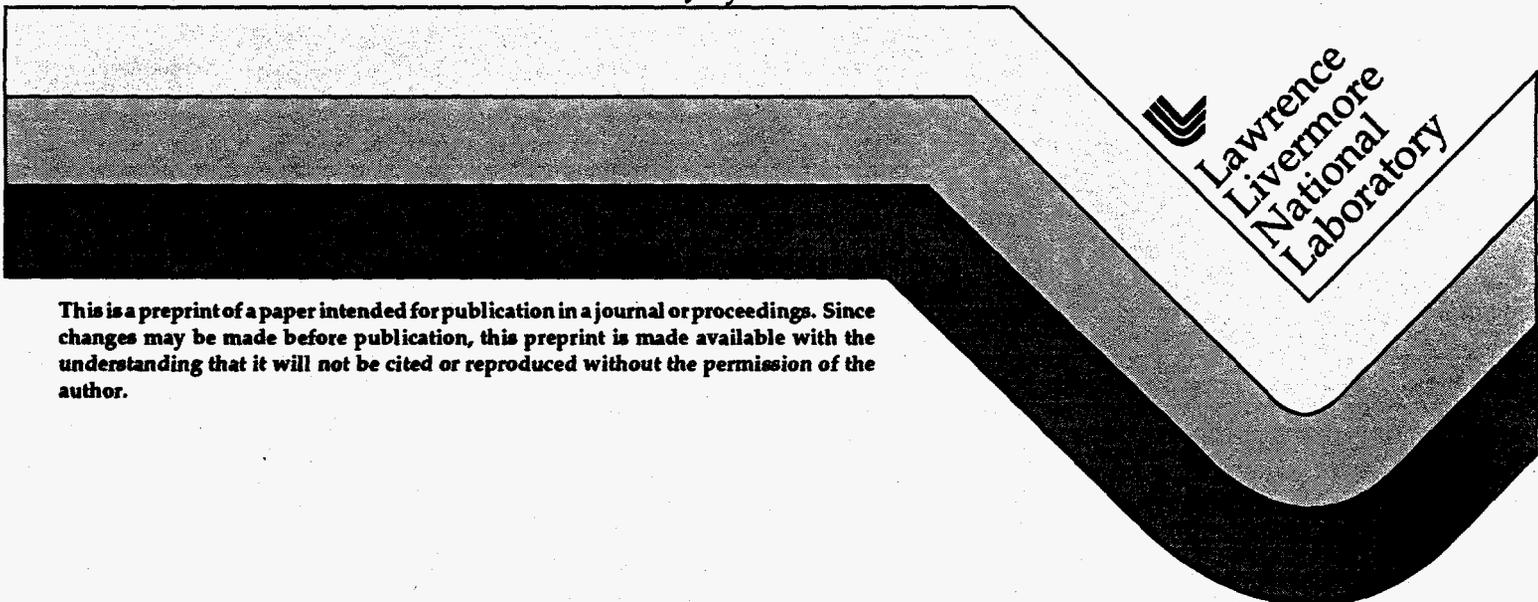


## Global Emissions Inventories

Jane Dignon  
Global Climate Research Division

This paper was prepared for presentation at the  
**Greenhouse Gas Emissions and Mitigation Research Symposium**  
*Washington DC*  
*June 27-29, 1995*

July 1995



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

## GLOBAL EMISSIONS INVENTORIES

Jane Dignon  
Global Climate Research Division  
Lawrence Livermore Laboratory  
Livermore, CA 94550 U.S.A.

### ABSTRACT

Many trace chemical species in the atmosphere are radiatively important and may affect climate and air quality. Detailed and accurate emissions inventories are essential for understanding the changing chemical composition of our atmosphere, and to establish compliance with international agreements. Currently climate and chemistry model predictions are limited by the paucity of quality emissions data input. This paper is designed to present a compilation of emissions inventories for radiatively important trace species. It reports the spatial and temporal characteristics of the emissions along with some interpretive comments.

### INTRODUCTION

Anthropogenic and natural factors affect the radiative forcing of the atmosphere. They have various magnitudes and different signs. The concept of radiative forcing allows us to compare the potential impacts of various factors. Different chemical species found in the atmosphere can affect the radiative forcing by acting as greenhouse gases. The amount that any individual chemical can effect the radiative balance is dependent on their concentration and their residence time in the atmosphere, i.e. their chemical lifetime. Their chemical concentrations and lifetimes are dependent on their sources and sinks, and/or the sources and sinks of their chemical precursors.

Carbon dioxide has received most of the attention in regard to the concerns of climate change and greenhouse effect. Model studies have shown that the sum of the radiative effects from other greenhouse gases, along with the indirect effects due to chemistry could be comparable to the projected effects of CO<sub>2</sub> alone [1]. The names, chemical structures, along with the direct and indirect ways these atmospheric constituents can influence the radiative forcing of the Earth/atmosphere system are listed in Table 1.

Most of the gases listed in Table 1 are greenhouse gases, or in other words, they are absorbers of long wave terrestrial radiation. Several of the other gases, e.g. nitrogen oxides, OH and CO, do not directly affect climate, but are important in relation to climate change because of their atmospheric chemical processes. They can have a strong influence on the atmospheric radiative forcing by affecting the concentration and distribution of the greenhouse gases.

Other species can form aerosols in the atmosphere that may affect climate through scattering of solar radiation and by altering cloud properties. From Table 1 we can see that the atmospheric concentrations of many of these radiatively important trace species are increasing. Evidence suggests that surface emissions, primarily from anthropogenic sources, are largely responsible for the increasing trends, particularly for gases such as CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, CFCs, and several of the

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U

MASTER

halocarbons [2]. The primary goal of this paper is to establish what we know about the emissions and budgets of the radiatively important atmospheric constituents listed in Table 1.

## CARBON DIOXIDE.

Atmospheric carbon dioxide concentrations have been measured at the Mauna Loa Observatory in Hawaii since 1958. The average annual concentration of CO<sub>2</sub> at Mauna Loa has risen from 315.8 ppmv in 1959 to 356.2 ppmv in 1992 [3]. CO<sub>2</sub> concentration in air bubbles trapped in ice cores indicate that the preindustrial concentration of CO<sub>2</sub> was approximately 280 ppmv [4][5]. Fossil fuel use and changing land use (i.e., deforestation and biomass burning) are the two types of human activities responsible for the increasing trends of CO<sub>2</sub>.

Burning of fossil fuels released about 6±.6 Pg of carbon into the atmosphere in 1990 [6][7]. From 1860 fossil fuel emissions have increased from less than 0.1 PgC per yr to greater than 6 PgC per year presently[8]. Emissions of CO<sub>2</sub> increased steadily at about 4.5 percent per year from 1945 through 1979, then declined from 1979 to 1983 but have increased since. Marland *et al.* [6] have presented inventories of CO<sub>2</sub> emissions on a country by country basis from 1950 to the present. In 1950 the U.S. was responsible for more that 40 percent of the total global emissions. This share has steadily declined to less than 25 percent today. Now the U.S., former Soviet Union, and Peoples Republic of China combined are responsible for about half of the worlds fossil fuel emissions.

Estimates of the net flux of carbon into the atmosphere for the year 1980 from land use range from 0.4 PgC/yr to 2.5 PgC/yr [2][9][10][11]. Prior to the impact of human activities, natural vegetation contained roughly 1000 Pg carbon [12]. This has decreased to current levels of about 560 Pg carbon [13]. It is clear that the magnitude of the carbon storage in contemporary landscapes is less than what was stored in the natural vegetation, however the rate of release and the timing of the major releases is very uncertain. Houghton and Skole [14] give estimates of carbon releases from vegetation and soils since 1800. They estimate that carbon storage in vegetation and soil has decreased by 170 Pg since 1800.

The observed increase in the carbon content of the atmosphere represents only 54 percent of the total release. Inconsistencies in our understanding of the relationship between observed increases in atmospheric CO<sub>2</sub> concentration and past fossil fuel emissions makes it difficult to make projections of future levels. All evidence indicates, however, that the CO<sub>2</sub> concentration can rise to double preindustrial levels within the next 50 years due to continued human activities.

## METHANE

Although its atmospheric abundance is less than 0.5 percent that of CO<sub>2</sub>, each molecule of methane (CH<sub>4</sub>) is about 21 times more effective at absorbing infra-red radiation than an additional molecule of CO<sub>2</sub> [12]. The globally averaged atmospheric concentration of CH<sub>4</sub> is about 1.72 ppmv, with slightly higher concentrations in the Northern Hemisphere (1.76 ppmv) than the Southern Hemisphere (1.68 ppmv). Methane concentrations increased at an average of about 1 percent per year (16 ppbv/yr) over the decade from 1979-1989. Khalil and Shearer [15] have shown that the rate of growth has actually decreased in the late 1980's and early 1990's with the annual increase more on the order of 10 ppbv per year. The change in growth rate may indicate that changes have occurred in the sources and/or sinks over the last few decades. Khalil *et al.* [16] suggest a decoupling of the increase of agricultural related sources (rice and animals) with the increase in human population.

Although methane is a naturally occurring greenhouse gas, its concentration is growing as a result of human activities including rice paddies, animal husbandry, landfills, biomass burning, and fossil fuel use. Globally CH<sub>4</sub> has increased by 7 percent over the decade from 1983. Because methane concentrations have been measured at global background sites for a number of years, the magnitude of the individual sources is less well known than the mass of atmospheric increase. The estimated

sources of methane to the atmosphere are broken down in Table 3 [2][9][17][18][19][20][21][22]. Complete spatially resolved emissions inventories of CH<sub>4</sub> are complex because of the large number of CH<sub>4</sub> source types. The best known source is probably emissions from domestic animals for which populations of animals are kept for commercial reasons. Rice is a large source of methane emissions, however measurements have shown more than an order of magnitude difference in CH<sub>4</sub> fluxes. Similar differences are found in wetlands and landfills. Carbon isotope measurements indicate that roughly 20 percent of the total emissions are from fossil fuel use [23]. Anthropogenic emissions are responsible for 60-80 percent of the total current methane source (see Table 3).

Photochemical oxidation with the hydroxyl radical (OH) is the largest sink for atmospheric CH<sub>4</sub>. Using current estimates of the global OH concentration the total quantity of CH<sub>4</sub> that reacts with OH is about 445 Tg/yr [20]. Microorganisms in the soil also remove CH<sub>4</sub> from the atmosphere. Microbial oxidation is estimated to remove 30±15 Tg/yr. There is also a relatively small (10±5 Tg/yr) stratospheric sink.

## HALOCARBONS

Halocarbons are of environmental concern because they have both the potential to affect stratospheric ozone as well as being greenhouse gases. With the exception of some natural emissions of CH<sub>3</sub>Cl and CH<sub>3</sub>Br, halocarbons present in the atmosphere are entirely from anthropogenic sources. Annual production and total sales are available from most of the world and are available from trade organizations. Release statistics of CFC-113, -114, and -115 have been compiled by Fischer *et al.* [24]. The spatial distribution of these releases are poorly characterized, because data shipment information is restricted by corporate confidentiality [25]. A summary of global sources is listed in Table 4.

Global observation networks have provided regular observations of CFC<sub>13</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CCl<sub>3</sub> and CCl<sub>4</sub> since 1978 [26]. CFC-11 and CFC-12 have the largest atmospheric concentrations of 0.2 and 0.5 ppbv respectively. The tropospheric concentrations of both gases were increasing at about 4 percent per year in the early 1990s but have slowed down to roughly 1-2 percent per year [8]. The concentration of CFC-113 was increasing at an even faster rate in the early 1990s, increasing at about 10% per year, but has also slowed since then. CH<sub>3</sub>CCl and HCFC-22 are increasing by about 2 and 7% per year respectively. CFC-113 and CH<sub>3</sub>CCl<sub>3</sub> are used as solvents. HCFC-22 is used in air conditioning and refrigeration.

All of the fully halogenated chlorofluorocarbons have very long atmospheric lifetimes with CFC-11 at 50 years, CFC-12 at 102 years [17]. These long lifetimes contribute to the sustained increasing concentrations of these gases. Bromine containing halons, used in fire extinguishing, have very small concentrations but they are very long lived and are much more effective at destroying stratospheric ozone. The peak tropospheric concentration of halocarbons is expected to have occurred in 1994 but stratospheric peak will lag by about 3 to 5 years [17]. The atmospheric lifetimes of HCFCs, HFCs and other halocarbons containing hydrogen tend to be much shorter (less than 15 years) due to their reaction with the hydroxyl radical.

Recent modifications of the Montreal Protocol call for the elimination of the production of CFCs by 1996 and an eventual phase out of the production CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub> and the halons. Some governments are reluctant to comply claiming it will have detrimental impacts on their economies [27].

## NITROUS OXIDE

Nitrous oxide N<sub>2</sub>O is a greenhouse gas where one molecule is 200 times more effective at absorbing in the infra-red than CO<sub>2</sub> and its atmospheric lifetime is about 120 yrs. N<sub>2</sub>O is also responsible for a significant fraction of the natural destruction of stratospheric ozone. The mean

atmospheric concentration of  $N_2O$  in 1990 was about 311 ppbv [20]. According to ice core records, the atmospheric  $N_2O$  concentration about 150 years ago was 285 ppbv [28]. Its concentration is currently increasing at roughly .2-.3 percent per year.

The various natural and anthropogenic sources of  $N_2O$  are not well quantified consequently the cause of the increase is not certain. The main anthropogenic sources are from agriculture especially development of pasture in tropical regions (~6 TgN/yr), biomass burning (2.5-5.7 TgN/yr), and a number of industrial processes (0.5 TgN/yr) [29]. Addition of nitrogenous fertilizers adds an additional 0.03 to 2.0 TgN/yr [30]. Bouwman *et al.* [31] produced an inventory from natural terrestrial ecosystems of ~4.4 TgN/yr. A best estimate of the current anthropogenic emission of  $N_2O$  is 5 to 20 Tg N/yr.

$N_2O$  is removed mainly by the photolysis in the stratosphere. Table 5 lists the known budget of  $N_2O$ . It is very difficult at this time to project future emissions of  $N_2O$  when such large uncertainties are associated with the numerous small sources. In order for  $N_2O$  levels to stabilize near current levels, anthropogenic sources would need to be reduced by more than 50 percent [20].

## NON-METHANE HYDROCARBONS AND VOLATILE ORGANIC COMPOUNDS

Non-methane hydrocarbons (NMHCs) constitute a large class of compounds containing only carbon and hydrogen. Volatile organic compounds (VOCs) include NMHCs and other organic compounds containing additional elements such as oxygen. A number of NMHCs and VOCs are potentially important greenhouse gases however their reactivity is high enough that these gases tend to have short lifetimes; consequently it is unlikely in the foreseeable future that their concentrations will be large enough to directly affect climate. The indirect climatic affect of NMHCs and VOCs lie in their tropospheric chemistry.

The indirect climatic effect of VOCs is most important through their controlling of tropospheric  $O_3$  and OH concentrations. For most VOCs, reactions with the hydroxyl radical provide the major loss and a significant source of carbon monoxide. In the presence of  $NO_x$  and sunlight, NMHCs can result in the production of tropospheric  $O_3$ . VOCs can also react with  $NO_x$  and produce a source of organic nitrogen. Organic nitrogen compounds can act as temporary reservoirs for  $NO_x$  allowing nitrogen oxides far greater global transport from their sources; which can again lead to tropospheric ozone production.

Inventories of VOCs are very complex not only because of the numerous source types but also because of the large number of species included. Sources of VOCs are associated with both natural and anthropogenic processes. In addition, because of their generally short lifetimes (order of hours for biogenic hydrocarbons to several months for ethane), combined with their highly localized sources, organic compounds are not distributed evenly through space and time. In some areas the natural sources dominate, while in urban areas anthropogenic emissions control VOC concentrations. Recent estimates of the total global anthropogenic VOC source is about 100-140 Tg C per year with 25 percent due to road transport, 14 percent from solvent use, 13 percent from fuel production and 34 percent from fuel consumption. The rest is from biomass burning (an important source in subtropical and tropical regions [32]) and other minor sources [22][30]. The annual emissions from natural sources are an order of magnitude higher at 1150 TgC/yr. Isoprene composes 44 percent of the total, with monoterpenes at 11 percent, other reactive VOCs at 22.5 percent, and the remainder is other VOCs [33].

## CARBON MONOXIDE

Measurements over the past 25 years have shown CO mixing ratios ranging from 40-200 ppbv [34]. Annual mean CO levels in the high latitudes of the Northern Hemisphere are about a factor of 3 greater than the Southern Hemisphere. Carbon monoxide levels are usually much higher over

continental regions than oceans reflecting the input from continental sources. Up until 1990, Northern Hemisphere concentrations of CO were increasing at roughly 1 percent per year. Recent data indicate that global CO levels have fallen sharply since 1990 from 1-7 percent per year depending on location [35][36]. There is no clear explanation for this rapid decrease, however one speculation is increasingly effective emissions controls.

Although CO is not important for its direct impact as a greenhouse gas, it is important to climate through its reactivity in the troposphere. The reaction of CO with OH is the primary sink for atmospheric OH, which yields an additional source of the greenhouse gas CO<sub>2</sub>. CO is also a local air pollutant and can contribute to the formation of infra-red absorbing tropospheric ozone in the presence of NO<sub>x</sub>. Soil uptake and stratospheric removal are also minor carbon monoxide sinks. Based on measured CO distributions and an OH field from model calculations the total global sink of CO is estimated at 865 TgC/yr [8]. Studies of <sup>14</sup>CO indicate that the global CO sink may be even higher [37][38].

The major sources of CO are anthropogenic, including transport, combustion, industrial processes, and biomass burning. Oxidation of methane and NMHCs from both natural and anthropogenic origin are also important. Oceans may also be an important natural source. All of these sources have large uncertainties. It is estimated that more than half of the current CO emissions are anthropogenic if one includes that derived from anthropogenic CH<sub>4</sub>. The source of CO from the oxidation of isoprene and other NMHCs is dependent on the uncertainties of the NMHC inventories. The source of CO from the oxidation of CH<sub>4</sub> on the other hand is somewhat more well characterized because the atmospheric concentration of CH<sub>4</sub> is more widely understood.

Emissions of CO from fossil fuel combustion peak between 30 and 60 degrees north latitude [39]. More than 70 percent of the biomass burning source is emitted in tropical regions [32]. Total anthropogenic sources are about 900 TgC/yr with a large uncertainty range and are listed in Table 6. On the global scale, inventories of CO have been developed at the 5°x5° scale by Muller [40]. The source from biomass burning has been estimated by Hao *et al.* [41] on a 5°x5° grid for tropical regions only, and Erickson [42] has developed a global inventory for the ocean flux of CO with a resolution of 4.5° latitude by 7.5° longitude.

## NITROGEN OXIDES

Nitrogen oxides (NO<sub>2</sub> + NO = NO<sub>x</sub>) have historically been considered important due to their role as primary pollutants in photochemical smog and their contribution to acidic dry and wet deposition. Though one of the nitrogen oxides, namely NO<sub>2</sub>, is an important absorber of visible solar radiation, and could affect the climate directly if tropospheric and/or stratospheric concentrations were to increase, NO<sub>x</sub> has little direct impact on the tropospheric radiation balance at present. Nitrogen oxides do however, have a large indirect effect owing to their importance in tropospheric chemistry. NO<sub>x</sub> is a catalyst promoting the formation of tropospheric ozone and controlling the concentration of OH. Through OH, emissions of NO<sub>x</sub> influence the lifetimes and therefore the abundances of many of the greenhouse gases. Nitrogen oxide species are relatively short lived, however, they can react chemically with NMHCs to produce organic nitrate. The strongly temperature dependent lifetimes of organic nitrates provide a reservoir for nitrogen oxides which can be transported long ranges to affect ozone chemistry well downstream from the sources.

NO<sub>x</sub> is emitted mainly in the form of NO. The major sources of reactive nitrogen are fossil fuel combustion, biomass burning, lightning discharges, microbial activity in soils and transport from the stratosphere (see Table 7). Fossil fuel combustion is the largest source of NO<sub>x</sub> and according to Hameed and Dignon [43] the global emissions from fossil fuel combustion increased from 18 TgN per year in 1970 to more than 24 TgN/yr in 1986.

Anthropogenic emissions of NO<sub>x</sub> have uncertainties ranging ±30 percent but in the case of natural sources, uncertainties may range by more than a factor of 2. NO<sub>x</sub> produced by lightning is

probably the most important natural source in the free troposphere. Price *et al.* [44] give a range for the  $\text{NO}_x$  source from lightning of 5 to 25 TgN/yr. Preliminary estimates suggest that in some geographical regions emissions from soils and lightning are the most significant source [45]. Dignon *et al.* [46] have determined an emissions estimate from natural soils at 5 TgN/yr. This is consistent with the 3.3 to 7.7 TgN/yr range given by Levy *et al.* [47].

Atmospheric oxidation of  $\text{NO}_2$  to  $\text{HNO}_2$  by OH in the daytime and to  $\text{NO}_3$  by  $\text{O}_3$  at night are the most important  $\text{NO}_x$  removal processes. Dry deposition of  $\text{NO}_2$  plays a lesser but significant role.

The tropospheric lifetime of  $\text{NO}_x$  varies from less than a day in the boundary layer to about a week in the free troposphere. Although the removal processes of  $\text{NO}_x$  are reasonably well defined the global distribution of  $\text{NO}_x$  is quite uncertain therefore an estimate of  $\sim 42$  Tg N/yr for the sink of  $\text{NO}_x$  can be made based on the work of Atherton *et al.* [48].

Because of the high variability in its tropospheric concentrations, it not possible to establish a clear trend for  $\text{NO}_x$  from atmospheric observations. The anthropogenic sources, particularly in the Northern Hemisphere, continue to increase and the concentration of nitrate in Greenland ice cores exhibits an increase during the last century[49]. There is evidence that tropospheric  $\text{O}_3$  in the northern mid-latitudes has increased [23] and much of this increase can be attributed to increased  $\text{NO}_x$  emissions[50].

## OZONE

Unlike the other greenhouse gases listed above, whose radiative effects are largely dependent on their concentrations, the climatic effect of ozone ( $\text{O}_3$ ) depends on its distribution throughout the troposphere and stratosphere. Ozone is the primary absorber of ultra-violet and visible radiation in the atmosphere and its concentrations determine the amount of ultra-violet radiation that reaches the Earth's surface. Ozone is also a greenhouse gas with a strong infra-red absorption band at 9.6  $\mu\text{m}$ . Changes in the ozone distribution can cause radiative forcing by influencing both the solar and infrared radiation. It is the balance between these radiative processes that determine the net effect of  $\text{O}_3$  on the climate.

Approximately 90 percent of the ozone in the atmosphere is contained in the stratosphere. Natural production of ozone in the stratosphere begins with the photodissociation of the  $\text{O}_2$  molecule at ultra-violet wavelengths less than 242 nm. This reaction produces two ground-state oxygen atoms that can then react with  $\text{O}_2$  to product  $\text{O}_3$ . Increases in ozone above roughly 30 km tend to decrease the surface temperature by decreasing the amount of solar radiation that reaches the Earth's surface. Ozone is also produced in the troposphere as a major component of photochemical smog resulting from anthropogenic emissions of  $\text{NO}_x$ , CO and hydrocarbons. Increases in ozone concentration below 30 km, where the infra-red greenhouse effect dominates, tend to increase the surface temperature.

Measurements of ozone from ground based stations and satellites indicate that the concentrations of ozone in the stratosphere are decreasing. The most obvious feature is the annual development of the Antarctic ozone hole which occurs in the Austral spring. The October average total ozone values over Antarctica are 50-70 percent lower than those observed in the 1960s [17]. The primary destruction of  $\text{O}_3$  in the stratosphere comes from catalytic mechanisms involving various free radical species, including oxides of nitrogen, chlorine, bromine, and hydrogen. Nitrogen oxide species are believed to be responsible for 70 percent of the total ozone destruction. Most of the nitrogen oxides in the stratosphere are believed to occur naturally; however, increasing anthropogenic emissions of  $\text{N}_2\text{O}$  at the surface are leading to growing amounts of stratospheric  $\text{NO}_x$ . Levels of reactive chlorine are increasing in the stratosphere from anthropogenic emissions of halocarbons. The reactive chlorine catalytic mechanism is particularly efficient at destroying ozone in the stratosphere and is believed to be the major contributor to the observed ozone depletion [11].

Downward transport of ozone from the stratosphere used to be considered the major source

of tropospheric ozone. It is now thought that the net tropospheric photochemical production of ozone is of a comparable magnitude [23][51]. The formation of tropospheric ozone occurs through mechanisms where NO reacts with HO<sub>2</sub>, in the presence of hydrocarbons and sunlight. Changes in tropospheric ozone are highly variable both regionally and vertically, making assessment of global long-term trends difficult. Ozonesonde balloon measurements indicate that northern mid-latitudes concentration of ozone in the troposphere have been increasing since 1969 [23] [52]. There is also some evidence that levels have increased in the NH since the early 1900s [53]. Dignon and Hameed [50] have shown that most of the observed ozone increase between the years 1966 and 1980 can be attributed to increasing anthropogenic fluxes of NO<sub>x</sub> and hydrocarbons.

## HYDROXYL RADICAL

The lifetimes of many of the radiatively important trace species depends on the concentration of hydroxyl radical (OH). Hydroxyl is the major scavenging species for removal of virtually all greenhouse gases except for CO<sub>2</sub>. The OH radical responds instantaneously to variations in O<sub>3</sub>, NO<sub>x</sub>, CO, CH<sub>4</sub>, VOCs and sunlight. The field can vary by orders of magnitude in space and time. It is not currently possible to measure the global field of OH therefore we are left to rely on numerical models to estimate the global, seasonal and vertical distribution of OH. Anthropogenic increases of greenhouse gases are removed by OH have the potential to reduce the global OH concentration, causing a chemical feedback decreasing the loss rate of greenhouse gases, and resulting in elevation of greenhouse gas concentrations.

## AEROSOLS

Aerosols are suspensions of particles in the atmosphere of the size range 10<sup>-3</sup> to 100 μm in diameter. Their distributions are highly variable regionally in both concentration and chemical composition. Tropospheric aerosols are formed by dispersal of material from the surface (e.g., soil and dust), by direct emissions of material into the atmosphere (e.g., smoke) and by chemical reactions in the atmosphere which convert gases into particles (e.g., sulfur dioxide to sulfate). Stratospheric aerosols have a longer lifetime than aerosols in the troposphere and therefore are more uniformly distributed. Large volcanic eruptions such as Mt Pinatubo influence the aerosol content of the stratosphere.

Addition of anthropogenic aerosols can influence the radiative balance of the Earth in two ways: (1) directly through absorption and through scattering of solar radiation back to space, and (2) indirectly by acting as cloud condensation nuclei thus changing the lifetime and radiative properties of clouds. There are many uncertainties associated with the climatic influence of aerosols one thing that is known is the direct and indirect effect of aerosols are both strongly influenced by particle size and composition. Therefore, the radiative effects can not be simply related to the aerosol mass loading. The radiative effect of anthropogenic aerosols are relatively large compared to their mass loading because their size distribution (< 1 μm) is in the range that is most radiatively active.

Natural sources of aerosols include sea-salts, resulting from the evaporation of sea-spray droplets, and volcanic emissions. Soil dust is also a major natural source in arid and semi arid regions. The diameter of windblown dust ranges from 1 to >100 μm, where the largest particles fall out very rapidly. The annual emissions amounts to about 1500 Tg/yr, which is of the same order as sea-salt production (1300 Tg /yr). Table 8 summarizes the annual emissions of aerosol into the troposphere and stratosphere [17]. Removal of aerosols is mainly achieved by deposition to the Earth's surface or by volatilization.

Release of sulfur dioxide from fossil fuel combustion and carbonaceous species mainly from biomass burning are the main anthropogenic sources of aerosols. There is evidence suggesting the concentration of anthropogenic aerosols have increased downwind of industrial regions and that this

increase is very large compared with the natural background. Owing to the effect of size distribution and chemical composition, anthropogenic aerosol contributes approximately 50% of the global mean optical depth but only 20% to the mass burden [17].

The impact of aerosol on the optical properties of low level clouds has been demonstrated in the localized observations of ship tracks[54], but has not been observed globally. There is, however, some observational evidence that mean sizes of cloud droplets are larger in the Southern Hemisphere than in the Northern Hemisphere, suggesting that sulfate emissions in the industrialized north may be having a widespread effect[55].

## SUMMARY

Atmospheric chemistry determines the concentrations of most of the important greenhouse gases except for carbon dioxide. The rate of removal of the greenhouse gases from the atmosphere is also controlled by atmospheric chemistry. The indirect effects of chemical forcing resulting from the chemical interactions of other species can also affect the concentrations of radiatively important gases such as ozone.

In order to establish the contribution of any possible climatic change attributable to individual greenhouse gases, spatially and temporally resolved estimates of their emissions need to be established. Unfortunately, for most of the radiatively important species the global magnitudes of their individual fluxes are not known to better than a factor of two and their spatial distributions are even more poorly characterized. Efforts to estimate future projections of potential impacts and to monitor international agreements will require continued research to narrow the uncertainties of magnitude and geographical distribution of emissions.

## ACKNOWLEDGMENTS

This work was partially supported by the Lawrence Livermore National Laboratory Directed Research and Development Program under the auspices of the U.S. Department of Energy Contract No. W-7405-Eng-48.

## REFERENCES

- [1] Ramanathan, V., R.J. Cicerone, H.B. Singh and J.T. Kiehl, 1985: Trace gas trends and their potential role in climate change. *J. Geophys. Res.*, **90**, 5547-5557.
- [2] IPCC (Intergovernmental Panel on Climate Change), 1992: *Climate Change: 1992*, Cambridge University Press, Cambridge UK.
- [3] Keeling, C.D. and T.P. Whorf, 1994: Atmospheric CO<sub>2</sub> records from sites in the SIO air sampling network, in *Trends '93 -- A Compendium of Data on Global Change*, eds. T.A. Bowden, D.P. Kaiser, R. J. Sepanski and F.W. Stoss, ORNL/CDIAC-65, Carbon Dioxide Information Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- [4] Neftel, A. E. Moor, H. Oeschger and B. Stauffer, 1985: Evidence from polar ice cores for the increase in atmospheric CO<sub>2</sub> in the past two centuries, *Nature*, **315**, 45-47.
- [5] Friedli, H., H. Löttscher, H. Oeschger, U. Siegenthaler and B. Stauffer, 1986: Ice core record of <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric carbon dioxide in the past two centuries, *Nature*, **324**, 237-238.
- [6] Marland, G., T.A. Bowden, R.C. Griffin, S.F. Huang, P. Kanciruk and T.R. Nelson, 1989: *Estimates of CO<sub>2</sub> Emissions from Fossil Fuel Burning and Cement Manufacturing, Based on the*

*United Nations Energy Statistics and the U.S. Bureau of Mines Cement Manufacturing Data*, ORNL/CDIAC-25, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[7] Bowden, T.A., G. Marland and R. Andres, 1995: CO<sub>2</sub> emission calculations and trends, *this issue*.

[8] Wuebbles, D.J., J. Edmonds, J. Dignon, W. Emanuel, D. Fischer, R. Gammon, R. Hangebrauck, R. Harriss, M.A.K. Khalil, J. Spence and T. Thompson, 1995: Emissions and budgets of radiatively important constituents, to appear in *The Engineering Response to Global Climate Change*, ed R.G. Watts.

[9] IPCC (Intergovernmental Panel on Climate Change) 1990: *Scientific Assessment of Climate Change*, Cambridge University Press, Cambridge UK.

[10] Detwiler, R.P. and C.A.S. Hall, 1988: Tropical forests and the global carbon cycle, *Science*, **239**, 42-47.

[11] Houghton, R.A., R.D. Boone, J.R. Fruci, J.E. Hobbie, J.M. Melillo, C.A. Palm, B.J. Peterson, G.R. Shaver, G.M. Woodwell, B. Moore, D.L. Skole and N. Meyers, 1987: The flux of carbon from terrestrial ecosystems to the atmosphere in 1980 due to changes in land use, *Tellus*, **39B**, 122-139.

[12] Olson, J.S., 1974: Terrestrial ecosystem, in *Encyclopedia Britannica*, 15th Edition, Helen Hemingway Benton, Chicago, Illinois.

[13] Olson, J.S., J.A. Watts and L.J. Allison, 1983: *Carbon in Live Vegetation of Major World Ecosystems*, ORNL-5826, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[14] Houghton, R.A. and D.L. Skole, 1991: Carbon, in *The Earth as Transformed by Human Action*, eds. R.L. Turner, W.C. Clark, R.W. Kates, J.F. Richards, J.T. Matthews and W.B. Meyer, Cambridge University Press, Cambridge UK.

[15] Khalil, M.A.K. and M.J. Shearer, 1993: Sources of Methane: An Overview, in *Atmospheric Methane: Sources, Sinks, and Role in Climate Change*, ed. M.A.K. Khalil, Springer-Verlag Berlin.

[16] Khalil, M.A.K., M.J. Shearer and R.A. Rasmussen, 1995: Rice agriculture: An important source of methane, *this issue*.

[17] IPCC (Intergovernmental Panel on Climate Change), 1994: *Climate Change 1994*, Cambridge University Press, Cambridge, UK.

[18] Khalil, M.A.K. and R.A. Rasmussen, 1990: Constraints on the global sources of methane and an analysis of recent budgets, *Tellus*, **42B**, 229-236.

[19] Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L.P. Steele and P.J. Fraser, 1991: Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, **96**, 13,033-13,065.

[20] WMO (World Meteorological Organization), 1985: Stratospheric Ozone 1985: Assessment of our understanding of the processes controlling its present distribution and change, Global Ozone Research and Monitoring Project Report No. 16.

[21] WMO (World Meteorological Organization), 1989: Scientific Assessment of Stratospheric Ozone: 1989, Global Ozone Monitoring Project Report No. 20.

[22] WMO (World Meteorological Organization), 1991: Scientific Assessment of Ozone Depletion: 1991, Global Ozone Monitoring Project Report No. 25.

- [23] Wahlen, M. N. Tanaka, R. Henry, B. Deck, J. Zeglen, J.S. Vogel, J. Southon, A. Shemish, R. Fairbanks and W. Broecker, 1989: Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon, *Science*, **245**, 286-290.
- [24] Fischer, D.A., T. Duafala, P.M. Midgley and C. Niemi, 1994: Production and emissions of CFCs, halons, and related molecules, in *Concentrations, Lifetimes and Trends of CFCs, halons and related Species*, eds. J. Kaye, S. Penkett and F. Ormond, NASA Report No. 1339.
- [25] Graedel, T.E., T.S. Bates, A.F. Bouwman, D. Cunnold, J. Dignon, I. Fung, D.J. Jacob, B.K. Lamb, J.A. Logan, G. Marland, P. Middleton, J.M. Pacyna, M. Placet and C. Veldt, 1993: A compilation of inventories of emissions to the atmosphere, *Global Biogeochem. Cycles*, **7**, 1-26.
- [26] Cunnold, D., F. Alyea, R. Prinn, R. Rasmussen, A. Crawford, P. Simmons and P. Fraser, 1990: Atmospheric inventories of the Chlorocarbons from Ten Years of ABLE/GAGE Observations, paper presented at the 7th International Symposium of Commission on Atmospheric Chemistry and Global Pollution, Chamrousse, France, 5-11, Sept., 1990.
- [27] Rawson, W.F., 1995: Arizona rejects 'irresponsible' Freon ban, *The Arizona Republic*, April, 18, 1995, Associated Press.
- [28] Pearman, G.I., D. Etheridge, F. deSilva and P.J. Fraser, 1986: Evidence of changing concentrations of atmospheric CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> from air bubbles in Antarctic ice, *Nature*, **320**, 248-250.
- [29] Bouwman, A.F., K.W. Van der Hoek and J.G.J. Olivier, 1995: Uncertainties in the global source distribution of nitrous oxide, *J. Geophys. Res.*, **100**, 2785-2800.
- [30] Matthew, E., 1994: Nitrogenous fertilizers: Global distribution of consumption and associated emissions of nitrous oxide and ammonia, *Global Biogeochem. Cycles*, **8**, 411-439.
- [31] Bouwman, A.F., I. Fung, E. Matthews and J. John, 1993: Global analysis of the potential for N<sub>2</sub>O production in natural soils, *Global Biogeochem. Cycles*, **7**, 557-597.
- [32] Dignon, J., 1995: Impact of biomass burning on the atmosphere, to appear in *Ice Core Studies on Global Biogeochemical Cycles*, Springer-Verlag, Berlin.
- [33] Guenther, A., C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor and P. Zimmerman, 1995: A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, **100**, 8873-8892.
- [34] Novelli, P.C., L.P. Steele and P.P. Tans, 1992: Mixing ratios of carbon monoxide in the troposphere, *J. Geophys. Res.*, **97**, 20,731-20,750.
- [35] Novelli, P.C., K. Masarie, P.P. Tans and P. Lang, 1994: Recent changes in atmospheric carbon monoxide, *Science*, **263**, 1587-1590.
- [36] Khalil, M.A.K. and R.A. Rasmussen, 1994: Global decrease of atmospheric carbon monoxide, *Nature*, **370**, 639-641.
- [37] Brenninkmeijer, C.A.M., M.R. Manning, D.C. Lowe, G. Wallace, R.J. Sparks and A. Volz-Thomas, 1992: Interhemispheric asymmetry in OH abundance inferred from measurements of atmospheric <sup>14</sup>CO, *Nature*, **356**, 50-52.
- [38] Mak, J.E., C.A.M. Brenninkmeijer and M.R. Manning, 1992: Evidence for a missing carbon monoxide sink based on tropospheric measurements of <sup>14</sup>CO, *Geophys. Res. Lett.*, **14**, 1467-1470.

- [39] Dignon, J., H.E. Eddleman and J.E. Penner 1995: A carbon monoxide emission inventory, manuscript in preparation.
- [40] Müller, J.-F., 1992: Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, *J. Geophys. Res.*, **97**, 3787-3804.
- [41] Hao, W.M., M.H. Liu and P.J. Crutzen, 1990: Estimates of annual and regional releases of CO<sub>2</sub> and other trace species to the atmosphere from fires in the tropics, based on the FAO Statistics for the period 1975-1980, in *Fire in the Tropical Biota - Ecosystem Process and Global Challenges*, ed. J.G. Goldammer, Springer-Verlag, New York.
- [42] Erickson, D.J., 1989: Ocean to atmosphere carbon monoxide flux: global inventory and climate implications, *Global Biogeochem. Cycles*, **3**, 305-314.
- [43] Hameed, S. and J. Dignon, 1991: Global emissions of nitrogen and sulfur oxides in fossil fuel combustion 1970-1986, *J. Air and Waste Management Assoc.*, **42**, 159-163.
- [44] Price, C., J.E. Penner and M.J. Prather, 1995: NO<sub>x</sub> from lightning Part I: Distribution based on lightning physics, *preprint*.
- [45] Atherton, C.S., J.E. Penner and J.J. Walton, 1991: The role of lightning in the tropospheric nitrogen budget: Model investigations, Lawrence Livermore National Laboratory Report No. UCRL-JC-107223.
- [46] Dignon, J., J.E. Penner, C.S. Atherton, J.J. Walton, 1991: Atmospheric reactive nitrogen: A model study of natural and anthropogenic sources and the role of microbial soil emissions. Lawrence Livermore National Laboratory Report No. UCRL-JC-107393.
- [47] Yienger, J.J. and H. Levy, II, 1994: Empirical model of global soil-biogenic NO<sub>x</sub> emissions, *preprint*.
- [48] Atherton, C.S., J.E. Penner, J.J. Walton and S. Hameed, 1991: Wet and dry nitrogen deposition: Results from a global three-dimensional chemistry-transport-deposition model, Lawrence Livermore National Laboratory Report No. UCRL-JC-103403 Rev. 1.
- [49] Neftel, A., J. Beer, H. Oeschger, F. Zurcher and R.C. Rinkel, 1985: Sulfate and nitrate concentrations in snow from South Greenland, *Nature*, **314**, 611-613.
- [50] Dignon J. and S. Hameed, 1985: A model investigation of the impact of increases in anthropogenic NO<sub>x</sub> Emissions between 1967 and 1980 on tropospheric ozone, *J. Atmos. Chem.*, **3**, 491-506.
- [51] Fishman, J., 1985: Ozone in the troposphere, in *Ozone in the Free Troposphere*, eds. R.C. Whitten and S.S. Prasad, Van Nostrand Reinhold, New York.
- [52] Lacis, A.A., D.J. Wuebbles and J.A. Logan, 1990: Radiative forcing of climate by changes in the vertical distribution of ozone, *J. Geophys. Res.*, **95**, 9971-9981.
- [53] Volz, A. and D. Kley, 1988: Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature*, **332**, 240-242.
- [54] Radke, L.F., J.A. Coakley and M.D. King, 1989: Direct and remote sensing observations of the effect of ships on clouds, *Science*, **246**, 1146-1148.
- [55] Han, Q.W, W.B. Rossow and A.A. Lacis, 1994: Near-global survey of effective droplet radii in liquid water clouds using ISCCP data, *J. Climate*, **7**, 465-497.

TABLE 1: RADIATIVELY IMPORTANT TRACE SPECIES

Trace Species	Common Name	Tropospheric Concentrations (ppmv)	Trend in Concentration (% per year)	Atmospheric Lifetime (yr)
CO <sub>2</sub>	carbon dioxide	356 (1992)	0.4	> 1
CH <sub>4</sub>	methane	1.71	0.7 to 1	8-10
CO	carbon monoxide	.12 (NH) .06 (SH)	1 (NH) 0 (SH)	0.3
N <sub>2</sub> O	nitrous oxide	0.31	0.2 to 0.3	120
NO <sub>x</sub> [=NO+NO <sub>2</sub> ]	nitrogen oxides	1 to 20×10 <sup>-5</sup>	unknown	≤0.02
CFCl <sub>3</sub>	CFC-11	2.7×10 <sup>-4</sup>	2	50
CF <sub>2</sub> Cl <sub>3</sub>	CFC-12	5.0×10 <sup>-4</sup>	4	102
C <sub>2</sub> F <sub>3</sub> Cl <sub>3</sub>	CFC-113	8.0×10 <sup>-5</sup>	6	85
CH <sub>3</sub> CCl <sub>3</sub>	methyl chloroform	1.6×10 <sup>-4</sup>	4	5
CF <sub>2</sub> ClBr	halon-1211	2.5×10 <sup>-6</sup>	6	20
CF <sub>3</sub> Br	halon-1301	2.0×10 <sup>-6</sup>	15	65
SO <sub>2</sub>	sulfur dioxide	1 to 20×10 <sup>-5</sup>	unknown	0.02
C <sub>2</sub> H <sub>2</sub> , etc.	NMHC/VOC	<1	unknown	
O <sub>3</sub>	ozone	.02 to .1	+(trop.) -(strat)	
OH	hydroxyl	4 to 100×10 <sup>-9</sup>	unknown	

TABLE 2: ESTIMATED BUDGET OF CARBON DIOXIDE [2][6][7][9].

<b>Sources of CO<sub>2</sub></b>	<b>Estimated value and range (PgC per year)</b>	
Gross ocean release	105	100-110
Gross release from land	110	40-120
<b>Energy</b>		
Fossil fuel use	6.2	5.5-6.5
Wood fuel use		
<b>Anthropogenic (non-energy)</b>		
Land use conversion	1.1	0.-2.3
Cement manufacture	0.15	0.1-0.2
<b>Sinks of CO<sub>2</sub></b>		
Gross ocean uptake	107.5	102.5-112.5
Net ocean uptake	2	1.2-2.8
Gross plant uptake	110	40-120
<b>Reservoirs of Carbon</b>		
Stock in atmosphere (1988)	745	
Ocean surface layer	630	570-690
Intermediate and deep ocean	38,000	34,000-42,000
Ocean sediments	100,000,000	
Marine biosphere	2	
Terrestrial biosphere	560	
Soils	1700	
<b>Recoverable fossil fuels</b>		
Oil and gas	250	
Coal	8000	
Oil Shale	40000	

TABLE 3: ESTIMATED SOURCES AND SINKS OF METHANE [2][9][15][17].

Sources	Best estimate and range (Tg CH <sub>4</sub> /yr)	
<b>Natural</b>		
Enteric fermentation (wild)	4	1-7
Wetlands	115	55-155
Lakes	5	1-25
Tundra	4	2-7
Oceans	10	5-50
Termites and other insects	20	10-50
Methane hydrates	5	0-100
Other	40	0-80
<b>Anthropogenic</b>		
Natural gas losses	40	25-50
Coal mining	30	15-60
Petroleum industry	15	5-30
Wood fuel	15	5-30
Landfills	40	20-70
Animal waste	25	20-30
Sewage treatment	25	15-80
Enteric fermentation (domesticated)	81	65-100
Rice Padies	60	20-100
Biomass Burning	40	20-80
<b>Sinks</b>		
Reaction with tropospheric OH	445	330-560
Stratospheric removal	10	5-15
Microorganism uptake in soils	30	15-45

TABLE 4: ESTIMATE SOURCES OF THE MAJOR HALOCARBONS IN TG PER YEAR [8].

Gas	Procuduction (Mid- to late-1980s)	Uses	
CFC-11	0.33	Refrigeration and air conditioning	8%
		Closed-cell foams	36%
		Open-cell foams	19%
		Aerosol propellants	31%
		Other uses	6%
CFC-12	0.44	Refrigeration and air conditioning	49%
		Closed-cell foams	8%
		Open-cell foams	5%
		Aerosol propellants	32%
		Other uses	6%
CFC-113	0.19	Aerosol propellants; cleaning agents	98%
		Closed-cell foams; refrigerants; heat transfer	2%
CH <sub>3</sub> CCl <sub>3</sub>	0.70	Cleaning agents	100%
HCFC-22	0.20	Blowing agents; aerosol propellant	15%
		Refrigeration and air conditioning	85%

TABLE 5: ESTIMATED SOURCES AND SINKS OF NITROUS OXIDE [20][29][30][31].

Sources	Estimated value and range (Tg N per year)	
<b>Natural</b>		
Oceans and estuaries	3.	1-5
Natural soils	4.6	3-8
Aquifers	0.8	0.8-2
<b>Anthropogenic</b>		
Fossil fuel combustion	0.5	0-3
Biomass Burning	4.0	2.5-5.7
Cultivated soils and pastures	6.0	2.5-10
Industrial processes	0.5	0-1.8
Addition of nitrogenous fertilizers	1.0	0-2
<b>Sinks</b>		
Stratospheric photolysis	12	9-17
Removal in soils	<0.1	

TABLE 6: ESTIMATED SOURCES AND SINKS OF CARBON MONOXIDE [8].

Sources	Estimated value and range (Tg C per year)	
<b>Natural</b>		
Plant emissions	75	60-160
Oxidation of natural hydrocarbons	250	50-500
Oceans	20	10-100
Oxidation of methane	400	260-500
<b>Anthropogenic</b>		
Energy use	400	300-550
Agriculture	110	40-170
Biomass burning	350	300-700
Oxidation of man-made hydrocarbons	40	0-80
<b>Sinks</b>		
Reaction with OH	865	500-1200
Soil uptake	250	100-390

TABLE 7: ESTIMATED SOURCES AND SINKS OF REACTIVE NITROGEN (NO<sub>x</sub>) [43][44][46][47].

Sources	Estimated value and range (Tg N per year)	
<b>Natural</b>		
Stratospheric oxidation of N <sub>2</sub> O	1.0	0.5-1.5
Lightning	15	5-25
Soil microbial activity	5	3-8
Oceans	0.15	<1
<b>Anthropogenic</b>		
Fossil fuel combustion	24	20-25
Biomass burning	8	3-13
<b>Sinks</b>		
Wet and dry deposition	42	25-85

TABLE 8: ESTIMATED SOURCES OF ATMOSPHERIC AEROSOLS [ 17].

Sources	Estimated value and range (Tg dry mass)	
<b>Natural Primary</b>		
Soil dust (mineral aerosol)	1,500	1,000-3,000
Sea salt	1,300	1,000-10,000
Volcanic dust	33	4-10,000
primary organic aerosols	50	26-80
<b>Natural Secondary (from gaseous precursors)</b>		
Biogenic sulfates	90	60-110
Volcanic SO <sub>2</sub>	12	4-45
Biogenic VOCs	55	40-200
Nitrates from NO <sub>x</sub>	22	10-40
<b>Anthropogenic Primary</b>		
Industrial dust	100	40-130
Soot	10	5-25
Biomass burning	80	50-140
<b>Anthropogenic Secondary</b>		
Sulfates from SO <sub>2</sub>	140	120-180
Nitrates from NO <sub>x</sub>	40	20-50
Biogenic VOCs	10	5-25