

UC Irvine

Faculty Publications

Title

Combustion's impact on the global atmosphere

Permalink

<https://escholarship.org/uc/item/4p34f2v7>

Journal

Symposium (International) on Combustion, 25(1)

ISSN

00820784

Authors

Prather, Michael J
Logan, Jennifer A

Publication Date

1994

DOI

10.1016/S0082-0784(06)80796-4

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

COMBUSTION'S IMPACT ON THE GLOBAL ATMOSPHERE

MICHAEL J. PRATHER

*Earth System Science
University of California
Irvine, CA 92717-3100, USA*

AND

JENNIFER A. LOGAN

*Department of Earth & Planetary Sciences
Harvard University
Pierce Hall, 29 Oxford St., Cambridge, MA 02138, USA*

The combustion of a hydrocarbon fuel removes molecular oxygen (O_2) from the atmosphere and releases equivalent amounts of water (H_2O) and carbon dioxide (CO_2), almost always with trace amounts of numerous other compounds including hydrocarbons (CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , C_6H_6 , CH_3CHO , etc.), carbon monoxide (CO), nitrogen oxides (NO , N_2O) and reduced nitrogen (NH_3 and HCN), sulfur gases (SO_2 , OCS , CS_2), halocarbons (CH_3Cl and CH_3Br), and particles. A review of the atmospheric budgets of these gases shows that burning of fossil fuels and recent biomass has led to global alterations in the composition of our atmosphere. Combustion is clearly responsible for most of the enhanced greenhouse forcing to date (through CO_2 , tropospheric O_3 , soot) and also some counteracting effects (through SO_2). It has had minimal impact on stratospheric O_3 (through CH_3Cl , CH_3Br , CH_4), but has likely changed the tropospheric oxidant levels (through CO , NO_x , NMHC), at least over the northern hemisphere. Most of the important greenhouse gases and tropospheric oxidant gases have significant natural sources, which are not well defined today and may be changing; and thus, quantifying the role of combustion is difficult.

Introduction

The combustion of a hydrocarbon fuel removes molecular oxygen (O_2) from the atmosphere and releases equivalent amounts of water (H_2O) and carbon dioxide (CO_2), often with trace amounts of other species. When recently photosynthesized material is burned, oxidation and decay of biomass are accelerated. When fossil fuel is burned, this activity reverses the geologic process whereby the biosphere has slowly accumulated an oxygenated atmosphere by laying down organic, carbon-rich sediments [1]. In either case, numerous other compounds are emitted in trace amounts, including nitrogen oxides (NO , NO_2 , N_2O), sulfur gases (SO_2 , OCS , CS_2), carbon monoxide (CO), hydrocarbons (CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , C_6H_6 , CH_3CHO , etc.), reduced nitrogen compounds (NH_3 and HCN), halocarbons (CH_3Cl and CH_3Br), and particulate matter. Some of these products are limited by the trace elements in the fuel (e.g., S, Cl, and Br), but overall the emission of trace products depends very much upon the conditions of combustion.

The burning of fossil fuels (coal, oil, and gas) and of recent biomass (savannas, forests, biomass fuels, and agricultural waste) leads to global alteration in

the composition of our atmosphere. Concern over such changes focusses on (1) the greenhouse effect, (2) depletion of the ozone layer, and (3) the level of tropospheric oxidants. Arrhenius [2] pointed out that CO_2 would act as a greenhouse gas, and recent scientific assessments [3] show that increases in CO_2 and other greenhouse gases (GHGs) will inevitably lead to a warmer climate. Stratospheric ozone loss associated with halocarbons [4] or with nitrogen oxides from high-altitude aircraft [5] has prompted international treaties (Montreal Protocol on Substances that Deplete the Ozone Layer, Final Act, 1987) controlling ozone-depleting gases (ODGs). Short-lived hydrocarbons and nitrogen oxides can produce unhealthful increases in oxidants (O_3 and NO_2) in polluted urban regions [6], and subsequent understanding of global tropospheric ozone has shown that these oxidant gases (OXGs) have likely increased concentrations of tropospheric O_3 throughout much of the northern hemisphere [7]. Concentration of the hydroxyl radical (OH), the primary sink for most atmospheric compounds, may have been modified by emissions of CO , hydrocarbons, and NO_x from combustion [8,9].

This paper reviews the role of combustion insofar as it changes the composition of the atmosphere on

a global scale, i.e., away from regional pollution in the boundary layer. We estimate how much of this change since preindustrial times can be ascribed to combustion. A summary of atmospheric chemistry given here emphasizes the troposphere and is taken from a chapter one of the authors (MJP) prepared for the new climate assessment [10]. We follow with an examination of how combustion affects the natural levels of each compound. For the consequences of an evolving atmosphere on both chemistry and climate, the reader is referred to recent international assessments [11,3,10] and reference texts [12,13,14].

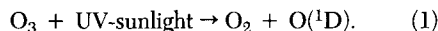
Atmospheric Chemistry—an Overview

The gases N₂ (78% of dry air), O₂ (21%), and Ar (1%) comprise the bulk of the Earth's atmosphere. Their abundances are controlled over geologic time scales by the biosphere, uptake/release from the crustal material, and degassing of the interior. Water vapor (H₂O) is the next most abundant, but highly variable, species in the lower atmosphere, where the cycles of evaporation and precipitation result in abundances ranging from 4% in the tropical boundary layer to 4×10^{-6} in the lower stratosphere. Of the remaining gases that play a role in the Earth's chemical or radiative balance, all but CO₂ are controlled in one way or another by chemical processes. The cycles of atmospheric aerosols also involve chemical reactions. Atmospheric trace gas composition and its change since the preindustrial era are summarized in Table 1.

The atmospheric abundances of these trace gases, most often designated in volume mixing ratios (e.g., parts per billion = ppb = 10^{-9} vol/vol), are determined by a balance between sources and sinks. The sources are typically surface emissions, such as those associated with combustion, and the sinks are chemical processes in the atmosphere that in general irreversibly oxidize the gas (e.g., CH₄ is oxidized to CO, and then to CO₂). The combined strength of these sinks determines the atmospheric residence time of a gas, i.e., the e-folding of an instantaneous emission. Most of the atmospheric mass, and consequently the mass of most trace gases (except O₃), resides in the troposphere, which comprises on average the lowest 13 km of the atmosphere. The bulk of the remaining atmosphere (~15%) resides in the stratosphere from 13- to 50-km altitude, the region containing most of the ozone (O₃). In the troposphere, the major sink for many gases is through reactions with the hydroxyl radical (OH), while in the stratosphere removal is dominated by ultraviolet photodissociation. Once a constituent becomes "sticky" or soluble, tropospheric removal in clouds and precipitation or surface deposition proceed rapidly.

Photochemical Loss of Trace Gases:

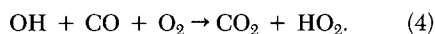
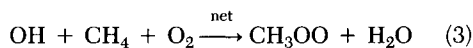
Most chemical cycles in the atmosphere are initiated by ultraviolet sunlight. Since only light with wavelengths greater than 290 nm reaches the troposphere, the number of compounds that can be photodissociated directly is limited. Most of the photochemical chains of interest begin with the dissociation of ozone (O₃) at wavelengths below 320 nm (e.g., Ref. 15).



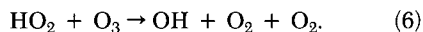
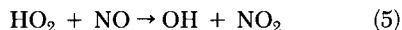
A fraction of this highly reactive, metastable form of atomic oxygen, O(¹D), reacts with water vapor (H₂O) to form the primary source of tropospheric hydroxyl radicals (OH),



In the troposphere, the OH radical is the most important cleansing agent. It reacts with virtually all molecules containing hydrogen atoms (e.g., CH₄) and also oxidizes species such as carbon monoxide (CO), nitrogen dioxide (NO₂), carbonyl sulfide (OCS), and sulfur dioxide (SO₂). In the unpolluted troposphere, the major reactions of OH are with the molecules:



This loss of OH is followed by production of peroxy radicals (HO₂, CH₃OO). When OH reacts with other, nonmethane hydrocarbons (NMHC) such as ethane, analogous organic peroxy radicals are formed. Subsequent oxidation of CH₃OO and NMHC analogues leads to production of one or more HO₂, which are recycled to OH by the reactions



The reactions (3) or (4) followed by (5) or (6) form a catalytic chain that destroys methane and carbon monoxide but regenerates OH. The cycling of OH and HO₂ is closed off by several reactions involving OH, HO₂, and NO₂. These regenerate H₂O or form hydrogen peroxide that is subsequently removed by clouds and precipitation. In a polluted environment with large concentrations of NO₂, the major loss of OH is through formation of nitric acid (HNO₃).



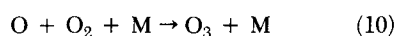
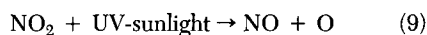
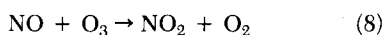
This reaction is also the major loss mechanism for

TABLE 1
Radiatively and chemically active gases

Compound	Concentration (10^{-9} vol/vol)		Residence time (yr)	% Change due to combustion	Impact
	Preindustrial	Current			
carbon dioxide CO ₂	278,000	356,000	120*	>90	GHG
methane CH ₄	700	1,714	14	10	GHG, OXG, ODP
nitrous oxide N ₂ O	270	310	120	20	ODP, GHG
chlorofluorocarbon-11 CFCl ₃	0.	0.268	50	0	ODP, GHG
chlorofluorocarbon-12 CF ₂ Cl ₂	0.	0.503	102	0	ODP, GHG
hydrochlorofluorocarbon-22 CHF ₂ Cl	0.	0.105	13	0	ODP, GHG
methyl chloroform CH ₃ CCl ₃	0.	0.160	5.4	0	ODP, GHG
methyl chloride CH ₃ Cl	<0.600	0.600	1.3	>0	ODP
methyl bromide CH ₃ Br	0.006	0.012	1.4	50	ODP
tetrafluoromethane CF ₄	0.	0.070	>999	0	GHG
carbon monoxide (northern hemisphere) CO	60	120	0.2	>90	OXG
nitric oxides (free troposphere) NO _x	?	10-1,000	<0.03	>50	OXG
nonmethane hydrocarbons NMHC	?	?	0-0.24	>0	OXG
tropospheric water (t)H ₂ O	10,000,000	same	a	0	GHG, OXG
stratospheric water (s)H ₂ O	3,500	5,500	~2	10	GHG, ODP
tropospheric ozone (t)O ₃	25	50	<0.10	>50	GHG, OXG
stratospheric ozone (s)O ₃	4,000	3,800	~2	<5	GHG, ODP, OXG
carbonyl sulfide OCS	<0.500	0.500	30	>0	anti-GHG, ODP
sulfates SO ₂ /SO ₄ ⁻	?	>?	a	>90	anti-GHG
black carbon aerosols soot C	?	>?	a	>90	GHG

*Variable, see text.

NO_x (NO + NO₂) throughout the troposphere, since most of the HNO₃ is washed out of the atmosphere. Like the OH-HO₂ pair above, the NO_x pair is tightly coupled through the reactions



where M is N₂ or O₂.

In addition to the daytime photochemistry, there

are some nighttime, nonphotolytic reactions that impact O_3 and NO_x . The most important process is the reaction of NO_2 with O_3 to form a nitrate radical (NO_3), which can further react to form nitrate aerosol, thereby removing both ozone and NO_x . Molecules that escape tropospheric oxidation by OH, or removal by clouds and precipitation, will reach the stratosphere where they encounter sunlight with much shorter wavelengths, as low as 180 nm. These photons have sufficient energy to dissociate directly many of the compounds that could not be destroyed in the troposphere. Photolysis initiates the oxidation processes that, for example, turn CFCs into CO_2 , HF, and a mix of chlorine compounds. In addition, concentrations of $O(^1D)$ [reaction (1)] are higher in the stratosphere and contribute to the loss of the more stable gases. For gases destroyed primarily in the stratosphere, lifetimes range from 40 to 200 yr and are limited by the rate of transport of air into the stratosphere. A few fluorinated gases (e.g., CFC-115 = CF_3CF_2Cl , CF_4 , C_2F_6 , SF_6) of concern as GHGs are identified with industrial sources, but not with combustion. They are not easily destroyed in the troposphere or stratosphere and have lifetimes exceeding 1000 yr [16,17].

Ozone:

Sunlight of wavelengths 180–230 nm also dissociates molecular oxygen (O_2), generating O_3 in the process [18]. Because of this absorption by a major atmospheric constituent, these wavelengths do not reach below about 20-km altitude in the atmosphere. The stratospheric column of O_3 is controlled by a balance between this production, atmospheric transport, and the catalytic loss cycles involving Cl and Br species, NO_x , OH, and HO_2 . Today about 80% of stratospheric chlorine and a large fraction of the bromine are released from the industrial halocarbons. Stratospheric NO_x is generated by N_2O and has increased by about 15% since preindustrial times, based on data from bubbles trapped in ice cores [19]. Stratospheric H_2O —the source of OH and HO_2 —is expected to increase along with the observed increases in atmospheric CH_4 . The stratospheric O_3 column is the major absorber of solar UV between 220 and 320 nm, and hence depletion of stratospheric O_3 is likely to change tropospheric chemistry in two ways: (1) by lowering the flux of O_3 into the troposphere, and (2) by increasing tropospheric UV, enhancing production of OH.

The exchange of air from troposphere to stratosphere in the tropics represents a loss for many of the long-lived species, and the return flux in the mid-latitudes brings significant sources of O_3 into the upper troposphere. There are four important contributors to the budget of tropospheric ozone—input from the stratosphere, deposition at the surface of the Earth, chemical production, and chemical loss,

all of the same order of magnitude on a globally averaged basis.

Ozone is produced in the oxidation of CO by reactions (4), (5), (9), and (10), with $(OH + HO_2)$ and NO being recycled. If insufficient NO is present, oxidation of CO leads to removal of ozone, reactions (4) and (6), with no effect on OH. Ozone is also produced by oxidation of CH_4 and NMHC. The balance between in situ production and loss of O_3 depends on the NO concentration: Production by reaction (5) is favored over loss by reaction (6) when the $NO:O_3$ concentration ratio exceeds about 10 ppt:30 ppb. (One ppt, or part per trillion, is 10^{-12} vol/vol mixing ratio.) In most parts of the troposphere, therefore, the addition of NO will induce additional production of O_3 , but in the heavily polluted urban environment, with already high concentrations of NO_x , addition of NO can lead to a reduction in local O_3 concentrations. CH_4 , CO, NMHC, and NO_x are considered as OXGs.

Atmospheric Chemical Feedbacks and Greenhouse Gases:

The varied chemical and physical couplings in the atmospheric system mean that a perturbation to one gas propagates through a series of feedbacks, perturbing many other species. Methane has an especially large number of identified couplings and is used as an example to illustrate this point. Methane originates primarily through biological processes, both current and ancient (i.e., fossil fuels) and is released near the surface of the Earth. The typical CH_4 molecule travels about 14 years from pole to pole and occasionally into the stratosphere before being destroyed by reaction with OH. During this period, the molecule acts as a GHG, second in importance only to CO_2 . When CH_4 is destroyed in the troposphere, its decay products can react with nitrogen oxides to produce additional O_3 , another GHG. When NO_x is not present, the CH_4 decay products help to destroy O_3 . In addition, the loss of CH_4 removes OH and thus increases indirectly the abundance of other OXGs (e.g., CO, NMHC, NO_x) and some GHGs (e.g., the HCFCs, HFCs, and CH_3CCl_3) that rely on OH for their sink. When CH_4 is destroyed in the stratosphere, it suppresses the chlorine and nitrogen cycles that destroy ozone, thus changing the effectiveness of some ODGs and increasing stratospheric O_3 abundances. The stratosphere is exceptionally dry and the H_2O from CH_4 decay contributes half of the water vapor in the stratosphere today. Even at these low abundances in the stratosphere, H_2O acts as a GHG and, by enhancing catalytic loss through HO_2 and OH reactions, as an ODG. The additional hydrogen that CH_4 carries through the cold trap at the tropopause reaches the highest altitudes of the Earth's atmosphere, the exosphere, where atomic H (half of it from CH_4) is the predominant constituent.

Budgets and Trends of Trace Gases

Our knowledge of the atmospheric budgets of most trace gases (i.e., sources and sinks) is based on a combination of source inventories, atmospheric observations, and chemical models. Rarely does a single approach give a reliable budget. The observed abundance of a compound together with an estimate of the residence time yields the total sink, and consequently the source if the compound is in steady state. Conversely, if the magnitude of the source of a gas and its abundance are well known, the magnitude of the sink can be estimated. The most useful example of this case is methylchloroform (CH_3CCl_3), an industrial solvent, which is removed primarily by OH. The budget of CH_3CCl_3 has been used to infer globally averaged concentration of OH (e.g., Ref. 20) and to test global models of OH (e.g., Ref. 21). A calibrated model for OH can then be used to infer the removal rate of other compounds such as CO, CH_4 , NMHC, and HCFCs that are removed by OH. Accurate source inventories are available only for primary compounds of industrial origin (e.g., CFCs). Estimates of emissions from processes such as deforestation, savanna burning, and agriculture practices (e.g., CH_4 from paddy rice and cattle) are uncertain, and constraints on the total source of a gas are particularly useful. For species with large natural sources (e.g., CH_4 and N_2O), it is difficult to partition the total emissions between anthropogenic and natural.

The balance between sources and sinks is most accurately inferred from the observed trends in atmospheric concentration. The long-term changes in many trace gases can also be used to infer the anthropogenic sources, providing natural sources (and sinks) remain constant. Critical data include both recent atmospheric observations [e.g., CO_2 [22]; CH_4 [23] and measurements of the composition of air bubbles trapped in large ice sheets (e.g., Refs. 24, 25, 19). The concentrations of CO_2 , CH_4 , and N_2O in ice cores that date from the preindustrial period before 1850 are all less than today's levels and consistent with recent atmospheric increases. Further, for the thousand years prior to 1850, the fluctuations in their concentrations (presumably a measure of the natural variations in their sources and sinks) were much smaller than the change from preindustrial to present.

Fuel Burned

Fossil-fuel use is reasonably well documented (e.g., Ref. 26). The total amount of fossil C burned in the 1980s was 5.4 Gt(C)/yr (i.e., 5.4×10^9 metric tonnes of carbon per year), and during 1991 emissions were 6.2 Gt(C)/yr [27]. (Cement production accounts for a small percentage of the CO_2 released

from industrial processes and is included in totals of fossil/industrial CO_2 released.) Individual events may seem to be a large perturbation; however, the Kuwaiti oil fires consumed about 4.6 million barrels of crude oil per day, only 3% of the worldwide emissions of CO_2 from fossil fuels at the time [28], and were even less important as sources of N_2O , CH_4 , and CO.

The amount of biomass burned each year is much more difficult to estimate. Savanna burning, deforestation, wildfires, burning of agricultural residues, and domestic use of wood and other biomass fuels provide important sources of fuel. The total amount of C burned is 3 to 5 Gt(C)/yr with about 80% of this in the tropics [29,30,31].

Emissions from fossil and biomass fuels depend on the combustion conditions and are typically more variable and less well known for biomass fuels than for fossil fuels. For fossil fuels, the largest yields of reduced gases such as CO and hydrocarbons are from gasoline-powered vehicles, while for biomass fuels, the largest yields are from forest fires [32,33,34]. In contrast to combustion conditions for fossil fuels, temperatures in biomass fires are not usually high enough to produce thermal NO_x .

CO_2 and O_2 :

There is currently an observed imbalance in the atmospheric carbon-oxygen cycles with increasing CO_2 [22,3] and a corresponding decrease in O_2 [35]. Although absolute changes are comparable, the relative change in O_2 is inconsequential to chemistry or climate, but the changes in CO_2 are large in terms of potential effects on climate: In the 1980s, CO_2 has changed by $+0.5\%/yr$ or $+1.6 \text{ ppm/yr}$ ($\text{ppm} = 10^{-6}$) or 3.4 Gt(C)/yr . The change in CO_2 is currently the single most important contribution to climate change [36]. Apparently only a little more than half of the fossil-fuel CO_2 [5.4 Gt(C)/yr] remains in the atmosphere; the ocean provides a sink for 2.0 Gt(C)/yr , and it has been proposed that there is an unknown terrestrial sink of 1.2 Gt(C)/yr [37,3]. Combustion of biomass that regrows quickly does not affect the CO_2 balance. However, deforestation releases carbon that has accumulated in the biosphere over decades, and represents a net source of CO_2 . Changes in land use are estimated to contribute 1.0 Gt(C)/yr to the atmosphere. The global carbon cycle involves exchange of the atmospheric CO_2 with carbon reservoirs in the ocean and biosphere over several time scales. Some are rapid enough to absorb about half of the fossil CO_2 within a year, but others take much longer to equilibrate. There is no simple lifetime for the decay of a CO_2 perturbation, but time scales are estimated to be about a century (IPCC, 1992).

There is clear evidence that CO_2 concentrations have risen in parallel with, and are caused by, combustion of fossil fuels. The ice-core record shows sta-

ble levels of 278 ± 10 ppm for 1000 years prior to the industrial era [19]. The increase to current levels of 357 ppm has been documented as part of a continuous record of atmospheric concentrations at Mauna Loa since 1957 [22], and at many other locations in recent years. Furthermore, changes in CO_2 isotopes, $^{13}\text{CO}_2$ and $^{14}\text{CO}_2$, have the same isotopic signature as fossil C. The best current models predict that even a freeze in current emissions would lead eventually to more than a doubling of natural levels [10]. Scientific assessments of climate change note that such CO_2 increases will eventually lead to a warmer surface climate, a colder stratosphere, and possible changes in weather patterns. CO_2 does not impact atmospheric chemistry except indirectly through changes in temperature and circulation.

H_2O :

Water in the form of vapor and clouds is the single most important atmospheric constituent controlling the temperature of the Earth. An increase in water vapor paralleling that of temperature significantly amplifies the expected warming for a doubling of CO_2 (IPCC, 1992). Although H_2O is a major by-product of combustion, this addition to the lower atmosphere is a small perturbation when compared with the global hydrological cycle of evaporation and precipitation. Emissions of H_2O from aircraft fleet cruising at 10–13 km in the drier regions of the atmosphere have a greater potential to augment natural levels, but recent estimates [38] suggest a minor impact. Similarly, rocket exhaust is expected to lead to minor enhancement in upper stratospheric water [39]. In the future, however, the impact of a proposed fleet of 500 High-Speed Civil Transports (HSCT, supersonic aircraft) cruising at 20-km altitude may be significant. Current assessments predict that a Mach 2.4 HSCT fleet would increase stratospheric H_2O by 10–20% in the lower stratosphere at northern midlatitudes [40].

CH_4 :

More than half of current CH_4 emissions, 375 of 550 $\text{Mt}(\text{CH}_4)/\text{yr}$, can be attributed to human activities. Many sources of CH_4 have been identified, with wetlands providing the largest natural source [41]. Anthropogenic sources that are associated with biological processes (e.g., rice paddies, cattle, landfills, and waste treatment) make up about 50% of the total; sources related to fossil fuels, about 18%. Most of the fossil-fuel sources are associated with fugitive release of CH_4 from coal mines, natural gas distribution, and petroleum processing. Low-temperature combustion of coal has been identified as a source at the 3% level [42], and combined with a biomass burning source of about 30–40 $\text{Tg}(\text{CH}_4)/\text{yr}$ [43], the

total direct contribution of combustion to the global methane budget is about 10%. If the fossil-fuel “industry” were included, this would rise to about 25%, which is consistent with observations of the isotopic abundances of CH_4 from live and fossil sources [44].

N_2O :

Nitrous oxide is important as a GHG and, by supplying the major source of NO to the stratosphere [45], as an ODG. The current imbalance in N_2O is substantial: The atmospheric content is currently increasing at a rate of about 4 $\text{Mt}(\text{N})/\text{yr}$ [46], and stratospheric losses are about 12 $\text{Mt}(\text{N})/\text{yr}$. The change in mixing ratio since preindustrial times is +15%, based on ice-core records, and much of this can be attributed to anthropogenic sources that are not well quantified. Originally, combustion of fuel-N in coal-fired power plants was identified as the major industrial source [47,48,49], but recent work has shown that artifact N_2O was being produced by secondary reactions in the sampling flasks [50]. Current estimates are that combustion is a minor source [51], providing at most 1 $\text{Mt}(\text{N})/\text{yr}$, with half from biomass burning and half from fossil fuels [52]. Fluidized-bed combustors emit a significantly higher yield of N_2O than other types of combustion systems [53]. The largest anthropogenic sources of N_2O appear to be agricultural activity and industrial processes involving nitric acid.

Halocarbons

Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) have long been thought to be the “natural” sources of stratospheric Cl and Br. Volcanic and other soluble sources of Cl/Br do not appear to penetrate the cold condensation trap between the stratosphere and troposphere [54]. The primary emissions of methyl halides were attributed to the oceans, but recent work has shown that biomass burning may contribute to current levels of both species [55,56]. Agricultural use of CH_3Br is an important anthropogenic source of CH_3Br . The atmospheric residence time for both species, about 1.4 yr, is determined by OH, although substantial oceanic uptake reduces the CH_3Br residence time [57]. Preliminary estimates suggest that combustion could provide 10–50% of the source of CH_3Cl and CH_3Br .

The major source of atmospheric chlorine today is from the chlorofluorocarbons (e.g., CFC-11 = CFCl_3 , CFC-12 = CF_2Cl_2 , CFC-113 = $\text{CF}_2\text{ClCFCl}_2$) and carbon tetrachloride (CCl_4). These are industrially produced compounds with long atmospheric residence times (>40 yr) and no known natural sources. Methyl chloroform (CH_3CCl_3) is also an industrial halocarbon with large emissions, with a shorter residence time (5.4 yr). There is no evidence for CFCs

in ice cores, and the current atmospheric abundance and trend are consistent with known production and emissions [58,59,60,61]. Likewise, the bromofluorocarbons (e.g., halon-1211 = CF_2ClBr , halon-1301 = CF_3Br) are also synthetic and emitted only over the last 50 years [62]. All of these compounds are insoluble and relatively long lived. They supply 80% of the Cl and 30% of the Br to the stratosphere today. Solid rocket motors provide an extremely small combustion-related contribution to the atmospheric Cl burden [63]. Ironically, the major use of halons is combustion related, as a fire extinguisher.

The dramatic rise in stratospheric Cl and Br in the past 20 years has led to the formation of the Antarctic ozone hole and is responsible for the extensive ozone depletion over the northern hemisphere today: about 5% loss over the past two decades at 45°N [11,64,65]. (Some of this recent loss may have been accelerated in 1992–1993 by the large enhancement of stratospheric sulfate aerosols from the Mt. Pinatubo volcano). These changes pose a significant environmental threat, and the Montreal Protocol (1987) and its subsequent amendments have led to the international phaseout of these compounds. The CFCs and halons also act as GHGs (e.g., Refs. 66, 67). The CFCs are being replaced by hydrochlorofluorocarbons (HCFCs), which have shorter residence times as they react with OH in the troposphere. Consequently, a much smaller fraction of the Cl reaches the stratosphere. These gases also act as ODGs and GHGs.

CO:

Carbon monoxide is emitted directly into the atmosphere by incomplete combustion, and it is produced in situ by the oxidation of CH_4 and NMHC (e.g., Ref. 15). The predominant sink is tropospheric OH, about $2100 \text{ Mt}(\text{CO})/\text{yr}$, with a small additional sink from uptake by soils. Oxidation of atmospheric CH_4 is the largest source of CO, about 33%. The source from biomass burning is hard to quantify accurately, since the combustion conditions determine the yield of CO and NMHC: Smoldering fires can emit several times as much per C atom burned compared to a fast-burning grass fire (e.g., Refs. 68, 31). Estimates range from 12 to 30% of the total source. The burning of fossil fuels, primarily gasoline, is responsible directly for about 14% of the total source, with an additional 3% from the oxidation of NMHCs from technological sources. Thus, combustion as a whole accounts for about 40% of the CO source if we include the secondary sources from CH_4 and NMHC. The fossil-fuel source is most important at northern midlatitudes, while the biomass source is most important in the tropics. Oxidation of isoprene, a natural hydrocarbon, also provides a source of CO, with the yield of CO depending on the local concen-

tration of NO. There are minor sources from the oceans, and vegetation.

Average CO levels are about 50 ppb in the southern hemisphere and about 120 ppb in the northern [69]. This imbalance is consistent with the short residence time of the gas, about 2.5 months, and the preponderance of sources in the northern hemisphere. Through the 1970s and 1980s, increases in CO concentrations of the order of $+1\%/\text{yr}$ have been observed in northern midlatitudes (e.g., Ref. 70) with no obvious changes in the southern hemisphere. Since 1990, however, CO in the northern hemisphere has decreased, a change caused in part by regulation of vehicular emissions in the U.S. since about 1970, and in Western Europe in the 1980s [68,71]. Overall, combustion has probably increased CO in the northern hemisphere by a factor of 2.

Carbon monoxide is the primary sink for OH in the troposphere. In the northern hemisphere, three times as much OH reacts with CO as with CH_4 , while in the southern hemisphere, the ratio is closer to 1:1. Thus, CO controls the level of OH; oxidation of CO in the presence of NO_x also provides an important source of tropospheric O_3 as discussed above.

NMHC/VOC:

The nonmethane hydrocarbons include gaseous compounds of the form C_xH_y . These are short-lived, highly reactive gases whose oxidation also leads to production of tropospheric O_3 in the presence of NO_x . The longest lived NMHC is C_2H_6 with a lifetime similar to CO. Another term used to describe hydrocarbons is volatile organic carbon (VOC), which includes NMHC as well as oxygenated species such as aldehydes and alcohols. A recent estimate of the anthropogenic source of VOC is $110 \text{ Mt}/\text{yr}$ [72] and includes significant contributions from gasoline vehicles, solvent evaporation, wood fuels, and biomass burning. Natural emissions of isoprene and terpenes from vegetation appear to be much larger than anthropogenic sources, but these estimates are highly uncertain, in the range of 400–800 Mt/yr . Oceanic emissions of C_2H_4 and C_3H_6 are important in remote environments. These biogenic hydrocarbons tend to be very reactive and are usually destroyed in the boundary layer near their source. The hydrocarbons in combination with NO_x (from fossil-fuel combustion) provide a source of ground-level ozone, elevating concentrations in the U.S. and other countries to unhealthful levels in warm, stagnant weather conditions [73]. Similarly, NMHC and NO_x from biomass burning provide an important source of O_3 in the tropics [31].

NO_x :

The nitrogen oxides, NO and NO_2 (NO_x), are essential to the photochemical formation of O_3 in the

troposphere [6]. They are the single most important OXG. The lifetime of NO_x is short, often less than 1 day. Thus, concentrations are highly variable throughout much of the troposphere and depend on the rapidity of transport from distant sources. In the free troposphere away from boundary-layer sources, concentrations range from 0.01 to 1 ppb (e.g., Ref. 74). NO_x is the limiting species for production of ozone in most of the troposphere.

NO_x is emitted primarily as NO by a large variety of sources. Lightning is the largest natural source of NO_x in the free troposphere but is not well quantified: Literature estimates range from 2 to 150 Mt(N)/yr (e.g., Refs. 75, 76), but it is likely that the source is much smaller, in the range 8–16 Mt(N)/yr [77]. Soil emissions represent a natural source of about 12 Mt(N)/yr. Fossil-fuel combustion is the largest source of NO_x , about 24 Mt(N)/yr centered equally in North America, Europe, and East Asia. Biomass burning is smaller, about 8 Mt(N)/yr, centered in the tropics (IPCC, 1994). Emissions from jet aircraft are often considered separately: Although only a fraction of the fossil-fuel source, about 0.4 Mt(N)/yr, they are emitted in the upper troposphere [78,79]. The large surface sources of NO_x are consumed primarily in the boundary layer, and only a small fraction is exported to the free troposphere (e.g., Ref. 80). Thus, aircraft and stratospheric injection [also a small source, <0.2 Mt(N)/yr] may compete with these much larger sources in remote regions. NO_x is converted to PAN (peroxynitric acid) in polluted source regions. Once PAN escapes the boundary layer, it is long lived, and its decomposition may provide a source of NO_x in remote areas.

Combustion has led to a fourfold increase in the source of tropospheric NO_x ; however, such increases would not be uniform as emissions near the ground (e.g., automobiles) are more readily oxidized than those aloft (e.g., lightning). The large variability in NO_x concentrations makes it inappropriate to assume an equivalent increase in the “mean” NO_x abundance throughout the free troposphere. Nevertheless, there is indirect evidence of NO_x increases since preindustrial times through the accumulation of nitrate (the end product of NO_x) in Greenland ice [81].

SO₂ and Sulfate Aerosols:

The sulfur in fossil fuel is usually emitted as SO_2 . The sulfur content of coal and oil is 0.5–2.5% by weight; in contrast, the sulfur content of biomass is small (e.g., S/C <0.001 in savanna), much smaller than the fuel nitrogen (e.g., N/C = 0.06 in savanna). The atmosphere continues to oxidize this S(IV) to S(VI) and eventually forms sulfates (SO_4^-), which become part of the atmospheric aerosols. The sulfuric acid formed from SO_2 (and to a lesser extent the nitric acid formed from oxidation of NO_x) is the primary source of acid deposition. The life cycle of

SO_2 from emission to sulfate to wet or dry deposition at the surface is only a few days.

Combustion of fossil fuels provides a source of SO_2 of about 80 MT/yr (as S), metal smelting about 8 MT(S)/yr, and biomass burning about 2 MT(S)/yr. Natural sources (oceanic emissions, vegetation, soils, and volcanoes) emit about 25 MT(S)/yr of various sulfur compounds (e.g., Ref. 82). Combustion clearly dominates the sulfur budget of the troposphere.

The reflective nature of the sulfate aerosols makes SO_2 an effective anti-GHG [83]. Sulfate aerosols can also impact cloud formation, generally producing more reflective clouds with more small droplets. It has been proposed that the increase in sulfate aerosols since the preindustrial era has offset a large part of the greenhouse forcing from CO_2 increases [84].

Sulfate aerosols in the stratosphere interact strongly with the NO_x chemistry and can greatly enhance catalytic loss of O_3 (e.g., Ref. 85). The large combustion source of SO_2 at the surface is rapidly converted to sulfate and does not reach the stratosphere, but explosive volcanoes can inject SO_2 directly into the stratosphere. Based on a possible decadal trend in background sulfate levels over Wyoming (between large volcanic injections) and a calculation of jet-fuel use, aircraft SO_2 was proposed as the major source of stratospheric sulfate layer [86]; a simple analysis of the stratospheric sulfur budget that includes OCS and simulation of aircraft SO_2 using an atmospheric model [87] ruled out this hypothesis.

OCS:

Carbonyl sulfide is moderately long lived in the troposphere (about 30 years against reaction with OH) with primarily oceanic sources [88]. As an insoluble sulfur compound with an abundance of about 500 ppt, it is believed to be the major source of the stratospheric sulfate layer during volcanically quiescent periods [89]. However, during the past two decades, the median stratospheric sulfate abundance was at least four times this background. Combustion sources of OCS from fossil fuel have been identified [90], but these are not believed to be important globally. There is an indication of possibly larger sources from biomass burning [91]. Significant uncertainty remains in understanding the global OCS budget [92]. It is possible that OCS from biomass burning has increased the nonvolcanic, background sulfate layer and impacted ozone, but we have no strong evidence for a change in OCS since preindustrial times.

Soot

Black carbon aerosols, comprised of graphitic carbon or soot, act as strong absorbers of sunlight in the

atmosphere [93]. Even small amounts of soot within liquid sulfate aerosols or water droplets can decrease the single scattering albedo and reduce the short-wave albedo of clouds [94,95]. Combustion is the only source of soot, and it is possible to distinguish fossil-fuel sources from biomass burning sources [96]. Combustion and subsequent photochemical generation from combustion products (e.g., SO₂, NMHC) generate very fine particles that, once lofted into the upper troposphere, have a long residence time and can be transported globally [97]. Arctic haze consists of graphitic carbon with some other particulate carbon produced in lower temperature combustion or from photochemical oxidation of VOC, but it is the absorbing properties of the soot that are of major concern [98]. Soot from fossil fuels and biomass burning [99] may have global impact as a GHG, but predictions are difficult as the formation of fine black carbon aerosols varies greatly depending on the conditions of combustion. For example, the Kuwaiti oil fires were expected to have a large climatic impact with soot production almost matching current global emissions of about 50 kt/day, but measurements [68] showed that these well fires were relatively efficient (96% as CO₂), and thus soot emissions were much smaller, only 3.4 kt/day.

Tropospheric O₃

Ozone can be produced rapidly by a mix of combustion products and natural emissions in the presence of sunlight (e.g., Refs. 6, 73). In the boundary layer over the U.S. away from cities, empirical evidence shows that between 5 and 8 ozone molecules are produced per NO_x molecule emitted, before the NO_x catalyst is removed by oxidation to nitrate [100]. Surface ozone values commonly exceed 100 ppb in the eastern U.S. in summer under meteorological conditions favorable for photochemical formation of ozone, high temperatures and stagnant air (e.g., Ref. 101). Emissions from biomass burning also produce enhancements of ozone [102]. The impact of massive burns in tropical regions during the southern dry season (August–October) can be seen in satellite data for tropospheric CO and O₃ [103,104,105]. There is a large region over South America, southern Africa, and the south tropical Atlantic Ocean where ozone and CO values are more than twice as high as over the central Pacific Ocean at the same latitudes. In remote marine air, photochemistry provides a net sink for ozone, as concentrations of NO_x are exceedingly low, <10 ppt in the boundary layer.

Combustion emissions, NO_x and NMHC, and products, O₃, are generally short lived in the boundary layer, with a lifetime of less than a few days. Lifetimes are much longer in the upper troposphere. Recent studies have proposed that the direct export of urban O₃ and of NO_x from combustion [80] and the

rapid transport of short-lived compounds from the boundary layer to the upper troposphere by cumulus convection [106] are important components of the tropospheric O₃ budget.

There is evidence that the concentrations of surface ozone in Europe, including high mountain sites, have doubled over this century [107,108]. Such are broadly consistent with global model simulations (e.g., Ref. 109). Measurements of the vertical distribution of ozone since the late 1960s show increases in tropospheric ozone over northern midlatitudes of <1–2% per year (e.g., Refs. 110,111). There are significant spatial variations in the trends, and indications that the trend over North America and Europe has levelled off in the last decade [112]. There is no evidence for long-term trends in ozone at southern midlatitudes, based on a 30-year data record. Long-term data for the tropics are lacking.

Nitrogen oxides are the limiting species for ozone formation, and emissions of NO_x from combustion have levelled off in both the US and Western Europe in the past decade, due to a combination of slow growth in fossil-fuel combustion, and regulation of vehicular emissions in the U.S. Emissions are growing rapidly in China and the far East (excluding Japan) because of large increases in consumption of fossil fuels, 5% per year [113]. Aircraft emissions of NO_x from have grown rapidly in the past 20 years, and there is much current interest in possible effects on ozone in the upper troposphere. Ozone is a GHG, and surface temperatures are most sensitive to changes in ozone near the tropopause. The budget of NO_x, and hence of ozone, in the upper troposphere is not well quantified at present.

Conclusions

Combustion of fossil and recent biomass has clearly changed the composition of the atmosphere. It is responsible for most of the enhanced greenhouse forcing to date (through CO₂, tropospheric O₃, soot) and also some counteracting effects (through SO₂). It has likely changed the tropospheric oxidant levels (through CO₁ NO_x, NMHC) but has had minimal impact on stratospheric O₃ (through CH₃Cl, CH₃Br, CH₄). Most of the important GHG and OXG have significant natural sources, which are not well defined today and may be changing; and thus, quantifying the role of combustion is difficult.

REFERENCES

1. Broecker, W. S., "Man's Oxygen Reserves," *Science* 168:1537–1538 (1970).
2. Arrhenius, S., "On the Influence of Carbonic Acid in the Air upon the Temperature of the ground," *Lon-*

- don, *Edinburgh, Dublin Philos. Mag. J. Sci.* 41:237–276 (1896).
3. Intergovernmental Panel on Climate Change, *Climate Change 1992*, J. T. Houghton, B. A. Callander, and S. K. Varney, (Eds.), Cambridge University Press, 1994, pp. 1–200.
 4. Molina M. J., and Rowland, F. S., "Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom Catalyzed Destruction of Ozone," *Nature* 249:810–814 (1974).
 5. Johnston, H. J., "Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust," *Science* 173:517–522 (1971).
 6. Haagen-Smit, A. J., "Chemistry and Physiology of Los Angeles Smog," *Ind. Eng. Chem.* 44:1342–1346 (1951).
 7. Fishman, J., Ramanathan, V., Crutzen, P. J., and Liu, S. C., "Tropospheric Ozone and Climate," *Nature* 282:818–820 (1979).
 8. Sze, N. D., "Anthropogenic CO Emissions: Implications for the Atmospheric CO-OH-CH₄ Cycle," *Science* 195:673–675 (1977).
 9. Thompson, A. M., "The Oxidizing Capacity of the Earth's Atmosphere: Probable Past and Future Changes," *Science* 256:1157–1165 (1992).
 10. IPCC, *Intergovernmental Panel on Climate Change, Radiative Forcing of Climate Change 1994* (J. T. Houghton et al., Eds.), Cambridge University, New York, 1994.
 11. World Meteorological Organization, *Scientific Assessment of Ozone Depletion: 1991*, Global Ozone Research and Monitoring Project, Report No. 25, 1992.
 12. Finlayson-Pitts, B. J., and Pitts, J. N., Jr., *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Wiley-Interscience, New York, 1986, pp. 1–1098.
 13. Seinfeld, J. H., *Atmospheric Chemistry and Physics of Air Pollution*, Wiley-Interscience, New York, 1986, pp. 1–738.
 14. Warneck, P., *Chemistry of the Natural Atmosphere*, Academic Press, New York, 1988, pp. 1–757.
 15. Logan, J. A., Prather, M. J., Wofsy, S. C., and McElroy, M. B., "Tropospheric Chemistry: a Global Perspective," *J. Geophys. Res.* 86:7210–7254 (1981).
 16. Cicerone, R. J., "Atmospheric CF₄: a Nearly Inert Gas," *Science* 206:59–61 (1979).
 17. Ravishankara, A. R., Solomon, S., Turnipseed, A. A., and Warren, R. F., "Atmospheric Lifetimes of Long-Lived Halogenated Species," *Science* 259:194–199 (1993).
 18. Chapman, S., "A Theory of Upper Atmospheric Ozone," *Mem. Roy. Met. Soc.* 3:103–125 (1930).
 19. Raynaud, D., Jouzel, J., Barnola, J. M., Chappellaz, J., Delmas, R. J., and Lorius, C., "The Ice Record of Greenhouse Gases," *Science* 259:926–934 (1993).
 20. Prinn, R., Cunnold, D., Simmonds, P., Alyea, F., Boldi, R., Crawford, A., Fraser, P., Gutzler, D., Hartley, D., Rosen, R., and Rasmussen, R., "Global Average Concentration and Trend for Hydroxyl Radicals Deduced from ALE/GAGE Trichloroethane (Methyl Chloroform) Data for 1978–1990," *J. Geophys. Res.* 97:2445–2461 (1992).
 21. Spivakovsky, C. M., Yevich, R., Logan, J. A., Wofsy, S. C., McElroy, M. B., and Prather, M. J., "Tropospheric OH in a 3-D Chemical Tracer Model: an Assessment Based on Observations of CH₃CCl₃," *J. Geophys. Res.* 95:18, 441–18, 471 (1990).
 22. Keeling, C. D. et al., "A 3-D Model of Atmospheric CO₂ Based on Observed Winds: 1. Analysis and Observational Data," in *Aspects of Climate Variability in the Pacific and Western Americas* (D. H. Peterson, Ed.), Geophysical Monograph 55, American Geophysical Union, Washington, DC, 1989, pp. 305–363.
 23. Dlugokencky, E. J., Masarie, K. A., Lang, P. M., Tans, P. P., Steele, L. P., and Nisbet, E. G., "A Dramatic Decrease in the Growth Rate of Atmospheric Methane in the Northern Hemisphere during 1992," *Geophys. Res. Lett.* (1994), in press.
 24. Etheridge, D. M., Pearman, G. I., and Fraser, P. J., "Changes in Tropospheric Methane between 1841 and 1978 from a High Accumulation-Rate Antarctic Ice Core," *Tellus* 44B:282–294 (1992).
 25. Chappellaz, J., Blunier, T., Raynaud, D., Barnola, J. M., Schwander, J., and Stauffer, B., "Synchronous Changes in Atmospheric CH₄ and Greenland Climate between 40 and 8 kyr BP," *Nature* 366:443–445 (1993).
 26. Marland, G., and Rotty, R. M., "Carbon Dioxide Emissions from Fossil Fuels: a Procedure for Estimation and Results for 1950–1982," *Tellus* 36B:232–261 (1984).
 27. Andres, T. J., Marland, G., Boden, T., and Bischoff, S., "Carbon Dioxide Emissions from Fossil Fuel Combustion and Cement Manufacture 1751–1991 and an Estimate of Their Isotopic Composition and Latitudinal Distribution," in *The Carbon Cycle* (T. Wigley, Ed.), Cambridge University Press, 1994 (in press).
 28. Ferek, R. J., Hobbs, P. V., Herring, J. A., Laursen, K. K., Weiss, R. E., and Rasmussen, R. A., "Chemical Composition of Emissions from the Kuwaiti Oil Fires," *J. Geophys. Res.* 97:14483–14489 (1992).
 29. Crutzen, P. J., and Andreae, M. O., "Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles," *Science* 250:1669–1678 (1990).
 30. Ward, D. E. et al., "Smoke and Fire Characteristics for Cerrado and Deforestation Burns in Brazil: Base-B Experiment," *J. Geophys. Res.* 97:14601–14619 (1992).
 31. Andreae, M. O., in *Biogeochemistry of Global Change: Radiatively Active Trace Gases* (R. S. Orem-land, Ed.), Chapman & Hall, New York, 1993, pp. 113–150.
 32. Crutzen, P. J., Heidt, L. E., Kranec, J. P., Pollock, W. H., and Seiler, W., "Biomass Burning as a Source of Atmospheric Gases CO, H₂, N₂O, NO, CH₃Cl and COS," *Nature* 282:253–256 (1979).

33. Hurst, D. F., Griffith, D. W. T., Carras, J. N., Williams, D. J., and Fraser, P. J., "Measurements of Trace Gases Emitted by Australian Savanna Fires during the 1990 dry season," *J. Atmos. Chem.* 18:33–56 (1994).
34. Lobert, J. M., Scharffe, D. H., Hao, W. M., Kuhlbusch, T. A., Seuwen, R., Warneck, P., and Crutzen, P. J., "Experimental Evaluation of Biomass Burning Emissions: Nitrogen and Carbon Containing Compounds," in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications* (J. S. Levine, Ed.), MIT Press, Cambridge, MA, 1991, pp. 289–304.
35. Keeling, R. F., and Schertz, S. R. "Seasonal and Interannual Variations in Atmospheric Oxygen and Implications for the Global Carbon Cycle," *Nature* 358:723–727 (1992).
36. Shine, K. P., Derwent, R. G., Wuebbles, D. J., and Morcrette, J.-J., "Radiative Forcing of Climate," in *Climate Change. The IPCC Scientific Assessment* (G. J. Jenkins, J. T. Houghton, and J. J. Ephraums, Eds.), Cambridge University Press, Cambridge UK, 1990, pp. 41–68.
37. Dixon, R. K., Brown, S. A., Houghton, R. A., Solomon, A. M., Trexler, M. C., and Wisniewski, J., "Carbon Pools and Flux of Global Forest Ecosystems," *Science* 263:185–190 (1994).
38. Schumann, U., and Wurzel, D., (Eds.), *Impact of Emissions from Aircraft and Spacecraft upon the Atmosphere*, Proceedings of Colloquium, Köln, Germany, April 1994, DLR Mitteilung 94-06.
39. Harwood, R. S., Jackman, C. H., Karol, I. L., and Qiu, L. X., "Predicted Rocket and Shuttle Effects on Stratospheric Ozone," in *Scientific Assessment of Ozone Depletion: 1991*, Chap. 10, World Meteorological Organization, Geneva, 1992, Global Ozone Research and Monitoring Project, Vol. 25, pp. 10.1–10.12.
40. Ko, M. K. W., Douglass, A. R., Grose, W. L., and McElroy, M. B., "Model Calculation of HSCT Effect," in *The Atmospheric Effects of Stratospheric Aircraft: Interim Assessment Report of the NASA High-Speed Research Program*. NASA Ref. Publ. 1333, Washington, DC, June 1993, pp. 103–125.
41. Cicerone, R. J., and Oremland, R. S., "Biogeochemical Aspects of Atmospheric Methane," *Global Biogeochem. Cycles* 2:299–327 (1988).
42. Khalil, M. A. K., Rasmussen, R. A., Shearer, M. J., Ge, S., and Rau, J. A., "Methane from Coal Burning," *Chemosphere* 26:473–477 (1993).
43. Hao, W. M., and Ward, D. E., "Methane Production from Global Biomass Burning," *J. Geophys. Res.* 98:20657–20661 (1993).
44. Quay, P. D. et al., "Carbon Isotopic Composition of Atmospheric CH₄: Fossil and Biomass Burning Source Strengths," *Global Biogeochem. Cycles* 5:25–47 (1991).
45. McElroy, M. B., and McConnell, J. C., "Nitrous Oxide: A Natural Source of Stratospheric NO," *J. Atmos. Sci.* 28:1095–1098 (1971).
46. Prinn, R., Cunnold, D., Rasmussen, R., Aleya, F., Crawford, A., Fraser, P., and Rosen, R., "Atmospheric Emissions and Trends of Nitrous Oxide Deduced from 10 Years of ALE-GAGE Data," *J. Geophys. Res.* 95:18369–18385 (1990).
47. Pierotti, D., and Rasmussen, R. A., "Combustion as a Source of N₂O in the Atmosphere," *Geophys. Res. Lett.* 3:265–267 (1976).
48. Weiss, R. F., and Craig, H., "Production of Atmospheric N₂O by Combustion," *Geophys. Res. Lett.* 3:751–753 (1976).
49. Hao, W. M. et al., "Sources of Atmospheric N₂O from Combustion," *J. Geophys. Res.* 92:3098–3104 (1987).
50. Muzio, L. J., and Kramlich, J. C., "An Artifact in the Measurement of N₂O from Combustion Sources," *Geophys. Res. Lett.* 15:1369–1372 (1988).
51. Linak, W. P. et al., "N₂O Emissions from Fossil Fuel Combustion," *J. Geophys. Res.* 95:7533–7541 (1990).
52. Berges, M. G. M., Hofmann, R. M., Scharffe, D., and Crutzen, P. J., "N₂O Emissions from Motor Vehicles in Tunnels and Their Global Extrapolation," *J. Geophys. Res.* 98:18527–18531 (1993).
53. Environmental Protection Agency, Supplement F to Compilation of Air Pollutant Emission Factors, Vol. 1, Stationary and Point Sources, Rep. AP-42, Research Triangle Park, 1993.
54. Tabazedeh, A., and Turco, R. P., "Stratospheric Chlorine Injection by Volcanic Eruptions: HCl Scavenging and Implications for Ozone," *Science* 260:1082–1086 (1993).
55. Tassios, S., and Packham, D. R., "The Release of CH₃Cl from Biomass Burning in Australia," *J. Air Pollution Control. Assoc.* 35:41–42 (1985).
56. Manö, S., and Andreae, M. O., "Emission of Methyl Bromide from Biomass Burning," *Science* 263:1255–1257 (1994).
57. Butler, J. H., "The Potential Role of the Ocean in Regulating Atmospheric CH₃Br," *Geophys. Res. Lett.* 21:185–188 (1994).
58. Lovelock, J. E., "Atmospheric Fluorine Compounds as Indicators of Air Movements," *Nature* 230:379 (1971).
59. Elkins, J., Thompson, T., Swanson, T., Butler, J., Hall, B., Cummings, S., Fisher, D., and Raffo, A., "Decrease in the Growth Rates of Atmospheric Chlorofluorocarbons-11 and -12," *Nature* 364:780–783 (1993).
60. Fisher, D., Duafala, T., Midgley, P., and Niemi, C., "Production and Emissions of CFCs, Halons, and Related Molecules," in *Concentrations, Lifetimes, and Trends of CFCs, Halons, and Related Species* Chap. 2 (J. Kaye and S. Penkett, Eds.), NASA Ref. Publ. 1339, Washington, DC, 1994.
61. Cunnold, D. M., Fraser, P. J., Weiss, R. F., Prinn, R. G., Simmonds, P. G., Miller, B. R., Aleya, F. N., and Crawford, A. J., "Global Trends and Annual Releases of CFCl₃ and CF₂Cl₂ Estimated from ALE/GAGE and Other Measurements from July 1978 to June 1991," *J. Geophys. Res.* 99:1107–1126 (1994).

62. McCulloch, A., "Global Production and Emissions of Bromochlorodifluoromethane and Bromotrifluoromethane (Halons 1211 and 1301)," *Atmos. Environ.* 26A:1325-1329 (1992).
63. Prather, M. J., Garcia, M. M., Douglass, A. R., Jackman, C. H., Ko, M. K. W., and Sze, N. D., "The Space Shuttle's Impact on the Stratosphere," *J. Geophys. Res.* 95:18583-18590 (1990).
64. Bojkov, R. D., Zerefos, C. S., Balis, D. S., Ziomas, I. C., and Bais, A. F., "Record Low Total Ozone during Northern Winters of 1992 and 1993," *Geophys. Res. Lett.* 20:1351-1354 (1993).
65. Gleason, J. F., Bhartia, P. K., Herman, J. R., McPeters, R. D., Newman, P., Stolarski, R. S., Flynn, L., Labow, G., Larko, D., Seftor, C., Wellemeyer, C., Komhyr, W. D., Miller A. J., and Planet, W., "Record Low Global Ozone in 1992," *Science* 260:523-526 (1993).
66. Wang, W. C., Yung, Y. L., Lacin, A. A., Mo, T., and Hansen, J. E., "Greenhouse Effect Due to Man-Made Perturbations of Trace Gases," *Science* 194:685-690 (1976).
67. Hansen, J., Lacin, A., and Prather, M., "Greenhouse Effect of Chlorofluorocarbons and Other Trace Gases," *J. Geophys. Res.* 94:16417-16421 (1989).
68. Laursen, K. K., Ferek, R. J., Hobbs, P. V., and Rasmussen, R. A., "Emission Factors for Particles, Elemental Carbon, and Trace Gases from the Kuwaiti Oil Fires," *J. Geophys. Res.* 97:14491-14497 (1992).
69. Novelli, P. C., Masarie, K. A., Tans, P. P., and Lang, P. M., "Recent Changes in Atmospheric Carbon Monoxide," *Science* 263:1587-1590 (1993).
70. Dianov-Klokov, V. I., Yurganov, L. N., Grechko, E. I., and Dzhola, A. V., "Spectroscopic Measurements of Carbon Monoxide and Methane 2: Seasonal Variations and Long Term Trends," *J. Atmos. Chem.* 8:153-164 (1989).
71. Bakwin, P. S., Tans, P. P., and Novelli, P. C., "Carbon Monoxide Budget in the Northern Hemisphere," *Geophys. Res. Lett.* 21:433-436 (1994).
72. Piccot, S. D., Watson, J. J., and Jones, J. W., "A Global Inventory of Volatile Organic Compound Emissions from Anthropogenic Sources," *J. Geophys. Res.* 97:9897-9912 (1992).
73. Seinfeld, J. et al., *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, DC, 1991, pp. 1-489.
74. Carroll, M. A., Ridley, B. A., Montzka, D. D., Hubler, G., Walega, J. G., Norton, R. B., and Huebert, B. J., "Measurements of NO and NO₂ during the Mauna Loa Observatory Photochemistry Experiment," *J. Geophys. Res.* 97:10361-10374 (1992).
75. Franzblau, E., and Popp, C. J., "Nitrogen Oxides Produced from Lightning," *J. Geophys. Res.* 94:11089-11104 (1989).
76. Liaw, Y. P., Sisterson, D. L., and Miller, N. L., "Comparison to Field, Laboratory, and Theoretical Estimates of Global Nitrogen Fixation by Lightning," *J. Geophys. Res.* 95:22,489-22,494 (1990).
77. Goldenbaum, G. C., and Dickerson, R. R., "NO Production by Lightning Discharges," *J. Geophys. Res.* 98:18333-18338 (1993).
78. Baughcum, S. L. et al., "Aircraft Emissions Scenarios," in *The Atmospheric Effects of Stratospheric Aircraft: A 3rd Program Report* (R. Stolarski and H. Wesoky, Eds.), NASA Ref. Publ. 1313, Washington, DC, 1993, pp. 87-208.
79. Hoinka, K. P., Reinhardt, M. E., and Metz, W., "North Atlantic Air Traffic within the Lower Stratosphere: Cruising Times and Corresponding Emissions," *J. Geophys. Res.* 98:23113-23131 (1993).
80. Jacob, D. J., Logan, J. A., Gardner, G. M., Yevich, R. M., Spivakovsky, C. M., Wofsy, S. C., Munger, J. M., Sillman, S., and Prather, M. J., "Factors Regulating Ozone over the United States and Its Export to the Global Atmosphere," *J. Geophys. Res.* 98:14817-14826 (1993).
81. Neftel, A., Beer, J., Oeschger, H., Zurcher, F., and Finkel, R. C., "Sulphate and Nitrate Concentrations in Snow from South Greenland 1895-1978," *Nature* 314:611-613 (1985).
82. Spiro, P. A., Jacob, D. J., and Logan, J. A., "Global Inventory of Sulfur Emissions with 1 x 1 Degree Resolution," *J. Geophys. Res.* 97:9023-9036 (1992).
83. Hansen, J. E., Lacin, A. A., Lee, P., and Wang, W. C., "Climatic Effects of Atmospheric Aerosols," in *Aerosols Anthropogenic and Natural Sources and Transport* (T. J. Kneip and P. J. Liroy, Eds.), Annals of the NY Academy of Science, New York, 1980, Vol. 338, pp. 575-587.
84. Charlson, R. J., Langner, J., Rodhe, H., Leovy, C. B., and Warren, S. G., "Perturbation of the Northern Hemisphere Radiative Balance by Backscattering from Anthropogenic Sulfate Aerosols," *Tellus* 43AB:152-163 (1991).
85. Hofmann, D. J., and Solomon, S., "Ozone Destruction through Heterogeneous Chemistry following the Eruption of El Chichon," *J. Geophys. Res.* 94:5029-5041 (1989).
86. Hofmann, D. J., "Aircraft Sulfur Emissions," *Nature* 349:659 (1991).
87. Bekki, S., and Pyle, J. A., "Two-Dimensional Assessment of the Impact of Aircraft Sulphur Emissions on the Stratospheric Sulphate Layer," *J. Geophys. Res.* 97:15839-15848 (1992).
88. Ferek, R. J., and Andreae, M. O., "Photochemical Production of OCS in Marine Surface Waters," *Nature* 307:148-150 (1984).
89. Crutzen, P. J., "The Possible Importance of CSO for the Sulfate Layer of the Stratosphere," *Geophys. Res. Lett.* 3:73-78 (1976).
90. Fried, A. et al., "Measurements of OCS in Automotive Emissions and an Assessment of its Importance to the Global Sulfur Cycle," *J. Geophys. Res.* 97:14621-14634 (1992).
91. Bingemer, H. G. et al., "Sulfur Gases and Aerosols in

- and above the Equatorial African Rain Forest," *J. Geophys. Res.* 97:6207–6217 (1992).
92. Johnson, J. E., Bandy, A. R., Thornton, D. C., and Bates, T. S., "Measurement of Atmospheric COS during the NASA CITE Project: Implications for the Global COS Budget," *J. Geophys. Res.* 98:23443–23448 (1993).
 93. Shaw, G. E., "Perturbation to the Atmospheric Radiation Field from Carbonaceous Aerosols," in *Particulate Carbon, Atmospheric Life Cycle* (G. T. Wolff and R. L. Klimisch, Eds.), Plenum, New York, 1982, pp. 53–73.
 94. Twomey, S. A., "The Influence of Pollution on the Short-Wave Albedo of Clouds," *J. Atmos. Sci.* 34:1149–1152 (1977).
 95. Ackerman, T. P., and Toon, O. B., "Absorption of Visible Radiation in Atmosphere Containing Mixtures of Absorbing and Non-absorbing Particles," *Appl. Opt.* 20:3661–3668 (1981).
 96. Clayton, G. D., Arnold, J. R., and Patty, F. A., "Determination of Sources of Particulate Atmospheric Carbon," *Science* 122:751–753 (1955).
 97. Heintzenberg, J., "Size-Aggregated Measurements of Particulate Elemental Carbon and Aerosol Absorption at Remote Locations," *Atmos. Environ.* 16:2461–2469 (1982).
 98. Currie, L. A., "Mankind's perturbations of Particulate Carbon," in *Radiocarbon After Four Decades*, Chap. 33 (R. E. Taylor, A. Long, and R. S. Kra, Eds.), Springer-Verlag, New York, 1992, pp. 535–568.
 99. Penner, J. E., Dickinson, R. E., and O'Neill, C. A., "Effects of Aerosol from Biomass Burning on the Global Radiation Budget," *Science* 256:1432–1434 (1992).
 100. Trainer, M. et al., "Correlation of Ozone with NO_x in Photochemically Aged Air," *J. Geophys. Res.* 98:2917–2925 (1993).
 101. Logan, J. A., "Ozone in Rural Areas of the United States," *J. Geophys. Res.* 94:8511–8532 (1989).
 102. Evans, L. F., Weeks, I. A., Eccleston, A. J., and Packham, D. R., "Photochemical Ozone in Smoke from Prescribed Burning of Forests," *Environ. Sci. Technol.* 11:896–900 (1977).
 103. Reichle, H. et al., "The Distribution of Middle Tropospheric CO during Early October 1984," *J. Geophys. Res.* 95:9845–9856 (1990).
 104. Fishman, J., Watson, C. E., Larsen, J. C., and Logan, J. A., "Distribution of Tropospheric Ozone Determined from Satellite Data," *J. Geophys. Res.* 95:3599–3617 (1990).
 105. Watson, C. E., Fishman, J., and Reichle, H. G. Jr., "The Significance of Biomass Burning as a Source of CO and O₃ in the Southern Hemisphere Tropics: a Satellite Analysis," *J. Geophys. Res.* 95:16443–16450 (1990).
 106. Pickering, K. E., Thompson, A. M., Scala, J. R., Tao, W.-K., Dickerson, R. R., and Simpson, J., "Free Tropospheric Ozone Production following Entrainment of Urban Plumes into Deep Convection," *J. Geophys. Res.* 97:17985–18000 (1992).
 107. Volz, A., and Kley, D., "Evaluation of the Montsouris Series of Ozone Measurements Made in the Nineteenth Century," *Nature* 332:240 (1988).
 108. Staehelin, J., Thudium, J., Buehler, A., Volz-Thomas, A., and Graber, W., "Trends in Surface Ozone Concentrations at Arosa (Switzerland)," *Atmos. Environ.* 28:75–78 (1994).
 109. Isaksen, I. S. A., and Hov, O., "Calculation of Trends in the Tropospheric Concentration of O₃, OH, CO, CH₄, and NO_x," *Tellus* 39B:271–285 (1987).
 110. Logan, J. A., "Tropospheric Ozone: Seasonal Behavior, Trends and Anthropogenic Influence," *J. Geophys. Res.* 90:10,463–10,482 (1985).
 111. World Meteorological Organization, *Scientific Assessment of Stratospheric Ozone: 1989*, Global Ozone Research and Monitoring Project, Report No. 20, Geneva, 1990.
 112. Logan, J. A., "Trends in the Vertical Distribution of Ozone: an Analysis of Ozonesonde Data," *J. Geophys. Res.*, submitted (1994).
 113. Kato, N., and Akimoto, H., "Anthropogenic Emissions of SO₂ and NO_x in Asia: Emissions Inventory," *Atmos. Environ.* 26A:2997–3017 (1992).

COMMENTS

P. Wiesen, University of Wuppertal, Germany. You have shown quite nicely the tremendous increase in the concentrations of different atmospheric trace gases during the last 150 years. More recently it was observed, however, that the rates of increase of the concentrations of carbon monoxide and nitrous oxide and, in particular, methane have decreased during the last two years. Could you please comment on that?

Author's Reply. Yes, the growth rates in many trace gases

have changed over the past decade. Most species have continued to increase, but their growth has slowed. In some cases, such as the CFCs, we can relate this to the phaseout of production (and hence emissions) as prescribed under the Montreal Protocol and its amendments. Some HCFCs used as CFC substitutes are increasing more rapidly. In the case of CO₂ and CH₄, the slowdown in growth during the period 1991–1993 cannot be easily explained, and measurements into 1994 indicate a return to more rapid growth. The immense injection of stratospheric sulfate by

Mt. Pinatubo changed global temperatures and stratospheric ozone over the two years following eruption in 1991, and may be in part responsible for some of these variations. For CO, the recent data show a dramatic decline in absolute concentrations that is not yet understood. For N₂O, the trend varies from year to year, but has been regular, about 0.25%/yr over the past decade. The record of CO₂, CH₄, and N₂O in ice cores shows that some natural variability in these trace gases preceded global perturbations by humanity.

●

Dr. Hans-Robert Volpp, University of Heidelberg, Germany. I would like to comment on Dr. Wiesen's (University of Wuppertal) question concerning the recently observed stagnation of the tropospheric methane concentration. Could it be possible that this effect is due to an increase in the OH radical concentration in the troposphere in recent years rather than due to an reduction of the global methane release rate?

Author's Reply. The slowdown in CH₄ growth to almost zero in 1992–1993 cannot be explained by increases in the CH₄ sink alone, because the most rapid observed change was in the latitudinal gradient, implying a drop in high northern latitude sources. There are several recent predictions that the decrease in stratospheric ozone driven by Mt. Pinatubo could have contributed to this decline in CH₄ growth, but these cannot explain the change in north-south gradient. Also, with the recent recalibration of the CH₃CCl₃ measurements made by the ALE/GAGE network, there is no longer any evidence for a change in the OH reactivity of the troposphere over the past decade.

●

David R. Crosley, SRI International, USA. You singled out aircraft as a special NO_x emission source because of the altitude at which the emissions occur. Would you comment on the effects of the current subsonic and projected supersonic fleets on the atmosphere?

Author's Reply. The current subsonic fleet is predicted by some models to increase background levels of NO_x in the upper troposphere by as much as 30% in the northern midlatitudes. The ensuing calculations of ozone increases due to this NO_x are typically 5% at the most impacted locations. These predictions need to be re-examined from scratch using three-dimensional models for tropospheric chemistry that are currently being developed, but they are not ready for such assessments. Moreover, we must develop a larger, more coherent database of upper-tropospheric measurements that provide the essential calibration for these models. It will still be difficult to quantitatively determine the role of aircraft NO_x relative to the other natural and anthropogenic sources.

The assessment of supersonic aircraft (High-Speed Civil Transports) cannot rely on a combination of measurements

and models for the current atmosphere alone. The models must predict the impact of large effluents of NO_x and H₂O at supersonic cruise levels (15–20 km) in a future stratosphere. The most recent NASA assessment from the High-Speed Research Program (Wesoky and Stolarski, 1994) notes that a large fleet of HSCTs would indeed perturb stratospheric NO_x (by up to 50%) and H₂O (by up to 25%), but that these changes in background trace gases would have only a small impact on stratospheric ozone. The crux of this evaluation is the recent recognition of heterogeneous chemical reactions on the stratospheric sulfate particles that reduce the role of NO_x as an ozone-destroying catalyst in the lower stratosphere.

●

Jan R. Pels, Delft University of Technology, The Netherlands. Fluidised-bed combustion of coal produces N₂O levels much higher than conventional methods. Please comment on the estimations given by G. G. de Soete, who calculates that, if all coal used for power generation would be burnt in FBCs, the emission of N₂O from combustion would be as big as the natural sources.

Do you think that knowing this, FBC should be limited unless it can be applied with strongly reduced N₂O emission?

Author's Reply. This question is appropriate. We have not yet found all of the anthropogenic sources of N₂O that we know are needed to explain the increase since the pre-industrial. The original identification of N₂O from coal-fired power plants was erroneous, and only recently has it been shown that these measurements were corrupted (N₂O was produced in the samples before measurement). The role of FBC as a significant N₂O source needs to be confirmed.

●

Bruce W. Gerhold, Phillips Petroleum Company, USA. Atmospheric mixing distributes the "greenhouse" gases (CO₂ for example) at least around a hemisphere. On the other hand, "anti-greenhouse" particulates (SO_x, soot) remain localized around a source, roughly around the continents. Thus, over North America and Europe, incoming solar radiation will be reflected, thereby counteracting part of the greenhouse warming. In contrast, the oceans have little particulate cover and the climate is subject to full greenhouse warming. Do models account for local variations? Might global warming be seen first in remote islands?

Author's Reply. Yes, the long-lived greenhouse gases like CO₂ and CH₄ are well mixed and have a rather uniform radiative forcing of the climate (although this simple view does not take into account that cloud cover and water vapor can dramatically change the regional impact of even these well-mixed gases). The two examples of radiative forcing that is spatially variable are aerosols and ozone (both strat-

ospheric and tropospheric). Several model studies have recently assessed the question of whether the aerosol "cooling" could offset an equivalent CO₂ "warming." The models do include the spotty distribution of aerosols around pollution regions, and do include the effects of clouds and land-ocean differences. Thus far the results are inconclusive, but the recent international climate assessment (IPCC) has strongly warned that equal but opposite radiative forcings may not cancel in terms of regional or even hemispheric climate impacts.



Ronald S. Sheinson, Naval Research Laboratory, Washington, DC. Combustion, or rather suppressing combustion via halons (brominated halocarbons), has a profound effect on stratospheric ozone. Halon production has already been stopped in the developed countries under the

Montreal Protocol process. Also significant is the effect of environmental concerns on combustion in spurring extensive halon replacement research. While global warming impact of suppression candidates at the quantities required should be very low, the restriction exercised by governments on their implementation in practical systems must be considered. Environment legislation, not the quantified impacts detailed in this paper, frequently dominates.

Author's Reply. Production of halons (used in fire suppression) has been halted. There is still a considerable bank of halons that can be recycled while substitutes are sought. The concentration of the short-lived halon-1211 has already been observed to decline.

Yes, it is the responsibility of the scientific community through national and international assessments to help guide policy so that regulations (which are almost always painful to some community) achieve the desired goal of improving the global environment.