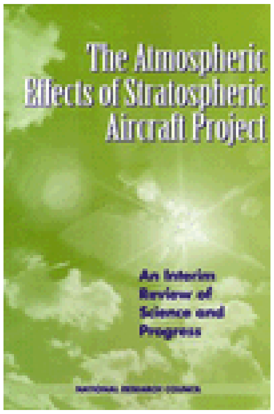

The Atmospheric Effects of Stratospheric Aircraft Project: An Interim Review of Science and Progress

Panel on Atmospheric Effects of Aviation, National Research Council

ISBN: 0-309-52392-3, 68 pages, 6 x 9, (1998)

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THE NATIONAL ACADEMIES
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The Atmospheric Effects of Stratospheric Aircraft Project

An Interim Review of Science and Progress

Panel on Atmospheric Effects of Aviation
Board on Atmospheric Sciences and Climate
Commission on Geosciences, Environment, and Resources
National Research Council

NATIONAL ACADEMY PRESS
Washington, D.C. 1998

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Support for this project was provided by the National Aeronautics and Space Administration under grant NASW-4938 order No. 109. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the above-mentioned agency.

International Standard Book Number 0-309-06095-8

Additional copies of this report are available from:
National Academy Press
2101 Constitution Ave., NW
Box 285
Washington, DC 20055
800-624-6242
202-334-3313 (in the Washington, D.C., metropolitan area)

Printed in the United States of America

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Preface

The Atmospheric Effects of Stratospheric Aircraft (AESA) project is the stratosphere-oriented half of NASA's Atmospheric Effects of Aviation Project (AEAP). A component of the High-Speed Research Program, AESA is a comprehensive effort to predict the atmospheric impacts of a future fleet of supersonic aircraft flying in the stratosphere. AESA, which began in FY 1990, completed its first phase and issued an assessment report in November 1995. NASA issued an interim assessment in 1993, which was evaluated by an NRC Panel on the Atmospheric Effects of Stratospheric Aircraft in a document issued in 1994. The project has now entered a second phase; its final assessment report is due in late 1998.

The present review of AESA is the product of the NRC Panel on the Atmospheric Effects of Aviation (PAEAN). PAEAN members were selected to provide expertise in relevant fields that include field observations, laboratory chemistry, atmospheric dynamics and modeling, aircraft engines, and climate. The charge from its NASA sponsor, AEAP, is to provide assessment of and guidance to AEAP by evaluating the appropriateness of the AEAP's research plan, appraising the project-sponsored results relative to the current state of scientific knowledge, identifying key scientific uncertainties, and suggesting research activities likely to reduce those uncertainties. In 1997 the panel published *Interim Review of the Subsonic Assessment Project* and *An Interim Assessment of AEAP's Emissions Characterization and Near-Field Interactions Elements*; this report completes PAEAN's first evaluation of AEAP's activities.

While the effects of the current subsonic fleet are perhaps of more urgent concern at the moment, PAEAN has been asked to assess how well the state of scientific knowledge will allow an informed decision to be made at the end of 1998 regarding the possible atmospheric impact of a future fleet of high-speed civil transport aircraft. The purposes of this panel's report on AESA are two: to evaluate the progress of AESA-sponsored research since 1990, and to provide recommendations for future direction of the project.

When PAEAN was formed, it included sixteen people. To produce its first reports, it broke up into working groups—supersonic/stratospheric, subsonic/tropospheric, and emissions. The original stratospheric group put together the initial draft of this document, and we thank them for their efforts. We appreciate the skill and perseverance of our study director and editor, Ellen Rice; the knowledgable assistance of staff officer Laurie Geller; and the administrative support of Doris Bouadjemi. Last, we are grateful to the many people, both those involved with AEAP and those outside it, who through briefings and reports have kept us apprised of the progress of AESA and the science.

Albert J. Kaehn, Jr.
PAEAN Chair

Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the NRC in making the published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The content of the final report is the responsibility of the NRC and the study committee, and not the responsibility of the reviewers. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals, who are neither officials nor employees of the NRC, for their participation in the review of this report:

Thomas E. Graedel, Yale University
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Robert D. Hudson, University of Maryland
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Lynn M. Russell, Princeton University
Anne K. Smith, National Center for Atmospheric Research
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While the individuals listed above have provided many constructive comments and suggestions, it must be emphasized that responsibility for the final content of this report rests entirely with the authoring committee and the NRC.

Contents

Executive Summary

Scientists and policy-makers alike are concerned that operation of a fleet of high-speed civil transport (HSCT) aircraft could significantly affect the global atmosphere. HSCT emissions may have a direct effect on the chemistry of the atmosphere, leading to changes in the distribution of ozone; they may also have indirect effects on ozone and on global climate through coupling with radiative and dynamical processes in the atmosphere. An assessment of the atmospheric impact of a fleet of HSCTs thus requires not only an understanding of the chemistry of the natural stratosphere and its possible perturbations by HSCT emissions, but also an understanding of the pathways for transport of HSCT emissions within the atmosphere, and the resulting temporal and spatial distribution of HSCT emissions.

The results of NASA's Atmospheric Effects of Stratospheric Aircraft (AESA) project were summarized in a 1995 NASA assessment. The present report looks at that summary and at more recent work to evaluate the state of the science. AESA has made good progress in the past few years. Satellite and aircraft observations have elucidated important aspects of large-scale transport processes. Field campaigns have provided a much better picture of the relative importance, below 20 km altitude, of the major catalytic cycles for ozone destruction. Careful intercomparisons of assessment models have led to reduction of some of the differences among the models. However, a number of uncertainties and inconsistencies still remain.

Transport Processes

Subsonic aircraft fly in the lowermost part of the stratosphere, where material is exchanged across the tropopause on time scales of a few months. HSCTs, however, would fly in the region of the stratosphere above about 16 km, from which exchange with the troposphere occurs only through a slow, global-scale vertical circulation. This slow movement determines the rate at which HSCT emissions are transported into the regions of the stratosphere in which exhaust components could be important catalysts for ozone destruction. Within the region above 16 km, horizontal transport by eddy motions is important for determining the distribution of chemical constituents. Accurate model treatment of these transport processes is necessary for estimating the spatial and temporal distributions of HSCT emissions, and is thus essential to prediction of the emissions' potential effects on ozone distribution and on climate.

Chemical Processes

Uncertainties related to gas-phase chemistry are less than those associated with heterogeneous chemistry on aerosol particles. Stratospheric aerosols arising from natural sources play a key role in the chemistry of the ozone layer as a result of the reactions that occur on their surfaces. Because emissions from a fleet of HSCTs might be a significant additional source of aerosols, and because reactions on aerosols appear to be important in converting nitric oxides to nonreactive species, it is important that reactions on both natural and aircraft-related aerosols be better understood. Predicted ozone reduction is greatly diminished if the heterogeneous reactions that occur on aerosols in the mid-latitudes are included in assessment models. However, substantial additional ozone depletion may occur in polar regions in response to HSCT emissions, because of heterogeneous chemistry involving polar stratospheric clouds (PSCs).

Assessment Models

The models used by AESA for assessment of HSCT-induced changes in the ozone layer have been two-dimensional (2-D) models with highly parameterized representations of transport and mixing. Model intercomparisons indicate that the 2-D models all predict similarly small impacts of HSCTs on total ozone. Within that total column amount, however, their predictions vary noticeably at some altitudes. There are also a number of differences between models and measurements that need to be resolved. How well 2-D models treat the sensitive role of transport can be tested only by comparison with 3-D chemical–transport models, such as the 3-D model being developed under AESA's Global Modeling Initiative.

Climate Impacts

Recent general-circulation model studies have examined the impact on surface climate of HSCT-induced changes in the global ozone and water-vapor distributions. These studies suggest that such emissions should have no significant direct impact on climate. HSCT-emitted sulfur aerosols are also expected to play a small role in climate compared to other aerosol sources, but more analysis is needed. Contrail formation is not expected to occur at the altitudes at which HSCTs will fly, although indirect radiative impacts may result if HSCT emissions enhance the formation of PSCs.

Recommendations

On the basis of its evaluation of the science and AESA's progress, the Panel on Atmospheric Effects of Aviation makes the following recommendations to NASA:

Transport Processes: There is still considerable uncertainty about atmospheric transport above 20 kilometers. **PAEAN recommends that AESA emphasize analysis of data from aircraft missions and satellites, in order to quantify better the meridional and vertical transport in the stratosphere, particularly at altitudes between 20 and 30 kilometers.**

Polar Processing: The processing of HSCT emission products in the polar regions is not adequately represented in current 2-D models, since the evolution of polar stratospheric cloud particles is not yet understood. **PAEAN recommends that AESA support field measurements as well as model developments that are specifically designed to unravel the complex formation process of polar stratospheric cloud particles.**

Assessment Models: Three-dimensional transport effects are of crucial importance for understanding the potential impact of a fleet of HCSTs, and the use of the NASA's GMI model will be required for future assessments. **PAEAN recommends that AEAP continue to support the development and testing of the Global Modeling Initiative model.**

Microphysics in the Plume-Wake Region: The processes (both gas-phase and heterogeneous) within the plume-wake region need to be properly described so that they can be incorporated into large-scale atmospheric models. **PAEAN recommends that the development of microphysical models of the plume-wake regime continue, in order to assess the role of the chemical and physical transformations that may occur before engine effluents mix into the background atmosphere**.

Climate Studies: Because of the complexity of the climate system, further climate studies by AESA may not yield significant progress in the near future. Research to date suggests that the globally averaged direct radiative impact of stratospheric aircraft emissions can be expected to be small, although the effects of aerosols must be better quantified. **PAEAN recommends that AESA continue its present policy of not undertaking model studies of the impact of aviation on climate, beyond calculating the degree of radiative forcing by components of HSCT exhaust.**

Beyond the 1998 Assessment: Many of the uncertainties discussed in this volume have not yet been sufficiently reduced to permit an informed assessment of the possible impact of a fleet of HSCTs to be made. Research in the years to come must focus on those critical uncertainties first. **PAEAN recommends that AESA draw up and execute an adequately detailed plan that sets priorities for research to reduce the remaining critical uncertainties.**

1

Introduction and History

Scientists and policy-makers alike are concerned that operation of a fleet of high-speed civil transports (HSCTs) could significantly alter important physical and chemical processes of Earth's atmosphere.* A recent NASA report (Stolarski et al., 1995) states that for every kilogram of current jet fuel burned, such future aircraft would typically emit the following mass amounts of these species of concern: 3155 g of carbon dioxide (CO_2), 1237 g of water (H_2O), 18 g of oxides of nitrogen (NO_x), 3.5 g of carbon monoxide (CO), and less than 1 g each of sulfur dioxide (SO_2), hydrocarbons, and soot or carbon (C). Each of these emission products is capable of directly affecting the atmosphere in one or more of the following ways: destruction of ozone, production of ozone, absorption and scattering of incoming solar radiation, absorption and emission of infrared (heat) radiation. Through various feedback processes these direct influences may lead to other, indirect effects on the chemistry of the atmosphere or on climate. To assess the impact of aircraft emissions, the aircraft component of each effect should be evaluated quantitatively and compared with the magnitude of the global natural component. NASA's Atmospheric Effects of Aviation Project (AEAP), in particular its Atmospheric Effects of Stratospheric Aircraft (AESA) portion, is largely devoted to these goals.

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*The inevitable increase in global demand for commercial air travel can be met either by a marked increase in the size of the subsonic-aircraft fleet, or by the introduction of supersonic aircraft. These options will have somewhat different environmental consequences. This report deals only with the projected atmospheric impacts of a supplemental fleet of 500 HSCTs.

The history of the study of atmospheric impacts of high-speed commercial aircraft began about 25 years ago with the Climatic Impact Assessment Program (CIAP), which was sponsored by the U.S. Department of Transportation over the period 1972 to 1975. Research on stratospheric ozone begun under CIAP has continued in NASA's Upper Atmosphere Research Program (UARP) since 1976. Although not specifically directed at assessing the effects of aircraft on the stratosphere, UARP contributes to the general understanding of the stratosphere that is essential for realistic assessments. In 1991, the UARP sponsored the first reviews of the impact of aircraft emissions on the stratosphere (Johnston et al., 1991; Douglass et al., 1991) that had been made in 15 years. The most recent effort, AESA, was initiated as part of NASA's High-Speed Research Program in 1988. For proper evaluation, AESA must be examined in the context of the entire NASA program of stratospheric research.

Since its inception, AESA has produced a number of significant reference publications. *The Atmospheric Effects of Stratospheric Aircraft* (Prather et al., 1992) reported on the three-day workshop in 1990 that defined seven critical needs for AESA, described the scope of the research being sponsored by AESA, and presented initial results. A second program report appeared early the following year (Stolarski and Wesoky, 1993a), together with a three-volume report on the 1992 Models and Measurements workshop (Prather and Remsberg, 1993). They were followed by the third program report (Stolarski and Wesoky, 1993b) and an *Interim Assessment Report of the High-Speed Research Program* (Albritton et al., 1993) that focused on AESA's research and the potential impact of HSCTs on the ozone layer.

The 1993 assessment report was formally reviewed by the National Research Council's Panel on the Atmospheric Effects of Stratospheric Aircraft. Their evaluation is contained in the report *Atmospheric Effects of Stratospheric Aircraft* (NRC, 1994). The report focused on the key scientific uncertainties associated with the impact of stratospheric aircraft. The top three uncertainties, in the opinion of the panel, were:

- Dispersion characteristics of HSCT effluents in the lower stratosphere
- Physical and chemical properties of stratospheric aerosols and PSC particles
- The climate effects of the HSCT fleet.

Also of importance, the panel thought, were issues related to the accuracy of flight and emissions scenarios, the modeling of plume and wake chemistry and dynamics, the adequacy of two-dimensional (2-D) models for the HSCT assessment, and model sensitivity studies. The 1994 NRC review closed with recommendations intended to guide NASA in their efforts to reduce uncertainties in predictions and to provide advice for better use of existing data. Highest priority was given to recommendations addressing the issues above; other recommendations included development of instruments for particle measurements, evaluation of how the Pinatubo aerosol cloud evolved, more model-to-model comparisons, and utilization of UARS and other satellite data for model development and verification.

In 1995 AESA commissioned an assessment of scientific predictions of the potential impact of a fleet of HSCTs. This second assessment, Stolarski et al. (1995), summarizes the topics of concern to AESA at the end of 1995 and offers strategies for reducing uncertainties about the effects of aviation. (It does not, unfortunately, include progress reports on microphysical models and aerosol instrumentation, evaluation of the lessons learned from the Pinatubo cloud, or discussion of the applications of UARS and other satellite datasets and their assimilation into models, as the AESA panel had requested.) The present NRC Panel on Atmospheric Effects of Aviation (PAEAN) has used Stolarski et al. as the focus of their evaluation of AESA's progress.

To fulfill the promise of the word "Science" in the title of the present report, *An Interim Review of AESA: Science and Progress*, this review repeats some material in Stolarski et al. as needed background (Chapter 2), gives in some detail aspects of pertinent science that are not fully stated by Stolarski et al. (Chapter 3), and comments on some more recent issues (Chapter 4). Chapter 5 presents PAEAN's recommendations, some of which echo the strategies in Stolarski et al., and some of which are new. The "Progress" in this PAEAN report's title can be seen as it restates the situation that existed just before and just after AESA research started in 1990, and compares it with the project's status as reported in later AESA publications, especially Stolarski et al., and with certain articles published during 1996 and 1997.

Thomas Graedel, Chairman of the NRC's AESA Panel, emphasized in his testimony (Graedel, 1994) to the Subcommittee on Technology, Environment, and Aviation of the U.S. House of Representatives that two years would not be enough to reduce the uncertainties associated with the effects of a fleet of HSCTs, and that "the assessment's overall reliability will not change significantly by 1995." Stolarski et al. confirms his statement; it remains to be seen how far those uncertainties will have been reduced by AESA's end.

2

Scientific Background for HSCT Concerns

ATMOSPHERIC STRUCTURE AND DYNAMICS

The simplest model for qualitatively understanding the observed distribution of trace constituents in the stratosphere consists of advection by a single meridional cell in each hemisphere with uniform rising in the tropics, poleward drift, and, by continuity of mass, a subsiding flow in the extratropics. Such a circulation was proposed by Brewer (1949) who pointed out that the observed aridity of the stratosphere (water-vapor mixing ratios of a few ppmv) could be understood only if water vapor were transported into the stratosphere by an upwelling circulation confined to the tropics, where air parcels would be "freeze-dried" as they went through the cold tropical tropopause. Somewhat later Dobson (1956) pointed out that poleward and downward advection by this type of mean circulation was consistent with the observed maximum concentration of ozone in the lower polar stratosphere, far from the region of maximum photochemical production. The "Brewer-Dobson" model, as it is now called, clearly demonstrated the importance of the global-scale circulation in determining the observed distribution of ozone. It also provided a partial, but by no means complete, model for transport in the stratosphere.

Stratospheric–Tropospheric Exchange

Stratospheric–tropospheric exchange is better understood now than it was at the time of the last NASA assessment. The work of Holton et al. (1995) described below provides a simple way to view this exchange, as far as the HSCT is concerned.

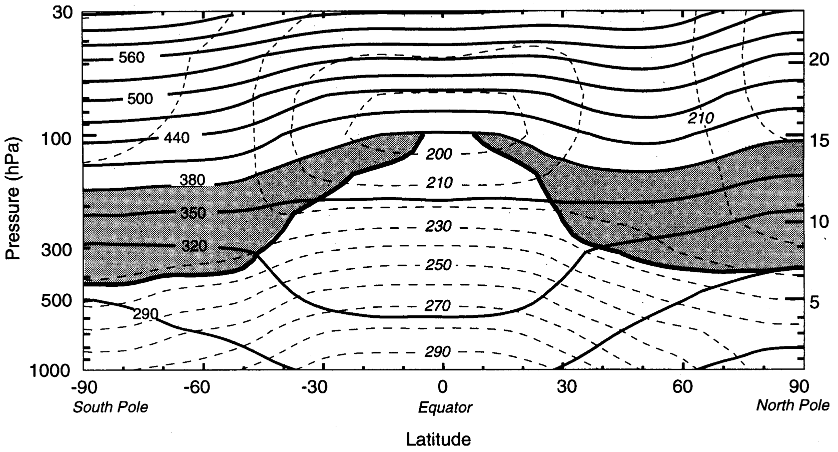

FIGURE 1 Latitude–altitude cross-section for January 1993 showing zonally averaged potential temperature (solid contours) and absolute temperature (dashed contours). The heavy solid contour (cut off at the 380K isentrope) approximates the tropopause outside the equatorial zone, while the 380K isentrope approximates the equatorial tropopause. The shaded areas denote the "lowermost stratosphere", where isentropic surfaces span the tropopause. (From Holton et al., 1995; reprinted with permission of the American Geophysical Union.)

Earth's atmosphere is classified in terms of a number of concentric layers. The two lowest layers, the troposphere and the stratosphere, are of primary concern for aircraft-related issues. Figure 1 shows in solid contours the meridional distribution of zonally averaged potential temperature (a measure of entropy) and in dashed contours the absolute temperature in January 1993 from the surface to 25 km altitude. The heavy dark line is the tropopause, which is the separation between the troposphere and stratosphere; the stratosphere extends up to 50 km altitude, and only the lower portion is shown. The shaded areas include the portion of the stratosphere in which lines of constant potential temperature (isentropes) connect the stratosphere and troposphere; in the field of atmospheric dynamics this region is called the "lowermost stratosphere". Above the shaded areas is the portion of the stratosphere in which the isentropic surfaces do not cross the tropopause; this region is called the "overworld" (see Holton et al. 1995), a specific technical term used to avoid confusion with qualitative statements such as "lower" or "middle" stratosphere. The temperature inversion throughout the stratosphere confers stability on the air against vertical mixing and vertical motion, but it does not inhibit horizontal motions. In contrast, tropospheric air undergoes strong vertical mixing, mainly because of moist convection.

As shown schematically in Figure 2, stratosphere–troposphere exchange oc-

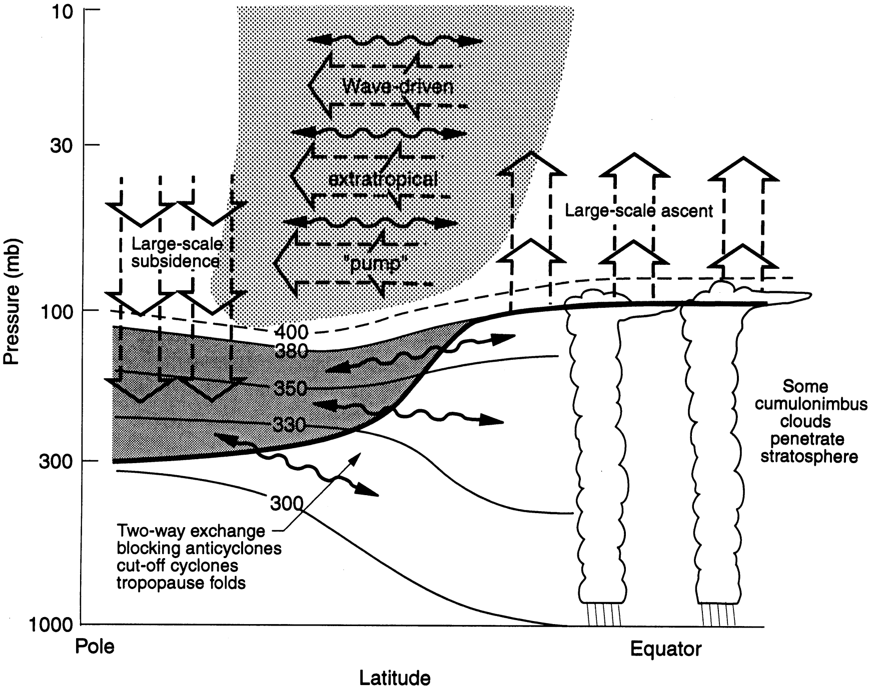

FIGURE 2 Dynamical aspects of stratospheric transport and stratosphere–troposphere exchange. The tropopause is shown by the thick line. Thin lines are isentropic (constant potential temperature) surfaces labeled in kelvins. The heavily shaded region is the "lowermost stratosphere" where isentropic exchange occurs by tropopause folding and small-scale mixing. The region above 380K is the "overworld", in which isentropes lie entirely in the stratosphere. Light shading denotes wave-induced forcing of the global-scale vertical circulation (shown as broad arrows). The wavy double-headed arrows denote quasi-adiabatic meridional transport by eddy motions. (From Holton et al., 1995; reprinted with permission of the American Geophysical Union.)

curs through both isentropic transport (i.e., transport along surfaces of constant potential temperature) and mixing in the lowermost stratosphere. Exchange of air between the overworld and the troposphere, however, occurs only through a global-scale cross-isentropic circulation driven by the pumping action of wave-induced forces in the extratropical stratosphere. This wave-induced pumping pulls air upward and poleward from the tropical troposphere into the stratosphere and pushes it poleward and downward into the extratropical lowermost stratosphere (Holton et al., 1995). Note that vertical transport from the overworld into the lowermost stratosphere, not quasi-horizontal exchange across the tropopause, is the rate-limiting process for exchange between the chemically important region of the stratosphere and the troposphere.

These considerations are important to AESA because they show that aircraft flying in the overworld represent a qualitatively different situation with respect to atmospheric effects from aircraft flying in the lowermost stratosphere, because of the persistence of exhaust components. The proposed fleet of HSCTs would spend most of its flight time in the overworld, while the current subsonic fleet flies in the upper troposphere and the lowermost stratosphere. Thus, transport and exchange processes for a supersonic fleet's exhaust components, and the time scales on which they operate, are expected to be quite different from those for the subsonic fleet emissions.

Differences in transport between the overworld and the lowermost stratosphere were also evident in the time evolution of stratospheric radioactive debris following the nuclear bomb tests of 1961-1962. For years after the conclusion of the bomb tests, all forms of radioactive fallout occurred with especially high intensity at mid-latitudes in the spring. Carbon-14 (written ^{14}C), in the form of gaseous carbon dioxide, moved rapidly with longitude around the globe in both regions of the stratosphere. The residence time of ^{14}C deposited in the overworld was about 2 years if deposited between 17 and 20 km and about 5 years if deposited between 25 and 30 km (Telegadas, 1967, 1971; Telegadas et al., 1972; Kinnison et al., 1994a). Both gaseous ^{14}C and the heavy-metal radioactive debris incorporated in stratospheric aerosols had stratospheric residence times of about six months if they were deposited in the lowermost stratosphere. The longer residence times of ^{14}C in the overworld, by comparison with ^{14}C and other radioactive debris in the lowermost stratosphere, demonstrate that for transfer of HSCT exhaust from the stratosphere to the troposphere, the rate-limiting step is the relatively easily evaluated vertical transport from the overworld into the lowermost stratosphere, not the intermittent, very complicated, quasi-horizontal exchange across the tropopause.

A simple mental picture of stratosphere–troposphere transport for both subsonic-aircraft and HSCT exhaust is to visualize the lowermost stratosphere as a large reservoir for chemical constituents that is replenished from above by diabatic descent across the boundary of the overworld, and undergoes horizontal leakage on its equator-facing side, especially in the springtime, as well as some down-directed leakage. Exhaust gases from subsonic aircraft accumulate continuously in this reservoir. The HSCT exhaust gases emitted in the overworld leak slowly (years) by diabatic descent into the lowermost stratospheric reservoir, where they also accumulate. In the spring a large "gate valve" opens for several weeks, and a large amount of air with its contained aircraft exhaust is flushed horizontally into the troposphere along the isentropes. The average residence time of subsonic exhaust gases in the stratosphere is about 6 months, but average residence time of HSCT exhaust gases in the stratosphere is more than 2 years.

Natural Ozone Distribution and Transport

The impacts of HSCT emissions must be assessed in the context of ozone's natural climatology. The global distribution of ozone by latitude and altitude is illustrated in Figure 3. The upper panel presents observed ozone concentrations. Relatively high ozone concentrations are found in an arching band from pole to pole, with maximum concentrations at ~19 km at the poles and ~23 km in the mid-latitudes. The lower panel of the figure shows the distribution of ozone mixing ratios by latitude and altitude. (A concentration is an absolute quantity, whereas a mixing ratio is the number of a given type of molecule relative to the sum of all molecules present. The decrease in atmospheric density with altitude makes both quantities useful.) The two heavy lines added to Figure 3 show two local ozone photochemical-replacement times, which are computed by dividing the local ozone concentration (from the upper panel) by twice the local rate of oxygen photolysis; the upper curve shows where the replacement time is 1 month, and the lower curve where it is 4 months. The band between these two curves can be viewed as separating the regions under chemical and dynamical control. The "chemically controlled region" is the ozone-formation region, where the ozone steady state is controlled primarily by local chemistry, but also by the past transport of ozone-destroying species in this region. The "dynamically controlled region" is the ozone-reservoir region, where the ozone steady state is controlled primarily by atmospheric dynamics, but also by the history of ozone destruction in this region.

During late fall, the tilting of Earth's axis in orbit shades the parcels of air above that hemisphere's polar region from sunlight. This "polar night" quenches both ozone production and loss, thereby "freezing" the existing high local ozone mixing ratio. This high mixing ratio is then further increased as ozone in the middle stratosphere is transported into the polar-night region by quasi-horizontal eddy motions. Within a few months, the ozone in the polar vortex is transported downward into the lower overworld by diabatic circulation (Rosenfield et al., 1994). Horizontal eddy diffusion, with net transport toward lower latitudes as shown in Figure 2, then replenishes ozone in the pole-to-pole arching band of maximum concentration shown in the upper panel of Figure 3.

Ozone concentrations in this maximum-concentration band thus depend on the chemistry in the mid-stratospheric region where the air entered the polar night, as well as on the dilution that occurred as the air descended into the lower overworld and spread into lower latitudes. Ozone production is quenched sooner than ozone destruction in the air entering polar night, so the ozone mixing ratio decreases. The changing photochemical steady state in that region also affects ozone concentration. The rate at which the air is transferred into the polar night thus can have an impact on the mixing ratios in both the polar-night region and the band of maximum concentration. Atmospheric-model results need to be compared with observations to determine how well the models currently repre-

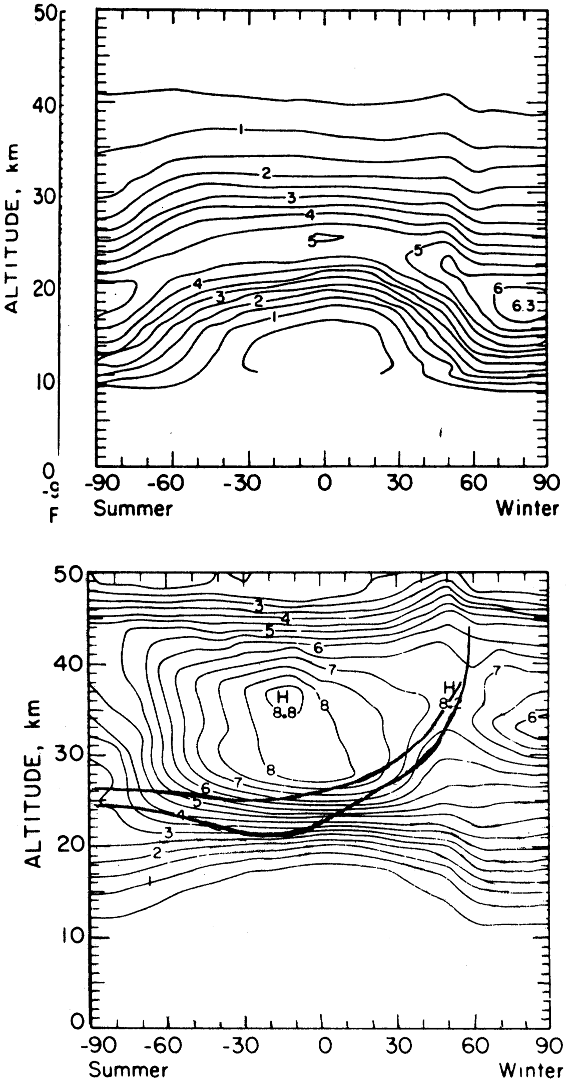

FIGURE 3 Contour plots showing examples of two-dimensional distributions of ozone. Upper panel: Concentration (number density) in units of 10^{12} molecules cm^{-3}. Lower panel: Mixing ratios in parts per million by volume. The superimposed heavy lines indicate where the local ozone photochemical replacement time ($[O_3]/2j[O_2]$) is 4 months (lower line) and where it is 1 month (upper line). The area above and to the left of the upper heavy line may be interpreted as the ozone-formation region; the area below and to the right of the lower heavy line may be interpreted as the ozone-reservoir region. (Upper panel is from Solomon et al., 1980; lower panel is modified from that article. Both reprinted with permission of Birkenhaeuser Publishers.)

sent this feature. Long model runs are needed to fully simulate these evolving processes.

Our quantitative understanding of the chemical and dynamical processes that control ozone distribution has been greatly improved by AESA-sponsored field campaigns. In 1990 (see Prather et al., 1992), AESA worked out plans and priorities for extensive simultaneous measurements of multiple species in the stratosphere using the NASA ER-2 aircraft up to the top of its flight range (20 km altitude), and later plans were made to use a proposed new unmanned aircraft in the 20 to 27 km altitude range. (Ultimately, development of the unmanned aircraft did not proceed fast enough for it to be used, and balloon measurements had to be substituted.) Stolarski and Wesoky (1995) describe the multiple-flight Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE), made in 1992-1993. In this campaign, almost all reactive species were measured simultaneously to provide definitive answers to some important chemical questions (discussed later in this chapter). The simultaneous observations of long-lived gases, in conjunction with recently developed understanding of atmospheric dynamics, provided investigators with quantitative new information about transport. Tracer data obtained by SPADE, and by more recent campaigns discussed under Atmospheric Measurements, have yielded extremely useful information about atmospheric motions that provides new structure and details to the Brewer-Dobson general-circulation model. These ideas are now being incorporated into models (see, for example, Plumb, 1996), and underlie the discussions of the formation and distribution of natural ozone in this report.

Transport Barriers Within the Overworld

Given the importance of transport history in understanding the distribution of ozone, it is desirable that the spatial and temporal variability of transport be well understood in order to account properly for transport in models. A key issue in this regard is the existence of so-called “barriers” to transport.

It has long been recognized that the tropopause acts to some extent like a quasi-permeable barrier to constituent transport and stratosphere-troposphere exchange. In more recent years it has become clear that there are also quasi-permeable transport barriers within the stratosphere itself. Such barriers separate the tropics from the mid-latitudes and the mid-latitudes from the winter polar vortex. These barriers are typically characterized by strong gradients in the zonal wind and steep gradients in various chemical species. Erosion at the edges of such barriers produces filamentary structure in chemical constituents determining the degree of “leakiness” across such barriers is key to understanding the fate of aircraft emissions and of other long-lived chemical constituents; the importance of such “transport barriers” for the HSCT assessment is clearly recognized in the 1995 NASA assessment.

The increase in global coverage of trace constituents in the stratosphere provided by the Upper Atmosphere Research Satellite (UARS) has made possible many advances in understanding the development and maintenance of the polar and subtropical barriers in the region above about 20 km, where the dynamics is dominated by planetary Rossby wave breaking (Plumb et al., 1994).

The theoretical behavior of the transport barriers in the bottom layer of the overworld (between about 16 and 22 km, or the 380-480K isentropes) is less well understood than their behavior at higher altitudes. In the 16-22 km region the upward extensions of tropospheric disturbances, including synoptic-scale extratropical storms and continental-scale monsoon circulations, can play a considerable role in transport. Evidence from a number of sources suggests a higher degree of leakiness in the 16-22 km altitude range across both the polar and subtropical transport barriers than at greater altitudes (see, e.g., Minschwaner et al., 1996). Since 18-21 km is the altitude range at which HSCT emissions will occur, it is important that accurate quantitative estimates (including temporal and spatial variability) be developed for the rates at which mass and trace constituents are transported between the mid-latitude northern hemisphere air corridors and the polar vortex as well as those corridors and the tropical-upwelling region. This is one of the objectives of the Stratospheric Tracers of Atmospheric Transport (STRAT) mission that is supported by the AESA project. It should be noted, however, that the 20 km level is the ceiling for ER-2 operations, and much of the new information obtained by AESA concerning atmospheric composition and dynamics is limited to altitudes below 20 km. Thus, evidence suggesting a change in transport regime at about this altitude must be treated with caution, because above this level nearly all observations are based on satellite remote sensing.

Meridional wave transport and mixing are inhibited at the edge of the polar winter vortex, so the vortex region is relatively isolated chemically. There is also evidence that an analogous inhibition of wave transport occurs in the subtropics. The possible existence of such a subtropical mixing barrier has led to suggestions that, to a first approximation, the transfer of trace constituents from the equatorial troposphere upward through the lower equatorial stratosphere can be viewed as occurring in a "tropical pipe" that is isolated from contact with the extratropical lower stratosphere (Plumb, 1996). (In other words, near the equator there is limited meridional mixing in the 16-24 km altitude band.) However, the tropical pipe is not airtight. Analysis of recent in situ observations of molecules with a wide range of lifetimes (Minschwaner et al., 1996; Volk et al., 1996) suggests that about 50 percent of air in the tropical ascent region at 21 km originates in the mid-latitudes. Substances emitted in the mid-latitudes thus have a significant probability of reaching the altitudes (about 25 to 38 km) at which NO_x chemistry is dominant in ozone destruction, as do emissions occurring on the significant fraction (38 percent) of flight paths that are above the tropics (see Chapter 3).

GAS-PHASE OZONE CHEMISTRY

Ozone is produced from oxygen by far-ultraviolet (UV) solar radiation (Figure 3, middle panel) in a two-step process: $O_2 + UV \rightarrow 2\,O$ followed by $O + O_2 \rightarrow O_3$ (twice). Ozone is destroyed in the chemically controlled region almost as fast as it is made, setting up a "photochemical steady state". Throughout the stratosphere, ozone is continually destroyed by several homogeneous gas-phase chemical reactions, including direct ozone destruction by the reaction $O + O_3 \rightarrow 2O_2$, and by reactions with active atoms and radicals, illustrated here for the case of nitrogen oxides (NO_x), nitric oxide (NO), and nitrogen dioxide (NO_2). At first sight it might appear that the nitrogen oxides present at a few times 10^8 molecules cm^{-3} could not destroy much ozone, which is present at a few times 10^{12} molecules cm^{-3}. Paul Crutzen showed (Crutzen, 1970), however, that ozone destruction does occur by way of the homogeneous catalytic cycle:

$$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2 \\ \underline{NO_2 + O \rightarrow NO + O_2} \\ \text{net: } O_3 + O \rightarrow 2O_2 \end{array} \qquad (1)$$

Many cycles can occur. Both NO and NO_2 are regenerated every cycle, whereas two molecules of ozone are lost for each cycle, since the oxygen atom in the second step is formed from sunlight and ozone ($O_3 + UV \rightarrow O_2 + O$).

There are other catalytic cycles perpetuated by trace concentrations of atoms and free radicals that destroy ozone in the stratosphere and troposphere. These processes are classified by the chemical family that contributes the catalytic chain carriers: (i) free radicals HO_x derived from water, H, OH, HOO; (ii) atoms and radicals ClO_x derived from chlorine (Cl_2), Cl, ClO; and (iii) atoms and radicals BrO_x derived from bromine (Br_2), Br, BrO. The great majority of ClO_x and BrO_x radicals come from photolysis of organo-halogen compounds. Bromine reactions parallel chlorine reactions in most respects, but for the radical–radical reactions that constitute the rate-limiting steps in catalytic ozone-destruction cycles, bromine reactions are faster than the corresponding chlorine reactions. For aircraft problems, the most important cycle in the HO_x family (out of five in all) and the most important cycle in the ClO_x family are written below:

$$\begin{array}{ll} \textit{Ozone loss cycle by } HO_x & \textit{Ozone loss cycle by } ClO_x \\ O_3 + OH \rightarrow O_2 + HOO & O_3 + Cl \rightarrow O_2 + ClO \text{ (twice)} \\ & 2ClO \rightarrow ClOOCl \\ O_3 + HOO \rightarrow 2O_2 + OH & ClOOCl + h\nu \rightarrow ClOO + Cl \\ \hline & \underline{ClOO + M \rightarrow Cl + O_2 + M} \\ \text{net: } 2O_3 \rightarrow 3O_2 & \text{net: } \quad 2O_3 \rightarrow 3O_2 \end{array} \qquad (2)$$

Each of these ozone-destroying cycles is diverted into a null cycle by NO:

$$\begin{array}{ll}
\textit{Null cycle by } HO_x & \textit{Null cycle by } ClO_x \\
O_3 + OH \rightarrow O_2 + HOO & O_3 + Cl \rightarrow O_2 + ClO \\
HOO + NO \rightarrow NO_2 + OH & ClO + NO \rightarrow Cl + NO_2 \\
NO_2 + h\nu \rightarrow NO + O & NO_2 + h\nu \rightarrow NO + O \\
\underline{O + O_2 + M \rightarrow O_3 + M} & \underline{O + O_2 + M \rightarrow O_3 + M} \\
\text{net: null} & \text{net: null}
\end{array} \qquad (3)$$

As directly demonstrated by atmospheric measurements, in the lower stratosphere NO_x catalysis is a minor mechanism, and ozone loss is dominated by HO_x catalysis with significant contributions from ClO_x and BrO_x (Wennberg et al. 1994; Stolarski et al., 1995). Atmospheric measurements also show that catalytic destruction due to NO_x is one of the significant background atmospheric ozone-loss mechanisms in the middle and upper stratosphere (Stolarski et al., 1995; Jucks et al., 1996). According to model calculations (see Figure 5 in Chapter 3), ozone destruction by NO_x is about 60 percent of the total in the tropics, 70 percent at mid-latitudes, and 80 percent in sunlit polar regions in the ozone-formation region between 28 and 38 km.

Chemically active species NO_2, OH, Cl, ClO, and BrO are reversibly converted to inactive "reservoir" species HNO_3, $ClONO_2$, $BrONO_2$, and HCl through the reactions:

$$\begin{array}{ll}
\text{by } NO_2 & OH + NO_2 \rightarrow HNO_3 \\
 & HOO + NO_2 \rightarrow HOONO_2 \\
 & ClO + NO_2 \rightarrow ClONO_2, \\
 & BrO + NO_2 \rightarrow BrONO_2
\end{array} \qquad (4)$$

$$\text{by } CH_4 \quad Cl + CH_4 \rightarrow HCl + CH_3 \qquad (5)$$

Solar radiation or hydroxyl radicals OH slowly re-convert the reservoir species to active radicals.

The two null reaction cycles in Equation (3) and the reactions in (4) are of importance in understanding the role of NO_x in the natural atmosphere and in an atmosphere with aircraft-added NO_x. In the natural atmosphere NO_x reduces ozone in the ozone-formation region in the middle stratosphere, and thereby determines the magnitude of ozone in its region of maximum concentration around 23 km. NO_x mitigates ozone destruction by HO_x and ClO_x systems (Equations 3 and 4), however, and thus protects lower-stratospheric ozone from almost total destruction by ClO_x and HO_x. The proper interpretation to be given to the null cycles in Equation (3) is that nitrogen oxides reduce the ozone reduction by HO_x and ClO_x systems, not that NO_x "produces" ozone.

In the lower atmosphere, UV photolysis of oxygen is not the only mechanism by which ozone is formed. Natural "smog" reaction mechanisms were first explained by Crutzen (1973). The essence of these mechanisms is the slow photochemical combustion of carbon monoxide or methane, or volatile organic compounds (VOCs) such as acetone. The reactions are cyclic in HO_x and NO_x but consumptive of VOCs. The number of ozone molecules produced by these reactions is generally a small multiple of the number of carbon atoms in the molecule that is consumed. However, the net effect of these reactions on ozone depends on the ambient $[NO]/[O_3]$ ratio. Low NO permits O_3 destruction by HOO, while high NO permits the production of O_3.

HETEROGENEOUS CHEMISTRY IN THE STRATOSPHERE

Stratospheric aerosols arising from natural sources play a key role in the chemistry of the ozone layer, because of reactions on their surfaces. Under some circumstances, such as large volcanic eruptions, they even influence stratospheric dynamics. Since the emissions from a fleet of HSCTs might become a significant additional source of stratospheric aerosols, it is important that reactions on aerosols be better understood.

Discovery of the Antarctic ozone hole in 1985 sparked coordinated campaigns of field measurement, laboratory studies, and modeling, including reconsideration of the potential role of heterogeneous processes in the chemistry of ozone at mid-latitudes. The special perturbed chemistry of the polar stratosphere requires the presence of at least one of the two types of polar stratospheric cloud (PSC) particles. The particles that compose PSCs are responsible for the catalytic heterogeneous chemistry that leads to the formation of the ozone hole (Molina et al., 1987; Tolbert et al., 1987; Solomon, 1990). These particles "activate" the reservoir species of chlorine (e.g., HCl and $ClONO_2$) and turn them into labile species (e.g., Cl_2), and "deactivate" the labile species of NO_x and turn them into inactive HNO_3.

Heterogeneous reactions that have been incorporated into chemical models of the Antarctic ozone hole include:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (6)$$
$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (7)$$
$$ClONO_2 + HCl \rightarrow C1_2 + HNO_3 \qquad (8)$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (9)$$
$$HCl + HOBr \rightarrow BrCl + H_2O \qquad (10)$$

At mid-latitudes, stratospheric temperatures are far too high to permit formation of PSCs. (Although ice particles can form at the tops of strong thunderstorms near the tropical tropopause, the air upwelling from the troposphere there contains mostly CFCs and N_2O, not HCl and $ClONO_2$.)

Figure 4 represents some interesting data obtained during the SPADE campaign. Instruments aboard the NASA ER-2 aircraft simultaneously measured many reactive species in the stratosphere up to the ER-2's 20 km flight ceiling.

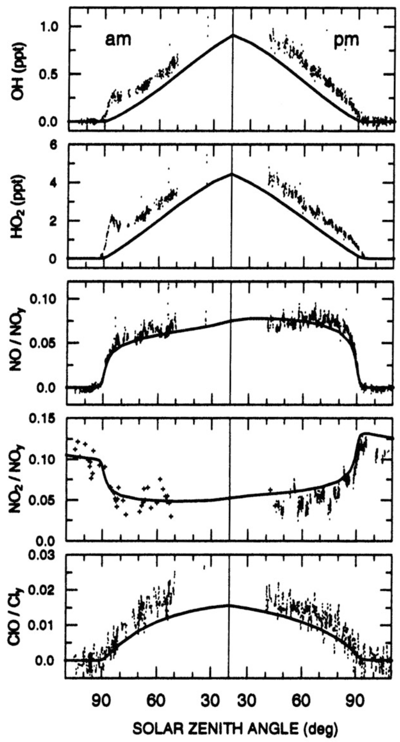

FIGURE 4 Diurnal variations of free radicals (OH, HO_2, NO, NO_2, and ClO) measured at 19 km, 37°N during SPADE. The lines show calculations made by a photochemical model. (Adapted from Salawich et al., 1994b; reprinted with permission of the American Geophysical Union.)

The measured data are plotted as points on each panel of the figure; for comparison, a line shows values calculated by a local atmospheric model specifically suited to the air mass in which the measurements were made. On Figure 4, time starts a few hours before sunrise, continues throughout the day, and ends a few hours after sunset. There is good agreement between model and measurement for the ratio NO/NO_y and for the ratio NO_2/NO_y, where NO_y is the sum of NO, NO_2, HNO_3, and all other molecules containing the NO group. However, there is a pulse of OH and HOO radicals shortly after sunrise; some substance had been accumulating all night and was dissociated by the early morning sunlight, and the observed OH and HOO were higher than the modeled values throughout the sunlit day. Also, the observed ratio ClO/Cl was higher than the model values, which is consistent with high OH, since the reaction $OH + HCl = H_2O + Cl$ increases active chlorine, including ClO.

It has been proposed that the heterogeneous hydrolysis of bromine nitrate

$$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr \qquad (11)$$

plays an important role in the bromine and HO_x chemistry at mid-latitudes. Hanson and Ravishankara (1995) have suggested that reaction (11) may be the source of the early-morning peak of OH and HOO and the higher-than-predicted OH and HOO (see also Salawitch et al., 1994b). Stolarski et al. (1995) reported unpublished work that tested this hypothesis: Inclusion of bromine nitrate hydrolysis in the LLNL and CSIRO models improves the agreement between models and measurements as far as the early peak and the excess OH and HOO are concerned, but it causes predicted NO_x to fall below observed values. There remains some suspicion of missing chemistry involving OH at altitudes below 20 km (see also Lary et al., 1996).

Hofmann and Solomon (1989) argued that volcanic eruptions could lead to enhanced depletion of ozone at mid-latitudes, according to laboratory studies by Mozurkewich and Calvert (1988), Tolbert et al. (1988), and Worsnop et al. (1988) of the kinetics of reaction (6) on liquid sulfuric acid and water surfaces. Depletion occurs through a reduction in the abundance of NO_x, and a consequent increase in the importance of ClO_x- and HO_x-catalyzed destruction of ozone (Equations 3 and 4). Changes in ozone observed by means of Dobson spectrophotometers, ozonesondes, and satellite-based instruments subsequent to the 1982 eruption of El Chichón, summarized by Hofmann and Solomon (1989), were consistent with the results of a photochemical model incorporating reactions on aerosol, but the uncertainties were large. Additional laboratory studies confirmed the potential importance of reaction (6), so modeling studies incorporated the occurrence of (6) on sulfate aerosol into reaction schemes for describing mid-latitude ozone chemistry (Rodriguez et al., 1991). Considerable improvement in agreement between predicted and observed vertical patterns of ozone depletion caused by chlorofluorocarbons and high ClO concentrations was obtained as a result, and the significance of the region below 20 km became apparent.

The eruption of Mt. Pinatubo during the second Airborne Arctic Stratospheric Expedition (AASE II, September 1991–March 1992) provided an early opportunity to test the aerosol hypothesis. Measurements were made of NO_x/NO_y and ClO/Cl_y at mid-latitudes before and after the onset of the effect of the Pinatubo eruption. The measurements showed a change in these ratios that could not be explained with gas-phase chemistry alone (Fahey et al., 1993). Models that included heterogeneous reactions improved prediction of the ratios of radical species involved in ozone chemistry for a large range of aerosol abundances (Kinnison et al., 1994b). Similarly, models that included aerosol reactions agreed well with ratios measured in situ during SPADE (November 1992–May 1993), whereas gas-phase-only models did not (Salawitch et al., 1994b). In a more recent modeling study, Solomon et al. (1996) confirmed the importance of heterogeneous chemistry in driving ozone depletion in the northern mid-latitudes.

Of course, the composition, size, and phase (solid or liquid) of aerosols vary greatly with latitude, altitude, and season. Aerosols composed primarily of sulfuric acid and water, or aerosols of mixed composition (including nitric acid), may dominate at any one time and place. The significance of aerosols for stratospheric chemistry at mid-latitudes, in addition to their role in polar ozone loss, has become clear over the last decade. Many of the major uncertainties remaining in the chemistry of the lower stratosphere involve heterogeneous chemistry occurring on atmospheric aerosols at all latitudes, and on polar stratospheric clouds. Heterogeneous chemistry at middle and polar latitudes exhibits a range of behavior determined by characteristics of aerosols that evolve with ambient temperature (Molina et al., 1993; MacKenzie et al., 1995; Peter, 1997).

At mid-latitudes, where aerosols are composed largely of sulfuric acid and water, only the hydrolysis of N_2O_5 and $BrONO_2$ may prove important. At the lower temperatures characteristic of polar regions, a supercooled ternary solution (called STS) of nitric acid, sulfuric acid, and water forms PSCs under conditions at which nitric acid trihydrate (NAT) would be expected to form in equilibrium (Hamill et al., 1996). The kinetics of some heterogeneous reactions have been studied on a variety of surfaces, including liquid and solid sulfuric-acid solutions, ice, and NAT, but PAEAN has found no reports of kinetic studies on STS. It should be noted, however, that the physical and chemical changes in PSCs caused by HSCT emissions, and the magnitude of the response of polar ozone chemistry to those PSC changes, will depend on both microphysical properties such as the aerosol surface-area-to-volume ratio and the specific composition of the aerosol (e.g., the proportions of NAT, STS, and sulfuric acid tetrahydrate). For example, STS and NAT absorb nitric acid with different efficiencies (Mackenzie et al., 1995), and the rates of several of the key heterogeneous reactions depend on the aerosol composition. Several of these factors are not yet understood quantitatively.

ATMOSPHERIC MEASUREMENTS

Observations show that the mixing ratios of long-lived species (e.g., N_2O and CH_4) show a simple, compact relation in the lower stratosphere (Ehhalt et al., 1983; Fahey et al., 1989a,b). This relationship results from the fact that the surfaces of constant mixing ratio (isopleths) are similar for all species whose quasi-horizontal mixing times are shorter than the chemical-loss times (Holton, 1986; Plumb and Ko, 1992). Successful field measurements of multiple reactive components by programs such as AASE, ASHOE/MAESA[*], and SPADE were carried out using the NASA ER-2 aircraft (see Wennberg et al., 1994; Salawitch et al., 1994a,b; Cohen et al., 1994; Stimpfle et al., 1994; Jaeglé et al., 1994), and the data from more recent campaigns such as STRAT. The use of the mixing-ratio relationships in a novel graphical approach has yielded useful information about atmospheric dynamics, leading to the development of the "tropical pipe" model and revealing that 2-D models cannot predict the NO_y/O_3 ratio well (Murphy et al., 1993).

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[*] Airborne Southern Hemisphere Ozone Experiment / Measurements for Assessing the Effects of Stratospheric Aircraft

These recent expeditions have shown that HO_x radicals (ultimately derived from H_2O and O_3) are the principal catalysts at mid-latitudes for removing O_3 at altitudes below 20 km (Wennberg et al., 1994). These results represent a major shift from the previously held notion that NO_x radicals were the principal catalysts for removing O_3 in this region of the atmosphere (Logan et al., 1978; McElroy and Salawitch, 1989). If the rates of ozone destruction caused by HO_x, ClO_x and BrO_x, and NO_x (according to SPADE data) are plotted against altitude between 15 and 20 km, HO_x is clearly the most important, the halogens are a close second, and NO_x the slowest (Wennberg et al., 1994).

Remote sensing methods measure several reactive species at altitudes above 20 km. The UARS limb-sounder measurements are less dense in time and space than what is really needed for evaluating the effects of aviation, and the UARS data set does not include all of the radical species whose concentrations are needed to “close” the chemistry. Nonetheless, it provides useful information on several of the crucial chemically important species in the chlorine, nitrogen, and hydrogen families, and it is the best source of data on the behavior of long-lived trace constituents at altitudes above 20 km. Observations of the spatial and temporal variability of such trace constituents, together with high-resolution Doppler imager (HRDI) wind data and meteorological analyses from the U.K. Meteorological Office and the National Centers for Environmental Prediction, can be used in diagnostic studies to assess transport and mixing rates in the 16-30 km altitude range.

From measurements of O_3, HO_2, OH, NO, NO_2, and ClO, Jucks et al. (1995) have inferred ozone-destruction rates between 24 and 38 km for HO_x, ClO_x, BrO_x, and NO_x. They find that while HO_x reactions are the dominant ozone destroyer below 20 km, NO_x reactions are the dominant ozone destroyer above 24 km. Figure 5, which appears in the next chapter, illustrates the altitudinal and latitudinal dependence of the various ozone-destroying processes.

3

Ozone Reduction by HSCT-Emitted Nitrogen Oxides

Even without model calculations, it has been obvious since 1971 that the possible reduction of ozone by a fleet of HSCTs is a problem worthy of serious consideration. Nitrous oxide (N_2O) is produced from soils and waters as a byproduct of biogeochemical nitrogen cycling. It is inert in the troposphere, is slowly transported up into the stratosphere by air motions, and reacts in the 30±5 km altitude range to form nitrogen oxides (Crutzen, 1971) at a rate of $1.8\pm0.5\times10^9$ kg as NO_2 per year (Crutzen and Schmailzl, 1983).

The 500 supersonic transports (SSTs) planned in 1971, emitting nitrogen oxides in the exhaust at the same percentage by weight as the existing Concorde engines (see Fahey et al., 1995), would have injected into the stratosphere $1.5\text{x}10^9$ kg NO_2 per year, an amount approximately equal to the natural input (NRC, 1974). Although the rate of NO_x emission from future HSCT engines is unknown, current estimates for a fleet of 500 Mach 2.4 HSCTs also give NO_x injection into the stratosphere at values close to or slightly lower than the natural input noted above. Figure 5, showing calculations by a Lawrence Livermore National Laboratory (LLNL) model, indicates that natural NO_x catalytically destroys ozone faster than the sum of all other ozone loss mechanisms at altitudes between 25 and 38 km, which is the production region supplying ozone to the region of its maximum concentration (see Figure 3). Thus, the possible near-doubling of the stratospheric input of NO_x via HSCT emissions is a problem worthy of serious consideration. However, the HSCT injection of NO_x into the stratosphere would occur at altitudes about 10 km lower than the altitude of natural NO_x input. As AESA has confirmed, this difference in altitude makes a considerable difference in the action of added NO_x on ozone (see Figure 5).

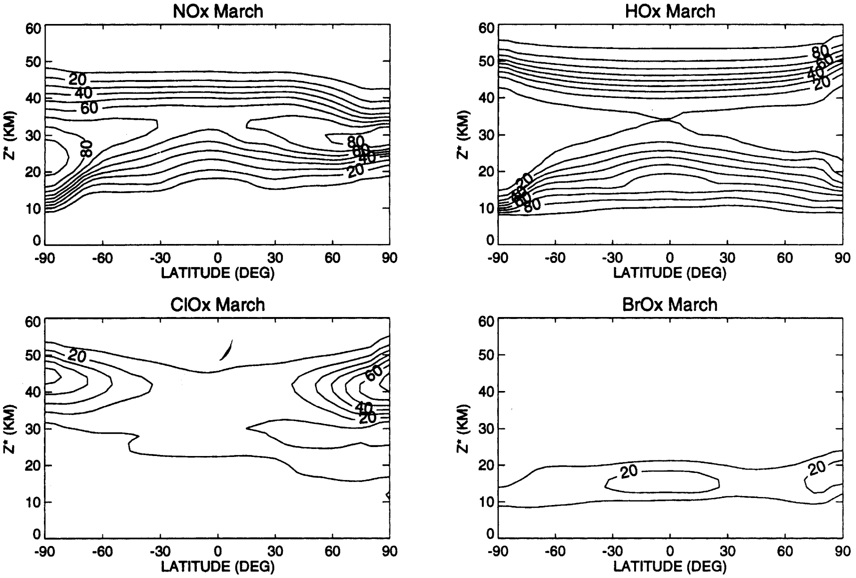

FIGURE 5 Calculated percentages of ozone loss caused by NO_x, HO_x, ClO_x, and BrO_x catalytic cycles, as a function of latitude and altitude, for the month of March. The LLNL model was used, with a background atmosphere and subsonic-aircraft emissions projected for 2015 (Stolarski et al., 1995) but with no HSCT emissions. The BrO_x chemistry used did not include the hydrolysis of $BrONO_2$ on aerosols (see reaction (11) in the text). The NO_x percentages include reactions involving nitrogen and hydrogen; the ClO_x chemistry includes reactions involving chlorine and nitrogen; the BrO_x chemistry includes reactions involving bromine and chlorine. (Reprinted from Stolarski et al., 1995.)

A HISTORY

The Department of Transportation's Climatic Impact Assessment Program, inspired by Boeing's work on an SST and the advent of the Concorde, was devoted to exploring the potential effects of supersonic aviation. It did the pioneering work on stratospheric composition and chemistry, including the first measurements of NO and NO_2 in the stratosphere; improved one- and two-dimensional atmospheric models; made systematic laboratory measurements of reaction rates applicable to the stratosphere; developed critical tables of chemical rate coefficients and light-absorption cross-sections; and sponsored studies of heterogeneous reactions in the atmosphere and of economic impacts and biological damage caused by ultraviolet radiation (CIAP, 1975a,b).

In 1976 Congress assigned NASA the role of primary agency for stratospheric research, and its Upper Atmospheric Research Program has been active since then. UARP has concentrated its efforts on the chlorofluorocarbon impact on stratospheric ozone, has systematically built up a data base from laboratory photochemistry, has measured stratospheric trace species by satellite remote sensing and by in situ methods, and has developed two-dimensional and is developing three-dimensional radiative-photochemical-dynamic numerical models. No general study of the atmospheric effects of supersonic aviation was made between 1976 and 1988, but LLNL kept a year-by-year record of the calculated ozone effect of 500 SSTs flying at 20 km, consuming $7.7\text{x}10^{10}$ kg fuel per year, emitting 1.8 MT NO_x (as NO_2) per year, using each year the best available dynamical models and values of photochemical data. For two years (1978-1979) these one-dimensional model studies predicted that NO_x from the standard CIAP fleet of supersonic transports would increase the ozone vertical column, but for all the other years between 1975 and 1988, the models predicted global ozone-column reductions of between 5 and 12 percent.

In 1988 and 1989, NASA and the aircraft industry showed renewed interest in supersonic (Mach 2.4 to 3.2) and hypersonic (Mach 4 to 10) aircraft. The LLNL two-dimensional (2-D) model was used to calculate the effect on ozone of 500 SSTs with CIAP fuel-consumption rates and with three different NO_x emission rates, corresponding to 1/3, 1, and 3 times the Crutzen and Schmailzl value of 1.8×10^9 kg NO_2 per year. Flights were assumed to occur at each of seven altitudes between 16.5 and 34.5 km, and in various assumed flight corridors, such as between 37° and 49°N (Johnston et al., 1989). The 1989 LLNL model did not include heterogeneous reactions (nor did other models at that time), such as those important for the Antarctic ozone hole. For a wide range of input parameters in this sensitivity study, the calculated ozone reductions over the northern hemisphere varied from 0.9 to 28 percent. These calculated ozone reductions were extremely sensitive to flight altitude: For the CIAP value of NO_x input, flight altitudes of 15-18 km, 18-21 km, and 21-24 km gave northern hemisphere ozone reductions of 0.9 percent, 10.4 percent, and 13.1 percent, respectively. These three altitude bands correspond approximately to the flight altitudes of aircraft with Mach numbers of 1.6, 2.4, and 3.2, suggesting that aircraft with a low, but still supersonic, Mach number might be able to operate under conditions such that their effect on ozone would be small. HSCTs with Mach numbers of 1.6, 2.0, and 2.4 were seriously discussed through 1993 in the various AESA reference publications.

A primary purpose of establishing AESA under the High-Speed Research Program in 1988 was to understand and if possible answer the question of the extent of potential ozone reduction by HSCTs, as indicated by model calculations. It was already known by that time that the ozone reduction by NO_x from HSCT exhaust calculated for a flight altitude of 20 km decreased rapidly as the flight altitude was moved down to 15 km, at which point the ozone reduction changed to an ozone increase, as anticipated by Johnston and Quitevis (1975). It was obvious that the calculated reduction would be diminished if the aircraft were equipped with low-NO_x engines. It was qualitatively recognized in 1990 that if the heterogeneous reaction ($N_2O_5 + H_2O \rightarrow 2HNO_3$) was fast, it would decrease the calculated ozone reduction by HSCTs, but if the heterogeneous reaction $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ was fast it would increase the calculated ozone reduction by HSCTs.

NASA took action on three fronts: First, shortly after the start of AESA, the HSRP dropped from consideration the high-altitude Mach 3.2 HSCT and selected the Mach 2.4 HSCT as the best candidate. HSRP also considered lower-flying Mach 1.6 and 2.0 models, partially in case the NO_x-ozone problem could not be solved. Second, HSRP set the goal of developing the technology for new types of HSCT engine combustors that would have an EI(NO_x) as low as 5, about a factor of 10 less NO_x than a high-efficiency 1990-technology engine equipped with a conventional combustor design. The completion of this design process and initial construction of an actual engine is not expected until well after the year 2000, however. (See *U.S. Supersonic Aircraft: Assessing NASA's High Speed Research Program* (NRC, 1997c) for a discussion of HSRP progress in these areas.) Third, AESA launched a major program of studying heterogeneous reactions in the laboratory and making meaningful measurements in the stratosphere. By 1991, Weisenstein et al. had already made model calculations including heterogeneous reaction (6), and found almost an order of magnitude decrease in the model-calculated ozone reduction by HSCT exhaust. Other modelers' results soon confirmed the importance of including heterogeneous chemistry. Since then, AESA has made diagnostic measurements in the atmosphere, extensively studied heterogeneous chemistry as it applies to the atmosphere, and considered other problems such as the role of HSCT aircraft in contributing to possible global climate change.

SCENARIOS AND CONDITIONS

AESA's initial status and its progress through the summer of 1991 are described in Prather et al. (1992). The conditions AESA established for its model explorations of possible effects are summarized below.

Flight Routes and Fuel Usage

With detailed consideration of every major airport in the world and flight paths between pairs of them, realistic HSCT flight routes were identified, flight-altitude patterns for fleets with different Mach numbers were worked out, the economically justified number of HSCTs was tentatively set at 500, and amount of fuel expected to be burned along the various routes was derived. The estimated mass of fuel to be used was 6.6×10^{10} kg per year, of which the fractional consumption is 2.8 percent from 30°S to the south pole, 32.4 percent from 30°S to 30°N, and 64.8 percent from 30°N to the north pole (Prather et al., 1992). All model calculations in the early years of AESA used these carefully derived flight patterns.

This 1992 plan has been modified somewhat (Baughcum and Henderson, 1995); the 1995 version is given by Figure 6, which shows at a glance the estimated latitudinal distribution of fuel consumption by HSCTs (top panel) and the vertical distribution of global fuel use by supersonic and subsonic aircraft as projected to year 2015 (bottom panel). The estimated mass of fuel to be used is 8.2×10^{10} kg per year, of which the fractional consumption is 3 percent from 30°S to the south pole, 38 percent from 30°S to 30°N, and 59 percent from 30°N to the north pole (Stolarski et al., 1995). While the most heavily traveled flight corridors are expected to continue to be north of 30°N, note that by 2015 more than one-third of the HSCT fuel may be expended in the tropics.

HSCT NO_x Emissions

The definition of "NO_x emission index" is the number of grams of NO_x (calculated as if it is all in the form of NO_2) per kilogram of fuel consumed by an aircraft engine. It is properly written "EI(NO_x) as NO_2", though sometimes "as NO_2" is omitted. Issues related to achieving a low NO_x emission index were discussed at the AESA planning workshop held at NASA Ames Laboratory, October 17-19, 1990 (see Prather et al., 1992). It was noted that "With no in situ measurements, Concorde emission studies have been limited to test-stand studies of the engines. . . It will be extremely difficult to measure chemical products in the exhaust plume of an aircraft without a visible clue (e.g., contrail or colored exhaust) to help find the wake." Exhaust products for current engines, as well as for new technologies that might reduce the NO_2 emission index (EI) from 40 to 5 g/kg of fuel, were described at that meeting.

A highlight of NASA's 1995 assessment is the report on the first measurements ever made in the plume region of a Concorde aircraft in flight (Fahey et al., 1995). The concentrations of NO_x found in the wake yielded an EI(NO_x) of 23 (±20 percent). In the 1970s, NO_x emission levels of the Concorde's Olympus engine had been measured in altitude-simulation-chamber tests that included supersonic cruise operating conditions; the resulting EI values varied from 15.5 to 19.3, with a "consensus value" of 18 (CIAP, 1975a). These test-chamber values are somewhat below those for the 1995 in situ measurements, but are still in reasonable agreement.

The Concorde's Olympus engines embody 1960s technology; the engines being developed for the HSCT will have as much as 30 percent greater fuel efficiency. With conventional combustor technology, however, the changed combustor operating conditions that yield these efficiency improvements would result in at least a doubling of the NO_x emission index. In 1989 NASA announced its intention of developing advanced low-emissions combustor technology that would permit HSCT engines with EI(NO_x) levels as low as 5 to be built. These

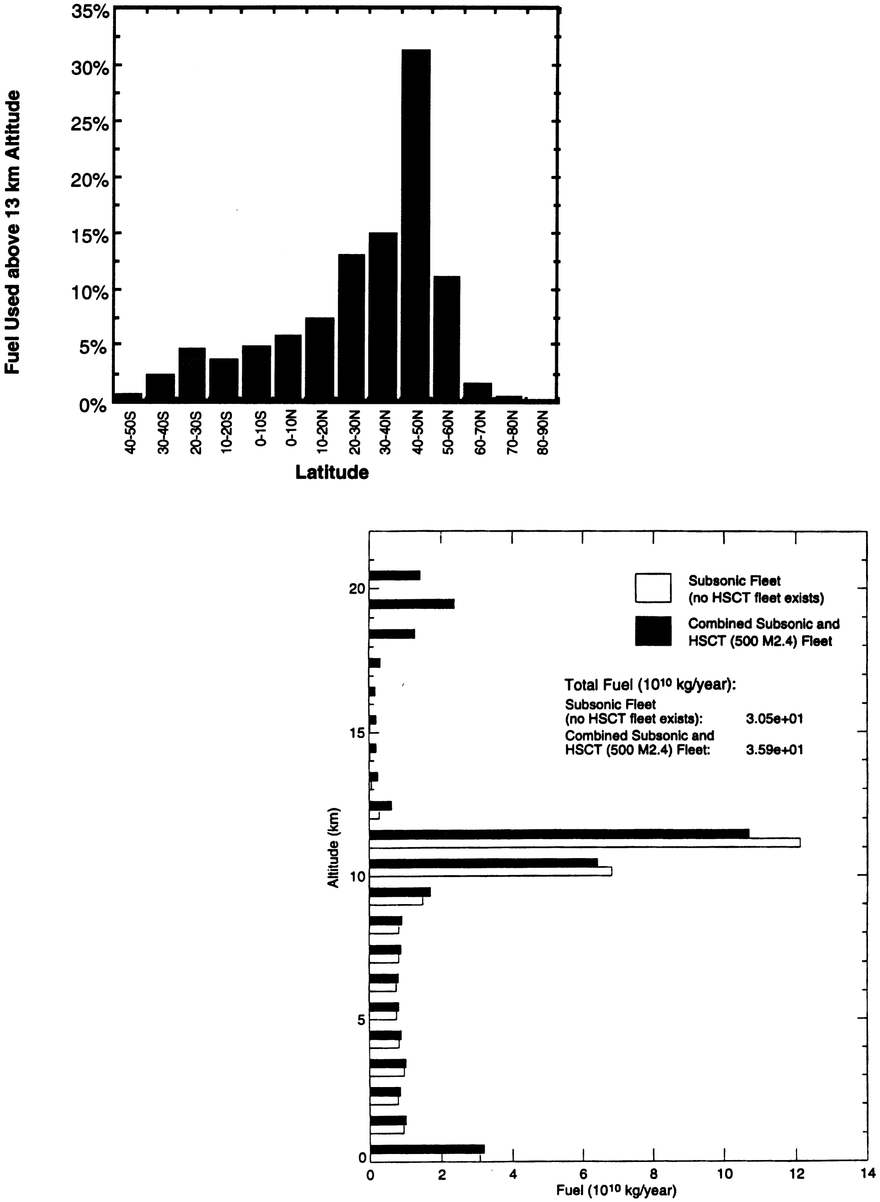

FIGURE 6 Projected HSCT fuel consumption in 2015. Top panel: Latitudinal distribution of fuel used above 13 km altitude by a fleet of 500 Mach 2.4 aircraft. Bottom panel: Total estimated fuel burn as a function of altitude for an enhanced all-subsonic fleet, and for a smaller subsonic fleet plus 500 Mach 2.4 HSCTs. (Reprinted from Stolarski et al., 1995.)

advanced combustor concepts employ multiple burning stages. Combustor testing and further technology development are under way, and altitude-chamber tests of an engine equipped with an ultra-low-NO_x combustor are expected to be made after the year 2000. Until such engines have been built and tested, the EI must be considered a large uncertainty in modeling HSCT NO_x input into the stratosphere.

MODELING HSCT OZONE REDUCTION

To represent the three reference points discussed above—a new engine based on 1990 technology with no concern for low NO_x, the existing Concorde Olympus engine, and the NASA goal for perhaps the year 2001—AESA modelers used 45, 15, and 5 as EI(NO_x) to calculate the effect of NO_x from HSCTs on ozone. These EIs cover the full range of reasonably expected final outcomes, and 15 (the geometric mean of 45 and 5) is reasonably close to the emission index of the Concorde. By about 1993, the favored HSCT was the Mach 2.4 type. To put this choice in perspective, AESA modelers calculated the ozone perturbation by HSCTs with Mach numbers 1.6, 2.4, and 3.2. The number of HSCTs was taken to be 500 unless otherwise noted, with a constant annual rate of fuel consumption.

Using Gas-Phase Chemistry Only

Seven models calculated the change of the ozone vertical column between 40°N and 50°N for various EIs and Mach numbers using gas-phase chemistry only. Their results (with the exception of one having limited runs), were presented in Stolarski and Wesoky (1993a) and are reproduced here in Table 1. They appear immediately below in a condensed form that gives an average ozone-column percentage change plus or minus two standard deviations:

Mach\EI(NO_x)	*45*	*15*	*5*
3.2		–8.6 ± 3.7	–2.6 ± 1.5
2.4	–14 ± 7	–3.9 ± 2.2	–1.3 ± 0.8
1.6		–0.9 ± 0.8	–0.16 ± 0.10

Relatively large ozone reductions, about 10 percent, are shown for (EI = 15, Mach = 3.2) and for (EI = 45, Mach = 2.4). At EI = 15, the calculated ozone reduction decreases a factor of ten in going from Mach 3.2 to Mach 1.6. At Mach = 2.4, the calculated ozone reduction decreases a factor of ten in going from EI = 45 to EI = 5. At Mach = 1.6 and EI of 15 or less, the calculated ozone reduction is less than 1 percent, and 0 percent reduction is barely outside the 95 percent confidence level. Results such as those given in Table 1A prompted aircraft

TABLE 1 Calculated percentage ozone-column changes between 40°N and 50°N by 500 HSCTs with various Mach numbers and various NO_x emission indices. (After Stolarski and Wesoky, 1993a.)

Mach No.	EI(NO_x)	AER	DuPont	GSFC	Italy	LLNL	NCAR	μ ± 2σ
A. Gas-phase chemistry only								
3.2	15	–8.8	–8.8	–10	–11	–5.8	–7.3	–8.6 ± 3.7
2.4	15	–4.6	–5.6	–3.7	–4.1	–2.7	–2.9	–3.9 ± 2.2
1.6	15	–0.91	–0.77	–1.4	–0.53	–0.5	–1.3	–0.9 ± 0.8
3.2	5	–2.5	–2.9		–3.3	–1.5		–2.6 ± 1.5
2.4	5	–1.3	–1.7		–1.47	–0.77		–1.3 ± 0.8
1.6	5	–0.23	–0.12		–0.15	–0.14		–0.2 ± 0.1
2.4	45	–14.0	–16.7		–17.2	–9.5		–14 ± 7.0
B. Gas-phase chemistry and heterogeneous reactions								
3.2	15	–3.3	–3.4	–4.1	–5.5	–2.2	–2.1	–3.4 ± 2.5
2.4	15	–0.95	–1.3	–0.63	–0.42	–0.56	–0.27	–0.7 ± 0.7
1.6	15	+0.09	+0.84	–0.01	+0.67	+0.08	–0.03	+0.3 ± 0.8
3.2	5	–1.2	–1.1	–1.3	–1.9		–0.20	–1.1 ± 1.2
2.4	5	–0.42	–0.31	–0.23	+0.04		–0.04	–0.2 ± 0.4
1.6	5	+0.03	+0.53	–0.04	+0.39		+0.04	+0.2 ± 0.5
2.4	45	–4.0	–7.4	–3.3	–4.8		–2.3	–4.4 ± 3.9

AER	Atmospheric and Environmental Research, Inc.
GSFC	Goddard Space Flight Center
LLNL	Lawrence Livermore National Laboratory
NCAR	National Center for Atmospheric Research

manufacturers and AESA to give serious attention to HSCTs with Mach numbers 1.6 and 2.0 in the early stage of AESA.

Including Heterogeneous Chemical Reactions in the Models

Although a laboratory study in 1975 reported no reaction of N_2O_5 with sulfuric acid, Mozurkewich and Calvert (1988) found this to be a fast reaction on sulfuric acid/water solutions:

$$\mathrm{N_2O_5}\ \text{(gas)} + \mathrm{H_2O}\ \text{(in sulfuric acid)} \rightarrow \mathrm{2HNO_3}\ \text{(gas)} \qquad (6)$$

Shortly thereafter several groups studied this reaction using different techniques, and found that the reaction occurs rapidly regardless of water concentration in the sulfuric acid and regardless of temperature over its atmospheric range, as long as the solution is not frozen solid. AESA carried out atmospheric-measurement campaigns to explore the reaction in situ; the measurements and their interpretation “proved beyond a reasonable doubt” that the heterogeneous reactions observed in the laboratory were indeed occurring in the stratosphere (Albritton et al., 1993).

Reaction (6) is of major importance to the HSCT-effect question. Homogeneous and heterogeneous chemistry relative to reaction (6) includes:

$$\begin{array}{lll}
\text{Night} & \text{Day} & \text{Day} \\
\mathrm{NO_2 + O_3 \rightarrow NO_3 + O_2} & \mathrm{NO_2 + O_3 \rightarrow NO_3 + O_2} & \mathrm{NO_2 + O_3 \rightarrow NO_3 + O_2} \\
\mathrm{NO_2 + NO_3 \rightarrow N_2O_5} & \mathrm{NO_3} + h\nu \rightarrow \mathrm{NO_2 + O} & \mathrm{NO_3} + h\nu \rightarrow \mathrm{NO + O_2} \\
\mathrm{N_2O_5 + H_2O \rightarrow 2HNO_3} & \mathrm{O + O_2 \rightarrow O_3} & \mathrm{NO + O_3 \rightarrow NO_2 + O_2} \\
\hline
\text{net: } \mathrm{2NO_2 + H_2O \rightarrow 2HNO_3} & \text{net: null (90\%)} & \text{net: } \mathrm{2O_3 \rightarrow 3O_2} \quad (10\%)
\end{array} \qquad (12)$$

The moderately slow reaction of nitrogen dioxide with ozone leads to inactive nitric acid vapor at night, if the surface area of the aerosols is large enough. During the day the NO_3 intermediate is almost instantly broken down by sunlight to NO_2 or to NO, and no N_2O_5 is formed. The net effect is to convert active NO_2 to non-reactive HNO_3 at night. Thus removed, NO_2 does not engage in reactions (4), which remove active OH, HOO, ClO, and BrO. In sunlight, NO_2 and NO are in photochemical steady state; reduction of NO_2 as the net effect of reaction (6) also reduces NO, and this loss of NO prevents ozone-destroying reactions (1) from occurring, replacing them with the null reactions (3).

Weisenstein et al. (1991) were the first to include a heterogeneous reaction, namely (6), in a 2-D model study concerning HSCTs. They found this single heterogeneous reaction greatly diminished the calculated ozone reduction, in some cases reversing the sign of the net effect. Weisenstein et al.'s article, which was not published in time to be included in the initial AESA review (Prather et al., 1992), marks a "watershed" with respect to estimates of ozone reduction by HSCTs.

Typical calculated ozone-column changes from models including both gas-phase and heterogeneous reactions are shown in Part B of Table 1. Those results are condensed here to give an average ozone-column percentage change plus or minus two standard deviations:

Mach\EI(NO_x)	*45*	*15*	*5*
3.2		–3.4 ± 2.5	–1.1 ± 1.2
2.4	–4.4 ± 3.9	–0.69 ± 0.75	–0.19 ± 0.38
1.6		+0.27 ± 0.76	+0.19 ± 0.50

The calculated ozone reductions in the models that included heterogeneous reactions (Part B of Table 1) are substantially less than those calculated using gas-phase chemistry only (Part A). All calculated ozone changes are less than ±1 percent except for the cases of (EI = 15, Mach = 3.2), (EI = 5, Mach = 3.2), and (EI = 45, Mach = 2.4). For both EI = 5 and EI = 15, the calculated ozone-column changes for Mach 1.6 HSCTs are positive. The average result for all cases with Mach = 1.6 and for all cases with EI = 5 includes zero within the two-sigma error limits.

The factors by which the inclusion of heterogeneous reactions lowers the calculated ozone-column reductions—gas only/(gas + heterogeneous)—are as follows:

Mach\EI(NO_x)	*45*	*15*	*5*
3.2		2.6	2.1
2.4	3.1	6.8	indeterminate
1.6		indeterminate	indeterminate

The ozone reductions calculated for the high-altitude HSCTs with Mach 3.2, which cruise at 21 to 24 km, are reduced by a factor of about 2 for an EI = 5; the reductions for the Mach 2.4 HSCTs, which cruise at 18 to 21 km, are reduced by about a factor of 7 for an EI = 15. For Mach 1.6 HSCTs, the calculated ozone changes indicate an increase of ozone column.

MODEL RESULTS REPORTED IN 1995

NASA's 1995 assessment gives a clear picture of the current status of model calculations of ozone change by a fleet of HSCTs. Figure 7 shows the calculated

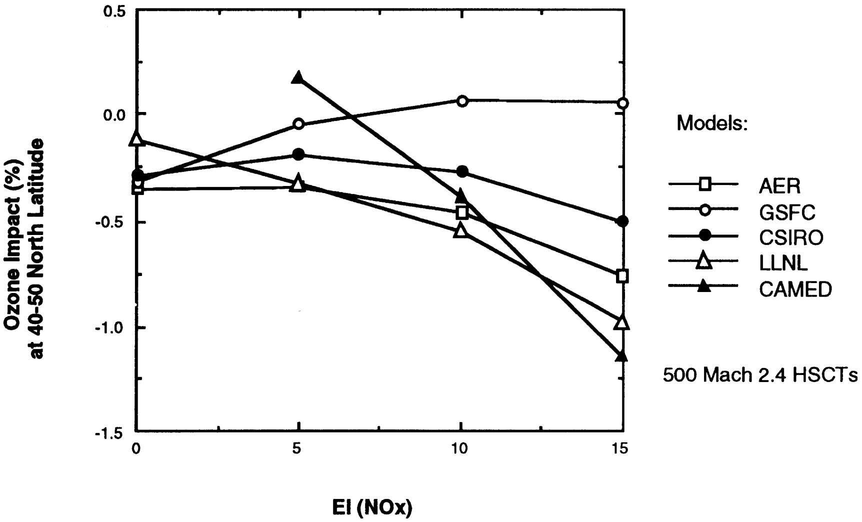

FIGURE 7 Five models' calculations of percentage changes in ozone column in the 40 to 50°N latitude band, as a function of NO_x emission index, for a fleet of 500 Mach 2.4 HSCTs.* (Reprinted from Stolarski et al., 1995.)

ozone changes for 500 Mach 2.4 HSCTs as a function of NO_x emission index for values of 0, 5, 10, and 15 as calculated by five 2-D assessment models. In general, the five models agree that there will be less than 1 percent ozone reduction for any NO_x emission index up to 15. If one looks for fine structure, of the four models that reported results with zero NO_x emissions, there is about 0.2 to 0.3 percent ozone-column reduction with no added NO_x, which on average remains about the same for a NO_x emission index of 5. One model shows essentially zero ozone reduction from EI = 5 to EI = 15, but the other four models give between 0.5 and 1.0 percent ozone reduction with EI = 15.

Figure 8 shows the calculated change of ozone concentration (molecules cm^{-3}) as a function of altitude at 45°N latitude for the month of March. The calculation is for 500 Mach 2.4 HSCTs with NO_x emission index of 5. Between 40 and 50°N (Figure 8), the five models all show very small changes in the ozone vertical column, from –0.3 percent to +0.2 percent (see Stolarski et al., 1995), which is excellent agreement. The striking feature of Figure 8, however, is the differences in the shapes of these five models' vertical profiles of ozone changes. The LLNL model results lie at one extreme, CAMED results at the other. At 20 km, two models show ozone increase, one model shows no change in ozone, and two models show an ozone decrease. The models differ from each other by large

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*CSIRO is the model of the Commonwealth Scientific and Industrial Research Organization, and CAMED is the joint model of the University of Cambridge / University of Edinburgh.

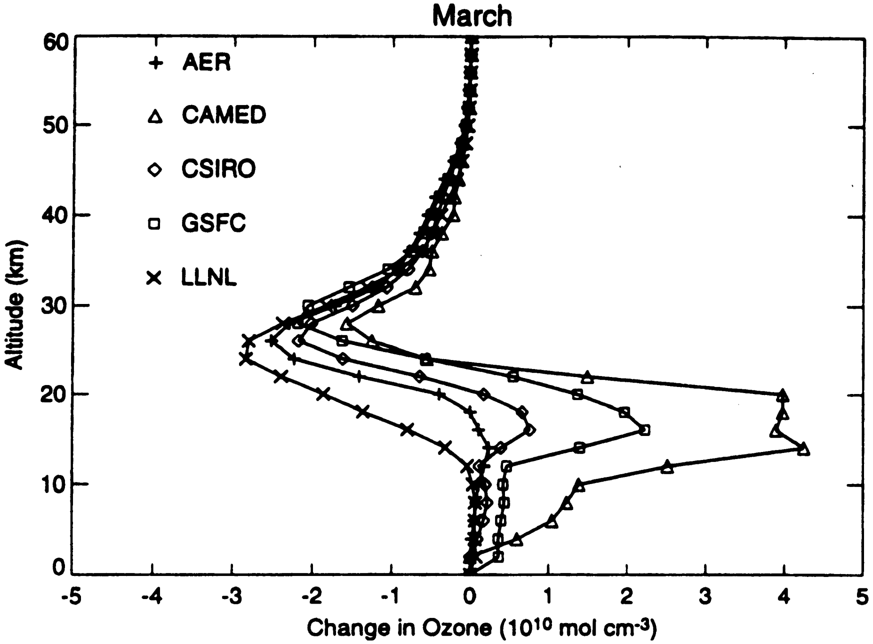

FIGURE 8 Five models' calculations of change in ozone concentration as a function of altitude for a fleet of 500 Mach 2.4 HSCTs with an EI (NO_x) of 5. The results shown are for March at 45°N latitude. Units are 10^{10} molecules per cubic centimeter. (Reprinted from Stolarski et al., 1995.)

ratios for the troposphere and the lowermost stratosphere. In the troposphere nitric acid is rained out in a few days, and there are large sources of nitrogen oxides (subsonic aircraft and lightning). It is surprising that a relatively small increase in NO_x in the overworld should increase ozone in the lower troposphere in two of the models; if it is correct, this is a matter of interest to current studies of the atmospheric effects of subsonic aircraft. These differences in model vertical profiles may represent uncertainty in formulating 2-D atmospheric models. On the other hand, they may be explicable in terms of some identifiable physical or chemical feature.

As new laboratory results, new atmospheric observations, or new theoretical insights are published, modelers may change their chemical coefficients, their boundary values, or their formulations of mixing. Model calculations of ozone changes therefore need to be updated almost every year. In recent years AESA has restricted its model calculations to HSCTs with Mach number 2.4 and its NO_x emission indices to 5 and 15. During the model-development stage, it saves computer time to omit other Mach numbers and emission indices. For a proper assessment, however, the surrounding space should be examined to see whether the results change rapidly or slowly outside the range of immediate interest. (Also, future practical considerations may call for information beyond the relatively narrow range of AESA's current scope.) For the final AESA reports, it would be useful (and require only trivial extra cost) if AESA modelers included in their calculations of ozone change Mach numbers 1.6 and 3.2, NO_x emission indices of 0 and 45, and a wider range of sulfate number densities in the wake. This expansion would show the context within which the chosen model of HSCT lies, and make sure that no nearby opportunity or possible hazard will be missed.

4

Outstanding Issues

Before an informed assessment of the potential impacts of HSCT emissions on the atmosphere can be made, a number of scientific issues need to be resolved, or at least better bounded. The manner in which emissions are transported horizontally and vertically away from the flight path needs to be better understood and modeled. The formation of aerosols in the aircraft's wake, and the heterogeneous chemistry that takes place on those new aerosols, require further exploration; reactions in the near field and in the polar regions are of particular concern. Atmospheric observations, together with development and refinement of both wake and global models, are called for to satisfy these goals. This chapter reviews the issues that, in PAEAN's judgment, deserve the highest priority within AESA.

ATMOSPHERIC DYNAMICS AND TRANSPORT

Correct representation of global-scale horizontal and vertical transport processes in the stratosphere, and of stratosphere–troposphere exchange, is essential for assessing the effects of HSCT aircraft emissions. Two-dimensional chemical–transport models will continue to be the primary tool for evaluating the impact of stratospheric aircraft emissions at least through this year, when a preliminary assessment of potential HSCT effects is expected.

Unfortunately, these models cannot yet treat the transport very realistically. As explained in Chapter 2, after global atmospheric forces have pushed air up into the tropical stratosphere, much of that air fans out in the mid-latitude middle stratosphere (where the ozone distribution is dominated by ultraviolet radiation and chemistry), and some air is transported by horizontal motions into the polar winter night (where the ozone distribution is determined by dynamics, and by the emission and absorption of infrared radiation) and then down to lower altitudes. Some of this descending air spreads out over the lowest "overworld" to constitute the region of maximum ozone density; some of it continues to descend into the lowermost stratosphere and then exits into the troposphere.

If a fleet of Mach 2.4 aircraft were to cruise at about 20 km altitude outside the tropics, approximately two-thirds of the emissions would be transported down into the region where ER-2 measurements and the current understanding of heterogeneous chemistry suggest that HSCT NO_x would have only minor effects on ozone. Only one-third of the emissions would remain in the region in which NO_x is active in reducing ozone. Of the emissions occurring at tropical latitudes (estimated to be more than one-third of total emissions in 2015), however, much will be transported by the tropical updraft into the region where NO_x dominates ozone destruction.

The AESA assessment models need to incorporate these atmospheric transport processes realistically if their results are to be useful for evaluating the potential impact of an HSCT fleet. Improvement of the models' transport parameterizations is needed, which in turn will require a database of the radicals and species at the relevant altitudes. Further measurements, and continuing analysis of existing data, will be necessary to reduce the existing uncertainties, particularly above 20 km and in tropical regions.

POLAR PROCESSING OF HSCT EXHAUST

Since late 1978, instruments aboard circumpolar NASA satellites have measured global ozone and its vertical distribution every day over the sunlit portion of Earth. Since the late 1950s, between 50 and 100 ground-based Dobson meters have measured local total ozone at unevenly spaced locations, mostly in the northern hemisphere. Figure 9 presents zonally averaged changes, measured and modeled, in total ozone between 1980 and 1990 as a function of latitude. The group of models, as a whole, show the same general arching pattern as the observations from pole to pole, and agree well in the low and mid-latitudes with each other and the observations. At the north pole the model-to-model comparisons vary by a factor of 3 (about 2 to 6.5 percent loss per decade), however, and at the south pole they vary by a factor of 5 (about 2 to 9.5 percent). These differences indicate that the assessment models do not yet represent polar processing realistically, and may lack or misrepresent other features of the chemistry or dynamics.

As noted in Chapter 2, the behavior of ozone in the polar regions may be worthy of special attention by AESA. Large seasonal decreases in ozone have been observed over Antarctica and the Arctic region, and it is known that heterogeneous processes play a key role. But ability to model particle-formation and

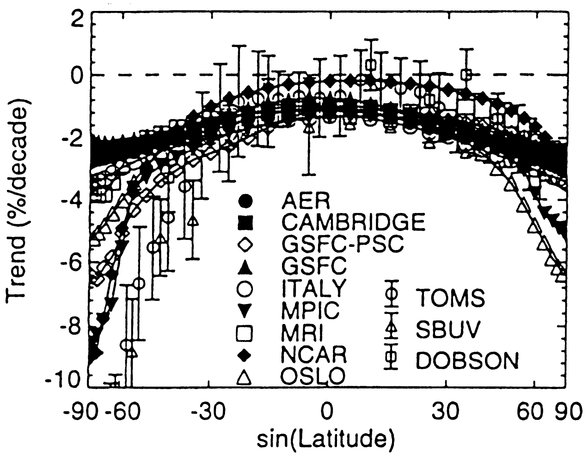

FIGURE 9 Changes in annual average ozone column from 1980 to 1990, as calculated by nine models, together with the trend derived from three sets of observations. MPIC is the model of the Max-Planck Institute for Chemistry; TOMS and SBUV are data from the Total Ozone Mapping Spectrometer and Solar Backscatter UV Spectrometer respectively. (From WMO, 1995; reprinted with permission of the World Meteorological Organization.)

-growth processes quantitatively remains limited, and the related uncertainties are considerable. This constraint is significant in the HSCT context, because attempts to incorporate polar processes into assessment models have shown that the ozone response to HSCT emissions is sensitive to the representation of particle microphysics (see Pitari et al., 1993, and Stolarski et al., 1995). Recent studies by De Rudder et al. (1996) and Tie et al. (1996), which include more realistic descriptions of particle microphysics, indicate additional depletion of ozone by HSCT emissions when polar stratospheric clouds are included. Also, recent modeling of PSC formation (Del Negro et al., 1997) indicates that additions of NO_x, aerosol, and water vapor in amounts characteristic of the assumed 500-craft HSCT fleet can enhance polar aerosol volume on the order of 100 percent for temperatures below 192K. This effect raises the possibility of substantial additional ozone depletion in the polar regions in response to HSCTs via heterogeneous processes involving PSC particles.

Furthermore, ozone in the polar regions appears to be sensitive to interannual fluctuations of temperature and aerosol to a degree that may indicate particular sensitivity to HSCT emissions. Empirical evidence for this sensitivity comes from interannual changes in ozone depletion caused by halogen compounds. Both increased aerosol concentrations (due to a volcanic eruption) and lower winter stratospheric temperature have apparently enhanced the depletion caused by halocarbons, which suggests that particular attention should be paid to aerosol resulting from HSCT emissions in the polar context (see Portmann et al., 1996). HSCT-related changes in NO_y or aerosol concentrations can affect the formation of PSCs, which in turn can alter the mechanisms and the temperature sensitivity of ozone-depleting processes.

HSCT exhaust could affect the polar regions not only as a result of transport from lower latitudes, but directly. Some projected routes, such as those between Europe and Alaska, pass directly through regions where the Arctic vortex is frequently established. In the Arctic region, reactions on aerosols and associated denitrification of the local stratosphere can cause rapid destruction of ozone during winter. An HSCT fleet could add NO_x, water vapor, and sulfate aerosol into the polar stratosphere, causing either reduction or enhancement of seasonal ozone loss already occurring due to halocarbons. Interactions among the NO_x, HO_x, and ClO_x chemical cycles in the gas phase mean that the NO_x in the exhaust may decrease rather than increase polar ozone depletion under some circumstances (Considine et al., 1994, 1995).

While HSCT emissions at non-polar latitudes may influence polar chemistry, as noted earlier, polar processes may also alter the effect of HSCT emissions occurring at non-polar latitudes. Polar processes shorten the atmospheric residence time of NO_x emitted by HSCTs (Pitari et al., 1993; Considine et al., 1994), which generally leads to lower calculated ozone depletion from HSCTs at northern mid-latitudes. Clearly, both further measurements and further modeling studies are needed to improve our understanding of PSC formation and evolution, and how those processes could be influenced by HSCT exhaust.

MODEL DEVELOPMENT

Modeling is a crucial aspect of AESA's effort to determine the atmospheric impact of a fleet of HSCTs. It provides the means of turning what is known about the atmosphere into predictions of what could become of it. Atmospheric measurements supply boundary values and initial conditions for models, laboratory measurements supply numerical coefficients for established physical and chemical equations, and atmospheric dynamics supplies concepts and equations for general 3-D motions in the atmosphere, which modelers approximate and parameterize in their 2-D and 1-D models. AESA's Models and Measurements study, described in the 1992 three-volume M&M report (Prather and Remsberg, 1993), compared the predictions of 14 different 2-D or 3-D models against a large body of selected atmospheric measurements. The spread among the models for most tests in M&M was comparable to that shown between 30°S and 60°N in Figure 9; no single model agreed with the measurements at all times.

AESA has a second Models and Measurements study under way for the 1997-1998 period. Of more concern to the PAEAN panel, however, are AESA's current efforts in the area of 3-D modeling. The NRC AESA Panel's earlier evaluation (NRC, 1994) recommended that increased 3-D modeling have a high priority, particularly given 3-D models' value for sensitivity studies. Not long thereafter, the AEAP initiated the Global Modeling Initiative (GMI), sometimes referred to as the "core 3-D model" effort. There was insufficient time for this effort to have yielded any results by the time of NASA's 1995 assessment, but it is clear that 3-D representations of transport effects are very important for understanding the chemical composition and climate of the lower stratosphere, and for evaluating the impact of the proposed fleet of HSCTs. The use of the GMI will be valuable to future assessments, particularly once it can include aerosol-related chemistry and processes.

The sensitivity of the ozone balance to horizontal transport in the region of transition between chemical and dynamical control places strong constraints on assessment models. It is not clear that parameterized transport in 2-D models can realistically compute the evolution of the ozone mixing ratio in regions where the balance between chemistry and dynamics will be highly dependent on whether transport takes place by rapid, large-scale wave breaking (in which air parcels move through large latitudinal ranges in a few days) or by slow meridional diffusion (which has a seasonal time scale); many models' transport parameterizations reproduce only the latter. Whether such transport details are significant for the overall ozone balance in the assessment models can probably be answered only through careful studies with 3-D chemical–transport models.

The GMI is based on the "science team" approach that has served well in research satellite missions and in many field campaigns. It is not at all clear, though, that this approach will be as effective in the modeling area. Successful field campaigns (e.g., AASE, ASHOE, and SPADE) have featured not only strong leadership and dedicated participants but also sufficient resources to accomplish their goals. The GMI science team, however, consists of many groups or individuals for whom the GMI is a relatively minor commitment. Although the goals of the GMI science team for the AESA assessment have now been formulated fairly specifically, the panel is concerned that the model may not be able to provide 3-D integrations that will fulfill the requirements of the 1998 stratospheric assessment. A fully realistic 3-D model is further off still. The value of continuing the GMI effort, however, even if its results benefit only later assessments, is not in question.

MODELING THE WAKE

Enhancement of AESA's plume/wake modeling effort was one of the earlier NRC panel's recommendations. Better understanding of the microphysics in the wake region is needed before the larger-scale models can properly represent HSCT effects. Two aspects of exhaust behavior and dispersion are of particular interest.

The first is important for NO_x reduction of ozone. The Mach 2.4 HSCT will cruise between 18 and 21 km altitude, and inert material deposited at that altitude has a stratospheric residence time of about two years (Kinnison et al., 1994a). In the sunlit stratosphere, NO and NO_2 reach a photochemical steady state within a few minutes, and NO_x attains photochemical steady state with HNO_3 within a few weeks. After the exhaust gases spread, the mixing ratio of NO_y from the exhaust is a thousandfold or more lower than that of ozone. Only cyclic processes such as reaction (1), occurring hundreds of times, change ozone significantly, so the details of the reactions of NO_y in the wake of the aircraft appear to be of little consequence with respect to ozone. However, if some form of NO_y is permanently incorporated into an atmospheric aerosol, which should have a stratospheric residence time of about 1 year (compare Kinnison et al., 1994a), then the detailed behavior of exhaust components in the wake becomes more important for ozone.

The second aspect of exhaust behavior that is of concern is the formation of sulfuric-acid particles in the wake. Fahey et al. (1995) measured aerosol concentrations in the exhaust of a Concorde SST in flight using instrumentation on board the ER-2. From the fuel's known sulfur content and the results of particle-counter measurements, it was inferred that a large fraction of the sulfur in the fuel was converted to SO_3 before leaving the engine, and new particles formed in the near wake before being intercepted by the ER-2. The measurements indicated that 12 to 45 percent of the total fuel sulfur was rapidly oxidized to sulfur trioxide, instead of appearing as sulfur dioxide. Uncertainties related to the instruments measuring particle sizes, however, made it necessary to use crude size estimates in converting the number of particles measured into inferred particle mass (Fahey et al., 1995). These percentages thus should be viewed with caution, and evaluations of potential HSCT impact need to include the related uncertainties about surface area available for heterogeneous reactions and other details of the relevant microphysical processes.

The high aerosol concentrations observed in the wake may have been unexpected, but their formation from a high-temperature combustion process should not be considered surprising. Sufficiently high supersaturation in the presence of suitably low available surface area for condensation is likely to result in rapid nucleation of particles. Similarly high concentrations of particles have been observed for natural, low-temperature processes in the troposphere and stratosphere over far more extensive regions. Clarke (1993) reported that concentrations equal to those measured in the Concorde's wake occur over regions of several hundreds of kilometers at altitudes of 8-10 km. Later observations near the tropical tropopause showed similarly high concentrations of small (circa 15 nm) nuclei; it has been argued that they provide a source of nuclei upon which oxidized sulfur gases in the stratosphere can condense (Brock et al., 1995). Hence, interpretations of the significance of high concentrations of aircraft-derived nuclei need to recognize that extensive natural sources of similar particles can be present at the altitudes at which aircraft operate.

Many reactions between atoms, radicals, and molecules are at chemical equilibrium under combustion conditions. High-temperature equilibrium product distributions in the engine can be "frozen out" during the rapid expansion and cooling of the combustion gases, and depending on the cooling rate and complex chemical kinetics of the system, the exhaust gases could contain significant amounts of gaseous sulfuric acid as well as gaseous SO_3 and SO_2. It appears that much of the sulfur in the exhaust forms fresh aerosol in the near wake (Kärcher and Fahey, 1997; Taleb et al.,1997), rather than accreting on existing atmospheric particles, which is consistent with much of the sulfur in the exhaust being in the form of SO_3 or H_2SO_4. This formation of aerosol would make a larger-than-expected surface area available for heterogeneous reactions. Weisenstein et al. (1996) used a 2-D model to calculate the change in annual average ozone column at 57°N caused by the emissions of a Mach 2.4 HSCT fleet. They assumed that the fleet would have an EI(SO_2) of 0.4. When they varied the percentage of sulfur emitted as particles (or particle precursors), the available aerosol surface area changed as shown below:

SO_2 Emission	*Aerosol Surface Area*
0% sulfur as particles	UNEP aerosol* + 30%
10% sulfur as particles	UNEP aerosol + 50%
100% sulfur as particles	UNEP aerosol + 150%

Sulfate aerosols at the UNEP level are known to have a strong impact on stratospheric chemistry by providing a site for the hydrolysis of N_2O_5. They may also be found to have a significant global impact on radiative forcing or other atmospheric properties. The consequences of an aviation-related increase in sulfate aerosols, in the context of these existing processes, must be considered. The possibility that aerosols from the exhaust might be transported into the troposphere, where they could affect cloud properties, should also be explored. Detailed modeling of aerosol particle formation and growth in the wake will be an important tool for determining the critical properties that govern the formation and the effects of the sulfate aerosols in the plume.

CLIMATE EFFECTS OF HSCT EXHAUST

AESA has taken an initial step toward evaluating the impact of 500 supersonic aircraft flying at Mach 2.4 with an EI(NO_x) of 15 on climate, using the

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*UNEP aerosol is defined in WMO (1992); it refers to the surface area of background stratospheric aerosol in a relatively clean period between major volcanic eruptions. It was estimated from measurements made by the second Stratospheric Aerosol and Gas Experiment.

Goddard Institute for Space Studies (GISS) general-circulation model (Rind and Lonergan, 1995). The radiative effects of changes in the vertical distribution of ozone and water vapor were evaluated separately. The ozone perturbations were found to cause a stratospheric cooling of a few tenths of a degree C, and a global mean surface-temperature increase of 0.025°C. This surface-temperature perturbation is not statistically significant when compared with the 0.09°C inter-annual standard deviation of surface temperature in the model, although a predicted high-latitude (70-90°N) stratospheric cooling of close to 0.5°C does appear to be statistically significant by comparison with model variability. The increase in water vapor in the stratosphere for the same 500-aircraft scenario has a similar effect: a stratospheric cooling of 0.5°C. The resulting mean surface-temperature increase (0.01-0.02°C) again is small compared with the model's standard deviation.

Soot and sulfate aerosols could also affect climate by altering radiative forcing in the atmosphere. Stratospheric sulfate aerosols may also contain substantial amounts of non-volatile solid particles (Farlow et al., 1977, 1978); although these solid components could affect the aerosols' radiative forcing properties, little work has been done to characterize their chemical composition. Other properties, such as size distribution, lifetime, and chemical reactivity, affect aerosols' climatic impacts as well. Certainly much remains to be understood before the potential impacts of increases in aerosol concentrations can be well quantified.

The NRC's AESA panel noted that NASA's 1993 HSRP Interim Assessment Report concentrated on the NO_x–ozone issue, and that no assessment of climatic impacts was included (NRC, 1994). They suggested that AESA should "conduct an immediate first-cut assessment" of possible effects of HSCT effluents on climate, including the modification of the thermal balance of the atmosphere by changes in the vertical ozone distribution, the alteration of the number or size distribution of cloud- or ice-nucleating aerosols, and the influence of added water vapor on cirrus clouds and contrails. From the research summarized above, it does not seem that significant impacts on climate from HSCT exhaust can be expected, although many uncertainties remain. The influence of contrails on cloudiness, a growing concern in the troposphere, is a very minor concern for AESA; over most of the stratosphere, HSCT aircraft emissions will not form contrails (Stolarski et al., 1995). (In the winter polar stratosphere, however, the HSCT exhaust constituents can contribute to the formation of PSCs, as noted earlier in this chapter.) Given the extreme complexity of accurately modeling the climate system, this panel does not recommend that AESA undertake further studies in this area.

UNCERTAINTIES AND UNPREDICTABILITIES

As Stolarski et al. (1995) note, the uncertainty related to gas-phase reaction-rate coefficients is the only readily quantifiable uncertainty associated with the various models used. The differences among the model results shown in Figures 8 and 9 suggest that the overall model uncertainties are considerably larger than those in the gas-phase rate coefficients alone. The spread of predicted ozone-column reductions among the nine models in Figure 9 sets a lower limit for the uncertainty of model-predicted ozone-column reduction. For example, at tropical latitudes, the observed ozone column decrease is 1±1 percent, and the models agreed with observations and among themselves within this range. At 60°S, however, the observed column decrease is 9±2 percent, and the models calculate a decrease of 3±1 percent. At the poles, the model uncertainties are even greater.

Similarly, in Figure 7 five AESA assessment models exhibit good agreement for calculated change of ozone vertical column, with a maximum spread of 1 percent. Figure 8, however, shows the uncertainty in the vertical distribution of the calculated changes in ozone concentration at 45°N. The models' vertical profiles agree fairly well among themselves at altitudes above 30 km, but they are noticeably different below that. For example, two models predict noticeable ozone production in the troposphere as a result of HSCT operation in the stratosphere, and two models give almost zero ozone production. These differences would yield different calculated warmings of Earth's surface. An ozone increase in the troposphere from HSCT exhaust would also affect ozone-change calculations for subsonic aircraft in the troposphere.

Chemical details not predicted by the models may also be quite important. For example, what if reaction (6) had turned out to be slow on sulfuric acid aerosols in the mid-latitudes, and reaction (8) had been fast? As shown by net reactions (12), reaction (6) leads to removal of active NO_x, but it does not directly increase the number of active chlorine species. However, the reaction sequence below (which includes reaction (8)) yields two units of active ClO, and converts one unit of active NO_x into nitric acid:

$$
\begin{array}{l}
NO_2 + ClO \rightarrow ClONO_2 \\
ClONO_2 + HCl \rightarrow C1_2 + HNO_3 \\
C1_2 + \text{near UV} \rightarrow 2\,Cl \\
2\,(Cl + O_3 \rightarrow ClO + O_2) \\
\hline
\text{net:}\; NO_2 + HCl + 2O_3 \rightarrow HNO_3 + ClO + 3O_2
\end{array}
\qquad (13)
$$

In the lower overworld and in the lowermost stratosphere, one unit of ClO is more active in destroying ozone than one unit of NO_2. In this hypothetical case, the addition of heterogeneous reactions to atmospheric models would have resulted in higher calculated ozone reductions from HSCT emissions in the mid-latitudes than those actually calculated.

This discussion illustrates the value of AESA's efforts to obtain a more complete understanding of the important features of stratospheric science. However, many uncertainties—for instance, those attached to transport processes, microphysics, and heterogeneous chemistry—will be challenging to resolve. AESA needs to identify the most critical uncertainties, and develop a plan establishing research priorities that will reduce those uncertainties as much as possible during AESA's lifetime. Such a plan will permit response and input to these activities from a wider scientific community, and may enable the international atmospheric-science community to cooperate on critical research issues.

5

Recommendations

AESA has made praiseworthy progress toward its goal of providing a scientific basis for assessing the potential impact of a fleet of HSCTs on the atmosphere, particularly on stratospheric ozone. Its models project the ozone reduction by a fleet of 500 Mach 2.4 HSCTs to be almost an order of magnitude less than was projected in 1990, under operating conditions that include a conceptual HSCT engine with a low NO_x emission index, and a choice of flight altitude and Mach number that would minimize the effect of added NO_x. Through laboratory measurements of the rates of newly recognized heterogeneous chemical reactions, and simultaneous in situ measurements of almost all active chemical species at altitudes up to 20 kilometers, AESA has shown that heterogeneous reactions involving sulfuric-acid aerosols deactivate NO_x in the lower stratosphere. Looking at patterns of correlation between reactive species and tracers such as N_2O and CH_4 has yielded new understanding of atmospheric chemistry and atmospheric motions. Although major uncertainties remain in how numerical models treat atmospheric motions (especially above 20 km), AESA's modeling work has been effective in translating both laboratory and in situ measurements into projected impacts. AESA has also identified new and important questions, such as how HSCT exhaust gases would interact with the polar stratospheric clouds that contribute to ozone depletion over the Antarctic. PAEAN commends AESA for its work; the recommendations that follow indicate areas that the panel feels are currently in need of greatest emphasis.

Transport Processes

Observations from aircraft and satellite programs have greatly increased our understanding of transport processes in the stratosphere. Major uncertainties in understanding air transport remain, however, especially above the tropical region and at altitudes above 20 kilometers, where fewer data are available. **PAEAN recommends that AESA emphasize the analysis and interpretation of data from aircraft missions and satellites, in order to quantify better the meridional and vertical transport in the stratosphere, particularly at altitudes between 20 and 30 kilometers.**

Polar Processing

The processing of HSCT emission products in the polar regions is not adequately represented in current 2-D models. Only when the evolution of liquid and solid PSC particles in the winter polar stratosphere is known can the effects of the additional input of HSCT-related gases and aerosols be properly assessed. **PAEAN recommends that AESA support field measurements as well as model developments that are specifically designed to unravel the complex formation process of polar stratospheric cloud particles**.

Assessment Models

Current assessments of the impact of a fleet of HSCT still rely on 2-D models. However, 3-D transport effects are of crucial importance for understanding this impact, and the use of the GMI model will be required for future assessments. **PAEAN recommends that AESA continue to support the development and testing of the Global Modeling Initiative model.**

Microphysics in the Plume-Wake Region

As the earlier AESA panel noted in 1994, the processes (both gas-phase and heterogeneous) within the plume-wake region need to be properly described so that they can be incorporated into large-scale atmospheric models. **PAEAN recommends that the development of microphysical models of the plume-wake regime continue, in order to assess the role of the chemical and physical transformations that may occur before engine effluents mix into the background atmosphere**.

Climate Studies

Because of the complexity of the climate system, it is not clear that any expansion of the limited climate studies AESA has sponsored will yield significant further progress on the issue of climate impacts within the time frame of the 1998 assessment. Research to date suggests that the globally averaged direct radiative impact of stratospheric aircraft emissions can be expected to be small, although the effects of aerosols must be better quantified. **PAEAN recommends that AESA continue its present policy of not undertaking model studies of the impact of aviation on climate, beyond calculating the degree of radiative forcing by components of HSCT exhaust.**

BEYOND THE 1998 ASSESSMENT

Many of the uncertainties noted earlier, such as those related to transport processes, microphysics, and heterogeneous chemistry, have not yet been sufficiently reduced to permit an informed assessment of the possible atmospheric effects of a fleet of HSCTs to be made. AESA management needs to identify the most critical uncertainties, and develop a strategy that will enable them to be reduced as far as possible during AESA's remaining lifetime and even beyond. **PAEAN recommends that AESA draw up and execute an adequately detailed plan that sets priorities for research to reduce the remaining critical uncertainties.**

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Acronyms and Other Initialisms

AASE	Airborne Arctic Stratosphere Expedition
AEAP	Atmospheric Effects of Aviation Project
AER	Atmospheric and Environmental Research, Inc.
AESA	Atmospheric Effects of Stratospheric Aircraft project
ASHOE	Antarctic Southern Hemisphere Ozone Experiment
CAMED	Universities Cambridge and Edinburgh of UK (universities' model)
CIAP	Climatic Impact Assessment Program
CSIRO	Commonwealth Scientific and Industrial Research Organization
EI	Emission index (grams of reference substance emitted per kilogram of fuel burned)
GISS	Goddard Institute for Space Studies
GMI	Global Modeling Initiative
GSFC	Goddard Space Flight Center
HRDI	High-resolution Doppler imager
HSCT	High-speed civil transport
HSRP	High-Speed Research Program
LLNL	Lawrence Livermore National Laboratory

MAESA	Measurements for Assessing the Effects of Stratospheric Aircraft (experiment)
MPIC	Max-Planck Institute for Chemistry
NASA	National Aeronautics and Space Administration
NAT	Nitric acid trihydrate
NO_x	Reactive nitrogen species ($NO + NO_2$)
NO_y	$HNO_3 + 2(N_2O_5) + NO_3 + HNO_4 + ClONO_2 + NO + NO_2$
NRC	National Research Council
NCAR	National Center for Atmospheric Research
OSLO	University of Oslo model
PAEAN	Panel on Atmospheric Effects of Aviation
PSC	Polar stratospheric cloud
SAT	Sulfuric acid tetrahydrate
SBUV	Solar Backscatter UV Spectrometer
SPADE	Stratospheric Photochemistry, Aerosols, and Dynamics Expedition
SST	Supersonic transport
STRAT	Stratospheric Tracers of Atmospheric Transport
STS	Supercooled ternary solution of nitric acid, sulfuric acid, and water
TOMS	Total Ozone Mapping Spectrometer
UARP	Upper Atmosphere Research Program
UARS	Upper Atmosphere Research Satellite
UKMO	U.K. Meteorological Office
UNEP	United Nations Environment Programme
UV	Ultraviolet (radiation)
VOC	Volatile organic compound
WMO	World Meteorological Organization