The Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) Version 3 data retrievals.


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Abstract

A new Version 3 of the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) dataset for some 30 trace and minor gas profiles is available. From the infrared solar absorption spectra measured during four space shuttle missions (in
1985, 1992, 1993, and 1994), profiles from over 350 occultations were retrieved from the upper troposphere to the lower mesosphere. Previous results were unreliable for tropospheric retrievals, but with a new global-fitting algorithm, profiles are reliably returned down to altitudes as low as 6.5 km (clouds permitting), and include notably improved retrievals of H₂O, CO, and other species. Results for stratospheric water are more consistent across the ATMOS spectral filters, and do not indicate a net consumption of H₂ in the upper stratosphere. A new sulfuric acid aerosol product is described. An overview of ATMOS Version 3 processing is presented, with a discussion of estimated uncertainties. Differences between these Version 3 and previously reported Version 2 ATMOS results are discussed. Retrievals are available at http://atmos.jpl.nasa.gov/atmos.

1. Introduction

The ATMOS experiment was designed to measure solar absorption spectra of Earth’s atmosphere from space and determine vertical volume mixing ratio profiles of trace and minor species spectroscopically active in the infrared. The instrument is a Fourier-transform interferometer that measures solar absorption at a spectral resolution of ≈0.01 cm⁻¹ (48 cm optical path difference). Its spectral response is 600 - 4800 cm⁻¹ over several bandpass filters. Flown on four Space Shuttle missions, ATMOS has returned data from inside and outside the Arctic and Antarctic vortices, from mid-latitudes, and from subtropics. Fig. 1 illustrates the observation geometry during a sunset occultation, and Fig. 2 illustrates the geographical distribution of ATMOS retrievals for the four flights. Table 1 and Fig. 3 summarize observations within each spectral filter. Details
about the instrument can be found in Ref 1., and its deployment on the shuttle can be found in Ref. 2.

ATMOS Version 2 retrievals used an “onion-peeling” algorithm.\textsuperscript{3-5} This approach was successful for stratospheric measurements (see Ref. 2 and references therein). However, for the ATLAS-1 and -2 missions, the instrument suntracker (using visible wavelengths) often lost lock on the sun as the ray passed through the optically-thick lower-stratospheric aerosol layer created by the eruption of Mt. Pinatubo in 1991. Significantly lower aerosol loading during the ATLAS-3 mission in 1994 allowed good quality spectra at tropospheric tangent altitudes, but Version 2 profile retrievals were often unrealistic at tangent heights in the upper troposphere (Fig. 3). Additionally, Version 2 software was designed to fit the absorption of only one gas at a time; generally, absorptions of non-target gases were calculated a priori from an assumed vertical volume mixing ratio profile, and remained fixed while the target gas was fitted. This rarely presented a problem in the stratosphere where the spectral lines of different gases tend to be well-resolved, and only occasionally would it be necessary to sequentially fit (and iterate on) two or more gases in one spectral window. However, at lower tangent heights, the stronger tropospheric absorption by minor gases, such as H\textsubscript{2}O, CO\textsubscript{2}, N\textsubscript{2}O and CH\textsubscript{4}, as well as increased pressure broadening, often caused spectral lines of interest to overlap on the wings. A sequential and iterative fitting procedure for tropospheric retrievals would have been too time-consuming to use routinely. Instead, for Version 3, a robust method of simultaneously fitting multiple gases within a window is employed. This is combined with a global-fit algorithm to retrieve a gas vertical volume mixing ratio profile simultaneously at all altitudes within an occultation. This procedure is much more
efficient at tropospheric tangent heights. The ATMOS Version 3 tropospheric retrievals
of gases such as CO, C₂H₂, C₂H₆, OCS, HCN and H₂O are significantly improved over
Version 2, and retrievals of gases such as O₃, NO, NO₂, and HNO₄ have been extended to
lower altitudes.

2. Algorithm description

The ATMOS Version 3 processing scheme is adapted from that of the JPL MkIV
FTIR interferometer program (referred to as the “GGG code” in Ref. 6.) The MkIV
instrument, similar to the ATMOS spectrometer, retrieves vertical gas profiles from
solar absorption spectra from balloon platforms, and total column measurements from the
ground. For ATMOS, the retrieval software was configured for space-based observation.
Simplified illustrations of the global-fit retrieval procedure are shown in Figs. 4 through
6. Details of the forward modeling and inversion procedure are given in Ref. 8, however,
in this work, we discuss features of the software that are specific to ATMOS.

The spectra used in Version 3 are the same as those used in Version 2. The
telluric limb spectra were ratioed against an averaged, near-simultaneous exo-
atmospheric spectrum (determined at altitudes greater than 165 km and free of telluric
absorptions). This procedure removed solar and instrumental features, such as the
spectral responses of the detector and filters, and lines of residual H₂O and CO₂ in the
housing. Self-calibrated limb transmittance spectra (i.e., on a scale of zero to unity) were
produced, greatly simplifying later calculations. (See, for example, Fig. 1 in Ref. 9.)
2.1 Model atmosphere

For Version 3, the atmosphere is modeled as homogeneous 1 km thick layers centered from 0.5 to 99.5 km in altitude. Between these layers, temperature and gas volume mixing ratios are assumed to vary linearly with altitude. Preliminary determinations of atmospheric temperature-pressure profiles using Version 3 software and temperature sensitive CO₂ lines, similar to the analyses of Ref. 10, did not produce temperature-pressure profiles statistically different from those of Version 2. The same pressure-temperature profiles retrieved for Version 2 were therefore used in Version 3. Between 12 and 18 km, temperatures retrieved from ATMOS spectra were merged with National Centers for Environmental Prediction (NCEP) profiles interpolated to the tangent point locations, with NCEP temperatures used at altitudes below 12 km. Temperature errors are estimated to be 2 K between 18 and 70 km for filters 1 and 12, and 4 K below 18 km. For other filters, temperature error is estimated to be 4 K at all altitudes below 70 km.

2.2 Zenith angle/tangent pressure determination

The Version 3 algorithm requires the zenith pointing angle of the instrument to ray trace from the instrument to the sun, and determine the tangent height and pressure of a spectrum. The zenith angle is determined by iterative adjustment to match a retrieved and a priori CO₂ “slant column” (the integrated amount of CO₂ in the line of sight). This a priori CO₂ slant column is determined using an assumed volume mixing ratio profile. Assumed CO₂ profiles used for ATLAS-1, 2, and 3 retrievals were the same as for Version 2 (Fig. 7). However, the Spacelab 3 profile was increased uniformly by 6 ppm below 90 km altitude for better agreement with NOAA Climate Monitoring and Diagnostics Laboratory CO₂ flask analyses. These pressure retrievals were made to a
maximum altitude of 100 km. No provision was made for non-LTE (Local Thermodynamic Equilibrium) effects; however, we note that a previous study of ATMOS Spacelab 3 results found that CO$_2$ ($v_2$) vibrational temperatures were very close to LTE up to 100 km for solar absorption measurements.$^{11}$

2.3 Selection of microwindows

As noted above, previous versions of the ATMOS retrieval software could fit the absorption of only one target gas at a time. The ability of the Version 3 retrieval software to simultaneously fit absorptions of several gases allows a more flexible selection of spectral microwindows for retrieval of several gases, with more reliable tropospheric results. Wherever possible, the spectral lines and altitude ranges of target gases were chosen to keep absorption depths between 10 and 50% (for good signal in the former case and to avoid saturation in the latter). Lines with ground-state energies below 400 cm$^{-1}$ were selected to reduce errors from temperature uncertainty. It was not always possible to use such unsaturated, temperature-insensitive lines, particularly at low altitudes where many of the spectra could be blacked-out. In this case, weaker high-J lines in a P or R branch with a concomitant increase in temperature sensitivity were used. Spectral ranges used in Version 3 retrievals are illustrated in Fig. 8, and a full listing of microwindows is available at the ATMOS web site, http://atmos.jpl.nasa.gov/atmos.

2.4 Spectral linelists

The spectral linelists used for Version 3 retrievals are the same as those used by MkIV retrievals, and correspond to the ATMOS main and supplemental linelists.$^{12}$ Additional differences between the linelists, and their effect on retrievals, are described below.
2.4.1 CCl₂F₂, CCl₃F, CHF₂Cl, HNO₄, N₂O₅, CCl₄, CF₄, and SF₆

For Version 2 retrievals, measured cross-sections were used for the forward model calculations for the broad or unresolved spectral features of these molecules. For the MkIV/ATMOS Version 3 linelist, “pseudo-lines” derived from these cross-section data were utilized, such lines preserving the individual band strengths. Comparison between stratospheric ATMOS Version 2 and Version 3 retrievals indicated no significant systematic biases introduced by using such pseudo-lines.

2.4.2 HNO₃

As described in Ref. 12, Version 2 analyses of ATMOS spectral data encompassing both the ν₂ and ν₅ bands indicated a systematic bias in retrieved profiles between the bands. For consistency across ATMOS spectral filters, the strengths of ν₂ band lines were therefore scaled by 1.1 for Version 2 results, which was within the estimated error of the line strengths. However, a later review of HNO₃ spectroscopy results indicated that, among different researchers, band strengths reported were more consistent for the ν₂ band than for the ν₅ band. Thus, for Version 3 results, we elected to use the HITRAN 1996 line compilation, with the ν₂ band strengths unchanged, but the strengths of the ν₅ lines scaled by 0.9. ATMOS Version 3 HNO₃ retrievals are therefore higher than those of Version 2 by about 10%.

2.4.3 CH₃D

Line parameters provided by Ref. 15 were employed. This allowed a larger number of CH₃D lines to be used in Version 3 analyses; however, profile results were comparable to Version 2.
2.5 Diurnal corrections for NO and NO$_2$

The stratospheric concentrations of NO and NO$_2$ are photochemically sensitive, and can vary along the line-of-sight, significantly so with the changing solar zenith angle across the terminator. Below 25 km, vertical volume mixing ratio profiles uncorrected for this effect can be in error by 20% for NO$_2$ and more than 100% for NO. Diurnal corrections for ATMOS Version 2 NO and NO$_2$ are discussed in Ref. 16, and for Version 3, we use a similar procedure described in Ref. 17. Diurnally corrected and uncorrected NO and NO$_2$ retrievals are given at the ATMOS web site.

3. Error Budget

The precision and accuracy of retrieved mixing ratio profiles can vary widely depending on species, spectral filter, and altitude. The signal-to-noise error calculation for mixing ratio retrievals uses a different scheme than that of Version 2. Errors have therefore been re-evaluated for Version 3. Despite the wider spectral windows and improved fitting, a more conservative error estimation scheme tends to make Version 3 random errors the same as or higher than those of Version 2.

3.1 Random error

Random errors for retrievals include finite signal-to-noise, uncertainty in the tangent pressure, uncertainty in the temperature profiles, and zero baseline offset. Estimated tangent pressure error by filter is illustrated in Fig. 9, while total random error for selected gases and filters is shown in Figs. 10 and 11. Complete data for all gases and filters are available at the ATMOS web site (http://atmos.jpl.nasa.gov/atmos/).
3.1.1 Finite signal-to-noise

The signal-to-noise ratio (SNR) of a particular spectrum is estimated from the root mean square of the fluctuations in a non-absorbing region. For individual spectra, SNRs determined by Version 2 processing was used in Version 3. The SNR of individual spectra is source noise limited, improves with either longer wavelengths or smaller spectral filter bandpasses, and decreases with increased atmospheric attenuation, particularly by the presence of moderate-to-heavy aerosol loading or cloud cover. Average SNRs for each spectral filter are listed in Table 1. Where possible, the effect of noise error is reduced by (a) averaging retrievals over several spectral windows and/or using broad windows and (b) avoidance of spectra where the target lines have absorptions greater than 50%. Generally, spectra with signal-to-noise ratios of 60:1 or below were not used for analyses.

Within a fitted spectral window, uncertainties are calculated from the covariance matrix of the fitted parameters. These uncertainties are proportional to the root-mean-square fit over the window, and inversely proportional to the depth and number of target absorption features. As discussed in a study comparing co-located FTIR spectrometers and spectral processing, the scheme used for Version 3 (‘GGG’) results in uncertainties consistent with statistical scatter when the results are truly random. However, if residuals are dominated by systemic features that are consistent spectrum-to-spectrum, then the uncertainties tend to be pessimistic. Details on Version 3 signal-to-noise error calculation are forthcoming.
3.1.2 Tangent pressure uncertainty

As described earlier, the tangent pressure is determined by fitting CO$_2$ and determining the pointing angle of the instrument (and therefore the tangent pressure and altitude) to match an assumed CO$_2$ profile. We estimate the tangent pressure random error as the quadrature sum of the fitting/SNR error in the retrieved column and an estimated error from the temperature profile uncertainty. Errors in the retrieved CO$_2$ column from the temperature uncertainty tend to be minor (< 2%) for all filters except filter 1. As the CO$_2$ lines used in filter 1 tend to have higher ground-state energies than those used in other filters, the temperature-uncertainty contribution tends to dominate the random error in filter 1 below 60 km. Tangent pressure uncertainties for each filter are illustrated in Fig. 9.

3.1.3 Temperature profile uncertainty

As mentioned, spectral lines were chosen, where possible, to have ground-state energies less than 400 cm$^{-1}$; thus errors from temperature uncertainty are generally less than 3%. Weaker high-J lines in a P or R branch used for minor gases, particularly H$_2$O, at lower stratospheric and upper tropospheric altitudes produced errors from temperature uncertainty of about 7%.

3.1.4 Intensity offset

Interferograms must be corrected for the non-linearity of the HgCdTe photoconducting detector of the ATMOS instrument; otherwise serious zero-level intensity offset errors will be introduced into the spectra. The error in a gas retrieval significantly increases with either higher intensity offset or absorption depth of a spectral feature. A combination of non-linearity correction to the interferogram (reducing the zero-level intensity offset of
the spectra to about 1%), as well as avoidance of spectra features of 50% or more absorption, keeps the intensity offset error to no more than 3%. A discussion of ATMOS detector non-linearity corrections and their effect on retrievals is given in Ref 18.

3.2 Systematic errors

Systematic errors include spectroscopic parameter uncertainty, errors in the inversion technique, and error in the assumed CO₂ profiles used to determine tangent altitudes. Unlike random error, calculation of systematic error for Version 3 is similar to that of Version 2. Estimated systematic errors for gases are listed in Table 2, and are similar to those listed in Ref 5.

3.2.1 Spectroscopic parameter uncertainty

Generally, the largest source of systematic error in gas retrievals is the accuracy of the spectral line intensities. As noted, the spectral line compilation used in Version 3 closely follows that described by Ref. 12, which discusses line parameters on a gas-by-gas basis, including line intensity errors.

3.2.2 Inversion technique

As discussed in Ref. 9, the previous retrieval algorithm was extensively intercompared with competing schemes, with results agreeing to within 5%. Comparison of Version 2 and Version 3 stratospheric retrievals are generally within this error. The Version 3 software, used in analyzing MkIV interferometer data, has been extensively intercompared with other algorithms in the analyses of ground-based solar absorption spectra with very good agreement.⁶,¹⁹,²⁰ A comparison of near co-located retrievals from MkIV balloon-borne limb spectra and ER-2 aircraft in situ measurements were generally
within 5\%. We therefore believe a systematic error of 5\% is appropriate for the inversion technique.

### 3.2.3 CO\(_2\) profile

Errors in the assumed CO\(_2\) profile will directly affect determination of a spectrum’s tangent height, and thus the retrieved volume mixing ratio of other gases. Considering the latitudinal variability of CO\(_2\), and differences in stratospheric and tropospheric mixing ratios, we estimate that assumed CO\(_2\) mixing ratios may be in error up to 5 ppmv in the free troposphere. This, in addition to estimated error of 2-3\% in the spectral intensities of CO\(_2\) lines,\(^{12}\) translates into a root-sum-of-squares systematic error of about 4\% in retrieved tangent pressures and volume mixing ratios. The retrieval software was configured such that only the \(^{16}\)O\(^{12}\)C\(^{16}\)O (\(^{44}\)CO\(_2\)) isotopomer was used except for the region from 1200 cm\(^{-1}\) to 1400 cm\(^{-1}\), where the weaker absorptions of \(^{18}\)O\(^{12}\)C\(^{16}\)O were used at lower stratospheric and tropospheric altitudes due to a lack of unsaturated \(^{44}\)CO\(_2\) lines. This introduces an additional systematic bias at tropospheric altitudes for filters 2, 9 and 12 of about 4\% in the tangent pressure determination due to isotopic enrichments relative to Standard Mean Ocean Water (SMOW). Although this enrichment is known to increase in the stratosphere (e.g. Ref. 22), the effect on tangent pressure determination is less as CO\(_2\) retrievals become more weighted to comparatively stronger, but unsaturated \(^{44}\)CO\(_2\) lines.

### 4. Results

This section discusses selected results for key trace and minor species from the Version 3 processing of the ATMOS data. Here, Version 3 results are mostly compared with those of Version 2. Elsewhere, however, Version 3 results have been compared with other
instruments for H$_2$O, H$_2$O$+$2CH$_4$, O$_3$, HCl, and ClONO$_2$, NO$_x$, NO$_y$, N$_2$O, and CH$_4$. Version 3 results have been compared with models for CO, N$_2$O, CH$_4$, H$_2$O, and O$_3$, HCl, and ClONO$_2$, HNO$_3$, and NO$_x$.

4.1 Tropospheric/stratospheric Cl and F budgets

The currently accepted understanding of the chlorine (Cl) loading in the atmosphere is that (a) the emissions of long-lived Cl-bearing source gases (both natural and anthropogenic), whose total Cl-atom sum is defined as CCl$_y$, are located at the ground and mix into the global troposphere; (b) primarily at tropical latitudes, they are progressively lifted above the tropopause and are transported throughout the stratosphere where (c) photo-dissociation by solar UV radiation decomposes them, with (d) the resulting formation of inorganic sinks and reservoirs whose total Cl-atom sum is defined as Cl$_y$. Therefore, the total atmospheric chlorine loading, Cl$_{Tot}$, at any altitude can be defined as

$$\text{Cl}_{Tot} = [\text{CCl}_y] + [\text{Cl}_y].$$ (1)

To within $\approx 3\%$, the main sources contributing to CCl$_y$ are CH$_3$Cl, CCl$_2$F$_2$, CCl$_3$F, CHClF$_2$, CCl$_4$, CH$_2$CCl$_3$, and C$_2$Cl$_3$F$_3$, while Cl$_y$ is approximated to within a similar uncertainty by combining the contributions from HCl, ClONO$_2$, ClO, and HOCl (except for the polar lower stratosphere where the ClO dimer plays a significant role.)

Similarly, the total atmospheric fluorine loading, F$_{Tot}$, is defined as

$$\text{F}_{Tot} = [\text{CF}_y] + [\text{F}_y],$$ (2)
which primarily involves contributions to CF$_y$ by CCl$_2$F$_2$, CCl$_3$F, CHClF$_2$, CF$_4$, C$_2$Cl$_3$F$_3$, and SF$_6$, and to F$_y$ by HF, COF$_2$ and COFCl.

Based on simultaneous or near-simultaneous ATMOS measurements of a large number of the species listed above, stratospheric budgets of Cl$_{Tot}$ and F$_{Tot}$ were readily derived for the 1985 Spacelab 3 mission$^{32}$ and of Cl$_{Tot}$ for the 1994 ATLAS 3 shuttle flight;$^{33}$ all results and conclusions regarding these budgets remain valid. Version 3 data, however, allow these earlier investigations to be extended further down into the troposphere, as shown in Figs. 12 and 13. The important source gases, i.e., CCl$_2$F$_2$, CCl$_3$F, CHClF$_2$ and CH$_3$Cl, contributing to CCl$_y$ and/or CF$_y$ can be retrieved down to nearly 6 km at northern midlatitudes. Clearly, such downward extensions of the VMR profiles allow better comparison with tropospheric in situ measurements. For the four gases just listed, this agreement is very good, well within the combined uncertainties of both techniques.$^{34}$ One noticeable discrepancy remains with CCl$_4$ whose VMR in the vicinity of the tropopause (~130 pptv) is substantially larger than the in situ concentration at the ground (102 to 104 pptv); this discrepancy was also present for ATMOS Version 2 results when compared with those from a gas chromatograph operated aboard an ER-2 during the ASHOE/MAESA campaign;$^{35,36}$ it may be caused by line mixing in a strong CO$_2$ Q–branch interfering with the ATMOS-adopted CCl$_4$ microwindow at 785-807 cm$^{-1}$.

The Version 3 VMR profiles of HCl, HF, and SF$_6$, have also been extended up to 62 km altitude, whereas Version 2 retrievals reached 55 km at best.$^{32,33}$ This allows better estimation of the HCl and HF VMRs in the vicinity of the stratopause. These are good surrogates of the total chlorine and fluorine loadings.$^{37}$
**4.2 $H_2O$ and $H_2O + 2CH_4$**

Fig. 14 compares selected Version 2 and 3 $H_2O$ profiles. For illustrative purposes, profiles are compared from different spectral filters, but these were observed in similar air masses (as measured by potential temperature and a scaled potential vorticity. See Refs. 24 or 28.) Version 3 profiles, both in Fig. 14 and in general, avoid the unrealistically low near-tropopause $H_2O$ mixing ratios often seen in Version 2. More importantly for the purposes of upper stratospheric water, the Version 3 $H_2O$ retrievals in Filter 12 (which were not done for Version 2) are consistent with other filters, including Filter 4 with which it has no spectral windows in common. There is better internal consistency, as well as an improved agreement with HALOE, MAS and MLS.24

The only significant stratospheric reservoirs for hydrogen are $H_2O$, $CH_4$, and $H_2$. Oxidation of $CH_4$ and $H_2$ are the only significant local sources of $H_2O$, so changes in the sum $[H_2O] + 2[CH_4]$ are indicative of changes in $H_2$ (where $[ ]$ is volume mixing ratio). In the absence of dehydration and if the stratospheric mixing ratio of $H_2$ is a constant, then the sum $[H_2O] + 2[CH_4]$ in a stratospheric airmass should be the same as when it entered the stratosphere, and $\partial[H_2O]/\partial[CH_4] = -2$ above the hygropause in extratropical and extravortex airmasses; deviations from this relationship indicate net production or destruction of $H_2$. A previous analysis of ATMOS Version 2 data showed a broad maximum for $[H_2O] + 2[CH_4]$ between 35 and 65 km in northern-latitude extra-tropical retrievals, evidence for a net oxidation of $H_2$ to $H_2O$.38 However, as discussed in Ref. 24 and illustrated in Fig. 15, a comparison of Version 2 and Version 3 results show lower volume mixing ratios for stratospheric water in this region for Version 3, while the VMRs for $CH_4$ are effectively unchanged. The sum $[H_2O] + 2[CH_4]$ is nearly constant
throughout the extratropical stratosphere to about 55 km; thus these Version 3 analyses do not provide evidence for any net changes in H\textsubscript{2} in the upper stratosphere. An analysis of the H\textsubscript{2}O retrieval process between Versions 2 and 3 indicated that a combination of modified spectral windows, slightly lower tangent heights above 30 km and algorithmic changes in Version 3 all contributed to the lower H\textsubscript{2}O mixing ratios compared with Version 2.

**4.3 NO, NO\textsubscript{2}, and CO**

Fig. 16 compares Version 2 and 3 NO, NO\textsubscript{2}, and CO. The profiles are averages of ATLAS-3 Filter 3 retrievals in the developing Arctic vortex (the “protovortex”).\textsuperscript{39,40} To simplify comparison, profiles are shown without diurnal corrections. For all three gases, the averages in Version 3 appear to be somewhat smoother than Version 2. There is good agreement for NO\textsubscript{2}, while for NO and CO higher mixing ratios are seen above 5 hPa, although the standard deviations tend to overlap. In the troposphere, retrievals of CO are much more realistic in Version 3 than Version 2. Statistically significant retrievals of NO and NO\textsubscript{2} were often difficult to obtain in the troposphere. With the possible exception of elevated regions of tropospheric NO or NO\textsubscript{2} (> 100 pptv), Version 3 results may only provide an upper limit of these gases in the troposphere.

**4.4 HNO\textsubscript{3}**

In a manner similar to H\textsubscript{2}O, Fig. 17 presents sample HNO\textsubscript{3} retrievals from Version 2 and 3 across filters 3, 9, and 12 selected for similar scaled potential vorticity (sPV) profiles. Version 3 results reflect increased mixing ratios of about 10% over Version 2 because of changes in the linestrengths described in Section 2.4.2.
4.5 Aerosol measurements

A new product in the Version 3 ATMOS data set is stratospheric sulfuric acid aerosol volume. Vertical profiles of the volume of aerosol composed of sulfuric acid and water are retrieved using the broad spectral features of sulfuric acid absorption. Using data from filters 1, 9, or 12 in the spectral region of 800-1250 cm\(^{-1}\), the aerosol retrievals are most sensitive to total aerosol volume and the weight percent of sulfuric acid. These retrievals are relatively insensitive to the aerosol size distribution. Aerosol volume peaks in the lower stratosphere (near 18 to 20 km) and ranges from 2-3 µm\(^3\) cm\(^{-3}\) (with approximately 1 to 15% error) in 1992 to values closer to 0.3 to 0.6 µm\(^3\) cm\(^{-3}\) (with error of 5 to 30%) in 1994. This reduction in aerosol volume was widely documented in the years following the eruption of Mt. Pinatubo.\textsuperscript{41-44} Four vertical profiles taken in 1992 in the same region are shown in the Figure 18. A complete discussion of the retrieval methodology is given in Ref. 45.

5. Conclusions

Version 3 of the ATMOS data set, containing volume mixing ratio retrievals of some 30 stratospheric and upper tropospheric species, has been described. The global-fit methodology of Version 3 requires significantly more computing resources than the computationally faster onion-peel algorithm of Version 2, but the increased reliability in tropospheric retrievals by the former technique merits its use. Compared with Version 2, results have been more reliably extended to tropospheric altitudes, and in some cases (e.g., HCl and HF), also extended to higher altitudes. There has been significant improvement in retrievals of upper tropospheric/lower stratospheric H\(_2\)O and CO, but more reliable retrievals have also been made for minor gases such as CH\(_4\) and N\(_2\)O, and
short-lived species such as C$_2$H$_2$ and C$_2$H$_6$. General agreement is maintained for stratospheric retrievals between Versions 2 and 3, although there are some differences. Version 3 HNO$_3$ is about 10% higher than that of Version 2. Upper stratospheric water vapor is slightly lower in Version 3, but shows better consistency across the ATMOS spectral filters. Unlike Version 2, Version 3 results show the sum [H$_2$O] + 2[CH$_4$] to be constant in the upper stratosphere to about 55 km, and do not suggest any net consumption of H$_2$. A new sulfuric acid aerosol retrieval product has been described, and initial results show the expected decrease in stratospheric sulfuric acid aerosol in the years following the Mt. Pinatubo eruption. Version 3 retrievals are available at http://atmos.jpl.nasa.gov/atmos.

Work on additional gas and aerosol retrievals and validation of current results continues. An improvement to the processing methodology can be made in the zenith angle/pressure-sounding determination by using assumed a priori CO$_2$ profiles more appropriate to a tangent latitude and season, as well as compensating for isotopic enrichments in $^{18}$O$^{12}$C$^{16}$O in spectral regions where use of $^{16}$O$^{12}$C$^{16}$O cannot be made. Additional improvement to the zenith angle determination for tropospheric spectra can be including water vapor in refraction calculations, although this would likely require an H$_2$O mixing ratio/zenith angle retrieval iterative loop. With advancements in algorithms and spectroscopic databases, the richness of broadband, high-resolution infrared spectra from space allows continual improvement in the quality and number of products from even “old” data sets.
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References


Figure captions

Fig. 1. Schematic of viewing geometry. Here, a sunset occultation is illustrated as the shuttle enters into Earth’s shadow. With selectable instrument fields-of-view of 1, 1.4, and 2.8 mrad, an observation field-of-view of 2, 3, or 6 km is achieved at the tangent altitude (defined at the central ray), typically about 2000 km from the shuttle. The sampling time of 2.2 seconds allows a vertical spacing between spectra of about 4 km in the upper atmosphere, decreasing through the lower stratosphere and upper troposphere to about 1 km due to refraction and drift of the suntracker up the solar disk.

Fig 2. Distribution of ATMOS sunset (blue) and sunrise (red) occultations from 4 space shuttle missions. The different symbols correspond to different spectral filters, as noted.

Fig. 3. Sample comparison of a single occultation methane gas profile from ATMOS Versions 2 and 3 retrieval software. Error bars are random errors. Version 3 random errors are calculated differently from Version 2, and tend to be the same or greater than Version 2 (see text). The Version 2 retrieval clearly produces an unrealistic profile in the free troposphere.

Fig. 4. Sample calculation of partial slant columns as function of altitude. C$_2$H$_6$ is used as an example. Assumed mixing ratio profiles are used to calculate the slant path and slant columns from the instrument to the sun through the model atmosphere for each spectrum. This is done for both target and non-target gases. Note that an observation’s field-of-view can encompass more than one model layer near the tangent point (the vertical resolution is worse than the model layer spacing). Thus,
contributions to the total slant column can be made from one or two layers immediately below the tangent point in addition to the contributions from all the layers above.

Fig. 5. Successive measured absorption spectra in a C$_2$H$_6$ microwindow (left panel) and a fitted spectrum and residual (right panel). The slant paths are used to calculate absorptions for target and non-target gases, and the slant columns (Fig. 4) are scaled until the best fit with observation is achieved. Where more than one microwindow is used for analysis, the retrieved slant columns are averaged.

Fig. 6. Using the partial slant column matrix (Fig. 4), the averaged slant columns (left panel) are inverted to the retrieved vertical mixing ratio profile (right panel). The procedure (beginning with the description in Fig. 4) is then iterated until convergence is achieved. (Note: The retrieved altitude grid is not the same as that for the tangent altitudes. Error bars only reflect signal-to-noise and fitting error.)

Fig. 7. Assumed CO$_2$ volume mixing ratio profiles for ATMOS zenith angle determination.

Fig. 8. ATMOS Version 3 spectral ranges for gas retrievals (upper panel) and ranges for spectral filters (lower panel). The numbers in the lower panel refer to the filter number.

Fig. 9. Median fractional random error in tangent pressure for an individual occultation.

Fig. 10. Median random error for minor gases by filter for an individual occultation.

Fig. 11. Median random error for selected trace gases and spectral filters for an individual occultation.
Fig. 12. Northern latitude zonal average volume mixing ratio profiles of chlorinated
species from ATMOS Version 3, ATLAS-3 retrievals. Species not measured by
ATMOS are in grey. The horizontal arrow indicates the level down to which
Version 2 profiles could be reliably retrieved. Triangles on the bottom scale
correspond to the measured in situ ground volume mixing ratios.

Fig. 13. Northern latitude zonal average mixing ratio profiles of fluorinated species from
ATMOS Version 3, ATLAS-3 retrievals. Species not measured by ATMOS are in
grey. The horizontal arrow indicates the level down to which Version 2 profiles could
be reliably retrieved. Triangles on the bottom scale correspond to the measured in situ
ground volume mixing ratios.

Fig. 14. Comparison of selected retrievals of H$_2$O. The upper row illustrates northern
mid-latitude retrievals, the middle row shows northern tropic and sub-tropic
retrievals, while the bottom row shows retrievals from within the Antarctic polar
vortex. The left column shows Version 2 retrievals, the middle column shows
Version 3 retrievals, and the right column shows sPV profiles for each retrieval. Note
that Version 3 retrievals avoids unrealistically low mixing ratios near the tropopause.
Reasonable consistency is maintained in Version 3 across spectral filters, including
Filter 12, for which H$_2$O retrievals are new.

Fig. 15. Zonal average mixing ratio profiles of CH$_4$, H$_2$O, and the sum H$_2$O + 2CH$_4$, from
ATMOS versions 2 and 3 retrievals. 34 sunset occultations between 31 and 49°N
(Filters 3 and 9) from the ATLAS-3 missions were used. Error bars are standard
deviations weighted by the inverse square error of the individual retrievals.
Fig. 16. Comparison of Versions 2 and 3 filter 3 NO, NO₂ and CO volume mixing ratios. Average volume mixing ratios are from ATLAS-3 northern “protovortex” retrievals. Error bars are standard deviations weighted by the inverse square signal-to-noise/fitting error.

Fig. 17. Comparison of selected retrievals of HNO₃. The upper row illustrates northern mid-latitude retrievals, the middle row shows northern tropic and sub-tropic retrievals, while the bottom row shows retrievals from within the Antarctic polar vortex. The left column shows Version 2 retrievals, the middle column shows Version 3 retrievals, and the right column shows sPV profiles for each retrieval. Version 3 retrievals tend to be larger due to modifications in the HNO₃ spectral strengths (see text).

Fig. 18. Vertical profiles of stratospheric sulfuric acid aerosol for a set of ATLAS-1 Filter 9 occultations taken over the southern tip of South America in 1992. Altitudes of different profiles have been slightly offset from each other for clarity.
Table 1: Number of occultations analyzed for ATMOS Version 3 retrievals

<table>
<thead>
<tr>
<th>Filter and bandwidth (cm^{-1})</th>
<th>Average signal-to-noise (1σ std. dev.)</th>
<th>Number of Occultations (SR = sunrise, SS = sunset)</th>
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<tr>
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<td>Spacelab 3 ATLAS-1 ATLAS-2 ATLAS-3</td>
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<tr>
<td>Filter 1 600-1200</td>
<td>242 ± 48</td>
<td>1 SR 7 SR 11 SR ——</td>
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<td></td>
<td></td>
<td>3 SS 7 SS 4 SS ——</td>
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<tr>
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<td>1 SR 8 SR ——</td>
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<tr>
<td></td>
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<td>3 SS 1 SS 7 SS ——</td>
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<tr>
<td></td>
<td></td>
<td>3 SS 11 SS 9 SS</td>
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<td>Filter 4 3100-4700</td>
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<td>2 SS 8 SS 4 SS 15 SS</td>
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<td>—— 7 SS 30 SS</td>
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Table 2: Estimated accuracy for gas retrievals

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<td>HCN</td>
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†Not including diurnal correction.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Gas window spectral ranges

Figure 8
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13
Figure 14
Figure 15
Figure 16
Figure 17
Figure 18

Figure 18