon chlorine, including estimates for the 21st century

4. The particular case of biomass burning

4.1. Introduction

During the last decade, considerable amount of work has been performed, often under IGAC sponsorship, to assess the role of biomass burning on the global budget of chemical species in the atmosphere. We have chosen to highlight the major outcome of these studies.

Biomass burning is a unique source of many atmospheric trace gases and aerosol particles, while other sources emit only a few compounds. Biomass burning has a distinct seasonality and most burning occurs in the tropics. This summary will discuss the major findings in biomass burning research during the past two decades and will propose areas for future research. Since 1980, the atmospheric chemistry community has made significant progress in understanding the impact of biomass burning on tropospheric and stratospheric chemistry and global climate. Crutzen *et al.* [1979] were the first to suggest that biomass burning is an important source of atmospheric trace gases. These findings have led to several multidisciplinary field campaigns in tropical, temperate, and boreal regions to study the interactions between biomass burning and photochemical processes in the atmosphere. Major field campaigns in Brazil have included NASA ABLE-2A (1988), BASE-B (1990), TRACE-A (1992), and SCAR-B (1995). Large-scale experiments have also been conducted in Africa, including DECAFE (1998) and FOS/DECAFE (1991) in western Africa, SAFARI in southern Africa (1992), and EXPRESSO in central Africa (1996). The major biomass burning experiment in boreal ecosystems (FIRESCAN) was conducted in Siberia in 1993. In addition to large-scale field campaigns, many small-scale experiments on biomass burning have been carried out in various ecosystems.

We will summarize the information necessary to evaluate the impact of biomass burning on atmospheric chemistry and global climate, including the sources of burning, combustion chemistry, and emissions of trace gases and particles from biomass burning. We will also discuss the effects of biomass burning on global budgets of atmospheric trace gases and aerosol particles, ozone concentrations in the troposphere, and global climate.

4.2. Extent of biomass burning

Most biomass burning takes place in tropical countries where rapid population growth has occurred during the past 30 years. These vegetation fires are mostly caused by human activities (lightning contributes only a small number). The primary reasons for burning in the tropics are deforestation, shifting cultivation, growth of fresh grass in savannas, demand for fuelwood, and clearing of agricultural residues. In contrast, prescribed fires and wildfires are the major burning sources in temperate and boreal ecosystems.

It has been estimated that the amount of biomass burned in the tropics accounts for more than 80% of the biomass burned globally in the late 1970s. This value is derived from FAO statistics on the rate of deforestation, the areas covered by forests and savannas, and fuelwood and agricultural production in tropical countries. Seasonal and inter-annual variations that affect the amount of biomass burned on a local level depend on weather conditions, land cover, and land uses. Thus, remote sensing used in conjunction with ground surveys of vegetation characteristics will be the best way to determine the extent of biomass burning on a global scale.

Spatial and temporal distributions of fires have been monitored in tropical, temperate, and boreal regions using satellite data from AVHRR, DMSP, and GOES. The AVHRR satellite provides daily fire locations in the early afternoon, and the DMSP satellite provides nighttime fire locations in 1-km resolution. The GOES satellite provides the diurnal cycle of fires with a spatial resolution of 4 km. Satellite images and statistical data have shown that the fire season starts in November and lasts until the following March in the northern hemisphere of Africa and South America. In the southern hemisphere, the fire season begins in May in the northern region, moves southward as the dry season progresses, and reaches South Africa and southern Brazil in September and October. Although satellite data can provide information on the distribution of fires, it cannot be used to quantify the areas burned. In future research, therefore, it will be critical to develop a better remote sensing technology to monitor the spatial and temporal distribution of burned areas.

There is limited information available on the percentage of aboveground biomass burned from the early dry season to the late dry season, primarily because all the field campaigns have been conducted during the late dry season. In fact, the portion of biomass that actually burns depends on its type, composition, and moisture content. In grassland savanna fires in Zambia during the early dry season, less than half the biomass is burned because of high moisture content in the fuel. As the dry season progresses, the percentage of biomass burned increases, and almost all of it is burned toward the end of the dry season. Only a small part of biomass is burned in woodland savannas during the early dry season. This portion also increases as the dry season progresses, until it reaches about 45% by the end of the dry season. In forest fires about 30% of the aboveground biomass is burned in the late dry season and unburned vegetation is often burned again during the following dry season. Overall, about half of total biomass is burned in tropical forests within a two-year period.

4.3. Combustion chemistry and emissions

Research on biomass burning during the past 20 years has progressed most significantly in the field of quantifying the emissions of trace gases and aerosol particles. Extensive field and laboratory experiments have been conducted to measure emissions from fires in tropical, temperate, and boreal ecosystems. Most of these measurements, however, were taken near the end of the dry season when biomass is low in moisture and is highly combustible. The emissions, in fact, are dependent on vegetation and meteorological conditions. The emission ratio of CO to CO_2 is about 14% in grassland savanna fires during the early dry season due to high moisture content in savanna grass. This ratio declines to about 4% - 6% by the late dry season when the grass is low in moisture. In woodland savanna fires, the emission ratio of CO to CO_2 is relatively constant at about 6% throughout the dry season. The emission ratio for forest fires is about 10% - 12% near the end of the dry season.

Most CO_2 is emitted during flaming combustion, while most CO is emitted during smoldering combustion. The emissions of CH_4, C_2H_4, C_2H_6, C_2H_2, C_3-C_6 alkanes and alkenes, CH_3OH, HCHO, HCOOH, CH_3COOH, CH_3Cl, CH_3Br, CH_3I, NH_3, and aromatic compounds are linearly correlated to the emissions of CO. The linear relationships vary considerably, depending on vegetation and combustion conditions. The emissions of NO and N_2O are linearly correlated to the emissions of CO_2 and the nitrogen content of biomass. NO is the dominant nitrogen compound of NOx ($=NO+NO_2$) produced from efficient combustion or low emission ratios of CO to CO_2. NO is further photochemically oxidized to NO_2 downwind of the plume. NH_3, on the other hand, is the major nitrogen compound produced from inefficient combustion or high CO to CO_2 emission ratios. The proportion of NO and NH_3 emitted is dependent on the efficiency of combustion.

Particles emitted from biomass burning have two modes of size distribution: 0.1-1 μm and >1 μm. In aged plumes the sizes of small particles will increase, due to condensation and coagulation of particles. The amount of particles emitted from forest fires is usually larger than the amount produced by savanna fires. The dominant composition of particles is organic material produced from incomplete combustion. Black carbon accounts for less than 10% of the particle content and is produced in high temperature combustion during the flaming phase. Inorganic elements comprise a small percentage of particles, with potassium the major component. Since potassium is enriched in smoke particles, it can be used as a tracer of smoke particles.

4.4. Contribution to global budgets

It is well established that biomass burning is an important source of many atmospheric trace gases and aerosol particles. Yet it is difficult to quantify the contribution of biomass burning to the global budgets of these trace gases and particles. The contribution also varies substantially in spatial and temporal terms. According to current estimates, the CO source from biomass burning is as great as that from industrial combustion, which accounts for a quarter of the total sources of atmospheric CO. Biomass burning also contributes 5% -10% of atmospheric CH_4. Approximately half of this source is caused by deforestation and shifting cultivation in the tropics. Fires in African savannas are a significant source of atmospheric ethene, ethane, ethyne, propane, propene, and benzene. It has been estimated as well that biomass burning may contribute about 30% of the CH_3Cl source and about 15% of the CH_3Br source, based on measurements of fires in tropical savannas and agricultural land. It is important to conduct field experiments in various ecosystems with different land uses (e.g., deforestation and shifting cultivation) in order to assess the overall contribution of biomass burning to the global budgets of these compounds.

The major nitrogen compounds emitted from vegetation fires are NO, NH_3, HCN and N_2O. The amount of NO emitted from biomass burning is about 30% of the amount of NO produced by industrial sources. Biomass burning is a minor source of atmospheric N_2O, contributing only about 2% of the global source of atmospheric N_2O.

4.5. Effects on tropospheric ozone

(Please add two paragraphs at the end of the following two paragraphs. One paragraph describes the aircraft observation of vertical ozone profile. The other paragraph describes the modeling results of vertical distribution of ozone as a result of biomass burning in the tropics and its spread to the mid-latitudes.)

The impact of biomass burning on ozone concentrations in the troposphere has been observed from satellites, in-situ measurements aboard aircraft, and photochemical modeling. Tropospheric ozone concentrations between 25°N and 25°S have been derived from the satellites of Nimbus 7 (1979-1992) and TOMS (1996-present). The trends of ozone concentrations throughout the year correspond to the extent of biomass burning activities in tropical Africa, Latin America, and Asia. In every September and October, ozone concentrations reach their highest levels in Brazil and southern Africa. Such high ozone levels can be attributed mostly to biomass burning, although industrial activities and biogenic emissions of ozone precursors from soils and plants are also potential sources.

In addition to having high ozone concentrations over the tropical continents, persistent high ozone levels have been observed by the TOMS satellite in the South Atlantic from July to October**.** These observations can be explained by the transport of CO, NO, and hydrocarbons, produced by fires in Africa and South America, to the South Atlantic. Further research is needed to examine whether other sources may contribute to the high ozone levels.

5. Global budgets of atmospheric compounds

It is instructive to summarize our understanding of the occurrence and fluxes of the key species in the atmosphere in the form of global budgets. Such budgets enables one to compare the magnitude of the various fluxes and to find out whether the estimates of total sources are balanced by the total sinks. The relative importance of natural and man-made sources will be easily seen. By comparing the atmospheric burden with the total sink strengths one can also get an estimate of the turnover time of the species in question. On the other hand, one must also realize the shortcomings associated with the global budget approach. Many species are not long-lived enough to have a uniform global distribution implying that their concentration varies from region to region depending mainly on the geographical distribution of the emissions. In such cases global totals may no be representative of the actual situation in specific places.

An additional problem with budgets occurs when one attempts to balance them by assigning numbers to fluxes whose magnitude are unceratin just to make the fluxes balance. Unless proper uncertainty ranges are included in the budget, uncritical readers may misinterpret such indirect estimates to represent solid numbers. We have tried to avoid this problem by not forcing the budgets to balance but rather used independent best estimates of their magnitude. An unbalanced budget is then an illustration of the limitations in our knowledge.

Carbon*:* The main carbon-containing compound in the atmosphere is carbon dioxide (CO_2). It is of fundamental importance to the climate system because of its strong absorption of infrared radiation giving rise to the greenhouse effect. No attempt will be made here to summarize the information about the processes affecting the atmospheric CO_2 budget, or indeed the global carbon cycle, including the oceans and the terrestrial ecosystems. The main reason being that this topic is covered in great detail in a separate IGBP volume (ref). An additional reason is that CO_2 related research has not been a major focus in IGAC (mainly because CO_2 does not participate in important ways in chemical reactions in the atmosphere).

Figure "bud 1" shows the global fluxes of CO_2 to and from the atmosphere as well as the atmospheric burden during preindustrial times and during the past decade. The current man-made emissions, from fossil fuel combustion, cement manufacturing and deforestation, amount to only about 5% of the natural (preindustrial) emissions. Nevertheless, the atmospheric burden has increased by 30% because of these man-made emissions. The main reason is that the natural exchanges between the atmosphere on the one hand and the oceans an the terrestrial ecosystems on the other are gross fluxes that essentially balance over a year, whereas the man-made emissions represent a net input. The atmospheric burden during preindustrial times – corresponding to an atmospheric concentration of about 280 nmol/mol – is the result of a complex interplay between volcanic CO_2 emissions, burial of organic sediments and storage of carbon in the biota and in the oceans.

The nominal turnover time of CO_2 in the atmosphere, obtained as the ratio of the preindustrial burden and the total removal rate in Figure bud 1, is about 3 years. This means that, on average, a CO_2 molecule in the atmosphere spends that time in the atmosphere before it is taken up by the biota or the oceans. But since most of the CO_2 molecules will re-enter the atmosphere within a few years, the effective lifetime before eventual removal into the deep oceans is much longer, of the order of 100 years. This longer time scale also represents the time scale of adjustment of atmospheric CO_2 to changes in emissions. If all man-made emissions were to stop, it would take hundreds of years before the concentration approached the pre-industrial level again.

The second most abundant carbon containing compound is methane (CH_4). Its budget is summarized in Figure bud 2. In this case the man-made emissions are more than twice as large as the natural emissions and the atmospheric burden has increased in the same proportion, i.e., by some 240%. As for CO_2, the pre-industrial burden of CH_4 has been estimated from measurements in air trapped in ice cores (ref. PAGES). The most important man-made CH_4 sources include rice cultivation, exhalations from domestic animals, biomass burning and coal mining. ***(Comment on how emissions might be deliberately reduced?).*** The atmospheric turnover time of CH_4 is around 9 years. This is long enough for it to be reasonable well mixed around the globe – still there are significant geographical and seasonal differences in its concentration - but short enough for the atmospheric concentration to respond within a few years to changes in emissions. This means that an emission reduction will be followed within a few years by an approximately corresponding reduction in the atmospheric concentration.

In absolute terms the man-made increase in CH_4 is much less than that of CO_2 - 1 vs. 90 mikromol/mol. Despite this, the contribution of the CH_4

increase to the greenhouse effect is as large as 30% of the corresponding contribution of man-made CO_2. This is because CH_4 is a much (25 times?) more efficient greenhouse gas than CO_2 counted per molecule.

The atmospheric concentration of carbon monoxide (CO) has also increased substantially because of man-made activities, c.f. Figure bud 3. The main man-made fluxes include combustion processes (mainly traffic, forest clearing and savanna burning) and oxidation of CH_4 derived from man-made sources. In the case of CO, no direct estimate is available of the pre-industrial burden; the number in Figure bud 2 is just scaled from the present burden and the ratio of the natural to total emissions. The turnover time of CO is about 2 months indicating a less uniform distribution around the globe than CO_2 and CH_4. The annual and latitudinal average concentration of CO in surface air *(**Will there be a figure showing this in Chapter 3?**)* shows a strong interhemispheric gradient with higher values in the Northern Hemisphere due to man-made emissions. A secondary maximum in the tropics is associated with the biomass burning.

Should we also say a few words about NMHC?

Nitrogen: As mentioned in Chapter 1, nitrous oxide (N_2O) is important both because of it being a greenhouse gas and because it influences the concentration of ozone in the stratosphere. Its sources include man-made emissions from cultivated (fertilized with nitrogen) soils, biomass burning and various industrial processes, several of them not very well quantified. They sum up to be almost as large as the natural emissions, c.f. Figure bud 4. The turnover time comes out to be around 10 years. The current rate of increase in the atmospheric concentration of N_2O is about 0.2 % per year, indicating an imbalance between sources ans sinks.

The global budget of NO_x is presented in Figure bud 5. Since the atmospheric turnover time of NO_x is limited to a few days, the geographical distribution of its concentration and rate of deposition is patchy with higher values concentrated in and aroujnd the most industrialized regions, c.f. Figure xx. The short turnover time also implies that any future change in emission will be immediately seen as corresponding changes in the concentration and deposition rate. The current man-made emissions are dominated by fossil fuel combustion and biomass burning. A fraction of the emission from soils is also likely to be of man-made origin.

Figure bud 6 shows the global budget of ammonia/ammonium (NH_x). Most man-made emissions are due to domestic animals, biomass burning and losses from fertilizers. Taken together the man-made emissions make for about 75 % (?) of the total. In addition to Europe and North America, India with its large cattle population, shows up as a major source of NH_3. The increasing use of nitrogen fertilizers worldwide points towards a continued increase in man-made emissons.

Ozone: The budget of ozone (O_3) is different from the other budgets discussed here in that ozone is not directly emitted into the atmosphere but formed in situ by chemcial reacitons, c.f. Section 4.x. An important source for ozone in the troposphere is influx of ozone from the main source reigons in the stratosphere. The pre-industrial and current budgets of ozone in the global troposphere are shown in Figure bud 7. It is clear that chemical reactions within the troposphere play an important role in these budgets, but also that the balance has changed substantially since pre-industrial times: the tropospheric burden has been estimated (through modelling) to have increased by 20 % (??).

Aerosols and their precursors: Man-made emissions of sulfur compounds (mainly SO_2) have a profound impact on the acid/base status of aerosols, clouds and precipitation. The aerosol sulfate resulting from these emissions also have a cooling effect which counteracts a substantial part of the heating due to greenhouse gases. Figure bud 8 indicates that about 70 % of the current emissions of gaseous sulfur compounds comes from man-made sources, mainly fossil fuels combustion. In the most polluted regions, this percentage exceeds 90 %. The concern about environmental effects, including acid deposition, has led to a substantial reduction in the man-made SO_2 emission in some parts of the world (mainly Europe and North America) during the 1980s and 1990s. In some other regions, including East Asia, emissions show a strong positive trend.

(Include figure showing the trend in man-made sulfur emission by region during the past 140 years, c.f. IPCC 1996??)

As an example of a primary aerosol component we show in Figure bud 9 the global budget of elemental carbon (black carbon, "soot"). Natural emissions of soot are believed to be small compared to those from fossil fuels combustion and biomass burning, but uncertainties are appreciable

6. Prospects for the 21st century

Anthropogenic influence on the chemical composition of the atmosphere will certainly evolve considerably over the next century. The developed countries of North America and Europe have now entered an era of environmental management, with strict emission controls aimed at abating urban and regional air pollution. Emissions of CO, anthropogenic hydrocarbons, and SO_2 in these countries have decreased by ~30% over the past decade, and the decrease is seen in atmospheric observations [Sickles *et al*., 1999; Dickerson *et al*., 1999]. Control of NO_x emissions has lagged behind, because the technology is less mature and because of greater economic cost, but large decreases in emissions are expected over the coming decades.

These decreases in emissions of the classical pollutants in the developed world will likely be compensated on a global scale by increasing emissions from the developing world. Eastern Asia (including in particular China and India) is at the vanguard of present economic development. Emissions of NO_x from that region have increased by ~5% yr^{-1} over the past decade and this exponential rate of growth is expected to continue for at least the next two decades [van Aardenne *et al*., 1999]. Although there is now some effort in China to curb egregious air pollution associated with large stationary combustion sources and with domestic use of coal, a rapid growth in mobile sources is expected in the decades ahead. Other developing regions in the tropics are expected to make increasing contributions to global anthropogenic emissions over the 21^{st} century.

Emission scenarios for the 21^{st} century were compiled by the Special Report on Emission Scenarios (SRES) as part of the IPCC [2000] report. The

SRES gives decadal estimates of emissions of greenhouse gases, NO_x, CO, hydrocarbons, and SO_2 for four possible socioeconomic scenarios. Forecasts are shown in Figure 8 for scenario A2 (most pessimistic) and scenario B1 (most optimistic). In scenario A2, the relative changes in emissions from 2000 to 2100 are +240% for NOx, +140% for CO, +160% for CH_4, +160% for NMHCs, and -10% for SO_2. In that scenario, emissions of SO_2 increase by 60% from 2000 to 2030 and then decline, presumably because of emission controls in the developing world and decreased use of coal. Scenarios A1 and B1, which assume more sustainable development, forecast in general lower emissions than scenarios A2 and B2. Even in scenarios A1 and B1, NOx emissions increase by 50-60% from 2000 to the mid-21th century before declining. Scenario A1 features a large increase of CO emissions from 2000 to 2100 (+140%) with only a moderate rise in NOx emissions (+24%), which would cause depletion of the OH radical with implications for CH4.

Figure X. Forecast trends in emissions of NO_x, CO, CH_4, NMHCs, and SO_2 for 2000-2100 in two socioeconomic scenarios of the IPCC 2000 SRES: scenario A2 (top) is the most pessimistic while scenario B1 (bottom) is the most optimistic.

A number of global 3-D tropospheric chemistry models have been applied under the auspices of IPCC 2000] to assess the implications of the different SRES emission scenarios for global changes in O_3 and OH during the 21st century. For scenario A2 the models predict a global mean increase in tropospheric O_3 of 17-27 DU from present-day conditions, corresponding to a percentage increase of 50-100%; they also predict 6-25% decreases in global mean OH concentrations.

The response of aerosol abundances to changes in emissions is expected to be more linear. As SO_2 emissions decrease and NO_x emissions increase, nitrate will eventually become dominant over sulfate as a component of anthropogenic aerosol [Adams *et al.*, 1999]. Another important aerosol precursor is NH3, which was not included in the SRES but may be expected to scale with N_2O emissions because of their common agricultural sources (+160% in scenario A2, -20% in scenario A1). Changes in soot emissions may be expected to scale with CO emissions, which more double in all scenarios except B1. It appears therefore that the next century will see large changes in both the abundances and composition of anthropogenic aerosols. These changes will be compounded by perturbations to biogenic and geogenic aerosols as a result of changes in climate and in land use.

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