5.3. AIRBORNE PROJECTS

The Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) [*Romashkin et al.*, 2001] and Lightweight Airborne Chromatograph Experiment (LACE) [*Moore et al.*, 2002] are GC instruments designed to measure CFCs, N_2O, SF_6, and other trace gases aboard aircraft (ACATS-IV and LACE) and balloon (LACE) platforms. Measurements of these trace gases in the lower stratosphere can provide insight into the chemistry and transport of that region. This section describes some of the science results deduced from measurements made during the Stratospheric Aerosol and Gas Experiment III (SAGE III) Ozone Loss and Validation Experiment (SOLVE) (with ACATS-IV and LACE) and the Atmospheric Chemistry and Combustion Effects Near the Tropopause II (ACCENT-II) campaign (with LACE).

SOLVE was an investigation of wintertime stratospheric ozone losses in the Arctic vortex using in situ and remotely sensed measurements made from aircraft and balloon platforms. The primary goal of SOLVE was to increase knowledge of the processes that influence northern polar ozone from late autumn through late winter. A second objective, validation of SAGE III ozone measurements, was not achieved because the satellite was not deployed prior to the campaign. SOLVE was conducted simultaneously with the Third European Stratospheric Experiment on Ozone 2000 (THESEO 2000), which included independent measurements from aircraft and balloons.

ACATS-IV was part of the NASA high-altitude ER-2 aircraft payload during the 2000 SOLVE campaign. The ER-2 aircraft flew 11 science flights from Kiruna, Sweden (67.9°N, 21.1°E), and 5 transit flight segments between Kiruna and NASA Dryden, Edwards, California, between January 9 and March 18, 2000. Science flights included deep vortex penetrations to 90°N, vortex edge and extra-vortex surveys, and multiple-level flights for vertical profiling. ACATS-IV produced science-quality data for each of these flights. As discussed by *Romashkin et al.* [2001], ACATS-IV was modified for SOLVE by decreasing the interval between measurements of N_2O, SF_6, CFC-12, and halon-1211 to 70 seconds, while CFC-11, CFC-113, $CHCl_3$, CH_3CCl_3, CCl_4, H_2, and CH_4 were measured every 140 seconds. *Romashkin et al.* [2001] also provided detailed information about the operation and calibration of ACATS-IV, the processing of data, and the precision and errors of measurements.

LACE was flown on two NASA-sponsored flights of the Observations of the Middle Stratosphere (OMS) balloon. The first flight, November 19, 1999, occurred just after the vortex edge had formed. The second flight, March 5, 2000, occurred just prior to vortex breakup.

Several significant alterations were made to the ER-2 payload for SOLVE. One important change was the replacement of the NASA Airborne Tunable Laser Absorption Spectrometer (ATLAS), a long-standing source of high-quality, 1-Hz N_2O data, with a new, compact, lightweight tunable diode laser spectrometer (Argus) designed to provide high-quality, 1-Hz N_2O data as well as high-precision measurements of CH_4 every 3 seconds. A comparison of coincident N_2O data from ACATS-IV, ATLAS, and the NASA Jet Propulsion Laboratory (JPL) Aircraft Laser Infrared Absorption Spectrometer (ALIAS) during two previous ER-2 campaigns [*Hurst et al.*, 2000] showed typical agreement of 1.9% between ACATS-IV and ATLAS, 2.7% between ACATS-IV and ALIAS, and 2.8% between ALIAS and ATLAS. A similar comparison of SOLVE N_2O data revealed typical agreement of 3.8% between ACATS-IV and Argus, 2.6% between ACATS-IV and ALIAS, and 4.0% between ALIAS and Argus [*Hurst et al.*, 2002]. The poorer agreement between N_2O instruments during SOLVE spawned the idea to construct a self-consistent, high-resolution N_2O data set from the data of the three in situ N_2O instruments. An objective statistical method was developed to reduce biases between the instruments, then combine their measurements into a "unified" N_2O data set with 3-s temporal resolution [*Hurst et al.*, 2002]. The quality of unified N_2O data was evaluated by integration of the data over the canister-filling periods of the National Center for Atmospheric Research (NCAR) Whole Air Sampler (WAS) during SOLVE ER-2 flights. The N_2O data from the canisters agree with the integrated unified N_2O data within about 1.5%, which is better than the agreement between any pair of N_2O instruments.

Record ozone losses for the Arctic stratosphere have been reported for winter 1999/2000 [*Richard et al.*, 2001*; Salawitch et al.,* 2002]. These losses are predominantly attributed to chemical O_3 destruction driven by the most widespread presence of polar stratospheric clouds (PSCs) in the Arctic since the 1970s [*Rex et al.,* 2002] and near-peak levels of total halogen (Cl + Br) in the lower stratosphere [*Elkins*, 2000]. Measurements of chlorinated and brominated source gases in the lower stratosphere, combined with CMDL surface measurements of these gases, attest to the high availability of inorganic halogen in the older air masses of the Arctic vortex. Figure 5.24 illustrates that organic chlorine (CCl_y) and organic bromine (CBr_y) are more than 50% converted to inorganic chlorine (Cl_y) and inorganic bromine (Br_y) in air masses with mean ages greater than 4.5 and 3.0 years, respectively. In addition, severe denitrification [*Popp et al.,* 2001] (Figure 5.25) greatly inhibited chlorine and bromine deactivation reactions that moderate O_3 destruction rates [*Gao et al.*, 2001]. *Fahey et al.* [2001] described the first in situ measurements of the large HNO_3-containing particles whose gravitational sedimentation resulted in the observed severe denitrification. In contrast, significantly dehydrated air masses (>10% H_2O loss) were rarely encountered between 17 and 21 km, indicating that temperatures in this altitude range were often below the temperature at which nitric acid trihydrate (NAT) forms, but seldom below the ice frost point. However, *Herman et al.* [2002] reported a slight decrease in total hydrogen with altitude that resulted from the widespread sedimentation of PSC particles during the winter.

Cumulative O_3 loss and O_3 loss rates in the Arctic vortex during SOLVE have been calculated from measurements made by instruments aboard the ER-2 aircraft and balloons. *Richard et al.* [2001] analyzed in situ data to determine a cumulative O_3 loss of 58 ± 4% at 19-km altitude between February 3 and March 12, 2000. Their calculations are based on the wintertime evolution of the vortex O_3:N_2O relationship (Figure 5.26a). Ozone loss rates at 19 km were as high as 51 ± 3 ppb d^{-1} during late winter (Figure 5.26b) [*Richard et al.*, 2001]. *Rex et al.* [2002] examined data from 770 O_3 sondes launched from 29 northern stations to sample distinct air masses twice over several day intervals as they circumnavigated the pole and reported 70% cumulative O_3 loss near 18-km altitude and a

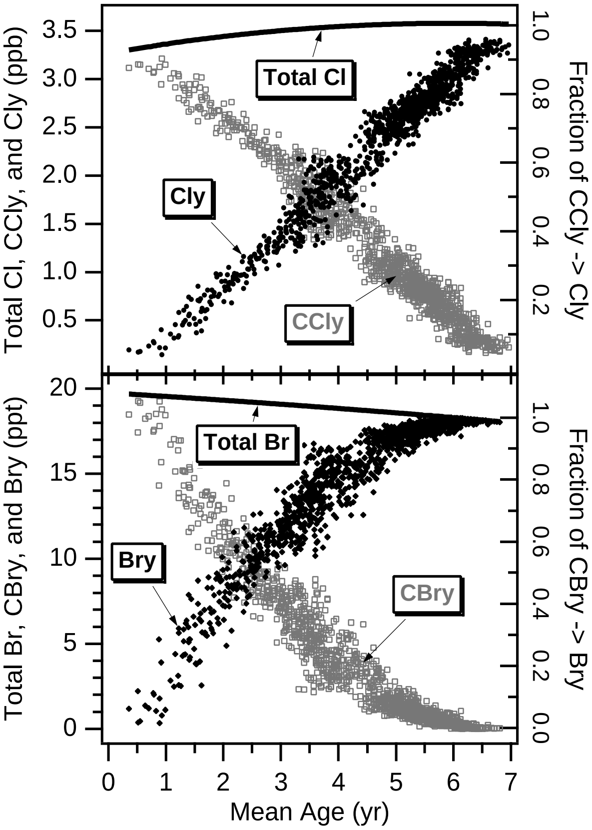

Fig. 5.24. Top: Total chlorine (solid curve), organic chlorine (CCl_y, gray squares), and inorganic chlorine (Cl_y, black circles) as a function of mean age for air masses sampled by ACATS-IV during SOLVE. The fraction of organic chlorine converted to inorganic chlorine reservoirs was approximated by the black circles using the right axis scale. Bottom: Same as the top graph, but for bromine. CCl_y and CBr_y are the sums of chlorinated and brominated source gases measured in the lower stratosphere by ACATS and the NCAR whole air sampler. Total chlorine and total bromine were determined from CMDL global surface trends of source gases with appropriate age spectral weightings. Cl_y and Br_y were calculated as the difference between total Cl (Br) and CCl_y (CBr_y). Mean ages were calculated from ACATS measurements of SF_6 in the lower stratosphere and the SF_6 global surface trend [*Geller et al.*, 1997].

cumulative column reduction of 117 ± 14 Dobson units (DUs) by late March 2000. *Salawitch et al.* [2002] studied the evolution of O_3:N_2O relationships to conclude that chemical O_3 loss between 14 and 22 km caused a 61-DU reduction of column O_3 between late November 1999 and March 5, 2000. The ozone loss and loss rates deduced in these three studies are in good agreement.

Grooss et al. [2002] used data from ACATS-IV and other instruments to initialize a stratospheric chemistry and transport model, the Chemical Lagrangian Model of the Stratosphere (CLaMS), that simulated Arctic ozone loss during SOLVE. Model simulations agreed well with the observed ozone loss at 450 K (about 19-km altitude) but tended to underestimate O_3 losses at higher altitudes, probably because of the limited amount of data used to initialize the model at higher altitudes and the absence of diabatic descent in the model.

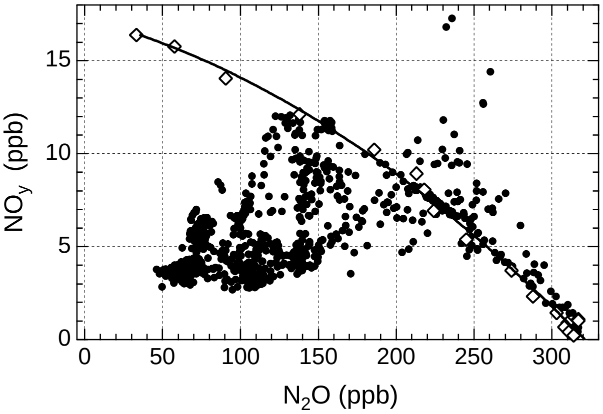

Fig. 5.25. Coincident in situ measurements of NO_y with the NOAA Aeronomy Laboratory total reactive nitrogen instrument [*Fahey et al.*, 1989] and N_2O with ACATS-IV on board the ER-2 aircraft during SOLVE (black circles). These data document severe and extensive denitrification in the Arctic vortex. The reference curve, a quadratic fit to NO_y and N_2O measured by the balloonborne MkIV interferometer on December 3, 1999 (open diamonds), represents the early-vortex NO_y:N_2O relationship before the onset of denitrification. Points below the reference curve indicate that air masses between 17 and 21 km altitude were denitrified by up to 75%. Nitrification at lower altitudes (14-16 km) is shown by points above the reference curve. (Figure adapted from *Popp et al.* [2001].)

Accurate differentiation between wintertime changes in vortex O_3 caused by chemistry and those caused by transport relies strongly on determinations of how much extra-vortex air mixes into the vortex. The vortex edge is a barrier to the exchange of midlatitude and vortex air. Previous work implied that differences between vortex and extra-vortex tracer-tracer relationships were due to large-scale, homogeneous descent in the vortex and significant in-mixing of extra-vortex air [*Plumb et al.*, 2000]. Descent can be roughly estimated by tracking the motion of air parcels with an inert tracer, as shown for N_2O in Figure 5.27. Most of the molecules measured by ACATS-IV and LACE are inert in the vortex, lacking local sources and sinks on the time scales of transport. Because these molecules have different vertical mixing ratio profiles, each molecule allows for an independent measurement of descent and other transport characteristics. This calculation of descent is only valid if mixing between air parcels of differing tracer concentration does not occur on similar time scales. In the absence of chemistry, this type of mixing can be seen as a shift in the curved tracer-tracer correlation plots (Figure 5.28).

Ray et al. [2002] were unable to produce the vortex tracer-tracer relationships observed by LACE and ACATS-IV during SOLVE by modeling homogeneous descent and in-mixing of extra-vortex air. They showed, instead, that differential descent and isentropic mixing within the vortex could produce the observed vortex relationships. These processes were folded into the descent calculations (dotted

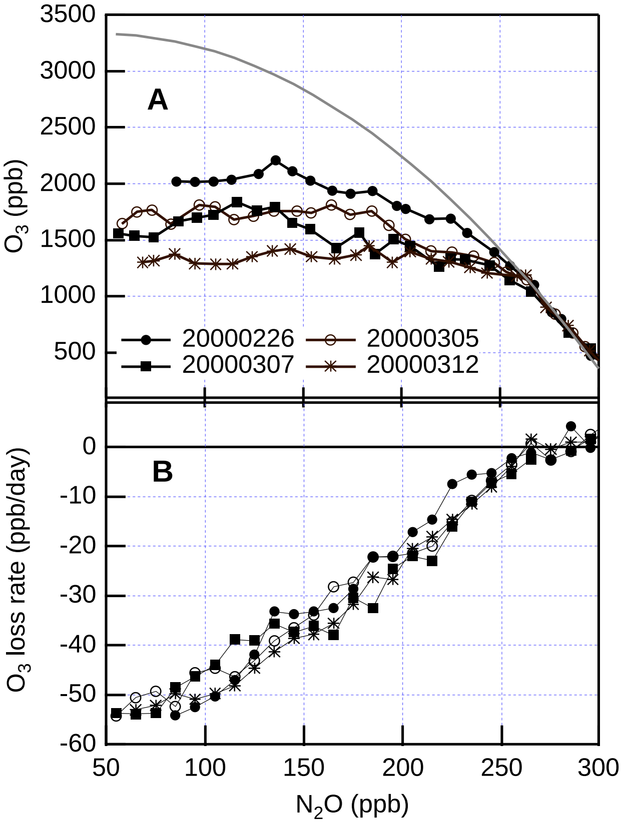

Fig. 5.26. (a) Coincident in situ measurements of O_3 with the NOAA Aeronomy Laboratory dual-beam ultraviolet photometer [*Proffitt and McLaughlin*, 1983] and N_2O with ACATS-IV on board the ER-2 aircraft during SOLVE. These data show the wintertime losses of O_3 in the Arctic vortex. The gray reference curve, a quadratic fit to O_3 and N_2O measured during four ER-2 and balloon flights between December 3, 1999, and February 3, 2000, represents the early-vortex O_3:N_2O relationship prior to ozone losses. Data from subsequent ER-2 flights demonstrate cumulative O_3 losses of up to 60% from early February to mid-March 2000. (b) Ozone loss rates calculated from differences between O_3:N_2O relationships in the early vortex and for the four ER-2 flights shown in (a). (Figure adapted from *Richard et al.* [2001].)

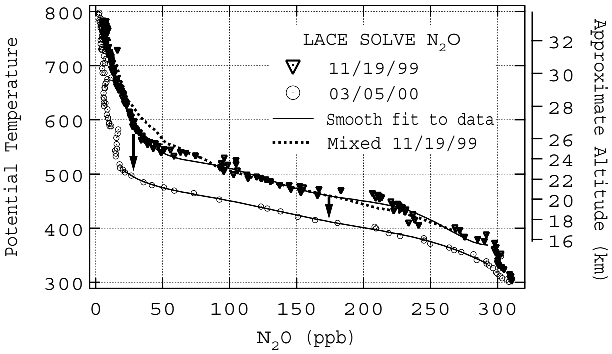

Fig. 5.27. Profiles of N_2O as a function of potential temperature (K) from LACE for the two OMS balloon flights during the SOLVE mission. Solid curves through the data are fits used in the calculation of descent in the vortex between the flights. Also included is a representation of a well-mixed early-vortex profile (dashed curve) from the differential descent mixing calculation.

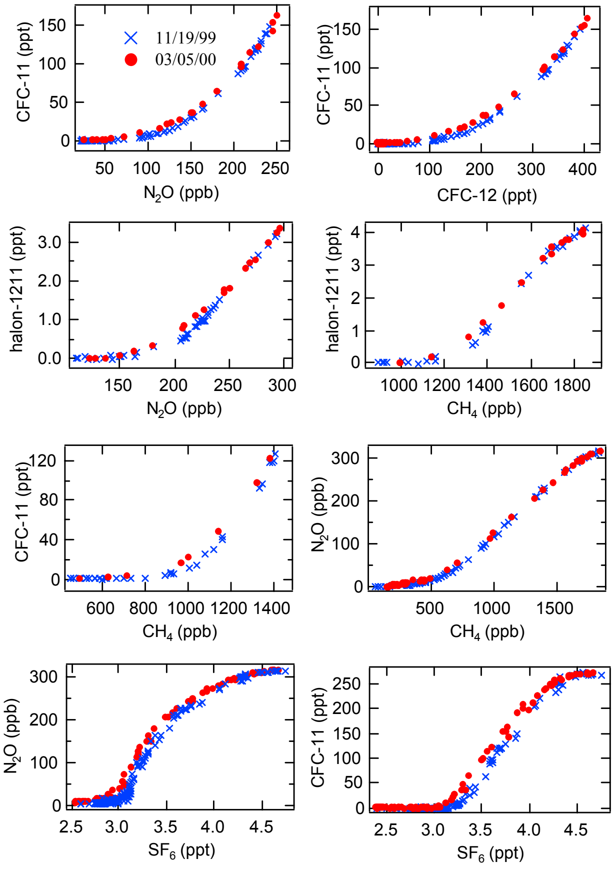

Fig. 5.28. Tracer-tracer correlation curves from the two LACE SOLVE flights. Data from the second flight are significantly shifted from the first flight toward the concave side of the curves, which suggests mixing of some type occurred.

line in Figure 5.27) to give the final descent rates shown in Figure 5.29a. Note the good agreement across all tracers. The differential descent needed to reproduce the changes in tracer-tracer correlations is shown in Figure 5.29b. The lack of significant in-mixing of extra-vortex air during winter 1999/2000 is an important finding because it identifies chemistry, not transport, as the predominant cause of the large ozone losses observed during SOLVE. Analyses by *Greenblatt et al*. [2002] and *Morgenstern et al.* [2002] using unified N_2O and ACATS-IV tracer data also conclude that the 1999/2000 Arctic vortex was strongly isolated and experienced little in-mixing.

The importance of accurate determinations of mean age distributions in the stratosphere has been stressed by *Andrews et al.* [2001]. Compared with mean ages calculated from in situ measurements of age tracers like SF_6 and CO_2, mean ages from many stratospheric transport models are underestimated by as much as a factor of 2. If general circulation rates in the models are decreased to increase mean ages, model tracer distributions fail to match observed distributions. Hence, model evaluations of important environmental issues related to trace gases, such as the impacts of exhaust from a proposed fleet of stratospheric aircraft and ozone layer recovery time scales, may be of limited accuracy until these discrepancies between models and observations are reduced. Using long-lived tracer data from ACATS, LACE, and other instruments, *Andrews et al.* [2002] have constructed accurate distributions of mean age in the stratosphere that will help improve the transport in models.

SF_6 is a strong greenhouse gas with a long lifetime. Estimating its atmospheric lifetime is important in terms of its contribution to the Earth's radiative budget as well as its use as a tracer of atmospheric motion. The stratospheric lifetime of SF_6 is dominated by loss that occurs in the mesosphere. Evidence of this loss is measurable in mesospheric air that descends into the polar vortices. Moore et al. [Measured SF_6 loss and its influence on age-of-air calculations, in preparation, 2002] calculated the stratospheric lifetime of SF_6 from OMS data assuming that (a) the age of air calculated with CO_2 data [*Andrews et al.*, 2002] is correct, and differences between CO_2 and SF_6 age-of-air estimates from vortex data (Figure 5.30) are due to SF_6 loss, and (b) the loss of SF_6 occurs over 6 months, and the mesospheric air descends only into the northern vortex (6 months later the process repeats into the southern

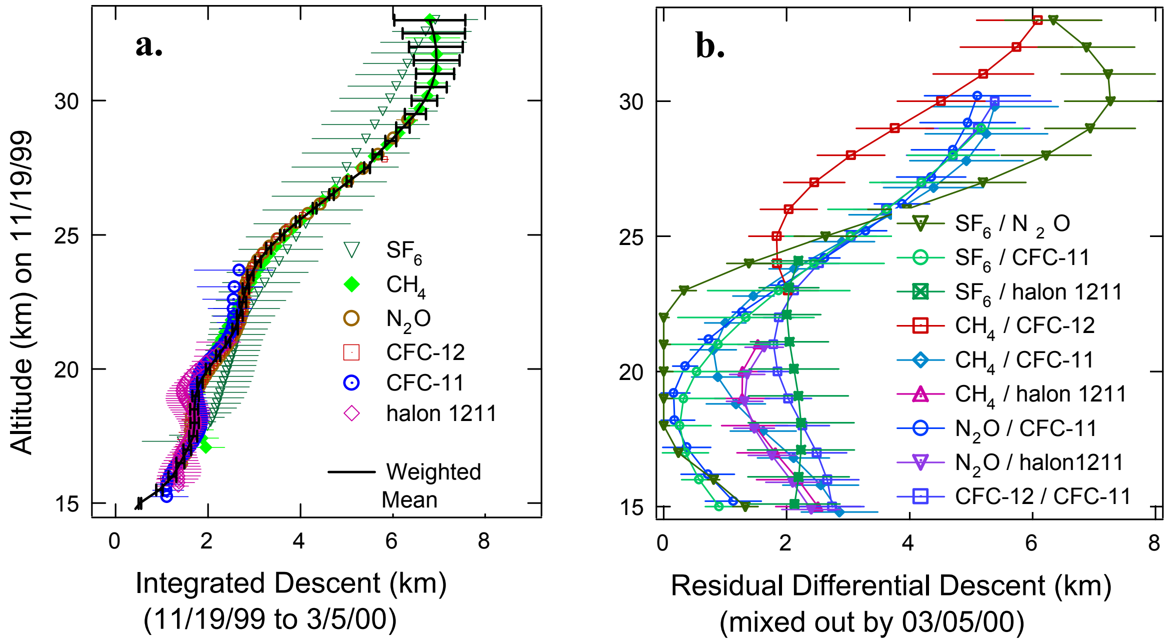

Fig. 5.29. (a) Integrated and (b) differential descent deduced from measurements associated with two LACE flights within the core of the Arctic vortex during SOLVE. Error bars represent the calculated statistical uncertainty.

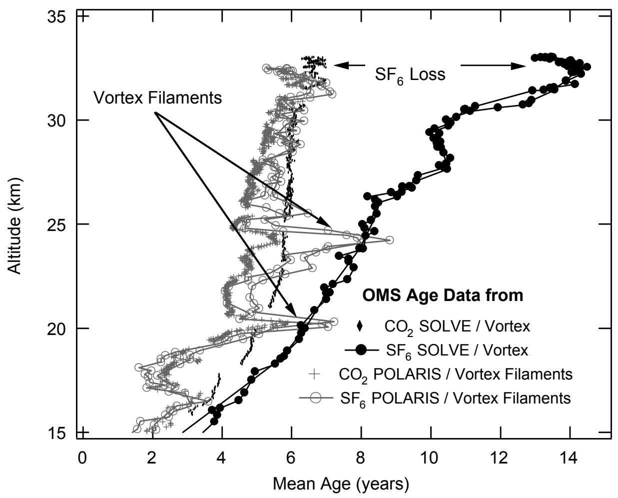

Fig. 5.30. Age-of-air estimates from both CO_2 and SF_6 data, assuming all stratospheric sources or sinks are taken into account. The difference between these two age estimates, seen both in the vortex filaments and the vortex core data, is then assumed to be due to SF_6 loss in the mesosphere.

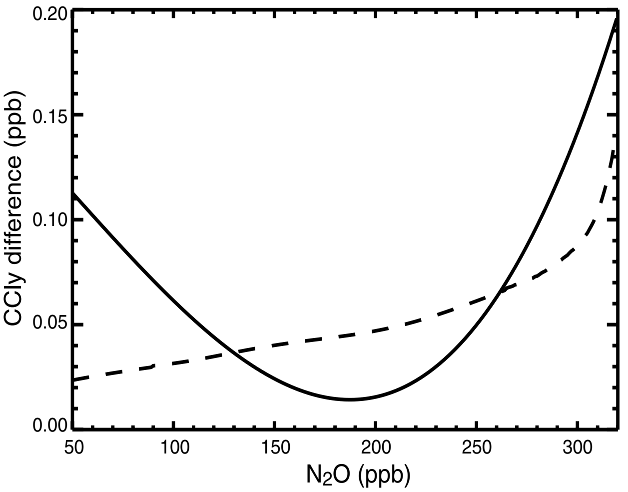

Fig. 5.31. Differences between WAS and ACATS-IV determinations of CCl_y as a function of N_2O (solid curve). Values range from 0.015 to 0.190 ppb. Partial differences in CCl_y that result from the ACATS omission of CFC-114, CFC-114a, CFC-115, CH_2Cl_2, C_2Cl_4, HCFC-142b, and HCFC-141b (dashed curve) range from 0.023 to 0.130 ppb. The remaining differences between WAS and ACATS-IV CCl_y result from calibration scale differences and the fact that CH_3Cl and HCFC-22 are calculated by ACATS-IV and measured by WAS. (Figure adapted from *Schauffler et al.* [2002].)

vortex). The net loss within the northern vortex was multiplied by two to estimate the yearly loss rate. Their new estimate for the stratospheric lifetime of SF_6 is 600 (+200, −100) years, which is better constrained than the previously reported range of 600-3200 years [*Morris et al.*, 1995]. The upper bound in the new estimate is less certain than the lower bound because of an uncertainty in SF_6 loss above 32 km within the vortex.

Significant global O_3 destruction will continue well into the 21st century because of the high halogen burden of the stratosphere [*Prinn et al.*, 1999]. Accurate predictions of future O_3 levels require accurate determinations of halogen budgets and their trends. Stratospheric chlorine [*Woodbridge et al.*, 1995] and bromine [*Wamsley et al.,* 1998] budgets are periodically calculated from ACATS, LACE, and WAS measurements of halogenated source gases, allowing the determination of trends. The calculation methods have been revised over time to reflect significant changes in the tropospheric trends of some halocarbons. An important, recent refinement in these calculations is the weighting of tropospheric trends with age spectra [*Hall and Plumb*, 1994; *Andrews et al.*, 2001] instead of mean age, to determine trends in total chlorine (Cl_{tot}) and total bromine (Br_{tot}) entering the stratosphere [*Elkins*, 2000]. These revisions improve calculations of total inorganic chlorine (Cl_y) and total inorganic bromine (Br_y) as the difference between total chlorine (bromine) and the sum of chlorinated (brominated) source gases CCl_y (CBr_y).

Schauffler et al. [2002] have recently revised the stratospheric chlorine budget based on WAS and ACATS-IV measurements made during SOLVE. A comparison of ACATS-IV and WAS CCl_y for SOLVE reveals differences of 0.015-0.190 ppb (Figure 5.31), with WAS values always larger because the ACATS-IV method does not account for chlorine from CFC-114, CFC-114a, CFC-115, CH_2Cl_2, C_2Cl_4, HCFC-142b, and HCFC-141b. These omissions account for 0.023-0.130 ppb of the CCl_y differences. The rest of the discrepancy results from calibration-scale differences and disparity in the HCFC-22 and CH_3Cl mixing ratios calculated by ACATS-IV but measured by WAS. The two independent data sets are complementary in that ACATS reports CCl_y more frequently (every 140 seconds) than WAS, but the WAS CCl_y data are inherently more accurate.

Trends in Cl_y determined from ACATS and LACE measurements near 19-, 20.5-, and 27.5-km altitude over the period 1992-2000 imply that Cl_y either peaked or leveled off by the year 2000 (Figure 5.32a). The sum of chlorinated source gases (CCl_y, or ETCl) measured at the surface by CMDL (Figure 5.32a) illustrates the decreasing trend in Cl_{tot} [*Montzka et al.,* 1999], largely because of the rapid decline in CH_3CCl_3. These surface CCl_y data represent an upper limit for Cl_y and are closely matched by Halogen Occultation Experiment (HALOE) Cl_y (HCl) data at 55-km altitude, where near-complete conversion of CCl_y to Cl_y has occurred (Figure 5.32a). Upward trends in Br_y, apparent at all three altitudes (Figure 5.32b), are driven predominantly by continued emissions of halons. The increasing sum of brominated source gases (CBr_y) measured at the surface by CMDL provides an upper limit for Br_y.

Of pivotal importance to stratospheric ozone are the combined influences of chlorine and bromine trends. The weighted sum of inorganic chlorine and bromine, namely equivalent inorganic chlorine ($ECl_y = Cl_y + 45 \times Br_y$), reflects the fact that Br_y is on average 45 times more efficient than Cl_y at the destruction of O_3 [*Daniel et al.*, 1999]. Trends in ECl_y (Figure 5.32c) mimic the decline or leveling off of Cl_y (Figure 5.32a), because Cl_y is 100-150 times more abundant than Br_y and the upward Br_y trend does little to offset the decreasing trend in Cl_y. Future trends in ECl_y, and hence O_3, are strongly dependent on this interplay between increasing bromine and decreasing chlorine abundance. Continued halon accumulation in the atmosphere may eventually overshadow reduced chlorine burdens, especially as the rate of CH_3CCl_3 decline approaches zero.

Up to this point, HATS airborne GCs were specifically designed to make measurements in the upper troposphere and lower stratosphere. Tropospheric issues such as air quality and the accumulation of greenhouse gases are expected to take a higher priority in this century. Funding was provided by the NASA Instrument Incubator Program to develop the PAN and other Trace Hydrohalocarbons Experiment (PANTHER) next-generation airborne GC. A mass selective detector will be combined with two or more ECD channels to focus on more reactive and shorter-lived species. The first test flight of PANTHER is scheduled for spring 2002 on the NASA ER-2 aircraft. Key molecules measured on this test flight will include peroxyacetyl nitrate (PAN), acetone ($CH_3C(O)CH_3$), and HCFCs. PAN comprises the largest fraction of oxides of nitrogen (NO_y) under natural conditions in the troposphere and is a precursor of O_3. Acetone is a precursor of PAN and an important source of hydroxyl radical in the upper troposphere.

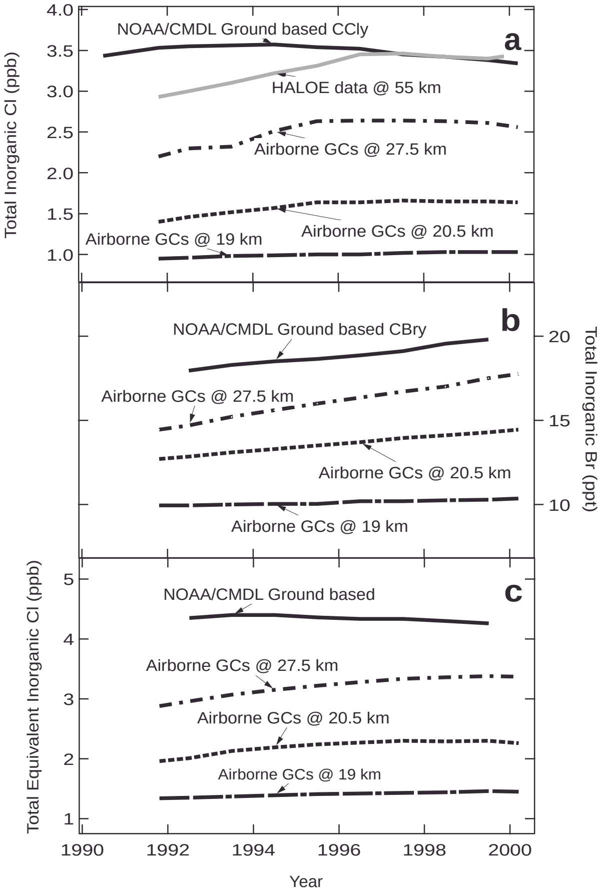

Fig. 5.32. Estimates of total inorganic halogen from airborne GCs (including ACATS and LACE): (a) total inorganic chlorine (ppb), (b) total inorganic bromine (ppt), and (c) total equivalent inorganic chlorine (ppb), at equivalent altitudes of 19, 20.5, and 27.5 km. HALOE inorganic chlorine data at 55 km are plotted in (a) (updated by *Anderson et al.* [2000]). CMDL ground-based data are plotted in (a)-(c).