

ASHOE/MAESA End of Mission Summary of Preliminary Results

This statement summarizes the observations and preliminary interpretations of the science team for Airborne Southern Hemisphere Ozone Experiment / Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA). ASHOE/MAESA was sponsored by NASA's Upper Atmosphere Research Program and by NASA's High Speed Research Program; NOAA and NSF contributed substantially, as did the meteorological services of New Zealand, Australia, United Kingdom and those signatory to the convention governing the European Centre for Medium - range Weather Forecasts (ECMWF). The mission was designed to address questions about the causes of the year round mid-latitude ozone loss observed in the Southern Hemisphere in the last 15 years, in particular the relative roles of vortex air transported to mid latitudes and in situ loss induced by heterogeneous chemistry on sulfuric acid aerosols. These questions are important for the general understanding of the composition of the lower stratosphere and its consequent effects on the radiative balance of the atmosphere, and hence for the assessment of the potential environmental effects of stratospheric aircraft upon this balance, a goal also served by the flights studying the exchange of air between the tropics and midlatitudes of both hemispheres. More detailed analyses will follow during the coming months and years. There will be continuing comparison of these results with those from previous missions, including the Stratosphere Troposphere Exchange Program (STEP) in 1987, the Airborne Antarctic Ozone Expedition (AAOE) in 1987, the Airborne Arctic Stratospheric Expedition (AASE) in 1989, the Airborne Arctic Stratospheric Expedition II (AASE-II) in 1991-1992, and the Stratospheric Photochemistry, Aerosol and Dynamics Experiment (SPADE) in November 1992 and May 1993. Because this document represents a preliminary view of what the observations mean, it is not referenceable in the scientific literature.

Flights of the NASA ER-2 high altitude aircraft, carrying as many as 16 instruments, provided new observations to diagnose the chemistry, physics and fluid motion of air in the lower stratosphere. Measurements span February to November, 1994 and from the edge of Antarctica at 70°S to upper Canada at 60°N, in conjunction with observations from the ground, balloons, and satellites. Most measurements were in the southern hemisphere and in the tropics; the former was being studied using in situ techniques over the entire evolution of the winter vortex, while the latter was being so investigated for the first time.

Operation

The observations are based primarily on 45 flights of the NASA ER-2 high altitude aircraft. For most flights, the ER-2 carried 16 instruments to measure the abundances of reactive and inert trace gases, aerosols, temperature, pressure, winds, ultraviolet light, and temperature profiles. For flights specifically to study dynamics and radiation, some of the trace gas instruments were removed and an instrument that measures infrared radiation was added. Among the 45 flights, 26 were from Christchurch, New Zealand, 5 were from Barber's Point, Hawaii, and 6 were transits between New Zealand, Fiji, Hawaii, and California. Also included were two full duration (8 hour) test flights north from Moffett Field in February, 5 short (2+ hours) test flights from Moffett Field between January and March and a northbound flight from Moffett Field in November, 1994. Thirty-two flights had the full payload, 11 had the dynamics and radiation configuration and 2 were test flights for individual instruments.

Observations from other instruments on the ground, balloons, and satellites provide valuable contributions to ASHOE/MAESA. Analyses of weather observations by UKMO, ECMWF, UK UGAMP, NMC, and GSFC aided flight planning and dynamical analyses. Satellite data from MLS and HALOE on UARS and TOMS on Meteor-3 give a global context for the local measurements of the ER-2. The GSFC Lidar and National Institute of Water and Atmospheric Research (NIWAR) column measurements from Lauder, New Zealand, and the MacQuarie Island ozonsondes provided valuable intercomparisons for aerosol and ozone measurements on the aircraft, extending the

observations well above and below the aircraft. All these observations will be combined with those from the ER-2 for study.

Objectives

An over-arching mission objective, as laid out in the mission booklet, was to investigate the causes of long term reductions of ozone in the wintertime midlatitudes in the southern hemisphere, which have been observed by ground-based measurements and satellites for the last 15 years. To meet this objective, ER-2 flights were designed to observe several aspects of ozone loss: the rapid decline of ozone each spring over Antarctica, the spread of ozone-poor and chemically-perturbed air to midlatitudes, and the activation of ozone-destroying chlorine directly in midlatitudes by reactions on the sulfate aerosols and by polar stratospheric clouds (PSCs) in polar regions. Flights were designed to determine the rate of chemical removal of ozone by nitrogen, hydrogen, chlorine, and bromine chemical radicals and to test our understanding of the processes that regulate the abundance of these reactive gases. Observations of tracers of lower stratospheric transport will permit study of the mixing of air between the midlatitudes and tropics because this process helps establish the ozone distributions and rates of ozone change. The radiative transfer in the infrared was studied in order to observe the thermal structure of the lower stratosphere in and around the vortex, and to make more direct estimates of the diabatic cooling rates than hitherto.

The evolution of the Antarctic polar vortex, with its circumpolar winds and low temperatures, was covered during the course of ASHOE/MAESA. The rapid loss of ozone, known as the ozone hole and reaching its maximum extent early in October each year (i.e. during austral spring) appears mainly within this vortex. Measurements of trace gases and meteorological parameters were made early in the life cycle of the vortex (Deployment I in March-April), prior to the onset of cold temperatures; after the vortex had formed and temperatures dropped below about 195 K, the formation temperature of polar stratospheric clouds (Deployment II in May-June); after the temperatures had dropped below ice saturation, when large scale loss of the condensable vapors HNO₃ and H₂O by sedimentation in PSC particles occurs (Deployment III in July-August); and when ozone was the most depleted (Deployment IV, October). The midlatitude regions equatorward of the maximum in the polar night jet stream were also the subject of close observation and study.

The other objective of ASHOE/MAESA was to obtain measurements for the assessment of the atmospheric effects of future supersonic (High Speed Civil Transport) aircraft that are now being considered. ASHOE/MAESA addresses three of the most uncertain aspects of this assessment.

First is the transport by air motions of the exhaust from midlatitudes, where most HSCTs will fly, to the tropics, where the exhaust could rise up and spread out to midlatitudes at higher altitudes. Model calculations suggest that HSCT exhaust could efficiently destroy ozone above about 25 km altitude, while at 20 km the exhaust is currently expected to cause some local increases in ozone. Understanding the transport of air between the lower stratosphere where the HSCTs will fly and the middle stratosphere where the exhaust can do the most damage to ozone is essential. Observations of a large number of tracers with a range of lifetimes will provide a good opportunity to quantify transport processes.

Second, the HSCT exhaust is calculated to increase stratospheric water vapor and gaseous nitric acid, which are the main components of polar stratospheric clouds (PSCs). HSCT exhaust near the cold regions at the winter poles and the equator could therefore possibly increase the frequency and range of PSCs, and also the reactivity of gases on cold, sulfate aerosols, which increases rapidly as the water content of the particles rises. Because chlorine is rapidly converted to its ozone-destroying forms on PSCs and cold sulfate aerosols by reactions of the reservoir gases on the particles, an increase in these clouds could result in increased ozone loss. The measurements of

aerosol size distribution and refractive index will enhance quantitative knowledge of these processes.

Third, the uncertainties in the laboratory measurements of chemical reaction rates and products that are used in assessment models directly affect the uncertainty in the calculations of ozone loss expected for projected injections of HSCT exhaust. Measurements of concentrations of hydrogen, nitrogen, chlorine and bromine radicals and of their reservoirs and precursors made during ASHOE/MAESA provide a rigorous test of our understanding of processes which regulate the abundance of reactive gases in the stratosphere. The measurements allow quantification of the effects of current laboratory uncertainties and chemistry not represented in the models on the calculated concentrations of reactive gases. Observations taken over a wide range of latitudes, altitudes, seasons, time of day, and abundances of chlorine, bromine, and nitrogen chemicals provide a stringent test of the processes controlling reactive species.

An uncovenanted bonus was an opportunity to measure directly the chemical composition of the exhaust plume from a Concorde supersonic airliner as it approached Christchurch, New Zealand. Of the currently operating aircraft, the Concorde is the one most similar to the projected HSCTs. Measurements of the chemicals in its exhaust over a range of times after emission tests the validity of the ground-based measurements of the emission indices of pollutants for the Concorde. It also tests atmospheric chemistry for the polluted conditions of the exhaust plume.

Summary of Observations and Results

These unique observations of variations of long-lived trace gases (including O₃, H₂O, N₂O, CO₂, CH₄, CO, H₂, SF₆ and a wide range of CFC's) in the lower stratosphere will help define the transport and mixing of air among the polar, midlatitude, and tropical regions of the stratosphere and the troposphere. Observations and models indicate that the transport of polar air, primed for ozone loss, occurs as filaments that are shed into the midlatitudes. Studies underway seek to quantify the midlatitude ozone loss that results from this mixing process. Tropical stratospheric air is also observed to be shed as filaments into midlatitudes. The aircraft observations suggest that midlatitude air mixes into the outer tropics from 23.5° to about 10° latitude, with the inner equatorial region showing signs of air which had entered the stratosphere more recently from below. The extent to which the outer tropical air can ascend to higher altitudes is crucial in the context of the potential effects of HSCT exhaust. Calculations show that such exhaust will destroy ozone if it gets to higher altitudes. These observations shed new light on the transport of air both in the stratosphere and between the stratosphere and troposphere.

The ASHOE/MAESA observations will improve the understanding of the processes that lead to the Antarctic ozone hole and to ozone loss at midlatitudes. These processes include the formation of PSCs, the conversion of chlorine from its reservoir forms to its ozone-destroying reactive form on cold, sulfate aerosols, and of the return of chlorine to the inactive forms after all ozone is destroyed inside the ozone hole. The transport mechanisms which redistribute the effects of these chemical processes will also be better understood. There will be a better understanding of the detailed mechanisms of the processes, which will help to improve numerical models used to simulate the stratosphere.

These observations, when compared to theoretical models, demonstrate a generally good understanding of the photochemistry in the lower stratosphere for the altitudes, latitudes, and seasons sampled during ASHOE/MAESA. The main disagreement between observation and current model calculation is the amount of chlorine in the form of HCl in the Northern Hemisphere during 1991 to early 1993; for both the Northern and Southern Hemispheres in 1994 the agreement is good. Generally, agreement is far better than expected from the stated errors in the measurements and the model parameters.

The simultaneous measurements of the reactive hydrogen, reactive chlorine and reactive bromine show conclusively that these species destroy ozone faster in the lower stratosphere than does reactive nitrogen, in the chlorine-laden stratosphere of the 1990's. Reactive nitrogen is now thought to be dominant only higher in the stratosphere, above altitudes sampled by the ER2. Thus, the calculated effect of HSCT exhaust on ozone is to produce small ozone increases in the lower stratosphere. The importance of reactions on sulfate aerosols which convert reactive nitrogen to reservoir forms is confirmed for a stratosphere with the low aerosol amounts characteristic of the period three or more years after a major volcanic eruption.

Observations and results from ASHOE/MAESA

The structure of this section is based in a consideration of three latitude regimes: polar, midlatitude, and tropical. A separate section is devoted to the Concorde exhaust encounter. Statements are presented as separate paragraphs under each heading.

Polar region

Ozone in the Antarctic polar vortex during October was substantially depleted, just as in the previous two years. Preliminary minimum ozone values reported by Meteor-3 TOMS were 90 Dobson Units and the average areal extent of intense ozone loss was about 23 million km², slightly larger than in 1992 and 1993 and almost twice the size of Antarctica. Ozone loss in the Antarctic polar vortex has now been severe in 7 of the last 8 years.

The aircraft observations of ozone, tracers and radicals provide a high quality set and span a wide range of latitudes and altitudes between 16 and 21 km in the lower stratosphere over the whole period from March to October. They provide the database to examine the chemical loss of ozone and its relationship to diabatic cooling and the transport it induces in the region of the polar night jet stream and the vortex. The greatest ozone losses in and near the vortex occurred at the lower altitudes in the range (16 - 20 km) sampled by the ER2.

Mean temperatures and other gross average indicators of dynamical activity associated with the Antarctic polar vortex were near the average values for the last 15 years, implying that observations from ASHOE/MAESA are representative of conditions in the recent past. These indicators include the stratospheric zonal mean winds and heat flux at 60°S and zonal mean temperature gradient. Minimum temperatures, important for PSC activity, were slightly lower than average by a few degrees for June through October. Temperatures less than 195 K persisted at 70 mb within the vortex into the third week of October, and at 100mb into early November.

Observations and model calculations demonstrate that air is transported out of the vortex as filaments that are sheared from the vortex edge and become thinner with time. The shedding of filaments was observed during all deployments, but was most intense in October. Studies of observed variations in the winds near the vortex edge will define the importance of smaller scale fluctuations for the exchange of air between the polar region and midlatitudes. There is on some flights preliminary evidence for a possible temperature signature associated with filaments from the vortex edge. Preliminary studies show examples of vertically laminated tracer structures correlated with the in situ winds. Some of these wind variations are undular, suggesting a role for gravity and inertia-gravity waves in cross-vortex transport. Turbulence was comparatively weak at the vortex edge as compared to the lower stratosphere over New Zealand.

Observations of ClO, HO₂, OH, NO and NO₂ were made in the air in and around the polar vortex during all four deployments. Analysis of these observations will allow us to quantify the the role of heterogeneous reactions on cold sulfate aerosols in regulating the abundance of radicals. Simultaneous observations of HOX and ClO will allow us to distinguish between the role of two processes that lead to production of reactive chlorine on sulfate aerosols: ClONO₂ + H₂O → HOCl + HNO₃ and HCl + ClONO₂ → Cl₂ + HNO₃ since the first of these produces HOX more efficiently than the second. Laboratory studies suggest that ClONO₂ + H₂O on sulfate aerosols is important when the temperature is below about 200 K. This process will probably become more important at higher temperatures with the addition of water vapor and NO_y from HSCT exhaust. Measurements made in type I PSC's at the vortex edge during late July challenge the commonly accepted notion that such clouds consist entirely of particles of nitric acid trihydrate (NAT). As in the Arctic, the main cloud did not appear until temperatures were 2-3 K colder than NAT saturation.

The clouds appeared to be made up of externally mixed particles, and could contain both liquid and frozen particles of various hydrates and ternary mixtures of water, sulfuric acid and nitric acid. Ice crystals may have been present. Surface areas of aerosols appeared to be much lower in cloud free vortex air which had earlier been colder than the frost point.

Tracer mixing ratios inside the vortex appeared to be higher than those encountered at similar altitudes and latitudes during the AAOE mission from Punta Arenas in 1987. Intense denitrification and dehydration were not encountered in horizontal flight above 16 km, except on one flight in early October when water vapor dropped sharply 7° of latitude poleward of the wind maximum; in 1987 the loss of condensable vapors was mostly evident closer to the wind maximum. There was no large asymmetry (z30%) of water vapor between the hemispheres outside the vortex, a feature which was observed in 1987.

Preliminary measurements of molecular hydrogen during August and October constrain its value at flight altitudes to between 0.45 and 0.70 ppmv. There is a low amplitude inverse correlation between H₂ and CH₄ in the lower stratosphere, indicating that a modest fraction of the methane molecules which originally entered the stratosphere are not converted to water vapor.

Greater than expected abundances of NO_y, caused by evaporation at ER2 levels of particles sedimenting from a higher altitude, were observed in early June near the vortex edge at about 16 km. Denitrification (irreversible removal of NO_y by particle growth and sedimentation) was observed in mid-winter (July) and later, mainly at and below 16 km. The amount of denitrification is an important process for the complete removal of O₃ observed in the Antarctic polar vortex. Observed dehydration was minimal in early August; in early October, intense dehydration occurred about 7° latitude south of the vortex edge at cruise altitudes (18-20 km). At and below about 16 km, some obviously dehydrated air was observed further equatorward.

Denitrification was observed on some flights at about 16 km in early June and early August, with no accompanying dehydration. The two processes are thus shown to be independent over Antarctica. Dehydrated air in August and October was also denitrified.

Large increases in ClO and decreases in HCl were observed after the occurrence of PSCs. Beginning in early June, for air which had been at temperatures below 195K, ClO was observed to increase to 700-900 pptv and HCl to decrease by amounts up to 1.5 ppbv. This air was in the outer regions of the vortex; penetration to the inner regions, where higher ClO abundances were present, was not possible given the combination of vortex motion, airfield weather and flight duration. Activated chlorine in the form of enhanced ClO was seen in the polar vortex on four flights. Loss of HCl was seen on other flights as well, because the instrument concerned was on the dynamics & radiation flights. These observations of ClO and HCl, and the stoichiometry for HCl loss vs. ClO + 2Cl₂O₂ production, show in detail the role of PSCs in creating enhanced levels of ozone-destroying reactive chlorine.

The observations confirm that ClO_x and BrO_x catalytic chemistry dominates ozone loss in the polar vortex. Although it had been suggested that OH and HO₂ might have a significant role for polar ozone loss, the observations of small OH and HO₂ abundances demonstrate an insignificant role for OH and HO₂ in ozone loss inside and around the vortex for fall through to spring.

Polar air nearly devoid of ozone was sampled in situ for the first time inside the vortex near the 400 K potential temperature surface (about 16 km altitude) on 10 and 13 October. Mid-October is late in the period of severe ozone depletion over Antarctica. This air contained little O₃ (<0.4 ppmv), little or no ClO (<100 pptv), high NO (1 ppbv), low NO_y (2 ppbv), and HCl equivalent to estimates of total inorganic chlorine (2.6 ppbv). The almost total loss of ozone creates a condition where chlorine is shifted rapidly from ClO to HCl via the reaction of Cl with CH₄ and NO_y is shifted into NO. Thus, HCl was observed to be the dominant remaining chlorine species, whereas in the

Arctic, with smaller ozone loss, ClONO₂ has been observed by others to be in this role. The implications of these interhemispheric differences in the final phases of the polar vortices on ozone loss at midlatitudes are being examined.

The dynamics & radiation payload provided evidence for a layer of warm air in the 14-17 km region at the base of the vortex which was not well reproduced in meteorological forecasts and analyses. Preliminary estimates of diabatic cooling rates in the polar night jet stream and in the vortex between the tropopause and 19 km showed somewhat larger cooling rates than those produced by numerical model calculations. At the latitudes of the polar night jet stream and the vortex, the lower stratospheric air below about 60 mb (the approximate cruise altitude of the ER2) during the dynamics & radiation flights was up to 5K colder than the temperatures in global meteorological analyses and in low vertical resolution soundings from operational satellites.

Observations from the UARS satellite made by the MLS and HALOE instruments were provided to the aircraft site in Christchurch. The ATMOS instrument on the Space Shuttle made measurements coincident with the ER2 in early November. Preliminary intercomparisons with the ER2 for all these instruments are encouraging, and lend both powerful support and a global context, including altitudes above the aircraft, to the in situ measurements.

Middle latitudes

The fast photochemistry of the lower stratosphere appears to be well understood for the altitudes, latitudes, and seasons that were sampled by the ER-2 during ASHOE/MAESA and SPADE. This ability to test the photochemical chain reactions is a direct result of careful, simultaneous measurements of a number of trace gases and meteorological parameters on the same platform, a capability which has not existed previously. The observed NO, OH, HO₂ and ClO are well simulated by a model that uses measured long-lived species as input data. Agreement is generally far better than expected from the stated errors in the measurements and the model parameters. This understanding greatly increases confidence in the chemistry incorporated into assessments models for studying the effects of HSCTs.

However there is an important deviation from the generally good agreement between observation and model calculation: the HCl/Cl_y ratio in the Northern Hemisphere. In 1991/1992 it was observed to be about 0.35±0.1, and in 1993 about 0.45±0.15, these fractions being only about 60% of model predictions. However, in four flights at the beginning and end of ASHOE/MAESA in February and November 1994 the measured HCl/Cl_y ratio was 0.55±0.15, in agreement with model predictions. Also, data from several flights in the Southern Hemisphere where the air had not recently been below a temperature of 195 K showed measured values of HCl/Cl_y ranging from 0.6 to 0.9. The Cl_y budget, which is constructed from measurements of organic chlorine, HCl and ClO, and ClONO₂ inferred from ClO and NO, was balanced in the Southern Hemisphere in 1994, but not in the Northern Hemisphere for 1991 through early 1993. The interhemispheric asymmetry in the HCl/Cl_y ratio, and the apparent evolution with time of the Northern Hemispheric ratio may be associated with the enhanced particle surface areas resulting from the eruption of Mount Pinatubo, but the responsible mechanism is not known.

Filaments of both polar and tropical air are observed at middle latitudes for potential temperature surfaces between 340 K and 520 K (roughly 14 to 20 km altitude) as they were during AASE II and SPADE. These filaments, which are contorted into thin, sheets by wind shear, are often predicted by contour advection and trajectory dynamical models. They may be a dominant way that air is transported among the polar region, midlatitudes, and tropics. The combination of in situ observations and these new, advanced modeling tools will provide new insight into transport processes.

The amount of aerosol in the stratosphere has decreased steadily since the eruption of Mt. Pinatubo. During ASHOE/MAESA, the aerosol surface area dropped from $2 \times 10^{-8} \text{ cm}^2 \text{ cm}^{-3}$ to less than $1 \times 10^{-8} \text{ cm}^2 \text{ cm}^{-3}$, with even lower values seen on 8 and 10 August near and inside the vortex. These values are comparable to background values observed before the eruption of Mt. Pinatubo. Thus, the influence of aerosols on the trace chemical species and on ozone loss is less now than it was for the previous missions: AASE-II in 1991-1992 and SPADE in 1993. The expected chemical response of the partitioning within the nitrogen, halogen, and hydrogen chemical families for this range of aerosol surface areas has been confirmed for all latitudes. Because HSCT exhaust is calculated to increase the amount of ozone in the lower stratosphere in the presence of these aerosols, this confirmation is important.

Observations of HO₂, ClO, BrO, and NO during ASHOE/MAESA show that the HO_x and ClO_x catalytic cycles dominate ozone destruction globally in the lower stratosphere. These results are similar to those from SPADE, but extend over a wide range of latitudes and seasons. On this basis, small increases in NO_y such as those that might occur from HSCTs, would decrease ozone loss in the lower stratosphere.

OH and HO₂ have been measured in the upper troposphere for the first time, along with NO, NO_y, O₃, CO, and CH₄. Analysis of these measurements, made during ascent, descent, and dives of the ER-2 into the troposphere, provides fairly complete first tests of the photochemistry for this region. Knowledge of the photochemistry of the upper troposphere is important for global climate change and for the effects of the current fleet of subsonic aircraft.

Tropics

Prior to ASHOE/MAESA, many gases that indicate atmospheric motion were either poorly measured or unmeasured in the tropics. A number of gases were observed during ASHOE/MAESA in both the tropics and midlatitudes, including N₂O, CO₂, CO, H₂O, CFC-11, CH₄, SF₆, and O₃. These gases have different trends and CO₂, H₂O, CO, and O₃ have seasonal variations as well. The variation of the relationships among these gases with season, latitude, and altitude, especially when compared to tropospheric values, gives new information about transport into the stratosphere and between the stratosphere and troposphere.

The relationships among these tracers is distinctly different in the tropics and middle latitudes. The tropical regime defined by trace gases is about 15° - 20° wide in latitude. The low value for NO_y/O₃ previously observed during STEP and AAOE in 1987 in the tropical regime was confirmed. Long-lived tracers approach tropospheric values in this region.

The tropical observations in late October showed a layered structure in the vertical near the equator between 16 and 20 km, which was present in H₂O, NO_y, CO₂ and aerosols; the minimum water was collocated with the tropopause. These measurements will shed new light on the entry and dehydration of air at the equatorial tropopause.

Poleward of the changes in the tracers, the values of NO_y/O₃ and long-lived tracers are observed to be intermediate between the observed values deep within the tropics and at middle latitudes. These observations suggest that information about mixing between the tropics and midlatitudes can be obtained from analysis of these observations. This information is crucial for understanding the potential transport of HSCT exhaust in the upwelling of the tropics to the middle stratosphere, where it will chemically destroy ozone.

Because stratospheric CO₂ is a conserved tracer with little production in the stratosphere and both a trend and a seasonal variation in the troposphere, the propagation of the secular and seasonal changes into the stratosphere, first observed during SPADE in 1992-1993, gives an indication of both transport and mixing. Its variation in the stratosphere of both hemispheres was approximately

in phase with the seasonal variation in the Northern Hemisphere troposphere in March/April from 61°N to 68° S. This behavior suggests that air enters the stratosphere in the tropics.

The NO and NO_y abundances are observed to increase, relative to expected values, in thin layers in the lower stratosphere and upper troposphere. The cause of these layers with enhanced NO_y is not yet known. However, understanding these features has implications for the NO_y budget in the lower stratosphere and upper troposphere, and thus for the assessment of the effects of current subsonic aircraft.

The effects of enhanced albedo from high, tropical clouds on the abundances of the reactive gases NO, OH, HO₂ have been observed for the first time. Because the rates of chemical decomposition by sunlight are calculated and not measured for the stratosphere, these observations test these photolysis rates. The agreement is generally good between observed and calculated abundances of NO, OH, and HO₂, implying that the calculated rates are reasonably accurate.

Stratospheric sampling of Concorde and ER-2

On October 8th, 1994, off the northeast coast of New Zealand, the NASA ER-2 aircraft sampled the exhaust plume of a Concorde aircraft being operated supersonically by Air France. The ER-2, in each of three separate legs, sampled a 320 km path that was traversed by the Concorde over a 10 minute period. Each of the ER2 legs required 30 minutes of sampling and was separated in altitude by about 1000 ft. The plume was encountered in the two legs at and below Concorde flight altitude.

Encounters with the Concorde exhaust plume were established by in situ observations of trace constituents made with instruments on board the ER-2 as follows: carbon dioxide (CO₂), water vapor (H₂O), nitrous oxide (N₂O), carbon monoxide (CO), reactive nitrogen (NO, NO₂, NO_y)⁷ reactive hydrogen (OH, HO₂) and condensation nuclei (CN).

The plume was sampled on approximately 10 occasions with a duration that varied from 4 to 14 seconds. Instrument sampling rates varied from 0.3 Hz to 8 Hz corresponding to a spatial resolution between 600 and 25 m, respectively. The age of the plume as determined by the position of the encounter along the Concorde flight path varied from 10 to 70 minutes.

CO₂ reached peak values up to 2 ppmv above ambient values of 356 ppmv. The integrated change in CO₂ above background values is needed to relate other constituent observations to the quantity of fuel burned. Such background values are determined by using the measurement of N₂O, which is not produced in jet engines in sufficient quantities to be detected, and the strong correlation between N₂O and CO₂ observed in the background atmosphere. The amount of water vapor observed in the plumes was less than the 1:1 mole ratio of H₂O:CO₂ expected from complete combustion. The relatively slow response of the water vapor instrument is considered to be the cause of the low peak values.

Carbon monoxide is a product of incomplete combustion. In all plume encounters, no CO increase was observed to coincide with that of CO₂ and other species, whereas CO increases were found in previous ER-2 exhaust plume measurements.

The reactive nitrogen, NO_y⁷ and the component species, NO and NO₂, were observed in each encounter. The abundance of NO_y ratioed to the abundance of CO₂ yields the emission index (EI) of nitrogen oxides for the engine operating conditions. The values for the emission indices will be calculable from these data, as they were for earlier encounters of the ER2 with its own exhaust during SPADE. Measured ratios near unity for (NO + NO₂)/ NO_y indicate that NO and NO₂ are the primary reactive nitrogen species in the exhaust plume up to an hour after emission.

Condensation nuclei are a measure of small particles emitted by the engine or produced from the condensation of gases in the exhaust. All plume encounters contained CN concentrations elevated significantly above background values of 6 - 18 cm⁻³. In most encounters, a large fraction of the particles were completely volatilized at 192°C, consistent with sulfuric acid composition. The absence of a plume signal in other particle sizing instruments on the ER-2 indicates that particle diameters are smaller than 0.09 micrometers. Values found in the ER-2 exhaust were generally below 200 particles cm⁻³.

Simultaneous measurements of OH and HO₂ were made during each encounter with a spatial resolution of 25 m. In the youngest plume samples, OH was found to increase and HO₂ to decrease. As the plume aged, the perturbation in OH decreased. The perturbation of the ratio of OH to HO₂ is consistent with the direct reaction of HO₂ with NO in the exhaust. The Concorde observations are similar to those made in the exhaust plume of the ER-2 aircraft in that they both implicate HONO as the source of OH in the exhaust plume. This is consistent with the time evolution of the HOX signal in the Concorde samples and with observations of the ER-2 exhaust plume at night. It should be possible to calculate an emission index for OH from the data; such a number will be a lower limit since all the nascent OH is assumed to be converted to HONO in the immediate wake of the aircraft.

As expected, no change in ozone was observed in the Concorde wake, if N₂O is used to infer background ozone values.

Appendix, dedicated to the further edification of those ASHOE/MAESA participants who are members of the society for the propagation of grey, homogeneous and boring prose; and who are also possessed of an insufficient appreciation and understanding of the role of the ER2 as the latter day Ark of the Covenant.

covenant

- n. ME [-OFr covenant, past participle of covenir, to agree; now co(n)venir]
 - 1. a mutual agreement between two or more persons to do or to refrain from doing certain acts
 - 2. a vow [CHAUCER]
 - 3. each of the terms of an agreement
 - 4. Law: a formal agreement, a promise or agreement under seal
 - 5. the matter agreed upon, undertaken or promised, as covenanted duty, wages etc.
 - 6. security [MILTON]
 - 7. Theological: applied to engagements entered into by and with the Divine Being, as revealed in the Scriptures
 - 8. Ecclesiastical History: the name given to the Solemn League and C. entered into in 1643 by the Scottish Presbyterians for the defense and furtherance of their ecclesiastical polity
 - Covenant of Works, Covenant of Grace: the two relations existing between God and man before and since the Fall
 - v. ME
 - 1. intransitive: to enter into a covenant, to contract
 - 2. transitive: to agree or subscribe to by covenant
 - 3. to stipulate
- They covenanted with him for thirty pieces of silver, Matt. 26:15
Nothing is covenanted as to any remainder [GROTE]

covenanted

- ppl a
 - 1. secured by covenant 1651
 - 2. bound by a covenant 1646
 - 3. having subscribed to the covenant 1638, 1643
 - 4. I. C.S.: applied to regular members of the service who used to enter into a covenant with the East India Company, and do so now with the Secretary of State for India

uncovenanted

- ppl a
 - 1. not promised or secured by covenant 1648
 - 2. not sanctioned by, not in accordance with a covenant 1727
 - 3. not bound by a covenant 1790
 - b. not having subscribed the Covenant 1818
 - c. The absence of a covenant between NASA and Air France for an ER2 to sample the exhaust of a Concorde 1994
- I will cast me on his free uncovenanted mercy 1806
To disclaim all allegiance to the uncovenanted Sovereign [MACAULAY]
An uncovenanted bonus was an opportunity to measure [ASHOE/MAESA]