Final Report

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Abstract

Consistent with the prime goal of the ASTRAEA project, as given in its peer-reviewed proposal, this Final Report is an informal report to DOE managers about a perceived DOE management problem, specifically, lack of vision in DOE's Atmospheric Chemistry Program (ACP). After presenting a review of relevant, current literature, I suggest a framework for conceiving new visions for ACP, namely, multidisciplinary research for energy policy, tackling tough (e.g., nonlinear) problems as a team, ahead of "political curves". Two "example visions" for ACP are then described, called herein the CITIES Project (the Comprehensive Inventory of Trace Inhalants from Energy Sources Project) and the OCEAN Project (the Ocean-Circulation Energy-Aerosol Nonlinearities Project). Finally, I suggest methods for DOE to provide ACP with needed vision. An executive summary of this report can be obtained by skimming the 12-page Section 3 (pp. 63-75).
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Appendices:

**Reprint A.** U.S. National Academy of Science Report "Interim Review of the Subsonic Assessment Project", co-authored by the PI and referenced in Section 3.

**Reprint B.** The original list of hazardous air pollutants (as given in the Clean Air Act) and EPA’s 7/8/96 draft update of this list, both from http://www.epa.gov/ttn/utw/

**Reprint C.** Chapter 4 (Recommendations) from the U.S. National Academy of Science Report "Aerosol Radiative Forcing and Climate Change", co-authored by the PI and referenced in Section 3.

Reprints removed for separate processing
1. Introduction

This is the final report of a 21-month contract, from 1 April 1996 to 31 December 1997, between the U.S. Department of Energy (DOE) and the Cascade Scientific Research Corporation (CSRC). The contract (DE-FG03-96ER62180) was part of the DOE's Atmospheric Chemistry Program (ACP) and was entitled "Atmospheric-Science: Transfer between Research Advances and Energy-policy Analyses" (ASTRAEA). The Principal Investigator (PI) of ASTRAEA was George Slinn, who devoted two-thirds of his time during the contract period to the project. During essentially the entire contract period the responsible DOE program manager was Rick Petty; currently, the DOE contact is Peter Lunn.

ASTRAEA was a service contract. Thus, the first line of the abstract of the peer-reviewed proposal states: "This proposal outlines and provides justification for the Principal Investigator's (PI's) plans to continue ongoing service activities for the U.S. Department of Energy (DOE)." As a service contract, a "final report" for ASTRAEA seems rather inappropriate, save as an apparent contractual necessity. Nonetheless, I have decided to use this reporting opportunity, and have focused this final report, to try to contribute further to the prime goal of ASTRAEA, viz., attempting to assist DOE managers in strengthening ACP. Thus, this "final report" is an informal management report to DOE managers about a perceived DOE management problem, specifically, ACP's lack of vision.

I approached the task of writing this report with the following relevant perspectives.

1. I have now been involved with ACP (and its predecessors) for exactly 30 years, during which time (as was documented in the proposal) I have been credited by previous DOE program managers with creating both the PRECP Program (the immediate predecessor to ACP) and the ACP's Ozone Project. I have thus been involved in the development of a substantial portion of ACP (as well as other successful DOE programs), and I therefore expect that I can assist the steering of ACP science in a successful direction for the future.

2. During the recent past (as a part of this ASTRAEA Project), I have served on two panels of the U.S. National Academy of Sciences (NAS). Portions of reports from these two NAS panels are referenced in Section 3 of this report and attached as Appendices A and C. With this NAS service (funded by ASTRAEA), I have improved my capabilities to view major science programs from an external perspective and focused on enhancing value of Federal research programs for U.S. taxpayers. Thereby, I expect that I have improved my capabilities to assist the steering of ACP to enhance its value to taxpayers.

3. I am now retiring from DOE-funded research. Therefore, perhaps my recommendations in this report will carry more weight when it is appreciated that I have no vested interest in the consequences of my recommendations, save my interest in seeing that something in which I have invested so much of my life's work continues to produce results of value to the public.

In this report, Section 2 is a review of recent literature to illustrate the type of research that ACP could potentially pursue. In Section 3, I illustrate the types of research projects that ACP might initiate and close with my recommendations for improving ACP.
2. Literature Review Relevant to ACP's Future

The following material has been taken from the recent scientific literature and is organized under the headings shown, listed alphabetically. If I have added comments within the quotations, they are put in brackets, viz. [...] This material gives suggestions for the types of research that ACP might pursue, as will be illustrated in Section 3.

2.1 AIR POLLUTION

2.1.1 Abelson's editorial criticizing EPA's proposed standard for particles

"How can the EPA minimize the effects of [ < 2.5 μm] particulates if it does not know what they are or which, if any, have deleterious physiological effects? How can the EPA produce reliable estimates of benefits and costs?"


2.1.2 Aerosol scattering can increase boundary-layer ozone

"More than 100 counties in the U.S. regularly violate the EPA's Ambient Air Quality Standard for ozone of 120 ppbv... averaged over 1 hour... On hot, smoggy summer days in many North American and European cities the cloud-free sky shows a milky white color—the result of particulate air pollution scattering solar radiation... We... present results from observations and computer simulations showing that scattering by aerosols can have a substantial and counterintuitive impact on the flux of UV radiation and the production of ground-level ozone... Our... simulation shows that aerosol scattering of UV radiation can increase boundary layer ozone mixing ratios by 20 ppbv or more. This represents an increase of about one-third in the amount of ozone produced over the 3-day model run..."


2.1.3 Aerosols can reduce beneficial UV-B

"In regions of intensive biomass burning in the tropics, the Amazon in particular, the photosynthetically active spectrum of sunlight (wavelengths of 400 to 700 nm) is reduced approximately 35-40% for 2 months. UV-B in natural sunlight kills airborne bacteria, and exposing drinking water to normal intensities of UV-B has reduced diarrhea in children in Kenya by 33%. Thus, the sharply diminished (by more than 80%) UV-B during the burning season in Brazil might enhance the populations of infectious pathogens suspended in air and water."


2.1.4 Isoprene: plants "waste" this energy to stay cool

"The research implies that plants produce one major haze ingredient, isoprene, as a strategy for coping with heat... Plant hydrocarbons, innocuous or even appealing on their own (the scent of a Christmas tree comes from one), are ingredients in photochemical smog... 'When plants did this 100 years ago, ozone formation was [probably] not being catalyzed,' says Ray Fall, a biochemist at the University of Colorado, Boulder... Isoprene production alone typically siphons off 2% of the carbon fixed through photosynthesis, carbon that could otherwise be converted into sugars. 'It's a puzzle', says Fall. 'Why would plants waste all this energy?"
"The thermal protection theory might explain not only why isoprene [a fat soluble, five-carbon chain molecule] emissions are highest on hot days but also why some plants emit more than others. Isoprene production generally comes into play in plant species that are subject to short burst of high temperatures. That may be why desert plants like the creosote bush don't seem to emit isoprene—presumably they have come up with other, more economical means for coping with constant high temperatures.

"Most oaks, for example, are on the high end of isoprene emissions, but a few, such as cork oak, emit little or no isoprene, even at high temperatures. [So, permit planting of only cork oak trees?]

'We're only beginning to learn about all the organic compounds plants are putting into the atmosphere,' says Fall."


2.1.5 Isoprene from the sea: may be significant, locally

"In this paper we show evidence that isoprene [2-methyl-1,3-butadiene] from the oceans is strongly seasonally dependent and is correlated with the chlorophyll content of the water from measurements in the North Sea and Southern Ocean. We estimate the seasonally average flux of isoprene to the atmosphere to be $1.7 \times 10^7$ molecules cm$^{-2}$ s$^{-1}$, which may be significant for atmospheric chemistry in locations remote from land as it is the only known source of atmospheric isoprene in these regions. We observe a strong seasonal cycle of several other NMHCs in seawater at high latitudes, with a maximum in summer... When averaged over the year, the isoprene flux from the North Sea... is an order of magnitude lower than the total flux from vegetation in Great Britain of 5-7 kt yr$^{-1}$... However, the emission may be significant on local scales considering the short lifetime of isoprene [3.9 hr, if [OH] = 6.5 $\times 10^6$ molecules cm$^{-3}$]."*


2.1.6 Organic aerosol from gasoline vapor varies as its aromatic fraction

"A series of sunlight-irradiated, smog-chamber experiments confirmed that the atmospheric organic aerosol formation potential of whole gasoline vapor can be accounted for solely in terms of the aromatic fraction of the fuel. The total amount of secondary organic aerosol produced from the atmospheric oxidation of whole gasoline vapor can be represented as the sum of the contributions of the individual aromatic: molecular constituents of the fuel."


2.1.7 Ozone and particle regulations coupled via nitrates

"A major fraction of ambient particulate matter arises from atmospheric gas-to-particle conversion. Attempts to reduce particulate matter levels require control of the same organic and nitrogen oxide emissions that are precursors to urban and regional ozone formation. Modeling of the gas-aerosol chemical interactions that govern levels of particulate components showed that control of gas-phase organic and NO$_x$ precursors does not lead to proportionate reductions of the gas-phased-derived components of atmospheric particles. The chemical coupling between ozone and particulate matter has implications for strategies to achieve the new ozone and particulate matter standards proposed by the U.S. Environmental Protection Agency.

"An important feature of the predicted response to VOC and NO$_x$ reductions [in the NO$_x$-rich conditions of the LA Basin] is the behavior of HNO$_3$, PAN, and PM2.5 nitrate as either NO$_x$ or VOC emissions are reduced. A 25% reduction in NO$_x$ emissions at the base VOC level is predicted..."
to lead to only a 3% reduction in peak HNO$_3$, a 4% increase in maximum PAN, and a 10% reduction in peak PM 2.5 nitrate; a 50% reduction in NO$_x$ leads to a 5% increase in PAN and a 21% reduction in maximum PM2.5 nitrate. That PM2.5 nitrate levels are substantially decreased when NO$_x$ and NH$_3$ are jointly reduced indicates that neither HNO$_3$ nor NH$_3$ individually dominates nitrate formation under current conditions."


### 2.1.8 Pitts & Pitts review: general concepts for ozone regulations

"Reactive intermediates in the oxidation of mixtures of volatile organic compounds (VOCs) and oxides of nitrogen play central roles: the hydroxyl radical (OH), during the day; the nitrate radical (NO$_3$), at night; and ozone (O$_3$), which contributes during the day and night. Halogen atoms can also play a role during the day. Here the implications of the complex VOC-NO$_x$ chemistry for O$_3$ control are discussed. In addition, OH, HO$_2$, and O$_3$ are shown to play a central role in the formation and fate of airborne toxic chemicals, mutagenic polycyclic aromatic hydrocarbons, and fine particles.

"Surface concentrations of O$_3$ found in other remote areas of the world now are similar, ~30 to 40 ppb, as compared with ~10 to 15 ppb in preindustrial times. This increase has been attributed to an increase in NO$_x$ emissions associated with the switch to fossil fuels during the industrial period... The sole known anthropogenic source of tropospheric ozone is the photolysis of NO$_2$... Although some NO$_2$ is emitted directly into the atmosphere by combustion processes, most is formed by the oxidation of NO (the major nitrogenous byproduct of combustion)... This conversion of NO to NO$_2$ occurs as part of the oxidation of organic compounds, initiated by reactive species such as the OH radical...

"Given the complexity of the chemistry as well as the meteorology, it is perhaps not surprising that quantitatively linking emissions of VOCs and NO$_x$ to the concentration of O$_3$ and other photochemical oxidants and trace species at a particular location and times is not straightforward. Particularly controversial for at least three decades has been the issue of control of VOCs versus NO$_x$.

"High NO$_x$ concentrations divert OH from the oxidation of VOCs by forming HNO$_3$, which also effectively short circuits the formation of O$_3$. Because of these reactions, decreasing NO$_x$ can actually lead to an increase in O$_3$ at high NO$_x$/VOC ratios; in this 'VOC-limited regime', control of organic compounds is most effective. However, these locations tend not to be the ones experiencing the highest peak O$_3$ concentrations in an air basin. Furthermore, NO$_2$ has documented health effects for which air quality standards are set.

"On the other hand, at high VOC/NO$_x$ ratios, the chemistry becomes NO$_x$-limited; in essence, one can only form as much O$_3$ as there is NO to be oxidized to NO$_2$ and subsequently photolyzed to O($^3$P). The issues are even more complicated, because the chemical mix of pollutants tends to change from a VOC-limited regime to a NO$_x$-limited regime as an air mass moves downwind from an urban center. This is because there are larger sources of NO$_x$, such as automobiles and power plants, in the urban areas. NO$_x$ is oxidized to HNO$_3$, which has a large deposition velocity, and hence is removed from the air mass as it travels downwind. VOCs do not decrease so rapidly because of widespread emissions of biogenics as well as less efficient deposition of many organic compounds. It is apparent that reliance on either VOC or NO$_x$ control alone will be insufficient on regional scales; control of both is needed."

[Science that's three decades old!]

2.1.9 Rural nonattainment for ozone will require major new controls

"An analysis from the Aerometric Information Retrieval System (AIRS) monitoring network showed that the new NAAQS would almost triple the number of nonattainment counties in the US. However, the AIRS monitoring sites are mostly urban and suburban, and thus this earlier analysis did not address the issue of rural pollution... Extrapolation of data from [other] networks, which are designed to characterize rural air quality... indicate that, although only 6 of the 85 sites were in nonattainment under the current NAAQS, 41 [i.e., approximately half] would have been in nonattainment of the proposed 8-hour standard [i.e., that the third highest, 8-hour averaged O₃ concentration (averaged over 3 years) not exceed 0.08 ppm vs. the current: daily, maximum 1-hr average O₃ concentration not to exceed 0.12 ppm more than three times in 3 years].

"Addressing rural nonattainment will necessitate a major change in the nation's pollution control strategies. Because current O₃ nonattainment is largely urban, control strategies have justifiably focused on emission controls within the nonattainment area. However, O₃ levels at any given rural location are probably affected by emissions from multiple urban areas as well as from local and distant rural sources. Thus, rural nonattainment will require regional control strategies. The economic impacts of this change, both in terms of total costs and on the sectors of the economy that bear these costs, could be significant."


2.1.10 Skepticism of epidemiological studies

"Most of the new epidemiological studies have examined short-term (daily) responses, including mortality. However, because of temporal colinearity among pollutants and uncertain exposures of the putative victims, it is not possible to apportion blame among potential environmental agents with certainty. The effects of carbon monoxide have often been neglected, and the effect of particle size (if any) remains unclear...

"Two recent mortality studies considered long-term survival rates of defined cohorts in relation to the average air pollution concentrations, as measured during periods of follow-up. Kasier describes the first of these studies as 'convincing'; it reported that about 26% of all deaths in six US. cities were attributable to air pollution, thus putting air pollution on a par with smoking and implying that eliminating air pollution could have about the same health benefit as eliminating all human cancers, for example. Kaiser quotes me as allowing that a systematic gradient in lifestyle across the six cities 'might' account for the mortality gradient that was attributed to air pollution. Such a regional gradient in physical activity exists, and its implied effect on longevity is almost exactly the same as that shown in an independent study of individuals in California. Accounting for this confounding variable would leave a mortality excess of only about 5% (in the most polluted city), and this excess could well be a result of the much higher historic exposures that were present in that city.

"Studies that conclude that current air pollution is as lethal as smoking or cancer have omitted known confounders such as diet, physical exercise, income, and employment status, and treat nonlinear factors (for example, body mass and education) as if they were linear. The second cohort study also suffered from most of these design faults, and it considered only two pollutants, neglecting the influence of their correlates.

"Finally, the scientific skepticism about this issue runs much deeper than just pro forma industrial opposition. A recent invited critical review of the particulate matter standards expressed doubt about the validity of both the short- and long-term mortality studies, and other academics have expressed similar opinions. EPA would be well advised to demonstrate the actual public health benefits already accrued from its existing air quality regulations before mandating the hefty additional investments that meeting the new regulations will require."

2.1.11 The Environmental Genome Project: "the wave of the future"

"National Institutes of Health (NIH) scientists are putting together a major effort to sequence DNA from perhaps 1000 people to try to demonstrate a link between certain genes and patterns of disease. 'This is information that can really revolutionize public health policy' by making it possible to identify and protect people susceptible to hazards,' says Ken Olden, director of the National Institute of Environmental Health Sciences (NIEHS), whose scientists conceived the so-called Environmental Genome Project.

"The idea for the undertaking follows several decades of work on common variations of genes involved in activation or detoxifying drugs and chemicals that we breathe, drink, or eat. 'Each person basically has his own unique fingerprint of drug-metabolizing enzymes and receptors, so we all handle drugs [and chemicals] differently,' says Dan Nebert, director of the Center for Ecogenetics and Environmental Science at the University of Cincinnati... 'This is kind of the wave of the future.'

"To have intelligent environmental regulatory policy, one has to begin to unravel the role of genetics in determining the differences in susceptibility', says NIEHS director Ken Olden... Olden's words are music to the ears of members of Congress who have been clamoring for better science behind regulations. Risk assessors at the EPA and elsewhere now craft rules with a standard fudge factor to try to protect sensitive individuals. They set the permissible exposure level to a chemical, for instance, at a tenth of that deemed acceptable for the general population... It would obviously become extremely expensive to protect a few individuals...

"Indeed, both scientists and regulators may struggle to 'digest and understand the meaning and importance' of the initial data on environmental genes... "I think the regulatory agencies need to really start getting their thoughts together about how this information will be used'."


2.1.12 Risk assessments for cancer: predisposed genetic traits

"Acting in concert with individual susceptibility, environmental factors such as smoking, diet, and pollutants play a role in most human cancer. However, new molecular evidence indicates that specific groups—characterized by predisposing genetic traits or ethnicity, the very young, and women—may have heightened risk from certain exposures. This is illustrated by molecular epidemiologic studies of environmental carcinogens such as polycyclic aromatic hydrocarbons and aromatic amines. Individual genetic screening for rare high-risk traits or for more common, low-penetrant susceptibility genes is problematic and not routinely recommended. However, knowledge of the full spectrum of both genetic and acquired susceptibility in the population will be instrumental in developing health and regulatory policies that increase protection of the more susceptible groups from risks of environmental carcinogens. This will necessitate revision of current risk assessment methodologies to explicitly account for individual variation in susceptibility to environmental carcinogens."


2.2 AIRCRAFT

2.2.1 Aircraft Aerosols

2.2.1.1 Background stratospheric aerosols increasing?

"Since the 1989 aerosol mass loading [of the stratosphere] was reported as 30-50% higher than that observed in 1979, it has been suggested [Hofmann, 1991] that human activity may already have..."
significantly affected the stratospheric aerosol burden. Herein we compare aerosol loading in 1979 and 1989-1991 using the global data sets provide by [SAGE & SAGE II]. These data strongly suggest that in 1989 and following years, the stratosphere was still significantly influenced by the earlier volcanic eruptions and that any underlying anthropogenic influence must be smaller than has been previously suggested.*


2.2.1.2 Life cycle of background stratospheric aerosols

[Their Fig. 2 shows that most of the nucleation of stratospheric particles (from H₂SO₄) occurs at about 18 km in the tropics, but there is also substantial nucleation in the troposphere (at ~ 10 km) [300/sec at 18 km; 1/sec at 10 km]—and probably a lot more at cloud tops.]

[Removal from the stratosphere is primarily via "isentropic mixing across the tropopause, primarily through tropopause folds" (if the entire polar vortex air is brought to the troposphere each year, that would remove only about 1/16 of the total stratospheric air per year at each pole, i.e., the lifetime of a stratospheric aerosol particle would be 8 years—which is too long.)]


2.2.2 Aircraft Contrails

2.2.2.1 Contrails from WW2 bombers (therefore, not just jet aircraft!)

"Reading the meeting brief 'Contrails may alter climate'... I was reminded of a personal observation of contrail persistence. Growing up in Germany in the spring of 1945, I watched the daily procession of U.S. bomber formations proceeding to and from their targets. Frequently, these formations would leave massive contrails that sometimes formed into persistent clouds covering a good fraction of the sky. To be sure, we are talking here about many planes—1 estimate that at times more than 300 bombers might have been in my view at a time, flying at altitudes between 6000 and 9000 meters. The clouds so formed looked like thick cirrus."


2.2.2.2 Contrails and Climate Change

2.2.2.2.1 Climate warming from contrails?

"Over the United States, cloud cover is up about 5% since jet travel mushroomed several decades ago, and most of the new clouds may be in the form of cirrus..."

"Climate-model simulations... suggest that a 5% increase in contrail coverage would indeed drive a small regional warming... If—and it's a big if...—the increase in U.S. cloud cover is mostly due to contrails, jet exhaust could be causing a regional warming as large as half that thought to be caused by increasing greenhouse gases..."


2.2.2.2.2 Or climate cooling?

"After reviewing the indirect evidence for the regional climatic impact of contrail-generated cirrus clouds (contrail-cirrus), the author presents a variety of new measurements indicating the nature and scope of the problem... The evidence indicates that the direct radiative effects of contrails display the potential for regional climate change at many midlatitude locations, even though the sign of the climatic impact may be uncertain. However, new information suggests that the unusually small
particles typical of many persisting contrails may favor the albedo cooling over the greenhouse warming effect, depending on such factors as the geographic distribution and patterns in day versus night aircraft usage.

p. 1886: "Other effects are less noticeable [than contrails], such as the potential alteration of natural cirrus through the enhancement of cloud-forming particles and water vapor, or the gradual buildup of reactive and greenhouse gases and soot particles in the upper troposphere.

p. 1889: "That contrails tend to be seen in advance of naturally occurring cirrus has been widely recognized. This linkage between natural and contrail-generated cirrus often makes it difficult, if not impossible, to distinguish aged, spread contrail veils from wide-spread cirrus.

"Table 2 reveals that contrails are identified on average about 20% of the time in the photographs, and that most of these are persisting contrails associated with, or apparently 'embedded' in, natural cirrus. However, a significant proportion of the contrails are observed either isolated from natural cirrus (~18%) or extending from the boundaries of advecting cirrus clouds (~25%).

p. 1900: "Although to help settle the issue of the climatic impact of contrails, better knowledge of the relative frequencies of the thin small-particle [favoring cooling] versus the vertically developed contrail [favoring warming] is needed, it is important to recognize that the composition of contrails are likely to be distinct from those of natural cirrus clouds because of their vastly dissimilar cloud formation mechanisms."


2.2.2.2.3 Or warming at night and cooling during the day?

"It is widely accepted that contrail overcasts are likely to suppress nocturnal cooling rates similar to the abilities of cirrus [i.e., warmer nights]. We are unaware, however, of any published study that associates the aerosol optical thickness (AOT) of contrails and contrail overcasts with localized temperature reductions during the daytime hours.

"During one particularly widespread occurrence of persisting contrails over the midwestern US on 17-18 April 1987, average maximum surface temperatures near the center of the contrail region were 2-5\° cooler than in surrounding locations just outside the contrail region, analysis of NWS data indicates.

"Further comparisons of the 30-year normals of [diurnal temperature range] DTR for the US prior to and immediately following the rapid increase in air traffic beginning in the early 1960s demonstrate a significant direct correlation between those regions estimated to have received the greatest amount of contrail coverage and those regions experiencing the greatest decrease in DTR... This may explain the unevenly distributed regional decreases in DTR in the US reported by Karl et al."


2.2.2.3 Improvements to SAGE data (for contrail climatology)

[Illustration of how to improve SAGE data, in this case for climatology of high altitude clouds. They used airborne lidar data to improve SAGE's algorithms.]

2.2.2.4 **Measurements in the Concorde's plume**

"Emission indices of reactive gases and particles were determined from measurements in the exhaust plume of a Concorde aircraft cruising at supersonic speed in the stratosphere. Values for NOx (sum of NO and NO2) agree well with ground-based estimates. Measurements of NOx and HOx indicate a limited role for nitric acid in the plume. The large number of submicrometer particles measured implies efficient conversion of fuel sulfur to sulfuric acid in the engine or at emission. A new fleet of supersonic aircraft with similar particle emissions would significantly increase stratospheric aerosol surface areas and may increase ozone loss above that expected for NOx emissions alone.

p. 72: "The EI (Emission Index) for nonvolatile particles was calculated from a direct integral of CN event data, where the integral precision was better than 1%. The count rates for total particles were too large in the selected plume events to be recorded accurately because of counter saturation. As a result of the excellent signal/background ratio, weaker plume events that did not saturate either CN channel were observed. In these events, 70 to 90% of the particles were volatile at 192°C. Using this ratio as representative..., we estimated the EI range for volatile particles to be (1.7 to 6.5) x 1017 (kg fuel)⁻¹. In previous CN observations made in the stratosphere 18 hours after the passage of an SR-71 supersonic aircraft, the ratios of volatile to nonvolatile particles were similar to those reported here, and the EI for total CN was estimated to be (2 to 9) x 1016 (kg fuel)⁻¹ for particles larger than 0.02 μm in diameter... At least 12 to 45% of the fuel sulfur... was oxidized to H2SO₄.*


2.2.2.5 **Model for contrail formation, with knowledge of 300-100 mb H₂O**

"Studies of recent climate trends based on surface observations of cloud amount suggest marked increases for Europe and North America during the twentieth century... A review of NWS cloud cover data by Angell indicates that there has been a statistically significant increase in the total cloudiness over the US since the middle of this century. An independent study by Seaver and Lee showed that the number of cloudless days suitable for aerial photography for the continental US decreased in the period 1900-82. This cloud cover increase has been suggested as at least a partial explanation for the asymmetrical variations in diurnal temperature range [DTR] noted for the US during the period 1951-1990. Cloud amount increases are concentrated at regional scales..., suggesting that the changes in cloud cover and their effects on surface temperature are produced by regional forcing mechanisms rather than larger-scale hemispheric or global processes.

"Anthropogenic influences on the high (cirrus) cloud fraction have been suggested primarily in relation to increases in jet aircraft activity. Machta and Carpenter (1971) and Liou et al. (1990) have investigated trends in cloudiness over Denver and Salt Lake City, respectively, and found increases in high cloud amounts coincident with the rise in jet fuel consumption. Changnon (1981) studied records of cloud, sunshine, and temperature for the midwestern US between 1901 and 1977. His results provided empirical evidence that the greatest increases in cloud cover in that portion of the country since 1960 have occurred within, and nearest to, the overflight zones of transcontinental commercial jet aircraft traffic. In addition, the percentage increase in cloud cover in these areas was not matched by an equal percentage decrease in sunshine (see also Angell 1990), suggesting that the increase is due primarily to high, thin clouds, which are possibly from the production of jet aircraft contrails.

"Lee and Johnson (1985) concluded that contrails are the most likely cause of the statistically significant decrease in the number of cloudless days found in 44 of 45 cities in the US for the period 1950-82, compared with the period 1900-36. Henderson-Sellers suggests a similar cause for at least part of the record of cloud cover increases identified for North America. Moreover, all sky camera observations taken from Champaign, Illinois and Albany, New York, have shown that contrails were present on about 30% of days when the upper cloud fraction could be seen.

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"This empirical study demonstrates that useful predictions of the occurrence of persisting contrails on the spatial scales typical of clusters (outbreaks) of this phenomenon can be made when knowledge of the 300-100 mb integrated water vapor data (from GOES image counts) are available. The model shows a high dependency on water vapor information, which suggests that the ambient moisture conditions at contrail levels may be more important than the ambient temperature conditions for predicting contrail occurrences."


2.2.2.6 Model for particle fate

"We demonstrate that the total number of particles in an evolving aerosol plume is limited in a predictable way by the competing rates of coagulation and atmospheric dispersion, and is generally independent of the details of particle nucleation or growth. Consideration of various microphysical processes contributing to aerosol plume development leads to the conclusion that the potential nucleation of enormous numbers of fine particles (for example, in high-altitude aircraft wakes and volcanic eruption clouds) does not affect the total number eventually dispersed throughout the atmosphere. We show that, after a suitable period of time (which is quite short relative to the time scales of regional and global dispersion), the aerosol population (total number, or concentration) is independent of the initial number, and instead, depends in a simple way on the average coagulation kernel and plume dispersion rate...

p. 1225. "The application of the principle of aerosol invariance to aircraft wakes implies that concentrations of the order of 10,000 particles/cm³ will typically be found after ~ 1000 sec, and 100/cm³ after 100,000 sec. These numbers are modulated by the actual rate of plume mixing in a particular situation, which in turn depends on the aircraft configuration, atmospheric stability, background turbulence, and other parameters. Overall, such factors are expected to introduce a relatively moderate range of variation in the aerosol properties."


2.2.2.7 Models for sulfate formation in jet exhausts

2.2.2.7.1 If high levels of oxidized SO₂

"Recent in-situ emission measurements of the Concorde in the lower stratosphere point to a surprisingly efficient conversion of fuel sulfur to H₂SO₄ in the exhaust plume. By means of a comprehensive model, the formation and evolution of aerosol particles and precursors are calculated in the diluting aircraft wake. The results provide strong evidence that high levels of SO₃ [yes, 3!] present in the nascent plume are required to explain the observations of large numbers of nanometer-sized aerosols.


2.2.2.7.2 If ion concentrations > 10⁸ cm⁻³

"We consider the effects on aircraft plume microphysics of ions generated by chemionization processes within the engine combustors. Ions provide centers around which molecular clusters rapidly coalesce, thus promoting the formation of electrically charged sulfonic acid/water aerosols. The resulting charged micro-particles exhibit enhanced growth due to condensations and coagulation aided by electrostatic effects. Simulations with a plume microphysics code show that volatile particles observed behind aircraft may be explained by such processes, as long as initial ion concentrations in the exhaust exceed ~ 10⁸ cm⁻³..."
2.2.3.2 Climatological estimates of soot

"... emissions by aircraft appear to be the most significant source of BCA [Black Carbon Aerosol] in the stratosphere. A strong gradient in BCA concentration exists between the northern and the southern hemispheres, indicating interhemispheric mixing times longer than [lower] stratospheric residence times... Applying the Concord Emission Index to fuel consumption by a projected future fleet suggest a twofold-threefold increase of stratospheric BCA by the year 2015."


2.2.2.8 U-2 contrails

"The fact that jet aircraft condensation trails are commonly observed in the dry stratosphere—Peters (1993) cites a 61% rate of contrail occurrence at altitudes from 40,000 to 63,000 ft and a 37% rate of occurrence above 63,000 ft in a database of 1040 U-2 aircraft observations...


2.2.3 Aircraft Soot

2.2.3.1 Climatology of aircraft soot (with some strange results)

"Black carbon soot from the upper troposphere and lower stratosphere has been systematically collected from 90°N to 45°S. The measured latitudinal distribution of this soot at 10- to 11-km altitude is found to covary with commercial air traffic fuel use, suggesting that aircraft fuel combustion at altitude is the principal source. In addition, at latitudes where the commercial air traffic is high, measured black carbon soot values are high even at 20-km altitude [A very strange result!!], suggesting that aircraft-generated soot injected just above the tropopause may be transported to higher altitudes. During the volcanically influenced period in which these samples were collected, the number abundances, total mass, and calculated total surface area of black carbon soot are 2-3 orders of magnitude lower than similar measures of sulfuric acid aerosol. During volcanically quiescent periods, the calculated total surface area of black carbon soot aerosol is of the same order of magnitude as that of the background sulfuric acid aerosol... It remains to determine the extent to which black carbon soot particles act as nuclei for sulfuric acid aerosol formation. However, mass balance calculations suggest that aircraft soot injected at altitude does not represent a significant source of condensation nuclei for sulfuric acid aerosols.

"One of the least understood atmospheric aerosols is soot. 'Soot' refers to two classes of carbonaceous aerosols: black carbon soot, which is the light-absorbing component of this aerosol (and is principally soot or amorphous elemental carbon), and carbon soot. Both are the product of incomplete combustion of fossil and other fuels. Depending upon source, the soot component may contain principally black carbon soot (as is the case in aircraft jet engines) or organic carbon soot (as is the case in some types of biomass burning). Individual black carbon soot particles are composed of chain aggregates of ~ 20-nm spheres which has various degrees of branching and compactness... Other sources of black carbon soot, such as acetylene burning in the lab... produce much larger aggregates... but the lacy fractal nature of the aggregates is typical and characteristic.

"Scanning electron microscope is a surface imaging technique, so that soot entrained within sulfuric acid droplets will not be accounted for in these measurements. [They may have systematically underestimated the number of carbon particles!] Thus, the value presented here do not account for soot that is 'internally mixed' with sulfuric acid aerosol..." [and surely many are!! And they may have underestimated the soot concentration because of their collection technique: for the wires they used on the ER-2, the collision efficiency for a 50 nm particle is 0.26 at 9 km and 0.95 at 20 km.]


2.2.3.2 Climatological estimates of soot from Concorde data

"... emissions by aircraft appear to be the most significant source of BCA [Black Carbon Aerosol] in the stratosphere. A strong gradient in BCA concentration exists between the northern and the southern hemispheres, indicating interhemispheric mixing times longer than [lower] stratospheric residence times... Applying the Concord Emission Index to fuel consumption by a projected future fleet suggest a twofold-threefold increase of stratospheric BCA by the year 2015."
2.2.3.3 Doubling sulfur in jet fuel doesn't double the number of particles

"The observations show visible and measurable differences between contrails caused by the different sulfur levels [in the two engines of the twin-engine jet]... Peak number densities [of particles in the plume, measured at ages of 20-30 s] were 30,000 cm\(^{-3}\) for particles of diameter above 7 nm and 15,000 cm\(^{-3}\) above 18 nm. The latter is a little larger than the estimated number of soot particles emitted. The high-sulfur plume show more particles than the low-sulfur plume. The difference are about 25% for particles above 7 nm and about 50% above 18 nm. The results indicate that part of the fuel sulfur is converted to sulfuric acid, which nucleates with water vapor heterogeneously on soot or nucleates acid droplets homogeneously which then coagulate partly with soot.

"Typically, jet engines emit 0.1 to 1 g of soot per kilogram of fuel, with peak diameters of 30 to 100 nm... The estimated soot particle number density is supported by the data of Pitchford et al. (1991) who measured a particle concentration of 300,000 cm\(^{-3}\) in the wake of a Sabreliner, 200 m behind engines with plumes of 5 m diameter.

[Implications: if 500 aircraft daily, consuming 60 Mg of fuel each within a corridor volume of 5000 km x 1000 km x 2 km, and if 2 x 10\(^{15}\) particles per kg of fuel] "one computes a mean increase in particle concentration of 6 cm\(^{-3}\), if the residence times is 1 day in the corridor, compared to typical background values of 100 cm\(^{-3}\). Emissions in the lower stratosphere will have longer residence times, get transported mainly poleward, and may cause enhanced cloudiness in particular near the tropopause.

"We cannot definitely decide on how the particles were formed. However, it appears that the measured particles neither originate from ambient aerosol entrained into the plume nor solely from homogeneous nucleation. The weak variation of the particle number with fuel sulfur content, the increase in mean particle diameter consistent with computed acid-coated soot-particle diameters, the change in color, and the estimated time scales for coagulation suggest that a major part of the sulfuric acid condenses with water directly on the soot particles or that most of the homogeneously nucleated droplets coagulate in the young plume with the soot particles."

[That is, here's another hint that soot is the key to forming sulfate particles.]


2.2.3.4 Formation of contrail particles: on soot?

"Constrained by the measurements, a lower bound is deduced for the number density of ice crystals initially present in contrails. This bound serves as a visibility criterion for young contrails. An analysis of the primary contrail particles (aqueous solution droplets nucleated in situ, emitted insoluble combustion aerosols, and entrained background aerosols) reveals that only soot must be involved as ice forming nuclei if the visibility criterion is to be fulfilled. Possible activation pathways of the soot aerosols are investigated, including an analysis of their wetting behavior and droplet scavenging and heterogeneous nucleation properties. To support these investigations, results of laboratory experiments concerning contact angles of acidic solution droplets on carbonaceous surfaces and the freezing probability of sulfuric acid tetrahydrate are presented.

"We conclude that under threshold conditions for contrail formation, when the plume becomes supersaturated with respect to ice but not water, a large fraction of the soot particles has to be activated and grow ice, leading to an observable contrail, for this is the only primary particle type which is present in sufficiently high abundances by the time of freezing. This result seems to be in
contrast to the findings of Blake and Kato (1995), who on the basis of measured soot abundances and hemispheric mass balance calculations, suggest that aircraft soot injected at altitude does not represent a significant source of CN for sulfuric acid aerosol. (We note, however, that these authors discuss possible far-field effects of soot, whereas we investigate its role in contrail formation.)

"Our findings are also supported by the experimental evidence that ice crystals in contrails observed near natural cirrus... are higher in abundance, initially of uniform size distribution, and smaller than cirrus crystals... Classical heterogeneous nucleation theory fails to give an explanation of how the soot aerosols acquire full or partial liquid coatings for jet fuel sulfur contents below ~0.2 g S per kg fuel, suggesting that processes are at work that are not considered by the standard approach (like activation after adsorption).... Assuming the soot particles to be coated by a supercooled liquid solution, heterogeneous freezing theory predicts sufficiently rapid ice germ formation in diluted H$_2$SO$_4$ solutions for contact angles below 60°. Above water saturation, the coating may grow by condensation and this liquid phase may become visible prior to freezing.

"In view of the potential importance of these processes regarding possible modifications of natural aerosols and their implications for ice nucleation, cloud formation, and subsequent heterogeneous chemical reactions in the upper troposphere and lower stratosphere, there is a strong need for more detailed measurements of particle characteristics and chemical composition in jet aircraft plumes. Certainly, aircraft-related laboratory and field measurements are required to acquire knowledge both on possible soot activation pathways in the presence of sulfur and other trace gases and on the capability of soot particles to act as ice forming nuclei under plume conditions. Such measurements might lead to important implications for the far-field behavior of aging combustion aerosols and could support future modeling work, which currently has to rely on classical nucleation theory with its well-known deficiencies. In addition, numerical modeling of the competitive aerosol interaction processes in aircraft plumes is needed to investigate the physico-chemical composition of contrails, to study their sensitivity on ambient conditions, and to support the interpretation of particle measurements."


2.2.3.5 Possible explanation for soot at 20 km: biogenic carbon?

"One of the surprising results of the Amazon Boundary Layer Experiment (ABLE-2) was the similarity of the concentrations of particulate organic carbon and "black carbon" over the central Amazon Basin between the wet and dry seasons. In both seasons, organic matter accounted for about 90% of the aerosol mass... Estimates for the global biogenic production of monoterpenes and other reactive volatile organics fall in the range of 300 to 500 Tg of C per year, with highest emissions in the tropics, particularly the Amazon basin.

"These production mechanisms, however, cannot explain the presence outside the burning season of black carbon (usually thought to be soot carbon from combustion...) These components must represent primary biogenic aerosol, which consists of microbial particles (for example, bacteria, fungi, algae, and spores), plant debris (for example, cuticular waxes and leaf fragments), and humic matter. Such a primary biogenic origin could explain the presence of K and Zn, both abundant in plant tissues. The light-absorbing properties of this aerosol may be related to the presence of humic-like substances rather than soot carbon."


2.2.3.6 Reduction reactions on soot?

"Such a large surface area [of individual soot particles] could therefore be a potentially important site for heterogeneous atmospheric chemistry, which really should be thoroughly investigated with a sense of urgency."
Carbon aerosols are produced by all combustion processes. This paper investigates some possible effects of heterogeneous reduction of atmospheric constituents on carbon aerosols. [i.e., the carbon grabs, e.g., oxygen — from almost everything, including HNO₃, NO₂, and O₃]... Reduction of HNO₃, NO₂, and O₃ on carbon aerosols may be an important effect of increased air traffic that has not been considered to date. It is shown that if HNO₃, NO₂, and O₃ are heterogeneous reduced on atmospheric amorphous carbon aerosols, then a significant, lower stratospheric [i.e., I think, "in the lower stratosphere"] ozone loss mechanism could exist. This ozone loss mechanism is almost independent of temperature and does not require the presence of sunlight. The mechanism can operate at all latitudes where amorphous carbon aerosols are present. The relative importance of the mechanism increases with height. The reduction of HNO₃ on carbon aerosols could also be a significant renoxification processes wherever carbon aerosols are present. Owing to the very different soot levels in the two hemispheres, this implies that there should be a hemispheric asymmetry in the role of these mechanisms. The renoxification leads to simulated tropospheric HNO₃/NOₓ ratios that are close to those observed. In contrast to the stratospheric response, the tropospheric production of NO₃ due to the reduction of HNO₃ would lead to tropospheric ozone production.

Thibis and Petit (1994) found that at temperatures close to those found in the atmosphere the gas/solid interaction quickly converted both NO₂ and HNO₃ into NO. NO was the main product formed, with CO₂, CO, N₂, and N₂O being minor products. NO reacted on the soot at a rate which was at least 1 order of magnitude slower than both NO₂ and HNO₃... If atmospheric NO₂ is reduced in this way on solid amorphous carbon then it represents a significant nighttime loss of O₃... There is, of course, the possibility that the active sites for physisorption will become saturated and so will take no further part in the heterogeneous process. If this is the case, then desorption could be initiated by heating and the presence of UV light. Another important issue is whether oxygen atoms are produced; if they are, this may partially or completely negate the ozone loss mechanism just described. These are all areas that need to be further investigated.

The present subsonic air traffic occurs mainly in the Northern Hemisphere (NH), with about 30 to 50% flying above the tropopause... In 1990, about 176 MT of aviation fuel was used. To put this into context, this aviation fuel constitutes about 6% of all petrol products and provides about 3% of the CO₂ released by the burning of fossil fuels. Global fuel consumption grows by about 3% per year, with a doubling within the next 18 to 25 years...

It has been found that graphitic carbon particles are present throughout the Arctic troposphere with upper layers typically containing more particles than at ground level...

Blake and Kato (1995) state that the carbon aerosol distribution they presented did not account for soot that had been entrained within sulfuric acid droplets. It is rather surprising that most of the soot aerosols are not actually entrained in sulfate aerosols. [So these authors, too, question Blake and Kato's results.] Blake and Kato speculated that aircraft-generated aerosols may constitute poor condensation nuclei; however, Kärcher et al. find strong evidence that aircraft soot is responsible for the buildup of visible contrails...

In the Arctic boundary layer a low HNO₃/NOₓ ratio has been inferred from measurement. Therefore, if the soot reduction actually occurs, since the Arctic is where soot accumulates, we would expect to see the low values that are seen. The observations therefore subjectively support the reduction of HNO₃ on soot.

It is not only nitrogen species that could be reduced on carbon aerosols. For example, HOCI could be reduced to HCl and HOBr could be reduced to HBr. This could be significant in polar regions, where the production of HCl can become the rate limiting step for further chlorine activation. These processes also need detailed examination.

Further laboratory studies are urgently required to precisely quantify the rate of reduction and investigate other possible heterogeneous reactions on atmospheric amorphous carbon aerosols. For example chlorine and bromine species such as HOCI and HOBr may also be reduced on carbon...
aerosols. Further field measurements are required to precisely quantify the amount of amorphous carbon aerosols present in the atmosphere. An assessment of the impact of carbon entrained within water or sulfuric acid droplets is also required.


### 2.2.3.7 Aircraft soot as CN and CCN

#### 2.2.3.7.1 If SO2 oxidation is fast

"The calculations indicate that the soluble mass fraction of sulfate added to soot particles (assumed to be totally hydrophobic at the point of exhaust) can be large enough to form activated particles within the exhaust plumes of aircraft operating on fuels with typical sulfur contents. However, for emissions from aircraft operating on extremely low sulfur fuels, the soluble material added to soot particles is not sufficient to activate them within the time frame observed for contrail formation. This result... suggest that heterogeneous interactions between soot and sulfur within the exhaust plume are not sufficient to explain the presence of activated particles and contrails in the wakes of high altitude aircraft if the emitted sulfur is in the form of SO2 only. It is probable that soot particles already have enough soluble material when emitted from the engine exhaust or and a higher conversion of sulfur into H2SO4 enable them to act as CCN for contrails."


#### 2.2.3.7.2 Or if it's H2SO4 condensation

"In addition to serving as nucleation sites for aerosols, black carbon particles may also provide surfaces for heterogeneous reactions. In the upper troposphere and lower stratosphere, the amount of black carbon collected on wire impactors represents less than 1% of the total aerosol mass. However, the fractal structure of the black carbon means that the black carbon surface area could be of the same order of magnitude as the sulfate aerosol surface area, particularly under volcanically quiet conditions... Fast reactions on black carbon surfaces could thus have a major impact on atmospheric chemistry.

"The experimental results support current assumptions in jet aircraft plume models that sulfuric acid condensation is involved in the activation of soot particles as condensation nuclei... We measured the uptake of SO2, NO2, O3, and HNO3 on an amorphous carbon sample at room temperature... to explore processes that may occur on combustion-generated soot. NO2, O3, and HNO3 reacted on the amorphous carbon while no reaction was observed for SO2. The reactions observed for NO2 and HNO3 may be important for nitrogen partitioning in the atmosphere. Water uptake was measured on amorphous carbon that had been exposed to SO2, NO2, O3, HNO3, and H2SO4. We observed that chemical treatment of the amorphous carbon with SO2, HNO3, and H2SO4 increased the water uptake, while treatment with NO2 and O3 had no observable effect. Our results indicate that the role of SO2 and HNO3 in the activation of soot particles in an aircraft exhaust plume is probably minimal, and support the condensation of H2SO4 as a mechanism for soot activation."  


### 2.2.3.8 Soot as ice nuclei?

"In the upper troposphere, the mixing ratio of water vapor is too low to produce much ice, and the vertical motions in the clouds are gentle. Thus, the impact of ice formation and growth in these clouds... on [Cloud Radiative Forcing] CRF is due primarily to the particle-radiation interactions themselves, rather than their effects on precipitation or cloud dynamics. ... [M]ost of the crystals
in mid-latitude cirrus clouds are smaller than 50 \( \mu \text{m} \) in their largest dimension. Most of the IR absorption and much of the reflectivity in the visible is due to the small crystals. In tropical cirrus clouds..., the results of a numerical model showed that small crystals (effective radius < 20 \( \mu \text{m} \)) contribute less than about 2% of the condensed water mass but backscatter about 4 W m\(^{-2}\) of incoming solar radiation, enough to offset the global effect of a doubling in the atmospheric concentration of CO\(_2\). Therefore, prediction of the contribution to CRF by cirrus clouds requires computation of the rates of formation, growth, and shape evolution of the small ice particles as functions of the thermodynamics, dynamics, and chemical properties of the upper atmosphere. Because of the difficulty of in situ sampling in this region, and because these parameter regimes had not been well studied in the laboratory previously, most current thinking about these processes is based on developments made in the past few years.

"These observations suggest that the dominant mechanism of ice formation at \( T \leq -35^\circ\text{C} \) is the homogeneous nucleation of ice by the freezing of small liquid-solution droplets; this suggestion is supported by the finding that the concentrations of ice nuclei in background air are often quite low in the upper troposphere... Soot has been mentioned... as a possibly important ice-nucleating component of jet contrails, suggesting that, as in the lower atmosphere, carbonaceous components of aerosol particles cannot be neglected in estimating anthropogenic effects on CRF. However, the importance of this source is unclear, in part because of uncertainties regarding the physical chemistry of the nucleation pathways..."

"The rates of formation and growth of ice particles in mid-latitude cirrus clouds appear to be primarily determined by the availability of water vapor rather than by the concentration of unfrozen haze droplets. These haze droplets may be responsible for the so-called subvisible cirrus, optically thin clouds at cirrus altitudes. An alternative explanation for subvisible cirrus is that they consist of small ice particles that sublime slowly because of high surface impedance, possibly caused by foreign (on-water) molecules near the particle surface.

"Current uncertainties about the shapes of ice particles in cirrus clouds can produce errors in retrieved optical depths at visible wavelengths of up to a factor of 3... It is not known whether impurities in the atmospheric environment have measurable effects on the evolution of crystal shape.

"The small-scale physical and chemical processes linking anthropogenic aerosol particles to droplet populations in the lower atmosphere and to ice-crystal populations in the upper atmosphere must be better understood in order to quantify the effects of anthropogenic aerosol particles on the albedos and extent of clouds. Similarly, detailed study of the physical chemistry and radiative properties of small atmospheric ice particles is necessary in order to interpret in situ measurements of the quantities determining the albedos, emissivities, cloud-top temperatures, and extent of cirrus clouds."


2.2.3.9 Uptake of gases on soot

"In general, the chemical composition of the aerosols controls their reactivity. The reactivity of liquid stratospheric aerosols depends on the solubility of HNO\(_3\) in the supercooled solution, which is in turn determined by the temperature evolution in the air parcel. Models indicate that small-scale temperature fluctuations can lead to the formation of supercooled, ternary H\(_2\)SO\(_4\)-H\(_2\)O mixtures in stratospheric lee-waves... or even in the early plume, by very similar nonequilibrium mechanisms. The key question to be answered is about how the perturbed wake composition and its dynamical evolution control the efficiency of heterogeneous chemical reactions.

"A basic problem concerns the applicability of uptake coefficients derived from laboratory measurements to heterogeneous reactions on the freshly nucleated microclusters present in young aircraft plumes... Another source of uncertainty is introduced by our incomplete knowledge of morphology and chemical reactivity of exhaust soot... At present, the role of soot in atmospheric chemistry is under discussion due to its potential to alter the NO\(_x\) to NO\(_y\) partitioning...
"The fractal nature of soot may cause a substantial enhancement of the total surface area (up to an order of magnitude compared to a spherical approximation), but it is unclear whether this additional surface area is fully available for a certain chemical reaction. It is likely that soot particles absorb oxidized sulfur gases at emission and collect volatile H$_2$SO$_4$ H$_2$O in the plume. It may therefore turn out to be very relevant to investigate how a thin coating of sulfuric acid and water, and probably also other soluble species, alters the chemical reactivity of soot when compared to a dry soot surface. Heterogeneous chemistry on dry soot surfaces can be inefficient if the reaction product remains on the surface and causes a saturation of active sites. In contrast, when soot is covered with a liquid (water) layer, the heterogeneous reactions occur at the solid-liquid interface, accompanied by a regeneration of active sites if the reaction product is soluble in water and therefore leaves the soot surface. Concerning plume processes, a rapid heterogeneous reaction of exhaust NO$_2$ with soot, as observed in the laboratory..., could possibly offer an explanation why the observed NO$_2$ values in the Concorde plume were a factor 2 lower than indicated by a photochemical steady state approximation."


2.3 AIR-SEA EXCHANGE

2.3.1 Huge emissions from ships

"The world's ships are primarily powered by diesel engines... Most marine fuels, or bunkers, are residual fuels. Since the 1973 fuel crisis, crude oils have been processed using secondary refining technologies to extract the maximum quantity of refined products (distillates). As a consequence, the concentration of contaminants such as sulfur, ash, asphaltenes, and metals in the residuals has increased... Most commercial shippers (70-80%) prefer to use the cheaper residual fuels.

"On average, 57 kg of SO$_2$ are released per ton of fuel by medium-speed engines (~40% of the fleet) and 87 kg NO$_x$ per ton by slow-speed engines (~55% of the fleet). Sulfur dioxide emissions (in kg) follow an empirical relationship: SO$_2$ per ton of fuel = 20 x (S%), where S% is the percent of sulfur contained in the fuel. Bunker fuel sulfur content varies from 2.1 to 5%..."

"Worldwide ship nitrogen emissions are... nearly half of the total emissions from the US. They are equal to 87% of nitrogen emissions from US stationary source and equal to 100% of those from US mobile sources... Ship sulfur emissions equal... 43% of total sulfur emissions from the US... These estimates indicate that ship emissions affect global background pollution levels of nitrogen and sulfur."


2.3.2 Huge influence on gas exchange from capillary waves

"An experimental study of gas transport across an air/water interface populated by a field of standing capillary waves is presented. The experiments were conducted in a small tank containing distilled water, enriched with carbon dioxide. The capillary waves were of the Faraday type, generated by providing a small vertical vibration to the water tank... The gas transport rate across the interface increased by almost two orders of magnitude as the wave slope was increased from zero to slightly above 0.2 m/m... The large enhancement in gas transfer was due to the effects of capillary waves alone, demonstrating their importance in gas exchange processes.

p. 2539: "A possible explanation concerns the drift velocities which occur on the surface of these capillary waves. ... While a perfect standing wave has an extremely small drift velocity, even a very small spatial modulation in the standing wave pattern can result in significant surface drift velocities. ... The surface velocities are random and have speeds on the order of several mm/s..."
Flow visualization experiments... qualitatively confirmed the results... By placing a drop of dye on the water surface, extremely rapid mixing in the horizontal direction was observed. It is natural to expect that these random surface velocities will combine to form points of stagnation and divergence at various regions on the surface. These regions would act to exchange the surface fluid with the bulk. While we were unable to prove or disprove this point, we did note that when dye was injected beneath the water surface, bulk mixing, while small, did occur at a rate which was larger than that which was observed in the absence of waves.


### 2.3.3 Influence of bubbles on particle and gas exchange—still unknown

[The problem of estimating the amount of air entrained by breaking waves (enhancing particle and gas exchange) is not here, but the paper illustrates where the field is: just working with a single jet. Recommendations, for both particles and gases, are obvious.]


### 2.4 EXAMPLES OF NEEDS FOR MULTIDISCIPLINARY RESEARCH

#### 2.4.1 Biologists and Botanists

##### 2.4.1.1 Biogenic "soot" and biological sources and sinks

"Atmospheric aerosols play important roles in climate and atmospheric chemistry: they scatter sunlight, provide condensation nuclei for cloud droplets, and participate in heterogeneous chemical reactions. Two important aerosol species, sulfate and organic particles, have large natural biogenic sources that depend in a highly complex fashion on environmental and ecological parameters and therefore are prone to influence by global change...

"[For DMS] fundamental gaps remain in our understanding of key issues in this biosphere-climate interaction, such as the processes that regulate the concentration of DMS in seawater... One reason for the absence of a correlation between plankton biomass and DMS is that the intercellular concentration of its metabolic precursor, dimethylsulfoniopropionate (DMSP), varies between different phytoplankton species over a range of five orders of magnitude. Although it is clear that some taxonomic groups typically contain higher amounts of DMSP, these relations are by no means clear cut... Biota-DMS correlations are further obscured by the complex set of interactions that regulate the concentration of DMS in the surface ocean. The release of DMSP into the water column is controlled by senescence or by grazing by viral, bacterial, and zooplankton, which in turn is influenced by the dynamics of the phytoplankton population. The subsequent breakdown of DMSP to DMS, which occurs with turnover times on the order of hours to days, is microbially mediated and can have a DMS yield between 12 and 66%. In the marine mixed layer, DMS is subject to a number of removal mechanisms, including bacterial and photochemical decomposition, emission to the atmosphere, and downward mixing, with a total turnover time of one to a few days. The rates of the dominant DMS sinks—biological decomposition, photodecomposition, and ventilation—are highly variable as a function of time, place, and meteorological conditions, but are of comparable overall importance for the removal of dissolved DMS. As a result of this complexity, attempts to predict the concentration of DMS in surface waters by a process model have been successful only on a regional level, and the construction of a global DMS concentration and emission fields has to rely on a heuristic extrapolations scheme.

"COS is the most abundant sulfur compound in the atmosphere... The major sources of COS are thought to be photo-oxidation of CS₂, biomass burning, and emissions from oceans and soils; its major sink, uptake by vegetation..."
"One of the surprising results of the Amazon Boundary Layer Experiment (ABLE-2) was the similarity of the concentrations of particulate organic carbon and 'black carbon' over the central Amazon Basin between the wet and dry seasons. In both seasons, organic matter accounted for about 90% of the aerosol mass... Estimates for the global biogenic production of monoterpenes and other reactive volatile organics fall in the range of 300 to 500 Tg of C per year, with highest emissions in the tropics, particularly the Amazon basin.

"These production mechanisms, however, cannot explain the presence outside the burning season of black carbon (usually thought to be soot carbon from combustion...). These components must represent primary biogenic aerosol, which consists of microbial particles (for example, bacteria, fungi, algae, and spores), plant debris (for example, cuticular waxes and leaf fragments), and humic matter. Such a primary biogenic origin could explain the presence of K and Zn, both abundant in plant tissues. The light-absorbing properties of this aerosol may be related to the presence of humic-like substances rather than soot carbon."


2.4.1.2 DMSP

"The main sources of DMSP in the natural environment are marine phytoplankton blooms, where high levels of primary production and biomass occur on a timescale of weeks, and phytoplankton assemblages in the vast areas of the open oceans, where steady-state populations exist for longer periods.... What is clear is that less than 10 per cent of the DMS in surface sea water ever enters the atmosphere. The rest is turned over by bacteria or oxidized by sunlight to form nonvolatile products... Grazing is a major route for the release of DMS to sea water.

"Marine organisms usually have a combination or organic osmolytes. DMSP is similar in both structure and function to the nitrogen-containing osmoregulatory compound glycine betaine (GBT). It has been proposed that, under conditions of nitrogen limitation, a common occurrence in the marine environment, organisms might preferentially change to making the sulfur-containing DMSP molecule.

"[By] increasing our understanding of the marine microbial maze, we can inch closer to the ultimate goal of being able to predict how changes in environmental parameters might impinge on natural inputs of sulfur to the atmosphere."


2.4.1.3 Isoprene

"The research implies that plants produce one major haze ingredient, isoprene, as a strategy for coping with heat.... Isoprene production alone typically siphons off 2% of the carbon fixed through photosynthesis, carbon that could otherwise be converted into sugars. 'It's a puzzle', says Fall. 'Why would plants waste all this energy?'

"The thermal protection theory might explain not only why isoprene emissions are highest on hot days but also why some plants emit more than others.... Isoprene production... generally comes into play in plant species that are subject to short burst of high temperatures. That may be why desert plants like the creosote bush don't seem to emit isoprene—presumably they have come up with other, more economical means for coping with constant high temperatures.

'We're only beginning to learn about all the organic compounds plants are putting into the atmosphere,' says Fall."

2.4.1.4 Oceanic sink of methyl bromide

"New modeling studies based on recent monitoring data... the oceans taking from the atmosphere more methyl bromide (a source of ozone-destroying bromine) than previously thought. This rapid removal by the ocean shortens the average lifetime of methyl bromide to just 0.7 of a year—much briefer than its former calculated lifetime of 2 years... Measurements show that in most of the oceans, methyl bromide is undersaturated... The additional degradation occurs through mechanisms other than the known chemical loss... These processes are assumed to be biological, although their exact nature has not been demonstrated."

"Knowledge about volatile organic compounds, like the biogeochemical cycles that we seek to understand, is changing. Only a few years ago, modeling studies (based on limited monitoring data and tentative relationships between chlorophyll levels and phytoplankton production of methyl bromide) suggested that the oceans were a huge source of methyl bromide.

"In the January [1997] issue of GRL, Juergen Lobert and coworkers reported that based on these [Antarctic] studies, the global ocean takes up 21 more gigagrams of methyl bromide from the atmosphere each year than it produces... Evidence that marine organisms take up and degrade methyl bromide from seawater is mounting... "We have taken the first step: identifying biological removal... There is a lot of work that biologists need to do, now, to figure out exactly what is causing the removal..."

EOS 78, p. 245, 17 June 1997

2.4.1.5 Oceanic source of methane

"The combined seasonal and zonal fluxes result in a total global ocean-to-atmosphere flux of 25 Gmol yr⁻¹ (0.4 Tg CH₄ yr⁻¹), which is an order of magnitude less than previous estimates [IPCC, 1994]."


2.4.2 Chemists and Meteorologists

2.4.2.1 A single example (of thousands!) in tropospheric chemistry

"Oxidative and transport time scales are often of similar magnitude, which leads to coupling between tropospheric chemistry and transport."

"Photochemical degradation of VOC and other reduced trace gases starts with oxidation by the hydroxyl radical. Tropospheric VOC oxidation, at a typical tropospheric OH concentration of around 10⁶ molecules per cc, proceeds within less than 1 hour for highly reactive olefinic compounds, to months for some of the less reactive alkanes and carbon monoxide, and years for the slowly reacting methane. The lifetime of NO₂ with regard to oxidation by OH to nitric acid is roughly 1 day.

"Interhemispheric exchange is achieved in about 1 to 2 years; meridional transport across latitude belts takes months; and zonal transport in bands of constant latitudes is achieved in about 2 weeks. Vertical mixing in the troposphere takes about 1 month on average. However, vertical transport can occur within 1 hour when, during active deep convection, boundary layer air is lifted to the uppermost levels of the troposphere in the cores of Cs.

"The similarity of oxidation and transport time scales leads to coupling between transport and chemistry, and generates principal and practical difficulties in the quest for a quantitative understanding of atmospheric chemistry.

Urban: "Dilution and mixing affect the complex nonlinear oxidation chemistry, depending on the relative importance of mixing and dilution compared to the chemical reaction rates..."
Global: "Atmospheric chemistry is also affected by advective transport, which may import trace species that originated far away. Tropospheric ozone serves as an example. The chemical lifetime of ozone against photolysis-initiated destruction, which leads to OH production, depends on the stratospheric column density of ozone [UV flux] and on the concentration of water vapor. In the upper troposphere, the lifetime approaches 1 year, whereas in the boundary layer of the tropics, the ozone lifetime is only a few days..."


2.4.2.2 Stratospheric chemistry

[Obvious: but NASA is doing well here.]

2.4.3 Health Scientists
2.4.3.1 A single example here, but see above re. genetics

"Many directly mutagenic mono- and di-nitro-PAH derivatives have been identified in extracts of primary combustion-generated particles collected from diesel soot, automobile exhaust, coal fly ash, and wood smoke, and in respirable particles collected from polluted ambient air... In summary, gas-phase nighttime OH and daytime NOx radical-initiated reactions of simple volatile and semivolatile PAHs to form nitro-PAH derivatives appear to be responsible for a substantial portion of the total direct mutagenic activity of respirable airborne particles—as much as 50% in southern California. Furthermore, the total vapor-phase direct mutagenicity of ambient air, at least in that region, is approximately equal to that of the particle phases... Clearly, reliable risk assessments of PAHs will require a great deal of new toxicological and chemical research on the atmospheric formation, fates, and health effects of these respirable airborne mutagens.


2.4.4 Oceanographers
2.4.4.1 See many examples, below, in Sec. 2.7.10

2.4.5 Statisticians
2.4.5.1 A single example here, of thousands!

"Analysis of observational temperature records for the Northern and Southern hemispheres indicates a statistical relationship in which NH temperature depends on temperature in the SH. This pattern, which has strengthened over time, can be explained by the climatic effects of anthropogenic trace gases and tropospheric sulfate aerosols. A similar statistical pattern is produced by model simulations of the historical atmosphere.

"Traditional regression or correlation analysis does not indicate whether the estimated relationship is coincidental or whether the 'dependent' variable is meaningfully dependent on changes in the 'independent' variables. This type of dependence can be examined by testing for Granger causality. The presence of Granger causality implies the presence of a statistical causal ordering. Granger causality tests are based on the notion of predictability, in particular whether past values of a variable X contain statistically meaningful information about current values of variable Y that is not contained in past values of variable Y and other relevant information...

[In the editor's summary: "... statistical techniques more familiar to economists than to climatologists..."]

2.5 OZONE

2.5.1 In the Stratosphere

2.5.1.1 Aerosol influences

"It is shown that short-term (interannual) and longer-term (decadal) changes in [stratospheric] aerosols very likely played a substantial role along with trends in anthropogenic chlorine and bromine in both triggering the ozone losses observed at northern midlatitudes in the early 1980s and increasing the averaged long-term ozone depletions of the past decade or so. The use of observed aerosol distributions enhances the calculated ozone depletion due to halogen chemistry below about 25 km over much of the past decade, including many periods not generally thought to be affected by volcanic activity... While the timing of the observed ozone changes over about the past 15 years is in remarkable agreement with the model predictions that explicitly include observed aerosol changes, their magnitude is about 50% larger than calculated. [But they used a 2D model and how well does the satellite detect submicron particles?]

"The results presented in this paper underscore the need to carefully consider any process that could increase aerosol abundances in evaluations of future ozone trends. For example, subsonic and supersonic aircraft emissions can increase the stratospheric aerosol burden... and hence deplete ozone. Indeed, the present study taken together with the work of [others] suggests that such processes could be more important for stratospheric ozone loss than aircraft NOX releases, at least until the stratospheric chlorine content is lowered substantially from current levels... [The] large particle size group of global stratospheric aerosol may already have been increased by about 60% due to subsonic aircraft emissions..."


2.5.1.2 Arctic ozone hole

"Our results indicate that 120 -160 Dobson units (DU) of ozone were chemically destroyed [in the Arctic polar vortex] between January and March 1996—a loss greater than observed in Antarctica in 1985, when the 'ozone hole' was first reported. This loss outweighs the expected increase in total ozone over the same period through dynamical effects, leading to an observed net decrease of about 50 DU. This ozone loss arises through the simultaneous occurrence of extremely low Arctic stratospheric temperatures and large stratospheric chlorine loadings. Comparable depletion is likely to recur because stratospheric cooling and elevated chlorine concentrations are expected to persist for several decades."


2.5.1.3 More on the Arctic ozone hole

"What has been peculiar about the past few winters is that the Arctic stratosphere has stayed cold for longer than average, and this seems to have led to low ozone concentrations in the Arctic vortex are as high as those seen in the Antarctic, more than about 1 ppbv..., and when such high concentrations are exposed to sunlight, it is well established that ozone loss will take place at a high rate. It is nitric acid that makes the difference: in the Antarctic, temperatures are low for long enough that particles containing nitric acid and water grow large enough to fall out of the stratosphere, leading to denitrification and dehydration. In the Arctic, temperatures are low enough for these particles to form, but not for long enough to lead to large-scale denitrification or dehydration. Because there is a lot more nitric acid in the Arctic atmosphere than in the Antarctic, ozone loss occurs in competition with recovery of CIO to chlorine nitrate via reactions with NOX released from nitric-acid photolysis.

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"The temporary lack of nitrogen allows more ozone removal; and, because absorption by ozone warms the stratosphere, these losses feed back and may keep the stratosphere cold later into the spring.

"Unusually large downward trends in ozone concentration have been observed in northern midlatitudes over the past decade and a half; but we still don't know how much of that is due to Arctic polar processes, and how much is a result of midlatitude chemistry or dynamic changes. Also, many details of the heterogeneous chemical mechanism are not established. For example, what form do the ice particles take at temperatures of 190-200K? Nor do we understand to what extent variability in dynamics, temperature, and aerosol concentration determine the year-to-year variations in Arctic ozone.

"Chlorine concentrations in the troposphere have peaked and are beginning their expected slow recovery... Stratospheric chlorine concentrations should begin to decrease soon, and ozone should then begin recovering to earlier amounts... How do we expect this recovery to proceed in the Arctic? The answer depends on what we expect to happen to the temperature, which is closely related to why the past few stratospheric winters have been so cold. There are three broad possibilities:

1) The temperature was low and the winter longer mostly because there was less ozone to absorb solar radiation (that is, an initial effect was amplified by the feedback mentioned above). This would imply that as ozone recovers, the temperature will recover with it. The timescale for ozone recovery would be similar to that expected in 'normal' winters.

2) The temperature was low as part of a climatological trend independent of ozone—perhaps via CO2 molecules radiating atmospheric heat to space. This would imply that ozone will not recover rapidly, and may remain low for another decade or more. It may be that ozone concentrations after a cold winter with 2 ppbv of chlorine are as low as those for a warm winter with 3 ppbv of chlorine.

3) The temperature was low because of climatological variability unrelated to ozone or a climate trend. This would imply that ozone recovery will occur on the timescale of 'normal' winters, but with considerable year-to-year variability, which will make it difficult to deduce when the recovery begins.

"A great improvement in our knowledge... is necessary if we are to predict the recovery of Arctic ozone as man-made, ozone-destroying chemicals decline, and understand how other sources of stratospheric pollution, such as supersonic aircraft, may influence Arctic ozone."


2.5.1.4 Influence of bromine

"New modeling studies based on recent monitoring data... the oceans taking from the atmosphere more methyl bromide (a source of ozone-destroying bromine) than previously thought. This rapid removal by the ocean shortens the average lifetime of methyl bromide to just 0.7 of a year—much briefer than its former calculated lifetime of 2 years.

"Measurements show that in most of the oceans, methyl bromide is undersaturated... The additional degradation occurs through mechanisms other than the known chemical loss.... These processes are assumed to be biological, although their exact nature has not been demonstrated."

"Following the CFC ban, concern has shifted to chemical species like bromine, which is 40 to 100 times more effective in depleting stratospheric ozone than chlorine. Industrially produced emissions, which constitute one-fourth to one-third of global methyl bromide sources, are thought to be responsible for approximately 3-10% of stratospheric ozone depletion... The shorter atmospheric lifetime estimated for methyl bromide is a result that decreases the global significance of man-made methyl bromide from what it was thought to be just a few years ago..."
"Knowledge about volatile organic compounds, like the biogeochemical cycles that we seek to understand, is changing. Only a few years ago, modeling studies (based on limited monitoring data and tentative relationships between chlorophyll levels and phytoplankton production of methyl bromide) suggested that the oceans were a huge source of methyl bromide.

"Open oceans take up more methyl bromide than they release, while in coastal areas and regions of upwelling, the balance is tipped the other way.

"In the January issue of GRL, Juergen Lobert and coworkers reported that based on these [Antarctic] studies, the global ocean takes up 21 more gigagrams of methyl bromide from the atmosphere each year than it produces... Evidence that marine organisms take up and degrade methyl bromide from seawater is mounting... "We have taken the first step: identifying biological removal... There is a lot of work that biologists need to do, now, to figure out exactly what is causing the removal"...


2.5.1.5 More on bromine

"The News story 'Ozone treaty... must tackle CFC smuggling' is seriously misleading when it states that 'molecule for molecule, methyl bromide is considered at least 50 times more destructive to the ozone layer than chlorine from CFCa.

"Because of oceanic uptake and removal by OH radicals in the lower atmosphere, only about 4% of methyl bromide molecules released at the surface survive the upward journey into the stratospheric ozone layer. Second, the dominant CFCs... have two or three chlorine atoms per molecule. Further, only about 35% of atmospheric methyl bromide can be shown to be under human control. Therefore, to say that atmospheric methyl bromide is 50 times more destructive than CFCs is incorrect and misleading, especially when focusing on anthropogenic effects. Once in the stratosphere, a bromine atom does destroy about 50 times as may ozone molecules as does a chlorine atom.

"Discoveries of the past several years demonstrate that removal of atmospheric methyl bromide is more rapid than had been thought, and imply the existence of unidentified sources. Are other human-controlled sources at play or are the missing sources mostly natural? Research on such questions should continue, partly because of the need to gauge how much ozone protection we purchase by banning the substance..."


2.5.1.6 SAGE trend errors

"Trends [for lower stratospheric ozone] as large as -2% per year [not per decade!] have previously been reported from SAGE II data below 20 km. We show how a significant proportion of this could be explained by the incorrect aerosol removal."


2.5.1.7 Trend data for stratospheric ozone

"For the trend results, above 30 km the SBUV, Umkehr, and SAGE data all show a statistically significant trend with the maximum values between 40 and 50 km of about -4 to -7% per decade. Also, the trends agree to within their stated statistical 95% confidence limits. At 25 km and above,
the ozonesonde data indicate an increase in ozone with time in contrast to the other observations, which may be related to the sensitivity of the results to changes in the sonde pump efficiencies. Below 25 km, the results all depict negative trends, with SAGE the most negative at about -10% per decade, and Umkehr the least negative at about -1% per decade. This latter number is misleading, however, in that it represents the sum of layers 1 through 5, and the ozonesondes indicate a substantial positive trend in the lower troposphere. We have calculated the sonde results for layers 1 through 5 to be about -2% per decade, which agrees quite well with the results for SBUV, about -3% per decade, and [with the results for] the Umkehr, -1% per decade. Overall, then, the trend results for the SBUV, Umkehr, and ozonesondes agree in the lower stratosphere. The somewhat larger value represented by SAGE is outside the 95% confidence limits from the sondes and will have to be examined further. [Sponsored in part by the ACP.]


2.5.2 Ozone in the tropopause region

2.5.2.1 Huge drop of ozone measured in tropopause ice clouds

"Raman lidar measurements of ozone, water vapor, and cirrus optical properties over northern Germany in autumn 1995 are presented. In contrast to smooth ozone profiles with values of 50 to 100 ppbv in a cloud-free and dry upper troposphere, pronounced minima in the ozone distribution with values close to zero were found several times in the presence of ice cloud layers."


2.5.2.2 Huge jump in CIO in tropopause ice clouds

"Cases of 'unusually low ozone in cirrus clouds' have recently been reported by Reichardt et al. [1996], and the potential of cirrus clouds for heterogeneous chlorine activation has been addressed by Borrmann et al.

"Airborne observations during descents of the ER-2 through layers of volcanic aerosol (Mount Pinatubo eruption of 1991) and a cirrus cloud are utilized to study the abundance of CIO and its relation to aerosol surface area in the midlatitude tropopause region. During a cirrus event near the tropopause, CIO mixing ratios up to 2.7 pptv were detected, and near the tropopause, CIO levels from a few to 70 pptv were found. These measurements are associated with large experimental uncertainties but demonstrate the possible presence of CIO inside cirrus clouds and near the tropopause. Model calculations show that possible enhancements of CIO by heterogeneous chemistry on cirrus cloud particles could have implications for the ozone budget in this region..."

"The effects on total ozone column are limited since most of the ozone resides at high altitudes. The model also shows that it can require many days for the CIO to be activated or return to pre-cirrus conditions. This suggests that correlations of CIO and aerosol surface need not be instantaneous if the cirrus or volcanic events are transient."


2.5.2.3 Modeled ozone loss in cirrus clouds

"Satellite observations of cloud optical depths and occurrence frequencies [from SAGE] are used as input to a two-dimensional numerical model of the chemistry and dynamics of the atmosphere to study the effects of heterogeneous reactions on cloud surfaces upon chemical composition and ozone..."
depletion in the tropopause regions. Efficient reactions of ClONO$_2$ with HCl and H$_2$O, and of HOCI with HCl, are likely to take place on the surfaces of cirrus clouds... and perturb chlorine chemistry, much as they do on polar stratospheric clouds present at higher altitudes and colder temperatures. Because of the very low predicted background abundances of ClO near the tropopause, such reactions could enhance the local ClO mixing ratios by up to 30-fold at midlatitudes.

Substantial perturbations are also predicted for related chemical species (e.g., HCl, HOCI, ClONO$_2$, NO$_2$, HO$_2$) in the midlatitude and tropical tropopause regions due to these heterogeneous reactions. If cirrus clouds occur with sufficient frequency and spatial extent, they could influence not only the chemical composition but also the ozone depletion in the region near the tropopause...

"Depletion of ozone close to the tropopause plays only a limited role in influencing the total ozone column trends, due to the low abundances of ozone found there compared to higher altitudes, but is important to the role of ozone depletion in radiative forcing of the Earth's climate system... Further, a key test of scientific understanding of ozone depletion processes is the accurate simulation of both the total column trend and the shape of the observed depletion profile. The latter has proven particularly problematic for present models at midlatitudes...

"[Cirrus] clouds are certainly observed at and slightly above the meteorological tropopause. Tropical cirrus are particularly widespread and often optically thick, but there is abundant evidence for cirrus cloud occurrence near the midlatitude tropopause as well, particularly subvisible cirrus. [They show ozone trends derived only from ozone sondes and Umkehr (max. of -8%/decade decrease at about 15 km) and show that the model of ozone depletion with cirrus can hit the curve.] [The] key result of [this figure] is that cirrus cloud chemistry in the tropopause region at northern midlatitudes probably makes a significant contribution to the observed [ozone] trends there...

"Perhaps most importantly, emissions from aircraft (contrails and/or chemical effluents) have certainly increased in recent decades, are likely to continue to increase in the future, and could influence cirrus cloud distributions and frequency... Clearly, if there were to be variability and/or trends in the frequency of occurrence of cirrus clouds or in their distribution, this could add substantially to their impact on the ozone layer based upon the chemical considerations presented here.

"Note that such ozone loss rates are sufficient to deplete ozone slowly over the course of many days... but are not rapid enough to produce locally large anticorrelations between ozone and cirrus clouds and hence fall short of explaining the measurements of Reichardt et al...

"In short, the modeling results presented in this paper suggest that the surfaces of cirrus clouds near the tropopause very likely provide sites for activation of chlorine (and perturbations to related species such as NO$_x$ and HO$_x$), much as polar stratospheric clouds do at higher altitudes over polar regions and for similar reasons... Our results suggest that consideration of cirrus cloud chemistry at midlatitudes may make important contributions to the shape of the ozone depletion profile in the lowermost stratosphere, which could play a role in reconciling discrepancies between observed and modeled ozone depletion profiles at midlatitudes."


2.5.3 Ozone in the Remote Troposphere

2.5.3.1 Upper troposphere in the tropics

"Over the tropical Atlantic, between 10 and 12 km, Sue et al. (this issue) found extremely high ozone concentrations of up to 500 ppb, together with high humidities, in convective regions 5-80 km across. These observations were made by automated instrumentation on an ordinary passenger aircraft. How can this be explained?"
"Leaving aside the unlikely explanation that lightning causes these very high ozone peaks [why "leave this aside"??], they must be due to transport from the stratosphere [with high humidities??
What about transport from below, via storm venting?]. There are two possibilities: downward
turbulent transfer through the tropopause, caused by convection; or advection of air masses from
outside the tropics through a break in the tropopause that is known to exist in the subtropics...."


2.6 MODELS FOR ATMOSPHERIC CHEMISTRY

2.6.1 Model for Particles, Regional Scale

"The Regional Acid Deposition Model has been modified to create the Regional Particulate Model,
a three-dimensional Eulerian model that simulates the chemistry, transport, and dynamics of sulfuric
acid aerosol resulting from primary emission and the gas phase oxidation of sulfur dioxide.... The mod-
" has been used to study how the degree of sulfuric acid neutralization by ambient ammonia
affects the total aerosol concentrations and particle size distributions over eastern North America." [They are using Slinn's dry deposition model, and for Part II of there paper, they say they'll use
Slinn's wet deposition model. DOE could have easily developed this model.]

Binkowski, F.S. and U. Shankar. The regional particulate matter model I. Model description and

2.6.2 Model Improvements for Removal Parameterizations

2.6.2.1 Dry deposition too large?

"A global three-dimensional chemical transport model is used to investigate seasonal variations of
anthropogenic sulfur in the troposphere.... Initial comparisons of model results with measurements
[air concentrations] reveal a systematic tendency of the model to overestimate SO2 concentrations
and underestimate SO4 concentrations while producing a reasonable fit to measured wet deposition
fluxes. Through a series of sensitivity tests we find that the addition of a nonphotochemical
pathway for converting SO2 to SO4 in the boundary layer with a pseudo first-order rate constant of
1-2 x 10^6 s^-1 provides the most reasonable method of bringing the model results into better
agreement with the ... data...

[But they used a sulfate dry deposition velocity of 0.2 cm/s, which for a 1-2 km boundary layer
height gives a dry removal rate of 1-2 x 10^6 s^-1!!! An appropriate reduction in their sulfate dry
deposition velocity will give them their "pseudo first-order rate constant" — and then fix up SO2
with more venting from the boundary layer!!!]

Kasibhatla, P., W.L. Chameides, and J. St. John, A three-dimensional global model investigation
of seasonal variations in the atmospheric burden of anthropogenic sulfate aerosols. J. Geophys.
Res. 102, 3737-3759, 1997.

2.6.2.2 Wet and dry parameterizations needing overhaul

"We estimate that the global direct radiative forcing is about -0.4 W m^-2 with a maximum over
Europe where the strongest anthropogenic sulfur emissions occur. With different approaches for the
formation of anthropogenic sulfate and its relation to aerosol size distribution, we estimate the
indirect forcing may range from -0.6 to -1.6 W m^-2. This range reduces to -0.4 to -1.1 W m^-2 if a
prescribed marine background particle number concentration is universally applied over the ocean.
Contrary to the direct effect which is more significant over continents, the calculated maximum of
indirect forcing is located over the Atlantic Ocean near the coastline of North America."

[See paper for their methods of including wet and dry removal... and gasp!]
2.6.3 Modeling and Measurements of Storm Venting

2.6.3.1 20 models compared

"Simulation of \(^{222}\text{Rn}\) and other short-lived tracers are used to evaluate and intercompare the representations of convective and synoptic processes in 20 global atmospheric transport models [an intercomparison sponsored by the WCRP]. Results show that most established three-dimensional models [there were 16 of them; 4 were zonally averaged] simulate vertical mixing in the troposphere to within the constraints offered by the observed mean \(^{222}\text{Rn}\) concentrations and that subgrid parameterization of convection is essential for this purpose. However, none of the models captures the observed variability of \(^{222}\text{Rn}\) concentrations in the upper troposphere, and none reproduces the high \(^{222}\text{Rn}\) concentrations measured at 200 hPa over Hawaii. Large differences between models are found in the rates of meridional transport in the upper troposphere (interhemispheric exchange, exchange between tropics and high latitudes). The four [2D] models... tend to underestimate the rate of vertical transport from the lower to the upper troposphere. The largest discrepancies between established 3D models and observations are found in the simulation of \(^{222}\text{Rn}\) in the upper troposphere. We see from Fig. 1 that all 3D models underestimate the observed median concentrations by typically a factor of 2. The maxima are underestimated by a greater factor; that is, the models do not capture the large relative variability in the observations." 

Jacob, D.J. and 29 other authors. Evaluation and intercomparison of global atmospheric transport models using \(^{222}\text{Rn}\) and other short-lived tracers. J. Geophys. Res. 102, 5953-5970, 1997.

2.6.3.2 Different parameterizations of rapid vertical transport

"The results of this study show that different moist convective parameterizations [as used in CCMs] can substantially change the amount of [inert] trace gas transported to the middle and upper troposphere. This can significantly change the vertical profile of the gas, which may result in substantially different scientific conclusions derived from CTM [Chemical Transport Model] studies sensitive to vertical transport. In the worst cases [but only under the restrictions of this study!!], predicted concentrations in the upper troposphere can change by more than an order of magnitude depending on the scheme chosen.

"The tests performed here are neither all encompassing nor (due to the column model used) conclusive. However, we feel that this analysis provides modelers of chemical transport some insight into the differences between and implications of choosing specific subgrid parameterizations...." 


2.6.3.3 Example of influences on upper-troposphere ozone

"The net effect of deep convection on free tropospheric ozone awaits global chemical-transport models with realistic treatments of convection and other processes that affect gas chemistry. Simulations must capture downdrafts as well as updrafts, stratosphere-troposphere exchange—as well as chemical reactions that can occur on and inside aerosols and hydrometeors... The required simulations are not yet available. Neither are global maps of tropospheric ozone, CO, and NO\(_2\) available for model input and validation..." [20-30% of seasonally enhanced ozone over the S. Atlantic... supplied by a combination of biomass burning, lightening, and deep convection over S. America.]

2.6.3.4 Example of influences on upper-troposphere particles

"This implies a deep convective removal efficiency [cf particles, by mass!!] of greater than 90%.*


2.6.3.5 Example of influences on upper-troposphere water vapor

"Feedback from the redistribution of water vapor remains a substantial uncertainty in climate models... Much of the current debate has been addressing feedback from the tropical upper troposphere, where the feedback appears likely to be positive. However, this is not yet convincingly established; much further evaluation of climate models with regard to observed is needed...

"Most global warming predicted by GCMs is due to positive water vapor feedback between water vapor and surface temperature variations... Here we define positive water vapor feedback as a decrease in the area-average clear-sky outgoing longwave radiation... with an areal average increase in surface temperature due to specific humidity increases alone, where averaging occurs over entire tropospheric circulation systems...

"The turbulent boundary layer, where the air is in 'direct' contact with the surface moisture source, likely contributes positively to the feedback. It is, however, less obvious how the free troposphere contributes, where detrainment of cloud condensate is the primary source of water vapor... Some research has suggested that free-tropospheric temperature and water vapor are not [so] closely coupled as climate models suggest during interannual climate variations...

"The dry subsidence zones are where much of the infrared energy that balances the solar energy being absorbed by the earth is being lost to space... Deep convection detrains at such high altitudes in the Tropics that the relative humidities produced in these subsidence regions have the potential of attaining the lowest values anywhere in the world. A major uncertainty is the amount of cloud condensate that detrains from the tropical precipitation systems and moistens the subsiding air through evaporation... Because this detrainment is, by definition, related to the precipitation efficiency of those systems, the handling of deep moist convection in GCMs is of obvious importance. This observation led Renno et al... to boldly conclude that, until cloud microphysical processes such as precipitation efficiency are well handled, it is premature to make climate change predictions...

"The nonlinear sensitivity of clear-sky OLR to humidity fluctuations at low humidities makes the newer satellite evidence of extreme aridity of particular importance to global warming predictions from GCMs. Because the source of most tropical free-tropospheric humidity is cloud detrained from deep convective systems, accurate GCM convective parameterizations of cloud microphysical processes, such as precipitation efficiency, are ultimately required to match the observed humidity distributions. As the climate system warms or cools, any changes in these microphysical processes must also be known in order to correctly predict the associated humidity changes and thus changes in OLR and the water vapor feedback on temperature. Thus, the evidence for widespread dry air makes accurate convective parameterizations even more critical for global warming predictions.*


2.6.3.6 General concern: testing models

"A current leading topic of discussion in the tropospheric chemistry community focuses on the degree to which chemicals released near Earth's surface influence the chemistry of ozone in the upper troposphere. Models that add small-scale convective mechanisms designed to move air even more efficiently through the mid- and higher-latitude middle troposphere do indeed calculate a more
substantial influence of surface sources on the chemistry of the upper troposphere. A question remains, however, as to whether or not such aggressive prescribed vertical mixing is correct. The obvious approach to determining what can be considered correct would be to use measurements of an atmospheric trace constituent with known sources and sinks to evaluate the various model performances. Unfortunately, there appear to be no trace constituents with known sources and sinks for which sufficient measurements exist to provide quantitative tests of 3D transport models; therefore, carefully considered extratropical tropospheric measurements of the vertical and horizontal structure of appropriately chosen traces constituents should be give a high research priority."


2.6.3.7 *Interactions with the lower stratosphere*

"Air inside the anvil was characterized by notably low concentrations of O₃ and high CO relative to the out-of-cloud environment. Elevated concentrations of NO and NO₂, due to lighting and upward transport, were observed in the anvil. A tongue of air with tropospheric characteristics lay above stratospheric air, showing that extensive stratosphere-troposphere exchange had occurred.

"[W]e estimate a minimum flux of 2 x 10¹⁰ g of O₃ into the troposphere and a maximum flux of 3-7 x 10¹³ g of H₂O into the stratosphere. This is a greater flux of water than the stratospheric water budget can support, and thus most of this water must return to the troposphere; the ice crystals were of sufficient size to have substantial settling velocity. If, however, even a small fraction of the mass of such anvils remains in the stratosphere, then convective transport of reactive tropospheric trace species such as NOₓ, CO, and NMHC may dominate the chemistry of the lower stratosphere in this midlatitude regions."


2.6.3.8 *Modeling for the above*

"If the chemistry and dynamics of this storm are typical of the roughly 100 MCCs occurring annually over midlatitudes, then this mechanism plays an important role in CO, NOₓ, and O₃ budgets and could be the dominant source of H₂O in the lower stratosphere and upper troposphere over midlatitudes.

"The observations-based estimate (Poulida et al., 1996) of this storm's flux of water (in the form of ice) into the stratosphere is 70 Tg, and even if only a small fraction of this ice disperses and sublimes (rather than falling back into the troposphere), then 100 MCCs are likely to dominate the H₂O budget (and strongly impact the heterogeneous chemistry) of the lower stratosphere in midlatitudes. By comparison, the total global input of stratospheric water vapor from the oxidation of methane is about 100 Tg/yr..."


2.6.3.9 *NOₓ via lightning*

"Estimates of the annual source strength of the global lightning emissions varies from 3 to 650 Mt NO₂/yr... Ridley et al. suggest a global emission of 7 to 18 Mt NO₂/yr between 8 and 12 km, based on measurements in two storms over New Mexico.

[They look at differences in calculations if a fixed amount of lightning NO₂ (16 Mt NO₂/yr) is distributed uniformly vs. with convection. Their result: for NOₓ, OH, and nonmethane HC, the
difference is of the same order of magnitude as the concentrations themselves; for ozone, 1 order of magnitude less than the ozone concentration.) This means that NO concentration from lightning may cause a variability in free troposphere composition which makes it quite difficult to distinguish the importance of other sources of free troposphere NO from that of lightning in periods when lightning occurs.

"Measurements of convective activity and investigations of the relationship between convection and NO emissions are needed... to develop... improved parameterization of the lightning emissions. The location of the lightning NO emissions and of the convective injection of boundary layer air with time and in space is seen to have a considerable impact on the results of model calculations of the chemical composition of the free troposphere."


**2.6.3.10 Radon modeling**

[Fairly good job of modeling $^{222}$Rn, worldwide, using the relaxed Arakawa-Schubert parameterization (RAS) for moist convection.] The midtroposphere is not playing a major role in RAS convection. Material moves directly from the PBL to the upper troposphere without dilution. Calculations... indicate that a substantial amount of material deposited in the upper troposphere originated above the cloud base. The absence of a downdraft parameterization... may also contribute to a possible high bias in the upper troposphere.

[But in general: good job for radon. Now, what for water, particles, and gases such as NO created within the convection systems?]


**2.6.3.11 Test of the Goddard Model for deep convective mixing**

"An accurate simulation of deep convective mixing is critical for climate assessments because deep convective mixing plays an important role in the transport of ozone precursors with surface sources to the upper troposphere. Deep convective mixing is parameterized in global models because it occurs at spatial scales too small to be resolved explicitly. Algorithms used to parameterize deep convective mixing vary, and errors in trace gas distributions introduced by its parameterization may be large...

"The location of deep convective mixing in the tropics is fairly well simulated, although its north-south extent is overestimated by $>5^\circ$. The frequency of deep convective mixing also appears to be overestimated in the tropics, resulting in... calculated upper tropospheric concentrations of CO in the tropics that are larger and less variable than those observed. The spatial extent of deep convective mixing in the subtropics is overestimated at several locations including the Caribbean throughout the year and the South Pacific Convergence Zone during June-August...

"On average,... calculated deep convective cloud top pressure differ from satellite-measured deep convective cloud top pressures by $<15$ hPa in the... tropics; however, the bias is a strong function of longitude. On average,... calculated cloud top pressures are too high... by 35-70 hPa over marine storm tracks and the Indian Ocean and too low by $>35$ hPa over Central America and Australia during December-February 1990-1992 and low northern hemisphere latitudes of Africa and Asia during June-August... Midlatitude deep convection is underestimated over marine storm tracks throughout the year and over land during the winter. It is slightly overestimated over land during the summer season. These biases will affect the [modeled] upper tropospheric concentrations of short-lived trace gases with surface sources... "

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Funded by NASA, Pickering has done a wonderful job pursuing this topic since 1985, when ACP's predecessor stopped funding him (his PhD thesis was derived from our PRESTORM results.)


2.7 SOME ASPECTS OF CLIMATE CHANGE

2.7.1 Abrupt Changes

2.7.1.1 Climate events in the past

"Not least, interest in the abrupt climatic events of the past stems from how they might affect us in the future. The present interglacial period (the Holocene, which commenced only about 10,000 years ago) is being analyzed to a finer and finer resolution... For example, most of the terrestrial cores contain a lot of high-frequency variations during the last glaciation, but the various explanations for such variations were rarely convincing. Only after glaciologists discovered the so-called Dansgaard-Oeschger events (temperature episodes in the glacial period), and paleoceanographers discovered Heinrich events (colder events associated with iceberg discharges into the North Atlantic ocean), has it been possible to give a climatic explanation to the fluctuations in vegetation seen in continental cores. These climatic events have now been recognized in pollen and loess cores from Florida to China..."


2.7.1.2 Seen from the equator to the poles

"Paleoclimatic records from equatorial East Africa, Antarctica, and Greenland reveal that atmospheric circulation changed abruptly at the early- to mid-Holocene transition to full post glacial conditions. A climatic reorganization occurred at all three sites between 8200 and 7800 years ago that lasted 200 years or less and appears to have been related to abrupt transitions in both marine and terrestrial records around the world."


2.7.1.3 Including Tibet

"The Late Glacial Stage record contains numerous 200-year oscillations in δ18O values and in dust, ammonium, and nitrate levels... Between 15 and 33 ka, the ice core record contains approximately 100 δ18O oscillations with amplitudes from ~ 2 to 21% and an average period of 200 years. The Greenland ice core δ18O record also reveals abrupt warm events, called Dansgaard-Oeschger (D-O) events, during Stage 2. These are postulated to reflect large changes in the temperature and atmospheric circulation around Greenland on centennial to millennial time scales and have been attributed to abrupt changes in the thermohaline circulation in the Atlantic Ocean... The mechanisms causing these abrupt, oscillatory changes in environmental conditions are not clear."

2.7.2 Aerosols and Climate Change

2.7.2.1 Atmospheric aerosols: general

**Andreae and Crutzen review**

"Atmospheric aerosols play important roles in climate and atmospheric chemistry: they scatter sunlight, provide condensation nuclei for cloud droplets, and participate in heterogeneous chemical reactions. Two important aerosol species, sulfate and organic particles, have large natural biogenic sources that depend in a highly complex fashion on environmental and ecological parameters and therefore are prone to influence by global change. Reactions in and on sea-salt aerosol particles may have a strong influence on oxidation processes in the marine boundary layer through the production of halogen radicals, and reactions on mineral aerosols may significantly affect the cycles of nitrogen, sulfur, and atmospheric oxidants.

"Reaction with OH is the major atmospheric sink for most trace gases, and therefore their residence times and spatial distributions are largely determined by their reactivity with OH and by its spatio-temporal distribution. Among these gases, methane reacts rather slowly with OH, resulting in an average residence time of about 8 years and a relatively even tropospheric distribution. The residence times of other hydrocarbons are shorter, as short as about an hour in the case of isoprene (C5H8) and the terpenes (C10H16), and consequently, their distributions are highly variable in space and time.

"COS is the most abundant sulfur compound in the atmosphere (atmospheric burden of about 5 Tg, about 15 times that of SO2 and three times that of aerosol sulfate (on a sulfur mass basis)... The major sources of COS are thought to be photo-oxidation of CS2, biomass burning, and emissions from oceans and soils; its major sink, uptake by vegetation...

"Analyses of the future climatic impact of growing SO2 emissions, and the resulting particle formations, that do not take into account the possible deposition of a substantial fraction of the sulfur on [alkaline] soil dust particle may thus substantially overestimate the climate cooling effect of SO2 emissions in several regions, such as India and China, in which major industrial developments are expected. It is estimated that 30-50% of the atmospheric mineral-dust loading is the result of human disturbance of Earth's surface, especially in semiarid regions.

"If the effects of atmospheric aerosols are to be included as interactive terms in models of climate and atmospheric chemistry, then a fundamental, quantitative understanding of their source and sink mechanisms is required. This understanding has not yet been achieved for most of the species discussed here, in spite of the considerable efforts and progress that have been made over the last decade, and such knowledge remains a major goal in biogeochemical and atmospheric research.

"In other areas, such as the chemical characteristics of organic and mineral aerosols and the chemical reactions taking place on or in these particles, basic information on composition and reaction mechanisms is still needed. Here, we are at a stage at which we have tantalizing glimpses into the complexity and potential importance of these processes but not even enough information to include them in a meaningful way into models of atmospheric chemistry. Fortunately, there are exciting developments in the fields of microanalysis and chemical-kinetics experimentation, which promise to shed light on these topics in the near future."


2.6.2.1.2 Clarke's most recent paper: sulfur condensing on soot?

"Meteorological conditions in the Atlantic Stratocumulus Transition Experiment (ASTEX) region favored advection of clean air from the central Atlantic during the early part of the experiment that was replaced by polluted air of European origin during the latter part of the experiment. Marked
differences in the aerosol size distribution, composition, and state of mixing existed in these air masses. Pronounced differences in their vertical structure also demonstrated that surface measurements often do not represent average boundary layer or column concentrations. Clean subsiding air from the free troposphere had concentrations of condensation nuclei that significantly exceeded concentrations in the boundary layer and had very low mass concentrations and volatility consistent with homogeneous nucleation aloft, supporting the hypothesis that these nuclei can provide a source for 'new' nuclei into the marine surface layer.

"This finding was in contrast to polluted air, characterized by high concentrations of aged aerosol but having no evidence for significant recent nuclei formation. Particles in polluted air consisted of more than 90% volatile mass (mostly sulfate) and a refractory residual remaining at 300°C. The refractory mass varied with the concurrently measured light absorption coefficient, associated with combustion-derived soot. In spite of 2 orders of magnitude more volatile sulfate in polluted air, most of the particle number in polluted air remained after volatilization at 300°C [that's a lot of soot particles!]. This finding suggests that the number of particles in polluted air may reflect the combustion process producing the primary soot aerosol more than the SO2 emissions responsible for much of the sulfate aerosol mass..."


**2.7.2.1.3 Soot climatology in Ireland**

"Black carbon mass concentrations have been measured... at Mace Head on the west coast of Ireland on an almost continuous basis from February 1989 to June 1996... A geometric mean mass concentration of 14.2 ng m\(^{-3}\) for black carbon is found for clean marine North Atlantic air masses... This compares with about 2.0 ng m\(^{-3}\) for southern hemispheric air masses..., 3.0 ng m\(^{-3}\) for Pacific air masses..., and 33.0 ng m\(^{-3}\) for Arctic air masses... Clean marine air masses in this region of the globe seldom contain greater than 75 ng m\(^{-3}\) of black carbon... A seasonal cycle has also been observed with a maximum concentration occurring in May. This has been attributed to a minimum in precipitation... with consequent minimal wet deposition... An approximately inverse relationship was found between the monthly average rainfall amount and black carbon mass concentration. However... other meteorological parameters are likely to play a large role in the seasonal cycle... Black carbon mass concentrations in air masses from the continental sector at Mace Head have... been found to be of the order of 15 times greater than for clean marine air masses..."


**2.7.2.2 Direct radiative effects of aerosols**

**2.7.2.2.1 Closure experiments**

[Show the derivation of formulae for aerosol-induced change in upwelling flux and suggest that closure experiments are feasible.]


**2.7.2.2.2 Global cooling**

"There is increasing evidence that the response of climate to increasing greenhouse gases may be modified by accompanying increases in sulfate aerosols. In this study, the patterns of response in the surface climatology of a coupled ocean-atmosphere GCM forced by increases in CO2 alone is compared with those obtained by increasing CO2 and aerosol forcing [direct only]... The
simulations are run from early industrial times using the estimated historical forcing and continued to the end of the twenty-first century assuming a nonintervention emissions scenario for greenhouse gases and aerosols. The comparison is made for the period 2030-2050 when the aerosol forcing is a maximum. In winter, the cooling due to aerosols merely tends to reduce the response to CO₂, whereas in summer, it weakens the monsoon circulations and reverses some of the changes in the hydrological cycle... The result of changes in aerosol concentrations of the magnitude projected in the scenarios would have a major effect on regional climate, especially over Europe and Southeast Asia."

[On p. 247, they "justify" ignoring indirect radiative effects because soot and tropospheric ozone may compensate—and estimates of indirect show a large cooling over the northern continents "which is incompatible with recent observed changes."]


2.7.2.3

Global cooling by direct effect may be negligible!

"We show that, in general, the climate response, specifically the global mean temperature change, is sensitive to the altitude, latitude, and nature of the forcing, that is, the response to a given forcing can vary by 50% or more depending upon characteristics of the forcing other than its magnitude measured in watts per square meter. The consistency of the response among different forcings is higher, within 20% or better, for most of the globally distributed forcings suspected of influencing global mean temperature in the past century, but exceptions occur for certain changes of ozone or absorbing aerosols, for which the climate response is less well behaved.

"Available data on aerosol single scatter albedo imply that anthropogenic aerosols cause less cooling than has commonly been assumed... [Our] results call into question the conclusion... that the direct aerosol effect has an impact on global temperature comparable to the indirect aerosol effect, with both causing cooling represented by a forcing of the order of 1 W/m². Other recent studies... have suggested that the magnitude of the direct aerosol forcing was being overestimated, as reflected in IPCC [1995]; the present results carry this one step further, suggesting that anthropogenic aerosols have little if any direct cooling effect.

"Aerosols with single scatter albedos as large as 0.9 can lead to net global warming, in part because of a semidirect cloud effect which reduces large-scale cloud cover in layers with absorbing aerosols. Present aerosol measurements are inadequate for a global assessment, but limited available data suggest that on average anthropogenic aerosols [have single scattering albedo] probably in the range 0.9-0.95. If so, the mean effect of aerosols on surface temperature is nearly neutral, excluding their indirect effect on cloud microphysics."


2.7.2.4

Measurements of the direct effect (of aerosols) from biomass burning

"Airborne measurements in smoke from biomass burning in Brazil have yielded optical parameters that permit an improved assessment of the effects of smoke on Earth's radiation balance. The global-mean direct radiative forcing due to smoke from biomass burning worldwide is estimated to be no more than about -0.3 W/m² (cooling), compared with +2.45 W/m² (warming) due to anthropogenic greenhouse gases. On regional scales, direct radiative forcing due to smoke can be large and might indirectly affect global climate... To quantify direct radiative forcing due to aerosols, the magnitudes of four optical properties of the aerosols are required: the mass light-scattering efficiency, the fraction of solar radiation backscattered to space, the single-scattering albedo [that is, the ratio of the light-scattering coefficient to the total extinction coefficient], and the effect of relative humidity on the light scattering."
2.7.2.2.5 Sulfate and soot for cloudy conditions: soot more important

"The contribution to the radiative forcing from cloudy sky regions is found to be negligible for sulfate aerosol; this is in contrast to recent studies... The radiative forcing due to fossil-fuel soot aerosol is enhanced in cloud regions if soot aerosol exists within or above the cloud. The global solar radiative forcing due to sulfate aerosol is estimated to be -0.38 W m⁻²... The uncertainties in the aerosol loading are far more significant. If a soot/sulfate mass ratio of 0.075 is assumed, then the global solar radiative forcing weakens to -0.18 W m⁻² for an external mixture and weakens further for an internal mixture... Although these results are extremely sensitive to the adopted soot/sulfate ratio and the assumed vertical profile, they indicate that fossil-fuel soot aerosol may exert a nonnegligible radiative forcing and emphasize the need to consider each anthropogenic aerosol species."


2.7.2.6 Uncertainty analysis: dominant uncertainty is from chemistry #1

"[Direct forcing] uncertain by somewhat more than a factor of 2. The principal sources of this uncertainty are atmospheric chemistry properties (yield, residence time) and microphysical properties (scattering efficiency, upscatter fraction, and the dependence of these properties on particle size, composition, and relative humidity)... Forcing is strongly dependent on dry particle size and relative humidity but is relatively insensitive to composition [of the sulfate particles]."


2.7.2.7 Uncertainty analysis: dominant uncertainty is from chemistry #2

"Within a plausible set of assumptions (sulfate aerosol resides in the accumulation mode size range and only interacts with water vapor and ammonia vapor) we show that this sensitivity is fairly small (±20%). This low sensitivity derives from a number of compensating factors linking the three optical parameters identified by Charlson et al. (1991). By implication these optical parameters (low RH scattering efficiency, the ratio of hemispheric backscatter to total scatter, and the RH dependence of scattering efficiency) should not be treated independently in either theoretical or experimental investigations of direct climate forcing. A suggested logical focus for such investigations is the backscatter efficiency at high RH. If borne out by future research, low sensitivity to sulfate aerosol size and chemistry would mean that direct sulfate climate forcing can be incorporated in global climate models with only a knowledge of sulfate mass concentration. We emphasize, therefore, the need to study the extent to which our assumptions break down, in particular, the fraction of anthropogenic sulfate that forms on coarse-mode particles... and the extent and effect of sulfate interactions with other accumulation mode components. Finally, we find that a significant fraction of direct aerosol forcing occurs in cloud-covered regions, according to a simple bulk parameterization."


2.7.2.8 Uncertainty analysis: dominant uncertainty is from chemistry #3

"Uncertainty in the direct radiative forcing by anthropogenic sulfate aerosols is analyzed for four different aerosol model structures with 13 uncertain parameters using a second-order probabilistic
collocation method. [Refining] uncertain input parameters may be more important than improving models in order to minimize the overall uncertainty in the direct radiative forcing by anthropogenic sulfate aerosols... The variance analysis indicates that the parametric uncertainty comes mainly from sulfate yield, sulfate lifetime, and ambient relative humidity. Variance contributions from aerosol size parameters are much smaller...


2.7.2.9

Upsetting the paradigm? Soot more important than sulfate for clear skies?!

"Aerosol column optical depths derived from airborne sun photometer and in situ measurements of aerosol properties in 14 vertical profiles off the mid-Atlantic coast of the United States in June show excellent agreement. Simultaneous measurements of the chemical compositions of the aerosol allow an assessment of the chemical apportionment of the aerosol column optical depths. The optical depths had essentially three chemical components, which, in order of descending average contributions, were condensed water, carbonaceous species, and sulfate. These results do not support the common assumption that sulfate dominates aerosol optical depths in polluted regions.

"All of the measurements... were obtained within about 150 km of the mid-Atlantic coast of the United States between New Jersey and North Carolina. The airflow was generally offshore and thus was dominated by continental influences.

"Analysis of the dry aerosol composition has shown that sulfates and carbonaceous species alone account for ~90% of the aerosol mass. On average, carbonaceous aerosols comprised 50% of the dry aerosol mass. Multiple regression of the dry aerosol light scattering coefficient (at... 550 nm) with these two aerosol components shows that the carbonaceous species contributed, on average, about two thirds to the total dry aerosol scattering. The carbonaceous species also acted as light absorbers, resulting in relatively low values for the dry aerosol single-scattering albedo... [0.90]. Even estimates of the upper limit of the mean (wet) single-scattering albedo... [0.94] are relatively low, an outcome with considerable significance to climate modeling.

"A budget analysis of the contributors to the ambient column optical depths show that, on average, condensed water was the most important single contributor (average value 35%, and on occasions as much as 63%). Next in terms of average contribution to the column optical depth was scattering by carbonaceous aerosols. Dry sulfate was the third most important average contributor... Even taking into account the fact that an appreciable portion of the condensed water is associated with sulfate, these results are at variance with previous speculations on the impact of aerosols on radiative forcing of climate... [On] average, dry sulfate constituted only 16% of the optical depth...

"The data presented here suggest that it is time to move beyond considering sulfate alone in modeling aerosol radiative forcing. More research on the role of organic aerosols is needed. Such issues as the hygroscopicity of organic aerosols, the fraction of these aerosols that derive from natural sources, and the vertical distributions of carbonaceous aerosols need to be investigated. The simple paradigm that sulfate dominates aerosol column optical depth has not been verified just offshore of the mid-Atlantic coast of the United States, where it seemed most likely to hold..."


2.7.2.3

Indirect radiative effects

2.7.2.3.1

-1.1 W m\(^{-2}\) over the oceans

"It is found that the annually and globally (over the oceans) averaged indirect shortwave forcing is -1.1 W m\(^{-2}\), with a hemispheric difference of 0.4 W m\(^{-2}\)... Our sensitivity studies indicate that
sulfate burden and its seasonal change is a major factor in the aerosol indirect forcing. Cloud amounts and types, as well as their seasonal changes, have much smaller effects.

"The sulfate amounts in this, as well as in other similar studies (Kiehl and Breigleb 1993, Jones et al. 1994, Boucher and Lohman 1995), are obtained using a particular chemical model that has its limitations (Langner and Rodhe, 1991). More studies based on other models are clearly necessary for comparison and verification of the current estimates of the indirect forcing. It has to be noted also that the sulfate 'data' from the chemical models is usually presented as monthly means, while the response time of cloud drop number to changes in the aerosol load is of the order of an hour. The nonlinear effect of time averaging on the indirect forcings needs further investigation.

"Finally we note that we used the same empirical CCN-cloud drop number relation as in the previous study by Jones et al. (1994). Although this relation distinguishes between maritime and continental environments, it does not account for the role of such physical factors as boundary layer decoupling, role of surface winds and sea salt nuclei, entrainment and mixing at the cloud top. The more accurate parameterization of the CCN-cloud drop number link will undoubtedly present a very challenging problem, but will be essential for improvement of the accuracy of the indirect forcing estimate."


2.7.2.3.2 As much as -30 W m^-2!

"The French Community Climate model... has been used in relation to four different warm-cloud droplet effective-radius parameterizations... The comparison between the results of the different simulations reveals that the model is very sensitive to the effective radius parameterization change. This change induced difference up to 30 W m^-2 in the global values of the radiative fluxes at the top of the atmosphere and at the surface level.

"The introduction into the model of expressions that link the subcloud layer aerosols to the cloud droplet concentration would most probably improve the accuracy of these parameterizations."


2.7.2.3.3 Measurements for biomass smoke

"Smoke particles from biomass burning can generate forcing of climate by modifying cloud microphysics and reflectance of sunlight. Cloud modification, critical to an understanding of climate change, is uncertain and variable. Satellite data over the Amazon Basin... were analyzed for cloud reflectance and droplet size and for smoke concentration. Smoke increased cloud reflectance from 0.35 to 0.45, while reducing droplet size from 14 to 8 μm. The regional variability of the smoke effect was correlated to the availability of water vapor. During the 3 months of biomass burning in the dry season, the smoke-cloud forcing of climate was only -2 watts per square meter in this region, much smaller than what can be inferred from model predictions.

p. 1638: "Previous estimates of indirect smoke forcing of -1 W/m^2 are for a global annual average as a result of smoke generated in the tropics during ~ 3 months per year. This would require a forcing of -20 W/m^2 during the 3 months of biomass burning in the 25° latitude belt where most smoke is generated, a requirement 10 times that of the present result... The value determined by Penner et al. of the global average indirect forcing by smoke could be an overestimate because (i) the study assumes a global homogeneous spatial distribution of the smoke aerosol...; (ii) it neglects the presently observed low forcing for low availability of precipitable water vapor; and (iii) it neglects the production of smoke in the dry season with low cloud fraction."
Potential problem: in Kaufman's case, there's potentially a huge nonlinearity (saturation): the -2 W/m² might be the saturated value (and might include a large amount of absorption where the smoke is so dense.)


2.7.2.3.4 Uncertainties for indirect effect: even larger

"We conclude that the uncertainties linked to the indirect aerosol effects on radiative forcing are much higher than was previously suggested. The indirect effect due to anthropogenic sulfate aerosols has been studied with a coupled microphysics-sulfate aerosol model (COUPL). This is the first time that the indirect aerosol effect due to a prolonging of cloud lifetime by changes in the precipitation efficiency and cloud albedo has been studied simultaneously with an interactive sulfur cycle module. To investigate the uncertainty in the indirect effect due to its dependence on cloud physics, sensitivity experiments with another cloud cover parameterization (COUPLCC) and with another autoconversion rate of cloud droplets (COUPLCC-Aut), have been concocted.

The findings of this study can be summarized as follows.
1. The sulfate burden is much higher in these coupled experiments... because of the longer residence time of water clouds.
2. The coupled model performs reasonably well, reproducing the main features of the observed surface sulfate concentrations, liquid water path, and shortwave cloud forcing.
3. In COUPL the indirect sulfate aerosol effect amounts to -1.4 W m⁻², approximately 60% of which is due to cloud albedo changes and 40% is due to changes in cloud lifetime. Thus, consideration of the albedo effect only, as in all previous model simulations, underestimates the indirect forcing.
4. The largest indirect effect occurs over the NH oceans in all experiments. It is roughly twice as large in the NH as in the SH and twice as large over oceans as over land in all experiments.
5. The indirect effect of sulfate aerosols depends very much upon the parameterization of cloud cover and of the autoconversion rate of cloud droplets. Changes in the cloud cover parameterization lead to an increase in the indirect effect from -1.4 W m⁻² in COUPL to -4.8 W m⁻² in COUPL-CC. Simultaneously, the cloud cover and liquid water path increases from 1% and 17% in COUPL to 3% and 32% in COUPL-CC, respectively. An autoconversion rate where the dependence on CDNC [Cloud Droplet Number Concentration] and cloud water is weaker (COUPLCC-Aut) results in a smaller indirect effect of -2.2 W m⁻² and a change in cloud cover and liquid water path of only 1% and 11%, respectively.

"A large uncertainty in our approach is the simple empirical relationship between CDNC and the sulfate aerosols mass (SO₄²⁻), because other aerosols, such as nitrates and organic species, are locally at least as important as sulfate in acting as CCN... The indirect effect of -4.8 W m⁻² obtained with this cloud cover parameterization (COUPL-CC) is as large as the forcing resulting from the doubling of CO₂..."


2.7.2.4 Sources of CCN

2.7.2.4.1 Biogenic S + nucleation in the free troposphere

"Bigg et al. (1984), Slinn (1992), Clarke (1992), and Raes (1995) postulated that, although CCN formation in the marine boundary layer is unlikely, a plausible CCN formation mechanism could result from DMS venting to the free troposphere, where it could form CN which would survive long enough to grow into CCN and, later, be entrained into the marine boundary layer."

2.7.2.4.2 More support for the free troposphere as the source of CN

"Conditions of strong subsidence and entrainment from the FT [free troposphere] produce an aerosol dominated by particles in the Aitken mode, about 25-60 nm or smaller in diameter. Residence time in the MBL [Marine Boundary Layer] of a few days or more results in a significantly modified aerosol which is bimodal with roughly equal contributions to the total number from the Aitken mode and the accumulation mode (between 150 and 200 nm diameter). In our extensive data set there was no indication of rapid new particle formation in the MBL; particle source seemed to be dominated by entrainment from the FT. However, the major source of new particle mass, resulting from a combination of vapor condensation and cloud processes, was most likely the MBL." Covert, D.S., V.N. Kapustin, T.S. Bates, and P.K. Quinn. Physical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport. *J. Geophys. Res.* 101, 6919-6930, 1996.

2.7.2.4.3 Still more support for the free troposphere as the source

"A box model has been developed to study the formation of CCN from DMS in the unpolluted marine boundary layer (MBL)... The description of the FT aerosol is based on the notion of new particle production in the UT (for which there is experimental evidence) and the notion that these particles evolve into a self-preserving aerosol (for which there is no clear experimental evidence yet)... [The results] show that entrainment of FT aerosols in the MBL quenches new particle formation within the MBL... We conclude that FT-MBL exchange is likely to be an important mechanism that can explain both the observed levels of CN and CCN (active in stratiform clouds) in the MBL and their lack of short-term variability." Raes, F. Entrainment of free tropospheric aerosols as a regulating mechanism for CCN in the remote marine boundary layer. *J. Geophys. Res.* 100, 2893-2903, 1995.

2.7.2.4.4 And still more support for the free troposphere as the source

"The relatively small diameter (55 nm) [of particles in the FT] during clean conditions indicates that the aerosol originated in the upper troposphere rather than over continental areas or in the lower stratosphere... The MBL site [on the Canary Islands] was not strongly affected by European pollution... The MBL aerosol size distribution was bimodal, but the relative concentration of Aitken and accumulation mode varied strongly. The accumulation mode can be related to cloud processing of the Aitken mode but also to pollution aerosol which was advected within the MBL or entrained from the FT. No bursts of nucleation were observed within the MBL." Raes, F., R. Van Dingenen, E. Cuevas, P.F.J. Van Velthoven, and J.M. Prospero. Observations of aerosols in the free troposphere and marine boundary layer of the subtropical Northeast Atlantic: discussion of processes determining their size distribution. *J. Geophys Res.* 102, 21315-21328, 1997.

2.7.2.4.5 And still more

"Recently Clarke (1993) has presented results of measurements taken in the remote North and South Pacific showing that the upper troposphere is a region of ultrasmall new nuclei production from gas-to-particle conversion associated with sulfur-containing gases. A simplified model described by Clarke indicates that the new nuclei can grow to large sizes and may contribute to the CCN concentration at lower altitudes. The aged new nuclei would eventually provide a source of CN in the upper troposphere, which is consistent with the maximum in the observed CN mixing ratio occurring in the upper troposphere [Hofmann, 1993]."
"The aerosol and its subsequent evolution as described by Clarke [1993] would seem to be consistent with many features of the background aerosol observed in this work [profiles over Laramie, Wyoming and Lauder, New Zealand]. The vertical distribution conforms to that expected for a high altitude tropospheric source, and the inferred background particle size is relatively small. Furthermore, the vertical profile and color index suggest that the largest particles are being removed at the top of the PBL consistent with a large particle CCN sink as suggested by Clarke.

"The main body of the newly generated aerosols reported by Clarke are most likely too small for direct detection by the backscattersonde.

"Assuming the above... is correct, and considering the large hemispheric difference in [anthropogenic] sulfur gases, one might expect to find a large difference in the background free tropospheric aerosol also. However, our results, as well as the findings of other quoted here, suggest similar concentrations of the background aerosol in both hemispheres. This seeming inconsistency could be resolved by the mounting evidence recently presented by Chin and Jacob [1996] that anthropogenic sulfur gases are quickly depleted at lower altitudes, while the more uniformly distributed natural sulfur-bearing gases are not [so] readily removed and eventually permeate the free troposphere. Thus, most of the sulfur-containing source gases may be of natural origin and [have] similar concentrations in both hemispheres."


2.7.2.4.6 Maybe ternary nucleation in the boundary layer?

"These results suggest that under conditions typical of the marine environment it may be possible to produce enough particles to balance the various particle sinks characteristic of the MBL. Nucleation rates calculated utilizing binary nucleation theory for average MBL conditions have yielded negligible particle production."

[But there is the possibility of "ternary" as opposed to binary nucleation. Others have looked at water-sulfuric acid-methane sulfonic acid: no significant impact. The point: to give the sulfuric acid-ammonia-water system a fair shake, data are needed.] "[Our results] simply demonstrate that this hypothesis [of this ternary nucleation] is worth pursuing and point out the need for a better models, better thermodynamic data, and laboratory studies of nucleation in the ternary HSO4-H3O system."


2.7.2.5 Sources of ice nuclei

"According to the most accepted theory, the great majority of atmospheric ice nuclei constitute soil mineral particles. But some evidence appears to favor the hypothesis of a nonnegligible contribution to the population of effective ice nuclei made by biogenic material, living or dead. Moreover, some specific human activities have been identified as prolific sources of particles on which ice crystals can be generated. In contrast, it has also been suggested that some anthropogenic effluents deactivated nuclei naturally occurring in the atmosphere.

"A standardization of measurement techniques and a more coordinated and systematic effort in the search for a general theory of heterogeneous ice nucleation are needed to answer the fundamental questions, what is the origin of atmospheric ice nuclei, and what is their activity spectrum?"

2.7.2.6 *Sources etc. for carbonaceous particles*

2.7.2.6.1 *Marine organic CCN?*

"The derived organic aerosol material (OCP) concentrations may represent lower limits because of the uncertainty in the collection of semivolatile organic material lost from the particles during sampling. Analyses of Cape San Juan samples show that (1) mass concentrations of OCP (average about 390 ng m$^{-3}$) exceed sulfate concentrations (average about 270 ng m$^{-3}$); (2) this organic aerosol material is water soluble (and the particles act as effective CCN); and (3) primary combustion aerosol does not appear to be a major contributor to OCP. The fact that OCP concentrations measured at the coastal site are similar to OCP concentrations (330-400 ng m$^{-3}$) measured at an Atlantic Ocean site removed from the coast suggests that a substantial fraction of the OCP in the Caribbean trade winds may be associated with natural oceanic emissions. [Why natural? What about ships powered by dirty diesels?] Results imply that background organic marine aerosol should be included in estimating the indirect forcing of climate by anthropogenic sulfate aerosol."


2.7.2.6.2 *Or from nearby forests?*

"Back trajectory analysis... shows that the air mass that Novakov and Penner studied was without continental contact for 8-12 days prior to being sampled. This implicates two possible sources for the gas phase organic [precursor to the organic CCN]: biogenic emissions from the Puerto Rican forest upwind of the mountain sampling site and emissions from the ocean surface... Using input parameters taken from the literature, it is shown that an assumed organic vapor flux for the forest scenario... generated size distributions similar to the observed aerosol. In contrast... estimates for the n-alkane vapor flux from the ocean are not consistent with the observed size distribution at the mountain site." [What about ships?]


2.7.2.6.3 *Or from ships? Recall:*

"The world's ships are primarily powered by diesel engines... Most marine fuels, or bunkers, are residual fuels. Since the 1973 fuel crisis, crude oils have been processed using secondary refining technologies to extract the maximum quantity of refined products (distillates). As a consequence, the concentration of contaminants such as sulfur, ash, asphaltenes, and metals in the residuals has increased... Most commercial shippers (70-80%) prefer to use the cheaper residual fuels.

Worldwide ship nitrogen emissions are... nearly half of the total emissions from the US. They are equal to 87% of nitrogen emissions from US stationary source and equal to 100% of those from US mobile sources... Ship sulfur emissions equal... 43% of total sulfur emissions from the US... These estimates indicate that ship emissions affect global background pollution levels of nitrogen and sulfur [and soot?]"


2.7.2.6.4 *Sampling and analytical problems*

"Some of the chemical characterization problems already evident at the first conference [in 1978] still exist today: characterizing carbonaceous aerosols even in relatively simple terms, such as total, organic, and black carbon, remains uncertain because of the operational and method-dependent definitions of these classes of materials and the absence of standard reference materials. The terms soot, black, elemental, and graphitic carbon are still used interchangeably because of the lack of generally accepted terminology.

10 December 1997

ASTRAEA Final Report
2.7.3

Data on Climate Change

2.7.3.1 Data for DTR (Diurnal Temperature Range)

"Discrepancies in organic and especially in black carbon determinations in samples with high organic content were found to be much larger... Organic carbon concentration measured in predominantly organic ambient samples influenced by wood burning differed by about 50%. Black carbon concentrations reported for these samples show a 10- to 50-fold difference among determinations by individual methods. Consequently the OC/BC ratios obtained by various methods differ by up to 2 orders of magnitude and vary significantly, even when obtained by seemingly similar methods.

"These analytical problems are aggravated by sampling artifact which, if not properly accounted for, may seriously underestimate or overestimate the actual organic aerosol concentrations... A method and sampling intercomparison activity... with samples collected in remote continental and oceanic environments, is urgently needed."


Data for DTR (Diurnal Temperature Range)

"Analysis of the global mean surface air temperature has shown that its increase is due, at least in part, to differential changes in daily maximum and minimum temperatures, resulting in a narrowing of the diurnal temperature range (DTR). The analysis, using station... data and improved areal coverage for much of the Southern Hemisphere [SH] landmass, indicates that the DTR is continuing to decrease in most parts of the world, that urban effects on globally and hemispherically averaged time series are negligible, and circulation variations in parts of the Northern Hemisphere [NH] appear to be related to the DTR. Atmospheric aerosol loading in the SH is much less than that in the NH, suggesting that there are likely a number of factors, such as increases in cloudiness, contributing to the decreases in DTR.

"Daily minimum temperature increasing at a faster rate (or decreasing at a slower rate) than the daily maximum... US... maximum temperatures have remained constant or have increased only slightly, whereas minimum temperatures have increased at a faster rate... In some areas the pattern has been different: in parts of New Zealand and alpine regions of central Europe, maximum and minimum temperatures have increased at similar rates, and in India, the DTR has increased as a result of a decrease in the minimum temperatures [drier air?]... Urbanized areas often show a narrower DTR than nearby rural areas... Large-scale climatic effects on the DTR include increases in cloud cover, surface evaporative cooling from precipitation, greenhouse gases, and tropospheric aerosols... Decreases in pan evaporation over the former Soviet Union and the US, suggesting that the DTR decreases in these areas is influenced by increases of cloud amount and reduced insolation...

"The overall global trend for the maximum temperature is +0.88°C per 100 yrs... However, the trend for the minimum temperature is +1.86°C per 100 years, which is considerably less than that found in previous analyses... trend in the DTR of -0.84°C per 100 years... The globally averaged time series for the annual maximum and minimum temperatures and DTR calculated using only nonurban stations show only slight differences from those calculated using all available stations [1300 urban stations; 5400 total stations]... Maximum temperatures have increased over most areas with the notable exception of eastern Canada, the southern US, portions of eastern Europe, southern China, and parts of southern South America."

2.7.4.1 

Decline in global solar radiation at the surface

"A statistically significant decrease in mean annual global solar radiation between 1964 and 1990 under completely overcast skies was found at five out of eight studied locations in Germany. A decrease of global solar radiation is also evident in partly cloudy conditions. The mean annual cloud cover fraction and sunshine duration did not significantly change, while the visually assessed mean annual horizontal visibility increased at six of the eight stations. The authors' findings point to a decrease of the cloud transmissivity, which in turn could be explained by an increased frequency of multilevel cloudiness, changing cloud types, or by indirect aerosol effects on clouds.

"Reliable long-term solar radiation measurements are rare. Stanhill and Moreshet, after analyzing data of 45 actinometric stations for the years 1958, 1965, 1975, and 1985, indeed found a statistically significant recent worldwide decrease of global solar radiation averaging 53%. The decline was largest between 45° and 30°N... Suggested explanation of the observed changes is not yet supported by physical models (!!!)"


2.7.3.3 

Precipitation increases

"The authors have analyzed global station data and created a gridded dataset of monthly precipitation for the period of 1900-88. Statistical analyses suggest that discontinuities associated with instrumental errors are large for many high-latitude station records, although they are unlikely to be significant for the majority of the stations. The first leading EOF [Empirical Orthogonal Function] in global precipitation fields is an ENSO-related pattern [ENSO = El Niño-Southern Oscillation] concentrating mostly in the low latitudes. The second leading EOF depicts a linear increasing trend (~2.4 mm decade−1) in global precipitation fields... Consistent with the zonal precipitation trends identified in previous analyses, the EOF trend is seen as a long-term increase mostly in North America, mid- to high-latitude Eurasia, Argentina, and Australia. The spatial patterns of the trend EOF and the rate of increase are generally consistent with those of the precipitation changes in increasing CO₂ GCM experiments."


2.7.4 

DMS

2.7.4.1 

$70 million spent because of CLAW?!

"Ten years ago, Charlson, Lovelock, Andreae, and Warren [CLAW]... In the years since publication of the CLAW hypothesis, over 700 papers have been published discussing the biogeochemistry of DMS (and its precursors) and its link to climate. [700 papers x $100 K/paper = $70000K = $70 Million !!!] In spite of this effort, fundamental gaps remain in our understanding of key issues in this biosphere-climate interaction, such as the processes that regulate the concentration of DMS in seawater, the rate of transfer across the air-sea interface, the mechanism and rate of CCN production from DMS oxidation, and the effects of climate on DMS production in the sea. As a consequence, we are still not able to represent the CLAW hypothesis in the form of a process-based, quantitative, and predictive model. Even the overall sign of the feedback cannot be deduced with certainty, because it is not yet known if a warming climate would result in an increase or decrease of DMS emissions. Glacial-to-interglacial changes in the amounts of DMS oxidation products in polar ice cores have not answered this question unambiguously, because they may reflect variations in atmospheric transport patterns as much as differences in DMS production.

2.7.4.2 Equatorial Pacific

"The equatorial Pacific Ocean is an ideal natural environment to assess DMS-climate feedbacks. The region is characterized by a westward flowing south-equatorial current (SEC), large-scale upwelling of nutrient-rich water along the equator, and a highly productive phytoplankton community. Periodically this characteristic pattern is disturbed by an ENSO event, which results in higher sea-surface temperature, lower nutrient concentrations, lower primary productivity rates, lower chlorophyll biomass concentrations, changes in phytoplankton speciation, and increases in rainfall... This region is especially interesting in light of the result from a recent iron fertilization experiment in the eastern equatorial Pacific Ocean that showed a factor of 3.5 increase in DMS concentration in iron-enriched waters...

"Measurements from 11 cruises between 1982 and 1996 show that the mean surface seawater DMS concentration in this region (15°N to 15°S) is relatively constant both seasonally and interannually... The large interannual variations in oceanic and atmospheric properties associated with ENSO events appear to have little effect on the concentration of DMS in surface ocean waters."

[Is it "an ideal natural environment to assess DMS-climate feedbacks"? Would higher SST increase productivity, compensating for the decrease from nutrients?]


2.7.4.3 Re. the above: is Gaia dead?

"[O]ceanographers Timothy Bates and Patricia Quinn... suggest this thermostat may not exist... Bates and Quinn have blown a hole in the scenario. They compiled a 15-yr record of DMS in tropical Pacific waters, predicting that if the feedback loop were operating, the DMS in the ocean would rise and fall. But in fact, they were surprised to find little variation despite wide, El Niño-induced swings in temperature and cloud cover... Charlon's not ready to give up yet. Just because there's no evidence for feedback in that part of the system 'doesn't mean a feedback doesn't exist,' he says."


2.7.4.4 Source of DMS

[Dimethylsulfoniopropionate (DMSP): algae synthesize to help maintain their osmotic balance with sea water. Two papers in the issue.]

"Gage et al. reveal the biochemical pathway for DMSP synthesis in a diverse group of marine algae. Wolfe and co-workers provide fresh insight into the involvement of grazing microzooplankton in releasing DMSP from marine phytoplankton cells."


"The main sources of DMSP in the natural environment are marine phytoplankton blooms, where high levels of primary production and biomass occur on a timescale of weeks, and phytoplankton assemblages in the vast areas of the open oceans, where steady-state populations exist for longer periods... What is clear is that less than 10 per cent of the DMS in surface sea water ever enters the atmosphere. The rest is turned over by bacteria or oxidized by sunlight to form nonvolatile products... Grazing is a major route for the release of DMS to sea water."
"Marine organisms usually have a combination of organic osmoles. DMSP is similar in both structure and function to the nitrogen-containing osmoregulatory compound glycine betaine (GBT). It has been proposed that, under conditions of nitrogen limitation, a common occurrence in the marine environment, organisms might preferentially change to making the sulfur-containing DMSP molecule... The papers by Gage et al. and Wolfe et al. are examples of how, by increasing our understanding of the marine microbial maze, we can inch closer to the ultimate goal of being able to predict how changes in environmental parameters might impinge on natural inputs of sulfur to the atmosphere."


2.7.5 Climate Influences from Tropospheric Ozone

2.7.5.1 Flux of ozone from the stratosphere

"The flux of ozone from the stratosphere is estimated to be 510 Tg of ozone per year (Danielsen & Mohren estimated 1000 Tg yr -1 Tg yr = 10^10 molecules cm^-2 s^-1)."


2.7.5.2 Global production of NO_x from lightning

"We have found that the annual mean production rate of NO_x by lightning... is between 11.3 and 13.1 Tg N yr^-1, with a mean of 12.2 Tg N yr^-1. The production of lightning (L) NO_x tends to be concentrated over the tropical land masses, with maxima over South America, African, and Southeast Asia. Approximately two thirds of the global LNO_x occurs in the tropics between 30°N - 30°S, while the NH produces twice as much LNO_x than the SH. The NH midlatitudes produce 23% of the global LNO_x, compared with 6% produced in SH midlatitudes. This large, factor of 4, difference in lightning NO_x implies that even prior to anthropogenic influences on the earth's climate, there existed a natural imbalance in NO_x and hence tropospheric O_3 between the hemispheres.

"The efficiency of NO_x in producing O_3 in the free troposphere is large. Values of the ratio of O_3 molecules produced per O_3 emitted range from about 30 to 60... A modest estimate would be that at least 50% of LNO_x is transported out of the boundary layer... and thus the global mean source of FT NO_x is at least 1.7 x 10^9 molecules cm^-2 s^-1. The expected source of O_3 from LNO_x is then 5-10 x 10^10 molecules cm^-2 s^-1, which is larger than the stratospheric source of about 4-6 molecules/cm^-2 s derived from either models... or data analysis... This NH source of O_3 would be a third larger than the average (twice that in the SH) and clearly dominate the stratospheric sources.

In the preindustrial atmosphere, lightning is expected to be the dominant source of NO_x and hence in situ O_3 production. We would thus predict that tropospheric ozone would have on the average a ratio of 3:2 between hemispheres, even in the absence of human activities over the past century."


2.7.5.3 Ozone production in warm clouds

[Argue that it's not so important as Lelieveld and Crutzen suggested] "It is found that the maximum perturbation to O_3 from cloud chemistry in the tropics and midlatitudes summer is less than 3%. The effect of cloud chemistry on O_3 cannot be decoupled from the effect on NO_x... Scavenging of HO_x radicals by cloud droplets slows down the photochemical oxidation of NO_x, so that O_3 production downstream of the cloud may increase..."
2.7.5.4 Radiative forcing by tropospheric ozone

"The radiative forcing of the Earth's climate system due to tropical tropospheric ozone is estimated using ozonesonde profiles and maps of the tropospheric ozone column derived from satellite data. The results suggest that a widespread radiative forcing of at least 0.5 to 1 W m⁻² exists over large areas in the topics for much of the year. This radiative forcing is comparable in magnitude, but opposite in sign, to estimates of the aerosol forcing from tropical biomass burning..."


2.7.6 Influences from Stratospheric Ozone

2.7.6.1 Surface cooling via stratospheric ozone depletion

"Since ozone is a strong absorber of both solar and terrestrial radiation, these ozone changes [lower in the stratosphere, higher in the troposphere] can affect the radiation budget of the surface-troposphere system in several ways: 1) Decreases in strat. ozone concentration result in reduced solar absorption by the stratosphere. Hence, more solar energy reaches the surface-trop. system [= trop. warming]; 2) Decreases in strat. ozone reduce the thermal emissivity of the strat. and, hence, less infrared radiation [from the warm strat.] reaches the trop. [= trop. cooling], 3) Lower ozone conc. in the strat. also tend to make the strat. cooler [less solar absorption by the strat.] and hence less thermal energy will be radiated by the strat. downward into the trop. [= trop. cooling], and 4) increases in trop. ozone will result in an increased greenhouse trapping of longwave radiation [= trop. warming]. It is not immediately clear which of the above effects is strongest. Since the observational evidence for changes in trop. ozone are highly variable and presently inconclusive..., we do not attempt to address the climate effects of the observed changes in trop. ozone here.

"[Importance of the vertical distribution of ozone changes ... 1) ozone depletion below about 30 km results in a net cooling of the Earth's surface, and 2) the surface temperature is most sensitive to changes in ozone that occur near the tropopause... The actual ozone profile in the layer between the tropopause and 17 km is highly uncertain ["since the SAGE measures ozone down to about 17 km"]

"We have estimated the climatic effects of sustained ozone changes relative to the other GHGs and have found that including decreases in stratospheric ozone (similar to those observed from 1979 to 1990) in the steady-state climate simulation reduced the modeled greenhouse warming by 39% relative to the fixed ozone case. We attribute much of this large compensation in global-mean annual-averaged greenhouse warming, resulting from the relatively small global-mean annual-averaged adjusted forcing, to increases in high-latitude meridional heat transport in the upper troposphere coupled with the low infrared opacity of the lower stratosphere, both a result of ozone loss in the lower stratosphere at high latitudes.

"Although our model results are very robust to small changes in model physics, the uncertainties in the spatial and temporal distribution of the ozone losses, especially near the tropopause, and uncertainties in the present ability of any model to simulate the real world, make our results correspondingly uncertain. However, we are confident that our results indicating the importance of large losses of high-latitude lower-stratosphere ozone to the global climate signal are qualitatively valid."

2.7.6.2 Counterbalancing GHG warming by stratospheric ozone depletion

"We show that, in general, the climate response, specifically the global mean temperature change, is sensitive to the altitude, latitude, and nature of the forcing; that is, the response to a given forcing can vary by 50% or more depending upon characteristics of the forcing other than its magnitude measured in watts per square meter. The consistency of the response among different forcings is higher, within 20% or better, for most of the globally distributed forcings suspected of influencing global mean temperature in the past century, but exceptions occur for certain changes of ozone or absorbing aerosols, for which the climate response is less well behaved.

"Negative forcing due to the net ozone change since 1979 appears to have counterbalanced 30-50% of the positive forcing due to the increase of well-mixed greenhouse gases in the same period. As the net ozone change includes halogen-driven ozone depletion with negative radiative forcing and a tropospheric ozone increase with positive radiative forcing, it is possible that the halogen-driven ozone depletion has counterbalanced more than half of the radiative forcing due to well-mixed greenhouse gases since 1979... This conclusion supports the expectation that a positive surge of net greenhouse forcing will accompany the expected recovery of lower stratospheric ozone abundance..."


2.7.7 Influences on Climate Change from Water Vapor

2.7.7.1 Drying via aircraft?

"Of course, there are many additional questions that need to be addressed. Most importantly, we need to better understand the current and projected areal and diurnal coverage of contrail-cirrus, the extent of the indirect cloud alterations caused by aircraft emissions of aerosols and water vapor in the UT, and whether aircraft operations are responsible for the moistening or dehydration (through ice crystal growth and sedimentation) of the UT."


2.7.7.2 Nonlinear response

"Feedback from the redistribution of water vapor remains a substantial uncertainty in climate models... Much of the current debate has been addressing feedback from the tropical upper troposphere, where the feedback appears likely to be positive. However, this is not yet convincingly established; much further evaluation of climate models with regard to observed is needed... Climate Change 1995, IPCC Second Assessment."

"The nonlinear sensitivity of clear-sky OLR to humidity fluctuations at low humidities makes the newer satellite evidence of extreme aridity of particular importance to global warming predictions from GCMs. Because the source of most tropical free-tropospheric humidity is cloud detrained from deep convective systems, accurate GCM convective parameterizations of cloud microphysical processes, such as precipitation efficiency, are ultimately required to match the observed humidity distributions. As the climate system warms or cools, any changes in these microphysical processes must also be known in order to correctly predict the associated humidity changes and thus changes in OLR and the water vapor feedback on temperature. Thus, the evidence for widespread dry air makes accurate convective parameterizations even more critical for global warming predictions.

"The sensitivity of OLR... to tropical tropospheric relative humidities change is much larger at very low humidities than at very high humidities; it is also greater for changes in the free troposphere than for boundary layer humidity changes... Due to this nonlinear relationship... humidity fluctuations at 10% RH have about three times as much impact on OLR... as do fluctuations around 90% RH..."
2.7.8 Some Climate Modeling

2.7.8.1 DTR decrease because of water vapor (shortwave feedback)?

"To examine the causes of the observed diurnally asymmetrical climate change over land, the roles of different physical mechanisms are evaluated using a radiative-convective model of the diurnal cycle. We find that feedbacks in the climate system are more important than forcings in producing diurnal asymmetry. The water vapor shortwave feedback dominates the diurnal distribution of the response. For all cases with warming, the DTR decreases, not due to the greenhouse effect of water vapor, but as a result of more intensive absorption of the solar radiation in the near infrared by water vapor and cloud water in a warmer, wetter climate, independent of the type of forcing. Aerosol reflection and absorption of solar radiation cool the surface and decrease DTR directly, but the negative daytime water vapor feedback virtually cancels out the diurnal asymmetry. In the combined case, with a 50% CO₂ content increase combined with tropospheric aerosol pollution [that] is not far from the current observed conditions over land, the greenhouse warming raises the temperature enough that the direct aerosol effect decreases the DTR. In all cases the time and spatial redistribution of clouds have a significant impact on the climate sensitivity and diurnal cycle. As in the observations, increasing of cloudiness and water vapor content occurs with decreasing of the DTR. In our model the cloudiness as... water vapor changes are produced by the same forcings that lower the DTR; they are not independent causes of changes of the DTR, but rather are important internal feedback mechanisms.

"Recently, Hansen et al. (1995) have used their Wonderland GCM... to further investigate the causes of diurnal asymmetry of climate change. They provide a very nice analysis of the importance of cloud feedbacks, which, in combination with aerosols and greenhouse gases overland are needed to produce the observed asymmetry but do not focus on the water vapor-shortwave radiation feedback. Their model, however, does not produce the needed cloud changes interactively, and they discuss them as an externally imposed forcing. They point out that the cloud changes could be a feedback caused by sulfates, but their model does not include this level of complexity.

"What we have left out may be of equal importance. This includes land surface soil moisture and biosphere feedbacks, snow-albedo feedbacks, aerosol effects on cloud microphysics, cloud ice microphysics, variable advective fluxes and vertical motion, more detailed boundary layer feedbacks, more detailed cloud distribution feedbacks, other greenhouse gases, and other aerosol types and distributions. Similarly, changing the methods we used to include the processes that we included may also affect the results. Further work will be necessary to evaluate their relevance."


2.7.8.2 Problems: aerosols and clouds

"[Bob Cess, SUNY Stony Brook] 'The [climate models] may be agreeing now simply because they're all tending to do the same thing wrong. It's not clear to me that we have clouds right by any stretch of the imagination.'

"Says one senior climate modeler who prefers not to enter the fray publicly: 'The more you learn, the more you understand that you don't understand very much'.

"Global warming is definitely a threat as greenhouse-gas levels increase,' says David Rind of NASA's Goddard Institute for Space Studies (GISS)... 'but I myself am not convinced that we have [gained] greater confidence' in recent years in our predictions of greenhouse warming.
"The NCAR modelers built a host of refinements into their new Climate System Model (CSM). But the key development, says CSM co-chair Byron Boville, was finding a better way to incorporate the effects of ocean eddies. The CSM includes a new parameterization that passes the effects of these unseen eddies onto larger model scales, using a more realistic means of mixing heat through the ocean. Even when run for 300 model years, the CSM doesn't drift away from a reasonably realistic climate. "Being able to do this without flux corrections gives you more credibility." The first results from this still vastly simplified model imply that future greenhouse warming may be milder than some other models have suggested—and could take decades to reveal itself. Doubling CO₂ in the model raised the global temperature 2°C, which puts the model's sensitivity to greenhouse gases near the low end of current estimates...

"But the assumptions about how haze [particles] affect climate may have taken a hit recently from... James Hansen of NASA's GISS. In a recent paper, Hansen and his GISS colleagues pointed out that recent measurements suggest that aerosols don't just cool; they also warm the atmosphere by absorbing sunlight. The net effect of this reflection and absorption, Hansen estimates, would be small—too small to have much effect on temperature.

"Hansen and his colleagues conclude that aerosols probably do have a large effect on climate, but indirectly, through clouds... 'I used to think of clouds as the Gordian knot of the problem,' says cloud specialist V. Ramanathan of Scripps. 'Now I think it's the aerosols. We are arguing about everything.'

Klaus Hasselmann of the MPI also sees a need to wait. He and his colleagues 'think we can see the [greenhouse warming] signal now with 97% confidence.' But 'the signal is not so much above the noise that you can convince skeptics,' he observes. 'It will take another decade or so to work up out of the noise'."


2.7.8.3 Problems: CO₂

"Addition of NH₄-N to NO₃-N deposition increased global terrestrial carbon storage to between 1.5-2.0 Gt C yr⁻¹, while the 'missing terrestrial sink' is quite similar in magnitude. Thus, global air pollution appears to be an important influence on the global carbon cycle. If N fertilization of the terrestrial biosphere accounts for the 'missing' C sink or a substantial portion of it, we would expect significant reductions in its magnitude over the next century as terrestrial ecosystems become N saturated and O₃ pollution expands.

[They use five different models; all have different wet and dry dep parameterizations; there are substantial differences in the predicted latitudinal distributions of the deposition—sort of factors-of-two floating around for annual average.]


2.7.8.4 Problems: hydrological cycle

"A reduction in the present uncertainties would significantly improve our confidence not only in the detection of climate change but also in its attribution to anthropogenic greenhouse warming. This requires further research not only on the impact of aerosols but also on the sources of the discrepancies in the global warming patterns predicted by different GCMs. Foremost among these are the role of clouds, the interactions between the tropical ocean and the global atmospheric circulation, the coupling between the atmosphere, ocean, and sea-ice in high latitudes, and the snow and soil water budget."

2.7.8.5  Problems with aphysical entropy production

"Motivated by the circumstantial evidence of the pervasive nature of the 'general coldness' of climate model simulations, a theoretical analysis is made of the model response expected from the presence of both physical and aphysical sources of entropy under the joint conditions that the net flux of energy through the upper and lower boundaries of the atmosphere and the isentropic temporally, areally integrated entropy source must vanish. These conditions are essential for a simulated global climate state to be without drift. The application of these conditions in the presence of positive definite aphysical entropy sources leads to the conclusion that the model-simulated climate state will be characterized by a general coldness, in particular in the upper polar troposphere and lower tropical troposphere as observed in 104 out of 105 possible outcomes from 35 different simulation by 14 climate models.

"In assessing the magnitude of this effect, a 10°C bias in mean temperate corresponds with a relatively small error of 4% in the mean heat addition of an isentropic layer. This correspondence reveals the extreme sensitivity of a climate model's temperature response to aphysical entropy sources introduced by spurious numerical dispersion/diffusion, Gibbs oscillations, parameterizations, and other factors..."

"The results of this analysis... reveals in the strict sense that the presence of positive definite aphysical sources of entropy in a climate model precludes the simulation of unbiased distribution of the heat addition and temperature. Since in the strict sense the true state cannot be simulated, several questions follow: are reasonable states of global and regional climate change simulated for the right reasons; just what are reasonable states; and how are the right reasons to be determined in view of the trade-offs among the several components of parameterized heat addition?"

[If you're reading this... this is part of what I was approaching, a decade ago, in that article with you to Jack E. that Larry G. squashed (limited in his knowledge of thermodynamics, as he seems to be, to only the first law!). The other part is in the next reference— which completes my feeling of vindication!]


2.7.8.6  Unpredictable? — but maximum entropy production

"Vertical heat transport through thermal convection of the earth's atmosphere is investigated from a thermodynamic viewpoint. The postulate for convection considered here is that the global-mean state of the atmosphere is stabilized at a state of maximum entropy increase in a whole system through convective transport of sensible and latent heat from the earth's surface into outer space. Results of an investigation using a simple vertical gray atmosphere show the existence of a unique set of vertical distributions of air temperature and of convective and radiative heat fluxes that represents a state of maximum entropy increase and that resembles the present earth...

One may expect general circulation models to represent the convective process. However, GCMs contain an artificial device for convection. The convective adjustment was first introduce by Manabe and Strickler... to adjust the vertical temperature profile to observations. The adjustment was necessary for GCMs since it was not possible to treat vertical instability of the atmosphere by a grid-scale dynamic motion... Even current versions of GCMs contain a sort of convective adjustment whose parameters are tuned to reproduce observations... Our reasoning... is that, despite nonlinearity and the consequent unpredictability of the individual motions of convection, the global-mean state is controlled so as to increase entropy in the whole system at a maximum rate..."

Some Policy Issues re. Climate Change

Climate change estimates (Mahlman)

"I... illustrate... using two extrapolations of the IPCC idealized scenarios of increases of 1% equivalent atmospheric CO₂ concentration per year... The first case levels off at a CO₂ doubling after 70 years; the second levels off at a CO₂ quadrupling after 140 years...

"These projections have a greater than 99 out of 100 chance of being true within the predicted range:
- The stratosphere will continue to cool significantly... If ozone continues to decrease, the cooling will be magnified...
- Global mean amounts of water vapor will increase in the lower troposphere (0 to 3 km) in approximately exponential proportion to the global mean temperature change (roughly 6% per 1°C of warming)...

"These projections have a greater than 9 out of 10 chance of being true within the predicted range:
- A doubling of atmosphere CO₂ over preindustrial levels is projected to lead to an equilibrium global warming in the range of 1.5° to 4.5°C... In effect, this means that there is roughly a 10% change that the actual equilibrium warming... could be lower than 1.5°C or higher than 4.5°C... 
- Sea level rise could be substantial. [Projections of 50±25 cm by the year 2100... caused mainly by the thermal expansion of sea water... Long-term melting of landlocked ice carries the potential for considerably higher values but with less certainty.
- As the climate warms, the rate of evaporation must increase, leading to an increase in global mean precipitation of about 2±0.5% per 1°C of global warming.
- By 2050 or so, the higher latitudes of the Northern Hemisphere are also expected to experience temperature increases well in excess of the global average increase. In addition, substantial reductions of northern sea ice are expected. Precipitation is expected to increase significantly in higher northern latitudes. This effect mainly occurs because of the higher moisture content of the warmer air as it moves poleward, cools, and releases its moisture.

"The following have a greater than two out of three changes of being true:
- Model studies project eventual marked decreases in soil moisture in response to increases in summer temperatures over northern mid-latitude continents...
- Climate models imply that the circum-Antarctic ocean region is substantially resistant to warming, and thus little change in sea-ice cover is predicted to occur there, at least over the next century or two.
- The projected precipitation increases at higher latitudes [and "temperature increases" and "reductions of northern sea ice"] act to reduce the ocean's salinity and thus its density. This effect inhibits the tendency of the water to sink, thus suppressing overturning circulation [i.e., suppressing North Atlantic Deep Water (NADW) formation]."


CO₂ stabilization

"The UN Framework Convention on Climate Change calls for a 'stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system.' However, the required level is still unclear. There are two main reasons. First, the climatological, ecological, and social impacts associated with any given level of atmospheric CO₂ concentration are still uncertain... Second, even if impacts were known with 100% certainty, the concept of 'dangerous... interference' is ultimately a question of value judgments that can only be settled in the political arena.

"It appears that to keep the changes in global temperature within the range of natural fluctuations during the past millennium, the climate sensitivity has to be low and the atmospheric CO₂ concentration has to be stabilized at around 350 ppmv... The burden of proof must lie on those who argue that it is safe and acceptable to cause changes in the global climate system that
substantially exceed the natural fluctuations during the past millennium... Until it has been proven that a temperature increase above 2°C is safe or that the climate sensitivity is lower than the central estimate, the projections... suggest that the global community should initiate policies that make stabilization in the range 350-400 ppm possible."


2.7.9.3 Climate change and human health

2.7.9.3.1 "Central clearing-house is needed for... data"

"Changes in temperature, precipitation, humidity, and storm patterns influence upsurges of waterborne diseases such as hepatitis, shigella dysentery, typhoid, and cholera as well as vector-borne pathogens such as malaria, dengue, yellow fever, encephalitis, schistosomiasis, plague, and hantavirus. Cycles of flooding and drought directly affect factors such as the multiplication rates of disease vectors, the biting rate of vectors, and the amount of host-vector interaction. Indirectly, climate influences parameters important to vector spread or survival such as agricultural practices, the disruption of ecosystems, or changes in social systems and practices, which in turn change the relationship between the parasite, the vector, its predators, and the host.

"Climate is only one of a complex suite of factors that cause the outbreak and spread of disease, but recent developments in forecasting short-term climate variability, such as that associated with El Niño, can indicate the climatic potential for a disease outbreak. This information could be crucial for identifying at-risk populations, making timely diagnoses, conducting outreach and education, preparing health facilities, and training personnel. In addition, an enhanced understanding of the connections between climate and health provides regional and national decision makers and planners with insight into disease outbreak and spread...

"The participants focused on two questions: Do we now know enough about the relationships between some types of infectious diseases that may be related to climate factors to use long-range climate forecasting to help prevent outbreaks? And, what climate products would help decision makers mitigate public health problems associated with vector-borne diseases and other types of infectious diseases, as well as other health risks related to changes in climate?...

"A key goal of the workshop was to consider ways to assess the feasibility of establishing an 'end-to-end' climate prediction and health early warning system. Such a system would monitor and disseminate climate and health-related information products, provide access to climate predictions at various lead times, utilize that information to develop health-warning tools, and provide useful information to decision makers.

"Participants agreed that a central clearing-house is needed for storing regional and country-specific data and information on human diseases that are influenced by climatic variations. The data should not be limited to vector-borne diseases but should include other ailments, such as asthma, which may be related to environmental changes, including climate variation... The main categories of health data to include are vector-borne diseases, animal-borne (terrestrial carriers) and marine-borne diseases, morbidity/mortality figures from extreme weather events, respiratory diseases, and nutritional diseases.

"More work is needed regarding the socio-economic implications of emerging linkages between climatic variations and human health problems... [A] suite of pilot application projects should be undertaken to look at the sensitivity of a select number of diseases (likely candidates being malaria, dengue, equine encephalitis, and schistosomiasis) to climatic variation. On particularly promising area for research on this topic is to determine the usefulness of ENSO forecasts and expected climatic impacts of ENSO on regional to local scales. Such activities would need to develop not only the appropriate scientific capabilities, but also foster close ties to the regional and local institutional entities needed to disseminate potentially beneficial information resulting from this process. Developing the links between El Niño and health will likely encourage studies on the
impacts of global climate and environmental change problems, which have much longer time horizons for action than those associated with seasonal to interannual climatic variations."


2.7.9.3.2 For public health, global warming is not the problem

"The story of global climate change and disease is what a newspaper reporter would call 'great copy.' It has dire predictions of pestilence and death, with the imprimatur of top-notch science. The plague is coming, and it's coming home to the developed world. The idea, as proposed by a handful of public health researchers, is that global warming and the attendant climate extremes of floods and droughts, storms and heat waves, may play havoc with public health."

"The salient word in all these stories, however, was 'may'. These predictions are getting renewed attention with the approach of the December climate change summit in Kyoto, Japan, and leading infectious-disease experts have taken to criticizing them sharply. Duane Gubler, for instance, director of the division of vector-borne infectious diseases and the Centers for Disease Control and Prevention (CDC), calls the prognostications 'gloom and doom' speculations based on 'soft data'. Johns Hopkins epidemiologist D.A. Henderson, who led the international smallpox eradication program from 1966 to 1977, says they are based on 'a lot of simplistic thinking, which seems to ignore the fact that as climate changes, man changes as well'. Henderson, Gubler, and others argue that breakdowns in public health rather than climate shifts are to blame for the recent disease outbreaks—and that public health measures will be far more important than climate in future disease patterns."

"Virologist Barry Beaty of Colorado State University... agrees: 'You don't have to be a rocket scientist to see we've got a problem', he says. 'But global warming is not the current problem. It is a collapse in public health measures, an increase in drug resistance in parasites, and an increase in pesticide resistance in vector populations. Mosquitoes and parasites are efficiently exploiting these problems'."


2.7.9.3.3 National Academy to define a research strategy — in ~ 3 years

"There's a potential for developing an early warning tool for many diseases,' says Juli Trtanj, international development specialist with [NOAA's] Office of Global Programs... Trtanj, through NOAA's pilot program for the application of climate forecasts, is coordinating 18 research teams around the globe that have agreed to include public health components in their ongoing projects... to take advantage of El Niño's changes in weather patterns..."

"Past associations of infectious disease with climate variability include malaria outbreaks in Rwanda in 1987 and in other locations, bartavirus in the southwestern U.S. and in Bolivia, and a 1991 cholera epidemic along the coast of Peru...

"The Clinton Administration is also looking into the issue of the spread of infectious disease due to climate variability and change. At a recent meeting at the National Academy of Sciences, Tim Wirth, U.S. under secretary for global affairs at the State Department, said that talking about infectious disease may be 'a way of telling the story about climate change' that effectively reaches the public. 'One doesn't want to be in the position of saying the plague and the locusts are coming,' he said, 'but the plague and the locusts are coming'."

"A 3-year study on climate, ecosystems, infectious diseases, and health will begin within a few months, according to Lowell Smith, staff officer for the study and a senior program officer with the National Research Council's Board of Atmospheric Sciences and Climate... The study, jointly managed by the board and the National Institute of Medicine's Division of Health Sciences Policy, will survey impact on human health that could potentially be caused by variability in the..."
atmosphere and marine and terrestrial ecosystems, identify the potential for using weather and other environmental data to develop an early warning and surveillance system for preventing and mitigating disease, and develop a research strategy to further clarify connections between climate variability and change and the transmission of infectious disease."

Showstack, R. Researchers say El Niño could bring increase in infectious disease. Fall Meeting Preview, EOS 78, p. 524, 18 November 1997.

2.7.10 The North Atlantic's Influence on Climate Change

2.7.10.1 Circulation in the North Atlantic

"Where does the water come from, where does it go, and what happens along its path? These seemingly simple questions about the oceans' (semi-) permanent circulations are at the heart of physical oceanography... The North Atlantic Ocean is the most completely observed and extensively studied of all the world's oceans, and yet it still resists thorough description and rationalization... Basically, what we do [in this paper] is describe a general circulation that is compatible with community wisdom...

"There are... a few circulation elements that we feel are well constrained by the observations. The northward transport of the Florida Current through the Straits of Florida is close to 30 Sv [1 Sv = 10^6 m^3 s^-1], and approximately 45% is from the South Atlantic. The net transformation of warm water to cold water in the North Atlantic is 13 Sv [i.e., 13 Sv flows southward as North Atlantic Deep Water = NADW]... Downstream from the Straits of Florida, the 30 Sv transported as the Florida Current is increased to roughly 100 Sv by recirculating gyres...

"The circulation above 7°C... [in the Florida Current] is broken down... into three layers (temperatures 7°-12°C, 12-24°C, >24°C)... [A] comparatively fresh 7 Sv at T>24°C in the upper 50-100 m [flow] into the Caribbean from the equatorial South Atlantic... [T]he water eventually flows out of the Caribbean into the Gulf of Mexico, then out through the Straits of Florida and into the Gulf Stream system. North of the Caribbean and Florida straits, this water is cooled by interaction with the atmosphere... Six Sv exit the Gulf Stream system through the North Atlantic Current system, possibly recirculating there, and being cooled on the way... finally sinking to form NADW [1 Sv in the Labrador Sea, 3 Sv near Iceland, and 2 Sv in the Greenland Sea]... The 12°-24°C range contains the bulk of the thermocline layer flow... [1 Sv to the Labrador Sea; 1 Sv from the Mediterranean to the Greenland Sea]... The 7°-12°C range [5 Sv to the Labrador Sea; bringing the total NADW to 13 Sv]."


2.7.10.2 Climate change and the North Atlantic

"The northern North Atlantic Ocean plays a key role in determining long-term changes in the climate system. At the northern subtropical latitudes [24°N] the oceans carry approximately half of the total meridional heat flux required by the global radiation budget, and 60% of that is accomplished by the overturning cell of the North Atlantic. The enormous transfer of heat to the atmosphere from northward-flowing surface waters and the subsequent loss of buoyancy [of the water] results in convective formation of intermediate- and deep-water masses.

"In the central Labrador Sea, deep convection in late winter creates the relatively homogeneous Labrador Sea Water (LSW)... [which] can be traced at depths between 1,000 and 2,000 m as the LSW spreads laterally into other regions... The wintertime formation of LSW is not a process of constant intensity or of constant characteristics every year... [varying] on decadal timescales. Two periods of intensified LSW production were identified during the past 30 years, from 1972 to 1976, and from the late 1980s onwards..."
2.7.10.4 Climate oscillations

"We] report rapid changes of intermediate-depth water-mass characteristics observed between 1990 and 1996... [The] trans-Atlantic travel time from the source region to the eastern boundary is estimated to be 4-5.5 years. This indicates a surprisingly high mean speed of about 1.5-2 cm s⁻¹. Our estimate exceeds those previously suggested... by about three to four times."


2.7.10.3 Climate dynamics and NADW

"The present-day paradigm of ocean climate dynamics implies... that the global ocean thermohaline circulation system, also known as the salinity conveyor belt... is strongly controlled by the production of North Atlantic Deep Water (NADW). Proxy data analysis indicates that this circulation system has undergone drastic changes... Moreover, various evidence shows that the ocean circulation has varied between two or three main states, or "modes", strongly controlled by a freshwater impact in the high-latitudinal North Atlantic..."


2.7.10.4 Climate oscillations

"Changes in Earth's orbit around the sun influence the seasonal distribution of energy on Earth, driving the climate system in and out of ice ages in a quasi-predictable manner. As paleoclimatologists struggle to solve remaining mysteries related to the ice ages, they are faced with the prospect of explaining large, rapid millennial climate changes, which are far too frequent to be a linear response to the relatively slow changes in Earth's orbital configuration, known as Milankovitch forcing. Milennial oscillations during the last glaciation are remarkable. The beginning of each cycle is marked by a 5° to 8°C rise in air temperature over Greenland in just decades to centuries. After 1000 to 2000 years of moderate temperatures, the region plunged rapidly back into frigid conditions, only to warm again and start the next millennial climate cycle...

"The origin of millennial-scale climate variability is unclear. The finding of millennial-scale oscillations during the [present] Holocene [warm period], in the absence of large ice sheets, rules out ice-sheet instability as the primary cause. The interplay between the primary Milankovitch frequency may account for climate variability at longer suborbital cycles, between 12,000 and 6,000 years... but it is unlikely that they are responsible for climate cycles of 1000 to 2000 years. Others suggest that variations in solar output may drive these climate oscillations. Bond et al. and Mayewski et al. favor an ocean-atmosphere mechanism but do not rule out primary forcing by external processes.

In the modern North Atlantic, the process of cooling surface water to form deep water, or convective overturn, provides roughly one-third as much heat as is directly contributed by the sun... Thus, variations in convective overturn can dramatically influence regional climate... Broecker introduced the concept of a 'salt oscillator'—essentially controlled by the balance between fresh water delivered by melting ice and salt removed from the surface by the export of saline deep waters from the North Atlantic—to explain millennial climate oscillations during glacial times... Heat released during convective overturn may have promoted the melting of the ice sheets fringing the North Atlantic, delivering fresh water to the surface ocean. Consequently, the density of the surface waters would decrease, eventually to the point where conditions were no longer favorable for deep-water formation. As a result of the reduced heat released in the process of convective overturn, less ice would melt, salinity would rise, and eventually the system would resume the convective phase of the salt oscillator. Marine evidence of linked surface and deep-water variability during glacial and deglacial millennial oscillations is consistent with this hypothesis...

"The recent findings of millennial climate oscillations in the Holocene [the present warm period], when large ice sheets did not surround the North Atlantic, may require modification of the 'salt...
2.7.1

Climate shifts from different climate states

"[W]e are able to directly compare in the North Atlantic two prominent series of abrupt climate shifts from completely different climate states: the Holocene climate episodes [during the current warm period] and the marine imprint of the Dansgaard/Oeschger cycles [abrupt shifts at the end of the most recent glacial period]. In addition to their similar pacings, events in both series document southward shifts of cooler, ice-bearing surface waters deep into the subpolar North Atlantic and a coupling of ocean surface circulation with atmospheric circulation above Greenland. As was the case for the glacial events, the Holocene shifts are abrupt, switching on and off within a century or two at least and probably faster, given the likely blurring of event boundaries by bioturbations. Sudden, recurring reductions in NADW production accompanied the glacial cycles...and the same appears to have occurred during at least one of the Holocene events.

"Hence, at least with respect to the surface circulation in the subpolar North Atlantic, it seems entirely consistent with the evidence to view the Holocene events as mini-Dansgaard/Oeschger cycles, and to regard the surface North Atlantic as a hydrographic system that shifts persistently in a Dansgaard/Oeschger-like mode, even when ice volumes are small. If that is correct, then the much larger amplitudes of the Dansgaard/Oeschger cycles relative to those of the Holocene reflect an amplification of the cyclic signal by a mechanism unique to the glaciations.

"The amplifying mechanism is uncertain, but it may have been linked to thermohaline circulation in the North Atlantic... During glaciation, the 1470-year cycle may have regulated iceberg discharges into the North Atlantic, thereby amplifying the signal through the impact of recurring increases in fresh water (icebergs) on rate of NADW production. An alternative mechanism is suggested by recent models demonstrating that a large-amplitude oscillatory mode can be induced in thermohaline circulation simply by increasing fresh water fluxes to the ocean, as would occur with growth of Northern Hemisphere ice sheets...

"We know too little thus far to identify the origin of the 1470-year cycle. Its constant pacing across major stage boundaries, especially the last glacial termination, almost certainly rules out any origin linked to ice sheet oscillations. Rather, the close correlation of shifts in ocean-surface circulation with changes in atmospheric circulation above Greenland is consistent with a coupled ocean-atmosphere process..."


2.7.10.6

Cloud radiative forcing over the North Atlantic

"On a annual-average basis, the reflection of insolation by clouds over the extratropical oceans exceeds the absorption of outgoing longwave radiation and contributes strongly to the net cooling effect of clouds on the earth's radiation budget... Over the Northern Hemisphere extratropical oceans during January... clouds have a near-zero, or small positive, net radiative heating effect on the total surface-atmosphere system. The reverse is true during July... clouds... are acting to oppose the seasonal warming... [cooling] often by more than 100 W m⁻². The magnitude of net cloud radiative forcing in the extratropics... is such that relatively small percentage changes in cloud cover or cloud properties could result in an anomalous climate forcing of several W m⁻², comparable to the direct forcing due to a doubling of CO₂. Thus, it is important to understand the physical mechanisms that control cloud radiative forcing in these regions."
2.7.10.7  

CO₂ and the thermohaline circulation

"Present estimates of the future oceanic uptake of anthropogenic CO₂ and calculations of CO₂-emission scenarios are based on the assumption that the natural carbon cycle is in steady state. But it is well known from paleoclimate records and modeling studies that the climate system has more than one equilibrium state, and that perturbations can trigger transitions between them. Anticipated future changes in today's climate system due to human activities have the potential to weaken the thermohaline circulation of the North Atlantic Ocean, which would greatly modify estimates of future oceanic CO₂uptake. Here we use a simple coupled atmosphere-ocean climate model to show that the Atlantic thermohaline circulation is not only sensitive to the final atmospheric CO₂concentration attained, but also depends on the rate of change of the CO₂concentration in the atmosphere. A modeled increase to 750 ppmv CO₂ within 100 years (corresponding approximately to a continuation of today's growth rate) leads to a permanent shut-down of the thermohaline circulation. If the final atmospheric concentration of 750 ppmv CO₂ is attained more slowly, the thermohaline circulation simply slows down. The reason for this rate-sensitive response of the climate system lies with the transfer of buoyancy in the form of heat and fresh water from the uppermost layers of the ocean into the deep waters below. This sensitivity of the simulated thermohaline circulation to the rate of change of atmospheric CO₂ concentration has potentially important implications for the choice of future CO₂-emission scenarios."


2.7.10.8a  

Geo-engineering: a dam at Gibraltar?

"If the Mediterranean Sea continues to increase in salinity, shifting climatic patterns throughout the world may cause high-latitude areas in Canada to glaciate within the next century. The Mediterranean is starved of freshwater by human activities: most of the annual flow of the Nile River is now used for irrigation and no longer enters the sea... The higher salinity will lead to a larger volume of the Mediterranean outflow at Gibraltar, which will modify high-latitude oceanic-atmospheric circulation and, in effect initiate new glaciation...

"CO₂ warming would probably trigger a new ice age by increasing Mediterranean evaporation losses, independently of Nile discharge. If CO₂ warming increases the sea surface temperature by 2°C... the increase in the hydrological deficit [of the Mediterranean] of 14%, as estimated from the ratio of future/present vapor pressures at the sea surfaces, would exceed the effect of Nile loss. The combined CO₂ warming and Nile loss might increase the hydrologic deficit to 29%. New ice sheet growth and a much colder Europe would then become extremely likely, and CO₂ concentrations will continue to rise.

"Initiation of new ice sheet growth is of great concern because the strong positive feedback of enhanced albedo and heavier cloud cover, much like the effectiveness of cloudiness over the Greenland Ice Sheet today, might lock in the ice-age growth mode despite CO₂ warming. The ultimate consequence might be a combination of two extremes. The strong CO₂ warming of lower-latitude land and sea surfaces would nourish—by ever stronger moisture advection—rapid expansion of ice sheets in Canada and Eurasia."

Johnson, R.G. Climate control requires a dam at the Strait of Gibraltar. EOS 78, p. 277, 8 July 1997.
Comment on the above

"While we appreciate the editor's desire to publish contributions of general scientific interest, societal relevance, and controversial nature, EOS should not sacrifice scientific rigor to achieve this. Publication of "Climate Control Requires a Dam at the Gibraltar" by R.G. Johnson (EOS, 8 July 1997) was irresponsible. The connection between Mediterranean salinity and ice age initiation is only postulated but not substantiated through quantitative reasoning supported by data.

"Climate is complex because many competing feedbacks act simultaneously. Even if every single one of the hypothesized mechanisms were correct, there would always be competing effects, so quantitative analysis is needed to determine the net response. For example, it is hypothesized that a warming of the Labrador Sea would lead to additional land ice formation, but one could argue equally well that the extra ice would simply melt because the surroundings were warmer.

"Some of the postulated mechanisms are blatantly inconsistent with what is known about fluid mechanics (e.g., the existence of the 'fluidic switch,' through which, apparently, a tiny current [from the Mediterranean] can deflect a large one [have these MIT boys never heard of Lorenz's butterfly??]) or about climate dynamics (if global warming could indeed lead to an ice age, i.e., global cooling, current climate would be unstable). [But the system is unstable!! That's what the paleoclimate data show! I thought MIT and Woods Hole were communicating!]

"To publish a demand for a societal response as enormous as building a dam across the Strait of Gibraltar when the scientific foundation is so tenuous is an affront to the many researchers who work hard to build a quantitative understanding of climate change and how society should deal with it." [Sounds like some linear programming boys got their toes stepped on! I hope Wally Broecker responds!]

Marotzke, J. and A. Adcroft. Comment on 'Climate control requires a dam at the Strait of Gibraltar'. Forum, EOS 45, p. 507.11 November 1997

Hemispheric asymmetry in global sea ice change

"From November 1978 through December 1996, the areal extent of sea ice decreased by 2.9±0.4 percent per decade in the Arctic and increased by 1.3±0.2 percent per decade in the Antarctic. The observed hemispheric asymmetry in these trends is consistent with a modeled response to carbon dioxide-induced climate warming. The interannual variations, which are 2.3 percent of the annual mean in the Arctic, with a predominant period of about 5 years, and 3.4 percent of the annual mean in the Antarctic, with a predominant period of about 3 years, are uncorrelated.

"The hemispheric difference in the climate response results in part from the influence of the thermal inertia of the much larger ocean area in the SH. Sea ice growth in the Southern Ocean, along with slight lowering of the surface water temperature, are attributed to a general freshening of southern circumpolar surface water and the resultant reduction of convective mixing..."


Sudden end of the previous warm period

"Much of humankind’s development as an agrarian and then industrial society has occurred during the current Holocene interglacial period, a roughly 9,000-year stretch of anomalously mild and stable climate... In geological time, such conditions are a rarity, and they can by no means be taken for granted. Hence the interest in finding out how stable interglacials really are, and what processes might act to bring them to a sudden close.

"On page 154 of this issue [13 Nov. 1997], Adkins and colleagues present one of the most detailed pictures yet of ocean conditions during the previous interglacial... They first show that the
interval during which global ice volume was comparable to or less than today's lasted from about 129,000 to 119,000 years ago. [Another 10,000 year warm period!] They then show that the 'conveyor belt' circulation which today carries ocean heat north from the tropics and warms much of Europe remained strong and relatively steady through the interval. Most interestingly, they also find evidence that the onset of ice growth marking the end of the interglacial was accompanied by a sudden reduction in conveyor circulation, which took only 400 years [or less] and from which the climate system apparently never recovered.

"If true, what caused the about-face in the climate system? There is no simple answer. But (tantalizingly) main characteristics of the terminal interglacial event recorded by Adkins et al. are similar to those reported from the Bermuda Rise for the Little Ice Age, a 'cold snap' which occurred a few hundred years ago. Arctic field geologists have long suspected that the end of the present interglacial was then very nearly at hand, as semi-permanent snowfields threatened to coalesce over the high plateau of Labrador and Baffin Island. If the coalescence had been complete, there would have reached a point at which the convective feedback along with decreasing summer insolation (on the decline locally for the past 9000 years) might have triumphed over interglacial warmth. Numerical models suggest that such a chain of events can be unleashed with very little forcing. In this context, a slight weakening of the ocean circulation can be likened to a sledge-hammer blow—one which could conceivably bring the present interglacial to a sudden end.

"...so much for the local changes within the domain of Labrador Sea Water. As these events were working themselves through, a sideways glance at the other two convective cells would have revealed that they too were undergoing unprecedented changes, in phase but in the opposite sense to those in the Labrador Sea. Thus, as Labrador Sea convection ground slowly to a halt in the 1960s, the production and density of '18° Water' (the mode water of the Sargasso Sea) reached a postwar maximum. And as the LSW layer cooled, freshened and thickened from the late 1960s to the 1990s, and its convection reached to new depths, so the deep waters of the Greenland Sea became warmer, saltier, and thinner, and its depth of convective overturn dwindled from over 3,500 m in 1971 to under 1,000 m in the 1990s. We now believe that we have an explanation for the pan-Atlantic coordination of extreme convective behavior—simply that all three cells underlie the..."
2.7.10.2 Recurrent atmospheric circulation mode known as the North Atlantic Oscillation (NAO), and reflect a long-term alternation in the ocean's response as the NAO changed from its 'low-index' extreme state in the 1960s to its record 'high-index' state in the 1990s. [Yah, but which is the chicken and which is the egg?! I expect that the ocean drives the NAO!]

"The potential importance of these convective changes devolves from this link with the NAO. It is still very much 'potential' at present, relying on several convergent lines of thought for which the evidence is fairly new or unproven..."

"Seen in this light, the coolings, freshenings, deepenings, and spreadings of Labrador Sea Water no longer seem parochial. Far from being a small deal in the northwest Atlantic, these changes may well be playing the major role in the largest deal of all—protracting, repeating, or in some way structuring the short-term behavior of the NAO into the long, slow shifts of global change."


2.7.10.12 Unstable climate

"The oceanic thermohaline circulation (THC) carries light, warm, surface water polewards and dense, cold, deep water equatorwards, thereby transporting a large amount of heat towards the poles and significantly affecting high latitude climate. The THC has been remarkably stable, and its variability quite low, over the Holocene period (the past 10,000 years). The much greater climate instability and high-frequency variability recorded in ice and deep-sea cores through the preceding 150,000 years have been linked to greater THC variability. Here we argue, using a global coupled ocean-atmosphere-ice GCM with realistic geography, that there is a wide range of weak mean states of the THC that cannot be stably sustained by the climate system. When the model THC is forced into a state in the unstable range, the THC may rapidly strengthen, collapse, or display strong oscillations. The existence of this unstable regime may account for the greater variability of the THC and climate before the Holocene period."


2.7.10.13 Variability of the North Atlantic thermohaline circulation

"Our data indicate that climatic shifts are strongly related to deep-water reorganizations and that these changes can occur in a time of the order of a few hundred years or less."


2.7.10.14 Variations in the future?

"One of the major elements of today's ocean system is a conveyor-like circulation that delivers an enormous amount of tropical heat to the northern Atlantic... The record contained in ice and sediment... indicates that this current has not run steadily, but jumped from one mode of operation to another. The changes in climate associated with these jumps have now been shown to be large, abrupt, and global. Although the exact linkages that promote such climate changes have yet to be discovered, a case can be made that their roots must lie in the ocean's large-scale thermohaline circulation... Might the ongoing build up of greenhouse gases in our atmosphere trigger yet another reorganization of the climate system?"

"All polar surface waters [italics added] are deficient in salt. The reason is that fresh water is transported as vapor from low to high latitudes where it enters the ocean as precipitation and continental runoff. This delivery of fresh water works to squelch deep water formation... In the Southern Ocean, seasonal growth of sea ice occurs along the perimeter of Antarctica. This ice holds the temperature of the underlying water at the freezing point... and the growth of sea ice leads to a
rejection of salt-rich brines into the underlying water [italics added]. In this way, the most dense waters [cold and salty] in today's surface ocean are generated. These water cascade off the shelves that surround Antarctica into the abyssal ocean...

"The situation in the northern Atlantic is different. Here the rapid throughput of Conveyor water [via the Gulf Stream] stems the buildup of fresh water. Furthermore..., the Atlantic loses more water by evaporation than it gains from precipitation and continental runoff... Hence, surface waters in the north Atlantic are saltier than those in the north Pacific. As a result of the combination of evaporative enrichment of salt and rapid throughput [of saltier, southern water] by the Conveyor, the northern Atlantic has the saltiest of all high-latitude surface waters [emphasis added]. When cooled to just 2° to 3°C, these surface waters become nearly as dense as the brine-densified winter waters beneath Antarctica's fringing sea ice.

"[In] cases where simulations include coupled atmosphere and ocean models..., large greenhouse [gas] buildups lead to collapses of thermohaline circulation... While these collapses are not accompanied by the type of global atmospheric responses seen in the glacial record..., this may well reflect an inherent inadequacy in the atmosphere models... [A] problem encountered... the current generation of coupled ocean-atmosphere models [is]: the sea-to-air heat and fresh water fluxes required to stabilize the model's atmosphere differ significantly from the air-to-sea fluxes required to stabilize the model's ocean... Examination of the geographic distribution of the flux-correction terms reveals that, especially for high-latitude grid squares, the fresh water flux corrections are often large (that is, comparable in magnitude with the actual fluxes). Indeed, it is by means of these difference terms that the polar surface water salinities are maintained at the values required for deep ventilation to balance the density loss created by the downward transport of heat...

"Clearly, if we are to prepare properly for the consequences of the buildup of CO₂ and other greenhouse gases in the atmosphere, we must greatly improve our knowledge of the deep water formation process. To me, it is the Achilles heel of the climate system..."

3. Visions and Recommendations

3.1 Introduction

At present, I'm serving on a National Academy Panel trying to ensure that taxpayer funds are being spent wisely by NASA in the Atmospheric Effects of Aviation (AEA) Project. As can be seen from the copy of the Panel's interim report in Appendix A, we were quite critical of the subsonic portion of NASA's project, especially because of its temporary leadership and its obscure strategic plan.

If I were serving on an Academy Panel charged with reviewing ACP (that is, if I accepted the assignment to try to ensure that taxpayer funds were being spent wisely by DOE in ACP), then I would argue for criticizing ACP even more intensely: not only is ACP's leadership inadequate and its strategic plan obscure, ACP even lacks vision! At least NASA knows what its AEA Project should accomplish. My blunt summary assessment of ACP is that it doesn't know where it's going, doesn't know how to get there, and doesn't know who's leading.

In what follows, my goal is to suggest how to improve ACP. ACP's critical need is for a vision of where it's going. To obtain a new vision for ACP, it must have visionary leadership. But before suggesting ways to provide ACP with new vision and leadership, it will be useful to sketch a framework through which ACP's vision should be sought, which is the subject of Section 3.2.

3.2 A framework for ACP visions

3.2.1 Research for energy policy

To do "good" atmospheric chemistry research is a necessary but insufficient goal of every proposal funded by ACP: ACP research should also be directed toward assisting future energy-policy decisions. There are, I would guess, at least 100 proposals to do "good" atmospheric chemistry research (submitted, e.g., to the NSF) for every one that has potential to assist energy policy.

The necessity for ACP research to be directed toward future energy policy is described already at the top of ACP's home page (at http://gonzalo.ear.anl.gov/ACP or at http://www.atmos.gov/ACP): "The overall objective of the ACP is to provide DOE with advanced information on the atmospheric environment that is required for long-range energy planning." But of late, DOE has not adequately enforced this objective. To improve ACP, DOE management should reassert itself by defining the energy-policy research that ACP is to pursue. Illustrative examples will be given in Section 3.3.

3.2.2 Research "ahead of political curves"

Sometimes, ACP should tackle immediate tasks (e.g., Chernobyl or Kuwait or...); therefore, in part, ACP should fund groups (typically at the National Labs) who will "spin on a dime" to "do the needful". And sometimes ACP should be involved in "current policy issues", such as was done in NAPAP and is now being done in NARSTO. But as the NAPAP experience painfully taught us, becoming involved in "current issues" is usually unproductive: unless some "silver bullet" is found, the research results will be too late to influence policy. That is, policy positions will be announced before the research is completed, and then not science but politics (including economics) will dictate policy decisions. Therefore, below I will encourage minimal involvement of ACP in NARSTO (e.g., only to continue funding the current NARSTO director), because already the topic of new controls on ozone and particles has become highly politicized.
More generally for ACP, DOE should seriously consider adopting the "rule": if lawyers and politicians have become involved with a subject, then research on it should be phased out. Some support for this "rule" can be found in an editorial in *Nature* (Vol. 388, 14 August 1997, p. 607). Concerning the "political demands" that environmental policy be based on "good science", the editorial states: "There is all the difference in the world between 'good' science and 'certain' science..." What politicians want (of course) is "certain science", which (of course) can never be delivered. Therefore, ACP should be doing "good science" on energy-policy topics that have not yet reached the political arena—and then should methodically phase-out the research when politicians start asking for "certain science".

In summary, ACP needs to get ahead of "political curves": engage in research, now, whose results will influence energy policy a decade-or-more from now. This is what Dave Slade (the program manager of a predecessor to ACP) was able to do, almost two decades ago, by starting what has now become the U.S. Global Change Program. Of course, to see decades into the future (as Dave was able to do) requires vision—which is the subject for which this framework is being constructed.

### 3.2.3 Multidisciplinary research

Actually, for there to be an "atmospheric chemistry program" in BER should be questioned. Three decades ago, DOE's Rudy Engelmann (preceding Dave Slade as the program manager of a predecessor to ACP) made major progress (which led, among many other accomplishments, to the Nobel Prize for Rowland and Molina) by stimulating interdisciplinary interactions between chemists and meteorologists. Three decades ago, creating an interdisciplinary atmospheric-chemistry thrust was a major and bold step ahead—with vision.

Now, though, decades later, such interactions are formalized even in academia, where courses and even degrees in atmospheric chemistry are now offered. And now, too, there are "program offices" for atmospheric chemistry in NSF, NASA, and other agencies. But it is questionable if there should still be an atmospheric chemistry program in DOE (or, if there is, probably it should be in BES). Instead, because ACP's goal is "to provide DOE with advanced information on the atmospheric environment that is required for long-range energy planning", DOE should assemble talents from whatever disciplines are appropriate to accomplish relevant tasks, e.g., atmospheric chemists (now a single discipline!) plus molecular biologists, or atmospheric chemists plus oceanographers, etc.

But even if the name "Atmospheric Chemistry Program" continues for whatever reason (historical, institutional inertia, because a majority of the people required to undertake a particular task should have skills in atmospheric chemistry,...) or if (as suggested in part of BER's home page) the name is changed to "Atmospheric Science Program", it is still essential that the ACP involve all people from whatever disciplines are needed to efficiently tackle assigned tasks. To be able to undertake "multidisciplinary research" is one of DOE's greatest strengths—but it's a strength essentially untapped by the current ACP, and its absence is one of the causes of ACP's current weakness. In Section 3.3, suggestions will be made for tapping this potential strength.

### 3.2.4 Tackle the tough problems as a team

And the fourth and final piece to be mentioned here about the framework for ACP's vision is that ACP's multidisciplinary, visionary research on topics relevant to future energy-policy issues should tackle only the tough problems: leave the "simpler" problems to "investigator-led" programs such as in NSF. ACP should tackle tasks too difficult for individual investigators. This team approach to difficult problems was being undertaken when I started working for DOE, 30-years ago (e.g., Josh Holland's leading the program in BOMEX). Subsequently, Dave Slade applied this team approach within a predecessor to ACP in the MAP3S program. And subsequently, this team approach has been used by NASA on many occasions and is now used even in many NSF programs.
Among the difficult, visionary, energy-related atmospheric-chemistry problems to tackle as a team, ACP should stay alert for potential and critical nonlinearities. A past example of a critical nonlinearity (a part of which was tackled by a predecessor to ACP) was the acidification of watersheds by atmospheric deposition (with the nonlinearity occurring when the pH fell low enough to liberate aluminum from the soil, leading to dramatic fish kills). Another example of a critical nonlinearity (one that ACP could have led if it had NASA's financial resources) was the precipitation of nitric acid on polar stratospheric clouds, freeing chlorine, causing the Ozone Hole (first hints of which were seen by Sherry Rowland during a coffee break at one of Rudy Engelmann's Chemist-Meteorologist Workshops). Still another example (one that ACP initiated but then discontinued funding, whereas NASA continued to fund) is the nonlinearity in atmospheric chemistry modeling caused by rapid vertical transport of pollutants from the atmospheric boundary layer by "storm venting". A nonlinearity that a future ACP research team could tackle is described in Section 3.3.

A summary of this "framework" through which new visions for ACP should be sought is sketched below:
3.3 Some potential new visions for ACP within OBER

Any new vision for ACP must be consistent with the vision and mission of BER. In principle, this is relatively easy to satisfy, for the mission of BER is stated to be

\[ \text{to develop the knowledge needed to identify, understand, and anticipate the long-term health and environmental consequences of energy production, development, and use} \]

and the vision for BER is stated to be

\[ \text{to bring revolutionary solutions to energy-related biomedical and environmental changes.} \]

What is needed, then, is to conceive visions for ACP that, in practice, will support BER's visionary mission.

To conceive new visions for ACP, it might be useful to examine BER from different angles. Therefore, granting that usually there's a huge number of ways to view the parts of any whole, I ask the reader to consider different ways that the whole BER "research pyramid" can be viewed, each time with different topics identified on different (nonhorizontal) triangular slices of the pyramid. For example, BER can be viewed with interconnections as follows:

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Energy Pollutants

BER RESEARCH

Human Health

Global Change
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As an illustration—and only as an illustration—of how a new, multidisciplinary project would be displayed in this view of the BER research pyramid, suppose BER adopted the recommendations of the workshop on human health and global change (see Section 2.7.9.3.1) and established (e.g., at ORNL) a "clearing-house" for data on human health and climate in the Americas, especially for El Niño events. To simplify reference to this project, suppose its acronym was chosen to be HACIENDA (Health Advisory and Climate Information for El Niño Disturbances in the Americas). Then, although this HACIENDA Project would need few-to-zero contributions from atmospheric chemists (and therefore it would not be a project within ACP; i.e., it would be a project within some other program within BER) it would appear in another slice of BER's research pyramid, more revealing for ACP, as follows:
The question now posed is what research should ACP undertake to make a difference to energy-policy decisions a decade- or-more from now? Based on the literature review given in Section 2 and the framework reviewed in Section 3.2, two suggestions are outlined below. The first deals with air pollution and health effects (a project that would require substantial involvement of atmospheric chemists and which would lie along the left side of the above triangle); the second deals with air pollution and climate change (which also would require substantial involvement of atmospheric chemists and would lie along the right side of the above triangle).

3.3.1 Example vision #1: air pollution and health effects

Items in the foreground of this "example vision" include the almost unbelievable "screw-up" that is now occurring related to EPA's proposed new regulations for surface-level ozone and aerosol particles. Given EPA's estimate (www.epa.gov/oar/sect8121) of $523 billion "for the total [cost] of 1970 to 1990 direct expenditures" for Clean Air Act compliance, future direct costs to meet new regulations for ozone and particles could easily be in excess of $1 trillion! On the other hand, if one accepts EPA's estimates for the benefits of Clean Air Act compliance (in 1990 dollars) "realized during the period from 1970 to 1990 in the range from 5.6 trillion to 49.4 trillion dollars, with a central estimate of 22.2 trillion dollars", then the cost/benefit ratio certainly appears favorable. But, as was indicated in Section 2, the scientific basis for EPA's benefit analysis is almost unbelievably weak. Even the EPA's report to Congress states (p. ES-5): 'Epidemiological research alone cannot prove whether a cause-effect relationship exists between an individual pollutant and an observed health effect." Yet the EPA went ahead, anyway: "this study uses the epidemiological finding about correlations between pollution and observed health effects to estimate changes in the number of health effects that would occur if pollution levels change." EPA estimates the benefits were 22.2 trillion, but EPA states they can't prove it. Why not choose any other number they can't prove?!

And the mess doesn't stop there. Thus, the draft for the new regulations on ozone (40 CFR Part 52, 10 October 1997; www.epa.gov/ttn) states, understandably without proof: "Ground-level ozone, the main harmful ingredient in smog..." Further, the EPA's "Fact Sheet" on "Health and Environmental Effects of Ground-level Ozone" (www.epa.gov/ttn) states: "10 to 20 percent of all summertime respiratory-related hospital visits in the northeastern U.S. are associated with ozone pollution" [I added the italics, to emphasize the new legal principle of "guilt by association"!]. And the "Fact Sheet" on "Health and Environmental Effects of Particulate Matter" (www.epa.gov/ttn) states: "They [fine particles] are of health concern because they easily reach the deepest recesses of the lungs"—based on that principle, just think about EPA's concern about ground-level oxygen! In summary, I
repeat my earlier recommendation: ACP should be only marginally involved in this entire mess (e.g.,
by funding the director of NARSTO), for already it’s far too politicized.

And the clutter in the foreground of this "Example vision #1" certainly isn't restricted to ozone and
aerosols: there is another mess in the area of 'hazardous air pollutants”. Appendix B (from
www.epa.gov/ttnluatw) shows the "original list of [190?] hazardous air pollutants" (listed in the
Clean Air Act), from acetaldehyde to selenium compounds (and including hydrogen sulfide,
apparently included because of a "clerical error" in the law) and then shows EPA's "7/8/96 Update...
current EPA staff recommendations for technical corrections and clarifications of the hazardous air
pollutants (HAP) list in Section 112 (b) (1) of the Clean Air Act..." If one then seeks a list of
measured concentrations of these hazardous air pollutants (as I have done for hours at various EPA
web sites), I predict that one will seek in vain. In fact, if one uses any of a number of EPA "search
engines" to seek air quality data for hazardous air pollution, the seeker is very conveniently referred
to EPA’s 9-9-97 "Fact Sheet: Notice of availability of the emissions inventory, and description of
EPA’s plans for the Integrated Urban Air Toxic Strategy...". This "strategy" is in response to a
September 1996 Sierra Club law suit against EPA for failing to act as required by the Clean Air Act
and to the consent decree in which EPA agreed "to analyze the urban air toxics problem and publish a
report." As for knowledge of existing air concentrations (let alone health effects of these hazardous
air pollutants at existing air concentrations!), this "Fact Sheet" states: "Further, EPA is requesting
any available ambient air quality data on the named air toxics that can be used in support of
subsequent analyses..." They can't find any data either!

In contrast, think of what BER could do—and indeed, should do. After a decade—or so of directed
(and nonpoliticized) research, with ACP’s involvement in (or leading of) a new multidisciplinary
thrust, BER could determine the specific energy-related air pollutants that cause specific human
illnesses—and why. Why are 30 million Americans suffering from asthma: is the cause ozone or
hydrogen peroxide or airborne pesticides, pollen, or cat hair, or a genetically related response to too
much stress, or too much dietary fat or...? How could "submicron aerosol particles" be causing
major health problems? If the particles are sulfuric acid, ammonia in the human respiratory tract
should neutralize the acid almost instantaneously; if the particles are (and remain) "submicron" (mass
mean diameter of -0.1 µm) and therefore "penetrate deep into lungs", their deposition velocity is so
small that they won't deposit but will be exhaled. Are the real culprits those described by Pitts and
Pitts (see Section 2.4.3.1) "the many mutagenic mono- and di-nitro-PAH derivatives that have been
identified in extracts of primary combustion-generated particles collected from diesel soot, automobile
exhaust, coal fly ash, and wood smoke...", or 13 of the 190 listed hazardous air pollutants, or 3 of
them acting in concert, causing a nonlinear physiological response, or...? It's a disgrace that we
don’t know—a disgrace to the entire scientific establishment, including science program managers
(e.g., in BER) responsible for steering Federal science programs.

The mission of BER is "to develop the knowledge needed to identify, understand, and anticipate the
long-term health and environmental consequences of energy production, development, and use." If
this mission is applied to ACP, then it seems obvious that ACP should immediately undertake, as a
minimum, the following:

- Identify as many as possible of the energy-related air pollutants in the U.S. (e.g., to start,
  identify, in a number of major urban areas in different regions of the country, essentially all
  inorganic and organic gases, as well as the chemical and elemental compositions of particles by
  size, including essentially all hydrocarbons, and certainly including the 190 (?) hazardous
  pollutants listed in Appendix B);

- Correlate multi-year data for all these air pollutants with reported instances of human illnesses
  suspected of being caused by inhalants;

- With biomedical research, understand the relationships between specific pollutants and illnesses.
Now, obviously there's a myriad of strategic details and decisions needed to undertake this project. Some obvious questions:

- Should the sampling be done at surface stations (e.g., at hospitals) first at, say, five cities near national labs (New York, Chicago, Phoenix, San Francisco, and Seattle), or at more cities, or should the sampling be done by helicopter(s);
- What sampling frequencies are appropriate and feasible for which inhalants;
- What procedures should be used for the needed sampling of pollen, other biological material (airborne viruses?), and other potential allergens;
- Should there be a central chemical laboratory to analyze the samples;
- Should plans be formulated for a ten-year project (2 years to define the sampling and analysis and to develop and/or obtain the instruments, 3 years of sampling, 2 years of analysis, and then plan on additional years of sampling and analysis to test hypotheses);
- Besides assigning a meteorologist to each sampling location to document meteorological conditions associated with each sample, what other meteorological services should be included (routine source/receptor modeling, airshed modeling?)
- How do health scientists want the project executed;
- Should the project be coordinated with the NIES, both to assist the fledging National Environmental Genome Program (which will almost certainly need much more complete specification of air pollution loads, e.g., airborne pesticides, beryllium, chlorinated solvents, etc.) and to facilitate obtaining illness reports from relevant health authorities?

But although there are many other questions and obviously there is need for strategic planning, I don't plan to pursue these matters here. Nonetheless, to simplify reference to this "example vision" in what follows, I will mention (and hereinafter use) a possible name for this project: the Comprehensive Inventory of Trace Inhalants from Energy Sources (CITIES) Project, as shown on the following.

In summary, a vision for ACP is to be able to state, in a decade or so: "This inhalant is causing that illness; therefore, these abatement techniques should be implemented". Talk about a "revolutionary solution to energy-related biomedical and environmental challenges"! What a contrast to EPA's current "trillion-dollar sledge-hammer approach".
3.3.2 Example vision #2: air pollution and climate change

Although air pollution from energy sources is currently the prime cause of climate-change concerns and although DOE's climate-change program may be the best in the world, DOE's climate-change program is now growing old (the politicians are currently involved in trying to regulate greenhouse gases) and, more importantly, DOE's climate-change program almost totally ignores what is arguably the single most important feature of the Earth's climate: the ocean's thermohaline circulation, driven in large part by North Atlantic Deep Water (NADW) formation. This is the "1000 pound guerrilla in the closet" that most climate-change programs are ignoring.

Changes to NADW formation should be of major concern (Wally Broecker calls it "the Achilles heel of the climate system") not only because of the enormous quantity of heat that is thereby transferred by the ocean from equatorial to polar latitudes in the resulting "thermohaline circulation" but also because there is a wealth of compelling evidence that this "conveyor belt" is unstable, i.e., responds nonlinearly to "small" perturbations. Thus, from Section 2.7.10.2, recall that (e.g., at the Tropic of Cancer): "The oceans carry approximately half of the total meridional heat flux required by the global radiation budget", carrying excess equatorial heat poleward, and "60% of that is accomplished by the overturning cell of the North Atlantic". And recall from Section 2.7.10.10: "Our data [for the termination of the previous interglacial warm period] indicate that climatic shifts are strongly related to deep-water reorganizations and that these changes can occur in a time of the order of a few hundred years or less." From a BER-ESD-ACP perspective, therefore, the obvious question is: what influences do energy-related air pollutants have on NADW formation and hence on the thermohaline circulation of the world's oceans?

Before addressing this question, it might be useful to review some of the major features of the thermohaline (or "thermosaline") circulation. As its name implies, it's driven by both temperature and salinity differences, i.e., by density (or buoyancy) differences of ocean waters. The temperature and salinity of ocean-surface waters are modified by (sensible) heat flux and by precipitation, evaporation, runoff, and the freezing and melting of ice. The relative influence on surface-water buoyancy from these different processes obviously depends on many factors; for typical ocean conditions, evaporation increases the weight of surface water mostly via cooling (being about four times larger than the weight increase from increased salinity). The cumulative ocean-wide increase in surface-water weight from all processes (e.g., cooling and evaporation of water over the entire Gulf Stream) results in two regions of the world where surface waters plunge to great depths: in the North Atlantic (especially in the Labrador and Greenland Seas, driving approximately half of the worldwide thermohaline circulation) and in the South Atlantic, surrounding Antarctica (where weight is added to the water when ice forms, expelling salt, driving the other half of the thermohaline circulation).

Given that the resulting, ocean-wide thermohaline circulation is a major way that the Earth redistributes solar energy, the imperative question is: are humans influencing NADW formation?

Some ways that humans could influence NADW formation via increasing atmospheric concentrations of greenhouse gases are under investigation, mostly numerically (e.g., see Section 2.7.9.1 and Section 2.7.10). These investigations suggest: if with increasing greenhouse gases the upper-ocean warms relative to the deeper-ocean (as is predicted), this will promote the ocean's stability, inhibiting NADW formation; if with increasing greenhouse gases polar regions warm more than equatorial regions (as is occurring), then warmer polar temperatures will result in warmer (and therefore less dense) ocean-surface water, inhibiting NADW formation; if with increasing greenhouse gases polar-region heating results in more ice melt (as is now occurring in the Arctic), then this release of fresh water will result in less dense ocean-surface water, inhibiting NADW formation; and if with global warming more (fresh) water is evaporated from equatorial regions, increasing precipitation in polar regions (as is now occurring), then this too will inhibit NADW formation. Thus, in summary, our increasing greenhouse gases is expected to inhibit NADW formation, weakening the global thermohaline circulation.
That may sound like great news! As humans add greenhouse gases (heating the lower atmosphere), NADW formation decreases, transporting less heat to northern latitudes, counteracting the warming (at least for us at high latitudes of the Northern Hemisphere). But it's a fool's paradise: paleoclimatic data clearly show (e.g., see Section 2.7.10) that the climate system is unstable (or, at least, metastable, with ice ages more stable than "interglacial periods", such as the current Holocene). It's unclear why there have been so many abrupt changes in the climate, e.g., the newly identified "mini-Dansgaard/Oeschger cycles", with a ~1500-year cycle, which occurred during the previous interglacial period and which almost certainly are not caused by orbital (viz., Milankovitch) forcing. Perhaps transporting to northern latitudes less heat (via oceanic circulation) and more water vapor (via atmospheric circulation) leads to more snow and ice (at polar latitudes) and maybe more clouds, therefore higher albedo for the Earth, and therefore less heat from the sun — a natural recipe for an ice age! In any event, if the past 30-and-more years of environmental research has taught us anything it should be not to expect environmental systems to respond linearly to our perturbations.

Now, certainly the ongoing research into the thermohaline circulation should continue, but it's not research that should be led by atmospheric chemists. In contrast, there is another huge area of research on NADW formation that should be led by atmospheric chemists. Thus, besides changes in NADW formation that are expected to arise from greenhouse gas emissions, atmospheric aerosol particles could be significantly influencing NADW formation, via influences on both precipitation and radiative heat transfers (both directly and through influences on radiative properties of clouds). There is no question that these potential influences should be investigated — and they must be investigated by scientists with competence in atmospheric chemistry.

Speculations on some possible influences of energy-related aerosols on NADW formation include the following:

- If the diurnal temperature range (DTR) has decreased over the North Atlantic (as it has, e.g., in the U.S.), generally because nights have become warmer than days have (possibly because of increased air traffic and associated cirrus clouds), then this decreasing DTR might inhibit NADW formation (especially because of the long winter nights of the North Atlantic and the heavy air traffic in this region).
- Soot from North America and from North Atlantic shipping is almost certainly also increasing atmospheric temperatures (absorbing solar radiation when soot particles are both in the air and on surface snow and ice), inhibiting NADW formation.
- But sulfur particles (from North America and from emissions of SO2 from ships) may cool surface waters, promoting NADW formation, with the cooling from direct scattering of solar radiation back to space, from increasing cloud albedo (e.g., "ship tracks"), and possibly from increasing the colloidal stability and therefore the lifetimes of clouds, which generally cool the North Atlantic. In this regard, recall the comments by Weaver and Ramanathan (Section 2.7.10.6): "Over the Northern Hemisphere extratropical oceans during January... clouds have a near-zero, or small positive, net radiative heating effect on the total surface-atmosphere system. The reverse is true during July... clouds... are acting to oppose the seasonal warming... [cooling] often by more than 100 W m-2. The magnitude of net cloud radiative forcing in the extratropics... is such that relatively small percentage changes in cloud cover or cloud properties could result in an anomalous climate forcing of several W m-2, comparable to the direct forcing due to a doubling of CO2. Thus, it is important to understand the physical mechanisms that control cloud radiative forcing in these regions."

The need for greater understanding of changes to radiative forcing of the climate from changes in atmospheric aerosols is clear. Demonstrating exemplary leadership, the previous director of DOE's ESD joined with directors of environmental programs at NASA, NOAA, and NSF to ask the National Academy to recommend a U.S. research program on this topic. I served on the resulting Academy panel; our recommendations (from the final chapter of our report) are shown in Appendix C.
Subsequently, the most recent RFP from ACP stated: "In coordination with other federal agencies, the DOE is addressing recommendations from [this Academy report]", and the RFP solicited "Research to understand the fundamental scientific phenomena associated with aerosol radiative forcing and climate change", listing specific topics shown in Appendix C.

Of course I strongly support investigations of the topics listed in the RFP and Appendix C, but this "shotgun approach" (generally led by individual investigators) is not the best that ACP can do. The target is too broad (the subject is too big), and pointing the program this way overlooks the best that DOE is capable of doing: tackling tough problems (especially those with potential nonlinearities) with a multidisciplinary team.

Instead, suppose ACP aimed at questions dealing with NADW formation. The general question would be: what are the influences of energy-related aerosols on ocean circulation in the North Atlantic? The general thrust would be: for energy-related aerosol particles in the North Atlantic, what's there, where are they from, and what are they doing to NADW formation. Aiming the project this way (rather than trying to illuminate the entire, worldwide blur of aerosol radiative effects) would focus ACP on what is arguably the most critical climate-change question (NADW nonlinearities).

But even aiming ACP this way would be shooting at a very broad target: the North Atlantic is huge! Therefore, almost certainly ACP should tighten the focus of such an initiative, e.g., geographically to the Gulf Stream between Florida and off Cape Hatteras (especially during the winter, when evaporation is most intense, and where the full ~30-40 Sv of warm water is flowing [1 Sv = 10^6 m^3 s^-1], feeding essentially the entire North Atlantic circulation) and to the Labrador Sea (especially during the summer, when any changes to cloud cover would significantly change cloud cooling and where, during the 1990s, approximately 7 Sv of surface water has been sinking). The new project could be viewed as an extension of DOE's ARM program to the Atlantic (in our original plan for ARM, a Gulf Stream CART site was included), but this new project would rely more on DOE's G-1 aircraft than on surface stations, would focus on two regions rather than a single CART site, and the emphasis would be on defining the influence of energy-related aerosols on the air-sea energy budget.

Some obvious questions that the project should address are the following:

- What effects from North American sulfur and soot, influencing both precipitation and evaporation, for both the Gulf Stream and the Labrador Sea;
- What influence from soot and sulfur from ships, which (because of their use of the dregs of the oil refining process) may be releasing as much soot over the North Atlantic as is being released along the entire east coast of North America;
- What influence from aircraft contrails, which if designed to have the most influence on NADW formation probably couldn't choose more influential flight patterns than those now flown over the North Atlantic (even choosing night-time flights, to maximize warming!);
- What changes to indirect radiative forcing, both from the Twomey effect (i.e., increased cloud albedo from more but smaller cloud drops and ice crystals, cooling the ocean during summer) and from colloidal stability (i.e., increased cloud cover, which would warm the ocean surface during winter but cool the ocean-surface during summer);
- What resulting changes in precipitation and surface albedo?

No doubt there are many other questions that need to be addressed (especially those posed by oceanographers, meteorologists, and numerical modelers) and obviously there's a huge number of strategic details that would need to be addressed before this project could get underway, but just as with the "CITIES Project" outlined earlier, I don't plan to address them here. There is even the trivial question of an appropriate acronym, such as the "OCEAN Project" (the Ocean-Circulation Energy-Aerosol Nonlinearities Project), which I'll use for convenience in what follows. Instead, I want to make a general comment and then, in the next section, turn to some more general questions.
My comment deals with my concern about potential changes to the North Atlantic circulation. I don't like to use the expression (in view of its source), but changes to the North Atlantic are potentially the "mother of all nonlinearities": heat the lower atmosphere enough (to shut down the thermohaline circulation) and we may usher in the next ice age! Those who don't understand how we could push a system one way and have it respond another way (e.g., see Section 2.7.10.8b) must never have lost their footing (a natural fluctuation!) while trying to push a heavy car up a steep hill! The point is: unless the Earth's albedo changes, greenhouse gases don't cause global warming (e.g., the stratosphere cools); they cause only a readjustment in the Earth's method of re-radiating the same energy from the Sun 'back to space' (a readjustment that happens to correspond with warmer surface temperatures); more snow, ice, and clouds, however, can decrease the amount of energy the Earth receives from the sun, which in the past has caused ice ages. As Lehman wrote (Section 2.7.10.10): "Numerical models suggest that such a chain of events can be unleashed with very little forcing. In this context, a slight weakening of the ocean circulation can be likened to a sledge-hammer blow — one which could conceivably bring the present interglacial to its knees..."

Now, I won't go quite so far as a particular, prominent, and very competent scientist who suggests that Federal-agency science-program managers should be indicted for criminal negligence for not steering their science projects more appropriately to improve understanding of what humans might be doing to ocean circulation in the North Atlantic, but I would argue as follows. I have no doubt that, if the rate of increase in technological and political competition of humans continues at roughly the pace of the past 50 years, then within 500 years, humans will be able to control the climate. Further, provided climate doesn't take control of humanity first (plunging us into an ice age), I expect that humans will choose to control the climate (within some reasonable bounds), choosing to eliminate not only the threat of climate jumps but even the costs of climate extremes. If, then, BER's mission is "to develop the knowledge needed to identify, understand, and anticipate the long-term health and environmental consequences of energy production, development, and use", and if BER's vision is "to bring revolutionary solutions to energy-related biomedical and environmental challenges", then it follows that BER should "do the needful" to understand what energy-emissions are now doing to NADW formation and to determine what solutions might be available for the future.

3.4 Acquiring vision and leadership

In the above, I have given two illustrations of the type of vision ACP needs, called here the CITIES Project and the OCEAN Project. For symmetry, I also mentioned the possible HACIENDA Project (which, in contrast, would not be led by atmospheric chemists). These three would fit within the previous view of the BER "research pyramid" as shown:
Do I recommend that DOE initiate any of these projects? No!—at least, not until these candidate projects are examined much more closely by scientists more knowledgeable than I. But that’s not the point I’m trying to make. What I wanted to demonstrate is the type of projects that should be undertaken by ACP. That is, I wanted to illustrate the type of vision that ACP needs. Stated more directly: my purpose, here, was not to identify specific visions that ACP should pursue; my purpose was solely to say: ACP needs vision!

How is ACP to acquire the needed vision? Who will supply it? Best for ACP would be the one who has the financial resources to make the vision reality! Next best: someone (or some committee) who can convince the person who has the financial resources, e.g., if not HERAC (BERAC), then a new “Visionary Committee” (e.g., an invited National Academy Panel). And if not the manager who controls the funding and not an advisory group reporting to this manager, then the manager reporting to the manager who controls the funds. And so on down the management chain—but my painful experience is that the farther one goes down the management chain, the less the likelihood of funding. And if none of the above, then the needed vision could be supplied by a strong ACP leader—who, we hope, can convince DOE management to secure the needed resources.

Actually, in the past, it was not unrealistic to expect DOE managers also to be leaders. During my 30-years experience with the ACP (and its predecessors), I had the good fortune to have experienced the leadership of Josh Holland, Rudy Engelmann, Dave Slade and Ari Patrinos. In the more recent past, though, DOE leadership of ACP has weakened. The previous director of the Office of Energy Research (ER) did stimulate the initiation of ACP’s ozone project, but the details of how this stimulation arose were quiet peculiar, not reflecting a continued strong leadership for ACP. Further, there was essentially zero leadership of ACP by previous heads of OHER (now OBER), some infamous examples of which will be omitted. Now, in contrast, ACP is in a better position than at any time during the past 30 years: ACP (via the principal scientist and/or the program manager and/or the director of ESD) can now present a new vision to the director of the OBER and has the once-in-a-lifetime opportunity of being understood!

But my goal, here, is not even to suggest how DOE should conceive of new visions for ACP! My goal is solely to alert DOE: ACP lacks vision. Further, if ACP doesn’t get some vision soon, then I predict that it will soon die—and, from my perspective as a taxpayer, if ACP doesn’t get vision soon, then its death would be desirable. I see little-to-nothing in the current ACP that couldn’t be done as well or better by NSF.

3.5 Summary and recommendations

In summary, I have argued that ACP lacks vision (and the necessary strategy to make progress toward making the vision a reality). The fault I find is lack of visionary leadership (which in general is different from strategic leadership and which, in turn, is generally much easier to find). A capable leader of ACP would have conceived and communicated a clear vision for ACP, obtained strategies to lead the program toward the vision, and marshaled the necessary resources to achieve the program’s goals.

The needed leadership of ACP could come from any of a number of sources: from the ACP’s Principal Scientist, from a panel of ACP’s leading scientists (which is the procedure now used in many NSF programs), from the ACP program manager, from higher administrative levels within DOE, or from any of a number of DOE advisory panels. In any case, though, it’s critically important that any new vision for ACP be seen and enthusiastically supported by DOE management, especially by those managers who control the purse strings! In fact, for ACP’s benefit, the best visionary leadership would be from a scientifically competent DOE administrator who is high enough in the hierarchy to obtain the funds needed to finance the visionary project.
I therefore recommend that DOE managers "do the needful" to define a vision for ACP. And if higher-level DOE managers conclude that neither any DOE manager nor any available (or specifically-charged) advisory committee is likely to accomplish the task adequately, then I recommend that DOE assign a visionary scientist "to do the needful" to define ACP's vision. My own prime candidates for this task are ACP scientists Steve Schwartz or Pete Daum, either of whom (I am confident) will appropriately engage others to accomplish the task. Then, with the vision clear and funding reasonably secure, either of these scientists (or others) should be charged with developing appropriate strategic plans.

And if it were concluded that the two visions used as illustrations here are among the visions that ACP should adopt, then I would recommend that DOE "do the needful" to convince Steve Schwartz to become the lead scientist of the Atmospheric Chemistry Program (or the Atmospheric Sciences Program, or whatever the program might be called), with Pete Daum leading the OCEAN Project and Jeff Gaffney leading the CITIES Project. Also, I would suggest that procedures for the proposals responding to ACP's recent RFP should proceed as planned, because the new OCEAN and CITIES Projects would each require at least two years of planning and easily $10 million per year of funding.

Finally, I would like to add that, viewed in an appropriate light, DOE managers can be seen to be in a most enviable position: they have the opportunity "to make a difference". If they have sufficient vision (and then the resourcefulness to transform their visions into reality), they can accomplish tasks that no others can. And then, when they, too, reach retirement, they will be able to look back at their life's work satisfied with their contributions—even proud of them. In this regard, I suggest that if the CITIES and OCEAN Projects evolve as I think they should, and if DOE managers are wise enough to design into these projects sufficient flexibility to allow surprises, then I essentially guarantee that, at retirement, all involved will take satisfaction from knowing they made a difference.
APPENDIX A

U.S. National Academy of Science Report "Interim Review of the Subsonic Assessment Project", co-authored by the PI and referenced in Section 3.

Reprint - removed for separate processing
APPENDIX B

The original list of hazardous air pollutants (as given in the Clean Air Act) and
EPA's 7/8/96 draft update of this list

Both from http://www.epa.gov/ttn/latw/
The original list of hazardous air pollutants as follows:

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<tr>
<th>CAS Number</th>
<th>Chemical Name</th>
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<tr>
<td>75070</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>60355</td>
<td>Acetamide</td>
</tr>
<tr>
<td>75058</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>98862</td>
<td>Acetophenone</td>
</tr>
<tr>
<td>53963</td>
<td>2-Acetylaminofluorene</td>
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<tr>
<td>107028</td>
<td>Acrolein</td>
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<tr>
<td>79061</td>
<td>Acrylamide</td>
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<tr>
<td>79107</td>
<td>Acrylic acid</td>
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<tr>
<td>107131</td>
<td>Acrylonitrile</td>
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<td>107051</td>
<td>Allyl chloride</td>
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<td>92671</td>
<td>4-Aminobiphenyl</td>
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<td>62533</td>
<td>Aniline</td>
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<tr>
<td>90040</td>
<td>o-Anisidine</td>
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<tr>
<td>1332214</td>
<td>Asbestos</td>
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<tr>
<td>71432</td>
<td>Benzene (including benzene from gasoline)</td>
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<tr>
<td>92875</td>
<td>Benzidine</td>
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<tr>
<td>98077</td>
<td>Benzoic acid</td>
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<td>100447</td>
<td>Benzyl chloride</td>
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<tr>
<td>92524</td>
<td>Biphenyl</td>
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<tr>
<td>117817</td>
<td>Bis(2-ethylhexyl)phthalate (DEHP)</td>
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<tr>
<td>542881</td>
<td>Bis(chloromethyl)ether</td>
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<tr>
<td>75252</td>
<td>Bromoform</td>
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<tr>
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<td>1,3-Butadiene</td>
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<td>156627</td>
<td>Calcium cyanamide</td>
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<td>105602</td>
<td>Caprolactam</td>
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<td>133062</td>
<td>Captan</td>
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<td>75150</td>
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<td>120809</td>
<td>Catechol</td>
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<td>57749</td>
<td>Chlordane</td>
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<td>7782505</td>
<td>Chlorine</td>
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<td>79118</td>
<td>Chloroacetic acid</td>
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<td>532274</td>
<td>2-Chloroacetophenone</td>
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<td>108907</td>
<td>Chlorobenzene</td>
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<tr>
<td>510156</td>
<td>Chlorobenzilate</td>
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</table>
Chloroform
Chloromethyl methyl ether
Chloroprene
Cresols/Cresylic acid (isomers and mixture)
o-Cresol
m-Cresol
p-Cresol
Cumene
2,4-D, salts and esters
DDE
Diazomethane
Dibenzofurans
1,2-Dibromo-3-chloropropane
Dibutylphthalate
1,4-Dichlorobenzene(p)
3,3-Dichlorobenzidene
Dichloroethyl ether (Bis(2-chloroethyl)ether)
1,3-Dichloropropene
Dichlorvos
Diethanolamine
N,N-Diethyl aniline (N,N-Dimethylaniline)
Diethyl sulfate
3,3-Dimethoxybenzidine
Dimethylaminoazobenzene
3,3- Dimethyl benzidine
Dimethyl carbamoyl chloride
Dimethyl formamide
1,1-Dimethyl hydrazine
Dimethyl phthalate
Dimethyl sulfite
4,6-Dinitro-o-cresol, and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
1,4-Dioxane (1,4-Diethyleneoxide)
1,2-Diphenylhydrazine
Epichlorohydrin (1-Chloro-2,3-epoxypropane)
1,2-Epoxybutane
Ethyl acrylate
Ethyl benzene
Ethyl carbamate (Urethane)
Ethyl chloride (Chloroethane)
Ethylene dibromide (Dibromoethane)
Ethylene dichloride (1,2-Dichloroethane)
Ethylene glycol
Ethylene imine (Aziridine)
Ethylene oxide
Ethylene thiourea
Ethylidene dichloride (1,1-Dichloroethane)
<table>
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<tr>
<th>Substance</th>
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<td>Hexamethylene-1,6-diisocyanate</td>
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<td>Hexamethylphosphoramid</td>
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<td>Hydrazine</td>
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<td>Hydrochloric acid</td>
<td>7647010</td>
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<td>Hydrogen fluoride (Hydrofluoric acid)</td>
<td>7664393</td>
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<td>Hydrogen sulfide</td>
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<tr>
<td>Hydroquinone</td>
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<tr>
<td>Isophorone</td>
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<td>Lindane (all isomers)</td>
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<td>Maleic anhydride</td>
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<td>Methyl bromide (Bromomethane)</td>
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<td>Methyl chloroform (1,1,1-Trichloroethane)</td>
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<td>Methyl ethyl ketone (2-Butanone)</td>
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<td>Methyl iodide (Iodomethane)</td>
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<td>Methyl tert butyl ether</td>
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<tr>
<td>4,4-Methylene bis(2-chloroaniline)</td>
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<td>4-Nitrobiphenyl</td>
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<td>4-Nitrophenol</td>
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<td>2-Nitropropane</td>
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<td>N-Nitroso-N-methylurea</td>
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<td>N-Nitrosodimethylamine</td>
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<td>Parathion</td>
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<tr>
<td>Pentachloronitrobenzene (Quintobenzene)</td>
<td>82688</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>87865</td>
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<tr>
<td>Phenol</td>
<td>108952</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>106503</td>
</tr>
<tr>
<td>Phosgene</td>
<td>75445</td>
</tr>
<tr>
<td>Phosphine</td>
<td>7803512</td>
</tr>
</tbody>
</table>
Phosphorus
Phthalic anhydride
Polychlorinated biphenyls (Aroclors)
1,3-Propane sultone
beta-Propioloctone
Propionaldehyde
Propoxur (Baygon)
Propylene dichloride (1,2-Dichloropropane)
Propylene oxide
1,2-Propylimine (2-Methyl aziridine)
Quinolone
Quinone
Styrene
Styrene oxide
2,3,7,8-Tetrachlorodibenzo-p-dioxin
1,1,2,2-Tetrachloroethane
Tetrachloroethylene (Perchloroethylene)
Titanium tetrachloride
Toluene
2,4-Toluene diamine
2,4-Toluene disocyanate
o-Toluidine
Toxaphene (chlorinated camphene)
1,2,4-Trichlorobenzene
1,1,2-Trichloroethane
Trichloroethylene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triethylamine
Trifluralin
2,2,4-Trimethylpentane
Vinyl acetate
Vinyl bromide
Vinyl chloride
Vinyldene chloride (1,1-Dichloroethylene)
Xylenes (isomers and mixture)
o-Xylenes
m-Xylenes
p-Xylenes
Antimony Compounds
Arsenic Compounds (inorganic including arsine)
Beryllium Compounds
Cadmium Compounds
Chromium Compounds
Cobalt Compounds
Coke Oven Emissions
Cyanide Compounds
Glycol ethers2
0 Lead Compounds
0 Manganese Compounds
0 Mercury Compounds
0 Fine mineral fibers
0 Nickel Compounds
0 Polycyclic Organic Matter
0 Radionuclides (including radon)
0 Selenium Compounds
This draft list includes current EPA staff recommendations for technical corrections and clarifications of the hazardous air pollutants (HAP) list in Section 112(b)(1) of the Clean Air Act. This draft has been distributed to apprise interested parties of potential future changes in the HAP list and is informational only. The recommended revisions of the current HAP list which are included in this draft do not themselves change the list as adopted by Congress and have no legal effect. EPA intends to propose specific revisions of the HAP list, including any technical corrections or clarifications of the list, only through notice and comment rulemaking.

<table>
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<th>Chemical Abstracts Service Number</th>
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<tbody>
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<td>75-07-0</td>
<td>Acetaldehyde</td>
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<tr>
<td>60-35-5</td>
<td>Acetamide</td>
</tr>
<tr>
<td>75-05-8</td>
<td>Acetonitrile</td>
</tr>
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<td>98-86-2</td>
<td>Acetophenone</td>
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<td>53-96-3</td>
<td>2-Acetylaminoethylfluorene</td>
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<tr>
<td>107-02-8</td>
<td>Acrolein</td>
</tr>
<tr>
<td>79-06-1</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>79-10-7</td>
<td>Acrylic acid</td>
</tr>
<tr>
<td>107-13-1</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>107-05-1</td>
<td>Allyl chloride</td>
</tr>
<tr>
<td>92-67-1</td>
<td>4-Aminobiphenyl</td>
</tr>
<tr>
<td>62-53-3</td>
<td>Aniline</td>
</tr>
<tr>
<td>90-04-0</td>
<td>o-Anisidine</td>
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<td>1332-21-4</td>
<td>Asbestos</td>
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<td>71-43-2</td>
<td>Benzene (including benzene from gasoline)</td>
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<td>Benzidine</td>
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<tr>
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<td>Benzotrichloride</td>
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<tr>
<td>100-44-7</td>
<td>Benzyl chloride</td>
</tr>
<tr>
<td>92-52-4</td>
<td>Biphenyl</td>
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<td>117-81-7</td>
<td>Bis(2-ethylhexyl)phthalate (DEHP)</td>
</tr>
<tr>
<td>542-88-1</td>
<td>Bis(chloromethyl) ether</td>
</tr>
<tr>
<td>75-25-2</td>
<td>Bromoform</td>
</tr>
<tr>
<td>106-99-0</td>
<td>1,3-Butadiene</td>
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<tr>
<td>156-62-7</td>
<td>Calcium cyanamide</td>
</tr>
<tr>
<td>105-60-2</td>
<td>Caprolactam (Removed 6/18/96, 61FR30816)</td>
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<tr>
<td>133-06-2</td>
<td>Captan</td>
</tr>
<tr>
<td>63-25-2</td>
<td>Carbaryl</td>
</tr>
<tr>
<td>75-15-0</td>
<td>Carbon disulfide</td>
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<td>56-23-5</td>
<td>Carbon tetrachloride</td>
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<td>532-27-4</td>
<td>2-Chloroacetylphenoxy</td>
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<td>Chlorobenzene</td>
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<td>CAS Number</td>
<td>Chemical Name</td>
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<td>510-15-6</td>
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<td>107-30-2</td>
<td>Chloromethyl methyl ether</td>
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<td>126-99-8</td>
<td>Chloroprene</td>
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<tr>
<td>1319-77-3</td>
<td>Cresol/Cresylic acid</td>
</tr>
<tr>
<td></td>
<td>(mixed isomers)</td>
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<td>95-48-7</td>
<td>o-Cresol</td>
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<td>108-39-4</td>
<td>m-Cresol</td>
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<td>105-44-5</td>
<td>p-Cresol</td>
</tr>
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<td>98-82-8</td>
<td>Cumene</td>
</tr>
<tr>
<td>N/A</td>
<td>2,4-D</td>
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<td></td>
<td>(2,4-Dichlorophenoxyacetic Acid)</td>
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<td>(including salts and esters)</td>
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<td>DDE (1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene)</td>
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<td>N/A</td>
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<td>51-79-6</td>
<td>Ethyl carbamate</td>
</tr>
<tr>
<td></td>
<td>(Urethane)</td>
</tr>
<tr>
<td>75-00-3</td>
<td>Ethyl chloride</td>
</tr>
<tr>
<td></td>
<td>(Chloroethane)</td>
</tr>
<tr>
<td>106-93-4</td>
<td>Ethylene dibromide</td>
</tr>
<tr>
<td></td>
<td>(Dibromoethane)</td>
</tr>
<tr>
<td>107-06-2</td>
<td>Ethylene dichloride</td>
</tr>
<tr>
<td></td>
<td>(1,2-Dichloroethane)</td>
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<tr>
<td>107-21-1</td>
<td>Ethylene glycol</td>
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<tr>
<td>151-56-4</td>
<td>Ethylenemimine</td>
</tr>
<tr>
<td></td>
<td>(Aziridine)</td>
</tr>
<tr>
<td>75-21-8</td>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>96-45-7</td>
<td>Ethylene thiourea</td>
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</tbody>
</table>
75-34-3  Ethyldiene dichloride
               (1,1-Dichloroethane)
50-00-0  Formaldehyde
76-44-8  Heptachlor
118-74-1  Hexachlorobenzene
87-68-3  Hexachlorobutadiene
           N/A
1,2,3,4,5,6-Hexachlorocyclohexane
           (all stereo isomers, including
           lindane)
77-47-4  Hexachlorocyclopentadiene
67-72-1  Hexachloroethane
822-06-0  Hexamethylene diisocyanate
680-31-9  Hexamethylphosphoramide
110-54-3  Hexane
302-01-2  Hydrazine
7647-01-0  Hydrochloric acid
           (Hydrogen chloride [gas only])
7664-39-3  Hydrogen fluoride
           (Hydrofluoric acid)
123-31-9  Hydroquinone
78-59-1  Isophorone
108-31-6  Maleic anhydride
67-56-1  Methanol
72-43-5  Methoxychlor
74-83-9  Methyl bromide
           (Bromomethane)
74-87-3  Methyl chloride
           (Chloromethane)
71-55-6  Methyl chloroform
           (1,1,1-Trichloroethane)
78-93-3  Methyl ethyl ketone
           (2-Butanone)
60-34-4  Methylhydrazine
74-88-4  Methyl iodide
           (Iodomethane)
108-10-1  Methyl isobutyl ketone
           (Hexone)
624-83-9  Methyl isocyanate
80-62-6  Methyl methacrylate
1634-04-4  Methyl tert-butyl ether
101-14-4  4,4'-Methylenebis(2-chloroaniline)
75-09-2  Methylene chloride
           (Dichloromethane)
101-68-8  4,4'-Methylene diphenyl diisocyanate
           (MDI)
101-77-9  4,4'-Methylenedianiline
91-20-3  Naphthalene
98-95-3  Nitrobenzene
92-93-3  4-Nitrophenyl
100-02-7  4-Nitrophenol
79-46-9  2-Nitropropane
684-93-5  N-Nitroso-N-methylurea
62-75-9  N-Nitrosodimethylamine
59-89-2  N-Nitrosomorpholine
56-38-2  Parathion
82-68-8  Pentachloronitrobenzene
           (Quintobenzene)
87-86-5  Pentachlorophenol
108-95-2  Phenol
106-50-3  p-Phenylenediamine
75-44-5  Phosgene
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<th>CAS Number</th>
<th>Chemical Name</th>
<th>Notes</th>
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<td>Phosphorus Compounds</td>
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<td>Phthalic anhydride</td>
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<td>1336-36-3</td>
<td>Polychlorinated biphenyls</td>
<td>(Aroclors)</td>
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<td>1120-71-4</td>
<td>1,3-Propane sultone</td>
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<tr>
<td>57-57-8</td>
<td>beta-Propiolactone</td>
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<tr>
<td>123-38-6</td>
<td>Propionaldehyde</td>
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<td>114-26-1</td>
<td>Propoxur</td>
<td>(Baygon)</td>
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<tr>
<td>78-87-5</td>
<td>Propylene dichloride</td>
<td>(1,2-Dichloropropane)</td>
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<td>75-56-9</td>
<td>Propylene oxide</td>
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<tr>
<td>75-55-8</td>
<td>1,2-Propylenimine</td>
<td>(2-Methylaziridine)</td>
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<td>91-22-5</td>
<td>Quinoline</td>
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<td>106-51-4</td>
<td>Quinone</td>
<td>(p-Benzquinone)</td>
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<tr>
<td>100-42-5</td>
<td>Styrene</td>
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<td>96-09-3</td>
<td>Styrene oxide</td>
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<td>1746-01-6</td>
<td>2,3,7,8-Tetrachlorodibenzop-dioxin</td>
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<td>79-34-5</td>
<td>1,1,2,2-Tetrachloroethane</td>
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<td>127-18-4</td>
<td>Tetrachloroethylene</td>
<td>(Perchloroethylene)</td>
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<td>7550-45-0</td>
<td>Titanium tetrachloride</td>
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<td>108-88-3</td>
<td>Toluene</td>
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<td>95-80-7</td>
<td>Toluene-2,4-diamine</td>
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<tr>
<td>584-84-9</td>
<td>2,4-Toluene diisocyanate</td>
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<td>95-53-4</td>
<td>o-Toluidine</td>
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<tr>
<td>8001-35-2</td>
<td>Toxaphene</td>
<td>(chlorinated camphene)</td>
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<td>120-82-1</td>
<td>1,2,4-Trichlorobenzene</td>
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<td>79-00-5</td>
<td>1,1,2-Trichloroethane</td>
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<td>79-01-6</td>
<td>Trichloroethylene</td>
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<td>95-95-4</td>
<td>2,4,5-Trichlorophenol</td>
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<td>88-06-2</td>
<td>2,4,6-Trichlorophenol</td>
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<td>121-44-8</td>
<td>Triethylamine</td>
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<td>1582-09-8</td>
<td>Trifluralin</td>
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<td>540-84-1</td>
<td>2,2,4-Trimethylpentane</td>
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<td>Vinyl acetate</td>
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<td>593-60-2</td>
<td>Vinyl bromide</td>
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<td>Vinylidene chloride</td>
<td>(1,1-Dichloroethylene)</td>
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<td>1330-20-7</td>
<td>Xylenes</td>
<td>(mixed isomers)</td>
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<tr>
<td>95-47-6</td>
<td>o-Xylene</td>
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<tr>
<td>108-38-3</td>
<td>m-Xylene</td>
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</tr>
<tr>
<td>106-42-3</td>
<td>p-Xylene</td>
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<tr>
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<td>Antimony Compounds</td>
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<td></td>
<td>Arsenic Compounds</td>
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<tr>
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<td>(inorganic including arsine)</td>
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<tr>
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<td>Beryllium Compounds</td>
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<td>Cadmium Compounds</td>
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<td>Chromium Compounds</td>
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<td>Cobalt Compounds</td>
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<td>Coke Oven Emissions</td>
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<td>Cyanide Compounds</td>
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<td>Glycol ethers</td>
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<td>Lead Compounds</td>
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<td></td>
<td>Manganese Compounds</td>
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</tbody>
</table>
Mercury Compounds
Fine mineral fibers
Nickel Compounds
Polycyclic Organic Matter
Radionuclides (including radon)
Selenium Compounds

NOTE: For all listings above which contain the word "compounds" and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

1X'CN where \( x \) = \( H \) or any other group where a formal dissociation may occur. For example, K\( \text{CN} \) or Ca(CN)\( \text{2} \).

2 (Under review)
Glycol Ether definition draft options:

Possible Correction to CAA 112(b)(1) footnote that would be consistent with OPPTS modified definition.

New OPPTS definition as published is:

\[
R-(OCH_2CH_2)_n-OR' \quad \text{where:}
\]

\( n = 1, 2, \text{ or } 3 \)
\( R = \text{alkyl C7 or less} \)
or \( R = \text{phenyl or alkyl substituted phenyl} \)
\( R' = \text{H or alkyl C7 or less} \)
or \( OR' = \text{carboxylic acid ester, sulfate, phosphate, nitrate or sulfonate} \)

CAA Glycol ether definition exactly as in the statute (errors included):

"Includes mono- and di ethers of of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH_2CH_2)_n-OR' where \( n = 1, 2, \text{ or } 3 \)
\( R = \text{alkyl or aryl groups} \)
\( R' = \text{R, H or groups which, when removed, yield glycol ethers with the structure R-(OCH_2CH)n-OH. Polymers are excluded from the glycol category.} \)

CAA Glycol ether definition with technical correction made.
(A 2 was left out of the last formula)

"Includes mono- and di- ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH_2CH_2)n-OR' where \( n = 1, 2, \text{ or } 3 \)
\( R = \text{alkyl or aryl groups} \)
\( R' = \text{R, H, or groups which, when removed, yield glycol ethers with the structure: R-(OCH_2CH_2)n-OH. Polymers are excluded from the glycol category.} \)

3 (Under Review)
5A type of atom which spontaneously undergoes radioactive decay.
APPENDIX C

Chapter 4 (Recommendations) from the U.S. National Academy of Science Report "Aerosol Radiative Forcing and Climate Change"

Co-authored by the PI and referenced in Section 3.

Reprint - removed for separate processing