Detection of elevated tropospheric hydrogen peroxide (H_2O_2) mixing ratios in atmospheric chemistry experiment (ACE) subtropical infrared solar occultation spectra

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Abstract

We report measurements of hydrogen peroxide (H_2O_2) profiles from infrared solar occultation spectra recorded at $0.02\,cm^{-1}$ resolution by the atmospheric chemistry experiment (ACE) during 2004 and 2005. Mixing ratios as high as 1.7 ppbv ($1\,ppbv = 1 \times 10^{-9}$ per unit volume) were measured in the subtropical troposphere. Back trajectories, fire count statistics, and simultaneous measurements of other species from the same occultation provide evidence that the elevated H_2O_2 mixing ratios originated from a young biomass-burning plume. The ACE time series show only a few cases with elevated H_2O_2 mixing ratios likely because of the short lifetime of H_2O_2 and the limited sampling during biomass-burning time periods.

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Keywords: Remote sensing; Tropospheric chemistry; Pollution; Spectroscopy

1. Introduction

A variety of techniques have been used to measure hydrogen peroxide (H_2O_2) [1], an atmospheric oxidant almost solely formed from the self-reaction of HO_2 radicals and thus can serve as sensitive indicator for HO_x ($OH + HO_2$) chemistry [2]. The H_2O_2 molecule is a HO_x reservoir with a relatively short lifetime in the

troposphere ($\sim$1 d) [2]. Emissions from surface sources can be transported to the upper troposphere by deep tropical convection [3]. Complex interactions in the troposphere affect the production of ozone (O_3) and atmospheric HO_x and NO_x ($NO + NO_2$) levels, though non-methane hydrocarbons cannot photolyze and participate in HO_x formation [2]. Volatile organic compounds (VOCs) include non-methane hydrocarbons (NMHC) and oxygenated NMHCs, are generally short-lived, although species such as ethane (C_2H_6) and acetone (C_3H_6O) are longer-lived and impact tropospheric chemistry on hemispheric scales [4].

Methods for measuring H_2O_2 include *in situ* sampling from an aircraft during the transport and atmospheric chemistry near the Equator-Atlantic (TRACE-A) experiment [5], far infrared stratospheric emission measurements from a balloon-borne platform ($34°N$, $104°W$) in September 1989 [6], and space-based limb emission measurements with a high spectral resolution Fourier transform spectrometer [7]. However, weak absorption by H_2O_2 in the mid-infrared combined with its short lifetime and the complex region where it absorbs make it a challenging molecule to detect and quantify with remote sensing techniques.

Atmospheric H_2O_2 is formed primarily by self-reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \tag{1}$$

although production can be suppressed at high NO_x in the troposphere where the peroxy radical (HO_2) reacts with NO, i.e.

$$HO_2 + NO \rightarrow HO + NO_2. \tag{2}$$

Loss of H_2O_2 is primarily through

$$H_2O_2 + OH \rightarrow HO_2 + H_2O, \tag{3}$$

$$H_2O_2 + h\nu \rightarrow 2OH. \tag{4}$$

In the troposphere gas-phase reactions are augmented by the loss of dissolved H_2O_2 mainly through reaction with dissolved SO_2 and rainout [2,7–9]. Photolytic loss is predicted to result in diurnal and seasonal variations in H_2O_2 [7].

H_2O_2 is an important sink for OH and an important oxidant of sulfur compounds in the aqueous phase and can be deposited both wet and dry as a result of its high solubility [2]. However, photochemical pathways may lead to substantial recycling to reform H_2O_2 [2]. Despite the importance, to our knowledge only zonal mean space-based profiles of H_2O_2 have been reported for the stratosphere and troposphere [7]. Mean measured profiles from that work did not show elevated tropospheric H_2O_2, but a three-dimensional model run for the same time period (September 2003) predicted an upper tropospheric peak of >0.33 ppbv (10^{-9} per unit volume) in the tropics [7].

The purpose of this investigation is to present H_2O_2 tropospheric retrievals obtained during 2004 and 2005 by the atmospheric chemistry experiment (ACE). We report several cases with elevated upper tropospheric H_2O_2 mixing ratios. We show back trajectories and fire count statistics for the measurement with the highest H_2O_2 mixing ratios. Those results support the hypothesis that the emissions originated from deep convective transport from a tropical biomass fire source regions to the upper troposphere [3]. Tropical fires are a well-documented source of elevated trace gases emissions and notably H_2O_2, as confirmed from measurements inside biomass-burning plume during aircraft flights near the equator as well as from laboratory biomass-burning emission experiments [5].

2. Measurements

The ACE payload, also known as SCISAT-1, was successfully launched on 12 August 2003 into a $74°$ inclined orbit by a NASA-supplied Pegasus XL at 650 km altitude [10]. Routine ACE FTS science measurements began in February 2004. This small Canadian-designed and built satellite contains three instruments with a shared field of view, and has the primary goal of recording high-resolution atmospheric spectra taking advantage of the high precision of the solar occultation technique. The infrared instrument is a Fourier transform spectrometer (FTS) that records solar spectra below altitudes of 150 km at a spectral resolution of 0.02 cm^{-1} (maximum optical path difference of ±25 cm) with a 1.25 mrad (10^{-3} rad) diameter

field of view. Full resolution FTS spectra are recorded by ACE in 2 s and cover 750–4400 cm^{-1} simultaneously. They are analyzed unapodized to take full advantage of the high spectral resolution. Low Sun solar occultation spectra are divided by exoatmospheric spectra from the same occultation to remove the wavenumber dependence of the instrumental response function. Mixing ratio profiles for several dozen atmospheric constituents and temperature are retrieved as standard products from occultation events between latitudes of 85°N and 85°S. Orbital coverage is optimized to achieve maximum coverage at northern high latitudes during early winter with limited latitudinal coverage in tropical regions, though measurements are obtained during the Austral spring dry season of maximum tropical biomass burning. Vertical spacing between successive measurements varies from 2 km for high β-angle (angle between the satellite velocity vector and the vector to the Sun) to 6 km for zero β-angle measurements. Typical vertical altitude spacing between successive measurements is 3–4 km. Additional instruments onboard SCISAT-1 are MAESTRO (Measurement of Aerosol Extinction in the Stratosphere and Troposphere by Occultation), a two-channel UV-visible spectrophotometer, and two imagers with optical filters at 0.525 and 1.02 μm. The two filter region were selected because they are relatively free of molecular absorptions. Analysis of those measurements provide line of sight extinction profiles from solar disk images coincident with the FTS field of view by taking ratios of intensities from the occultation images to those from coincident exo-atmospheric scenes.

3. Retrieval

Profiles with statistical uncertainties are retrieved for individual molecules from fits to multiple species in pre-selected microwindows over pre-specified altitude ranges [11]. Temperature profiles are retrieved assuming a realistic CO_2 volume mixing ratio profile accounting for its increase as a function of time. Profiles are retrieved from fits to measurements in microwindows selected to provide CO_2 lines covering a wide range of sensitivities with respect to temperature and are constrained to yield an atmosphere in hydrostatic equilibrium. Retrievals below 12 km altitude assume temperatures derived by the Canadian Meteorological Centre (CMC) for the location of the observation. Spectroscopic line parameters from HITRAN 2004 [12] are assumed. The key papers reporting the high-resolution spectrum and analysis of H_2O_2 in the infrared and far infrared include those by Perrin et al. [13,14] and Klee et al. [15].

The ACE retrieval approach differs from that employed by most other space-borne experiments as it does not adopt the optimal estimation method [16], where a retrieved product is a weighted combination of information from the measured spectrum and the *a priori* profile. Validation of the current ACE version 2.2 standard products through comparison of those measurements with space-based, balloon-borne, ground-based and aircraft measurements is in progress. We compare version 2.2 retrievals with those derived from the same spectra with an algorithm developed at the NASA Langley Research Center [17] also assuming the HITRAN 2004 parameters [12] and a common set of temperature profiles, though with a different algorithm for atmospheric ray tracing and independently derived selections of microwindows and interferences and their altitude ranges. The Langley Research Center algorithm uses a similar retrieval approach (multi-microwindow non-linear least-squares spectral fitting) as the ACE code [11].

4. Analysis

The strongest infrared band of H_2O_2 is the ν_6 with a band center of 1266 cm^{-1}, a region containing strong absorption by multiple interferences with absorption that increases with increasing wavenumber. Potential windows for measurement in the upper troposphere are limited to the P-branch region below 1245 cm^{-1}. Fig. 1 illustrates ACE version 2.2 H_2O_2 profiles for 2004 and 2005 with the highest mixing ratios in the upper troposphere. Version 2.2 profiles are interpolated from the measured altitudes to a 1 km altitude grid.

Molecule-by-molecule simulations are presented for H_2O_2 and the most significant interferences for that region in Fig. 2. The comparison is shown for ss6185, the occultation with the highest mixing ratios of H_2O_2 at the version 2.2 tangent altitude of 6.47 km. The simulated and measured spectra are offset vertically for clarity. The strong absorptions by interfering species highlight the complexity and difficulty in quantifying middle and upper tropospheric H_2O_2 despite the high spectral resolution of the ACE Fourier transform spectrometer. The mixing ratio for H_2O_2 from a reference profile has been multiplicatively scaled at all altitudes to increase the
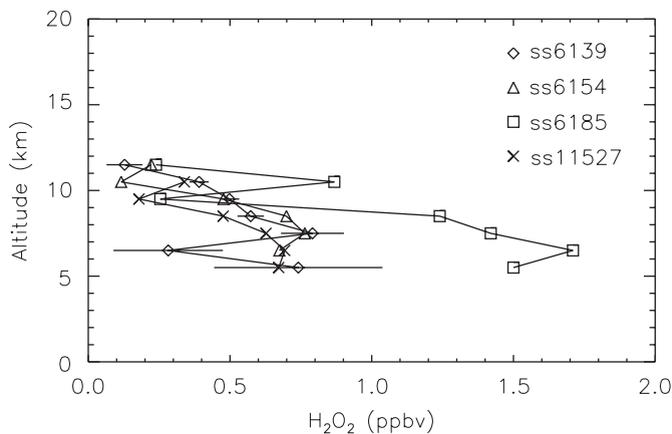
Fig. 1. ACE version 2.2 profiles from 2004 to 2005 with elevated H_2O_2 mixing ratios in the middle and upper troposphere. Error bars indicate 1-σ standard deviations. Occultation ss6185 was measured on 5 October 2004 at 18.57°S, 354°E longitude. Occultation ss6139 was measured on 2 October 2004 at 34.53°S, 39.43°E longitude. The β-angle was 52.75°. Occultation ss6154 was measured on 3 October 2004 and was located at 29.88°S, 32.44° longitude. The β-angle was 48.09°. Occultation ss11527 was recorded on 3 October 2005 at 36.75°S latitude, 197.9°E longitude. The β-angle was 44.33°.
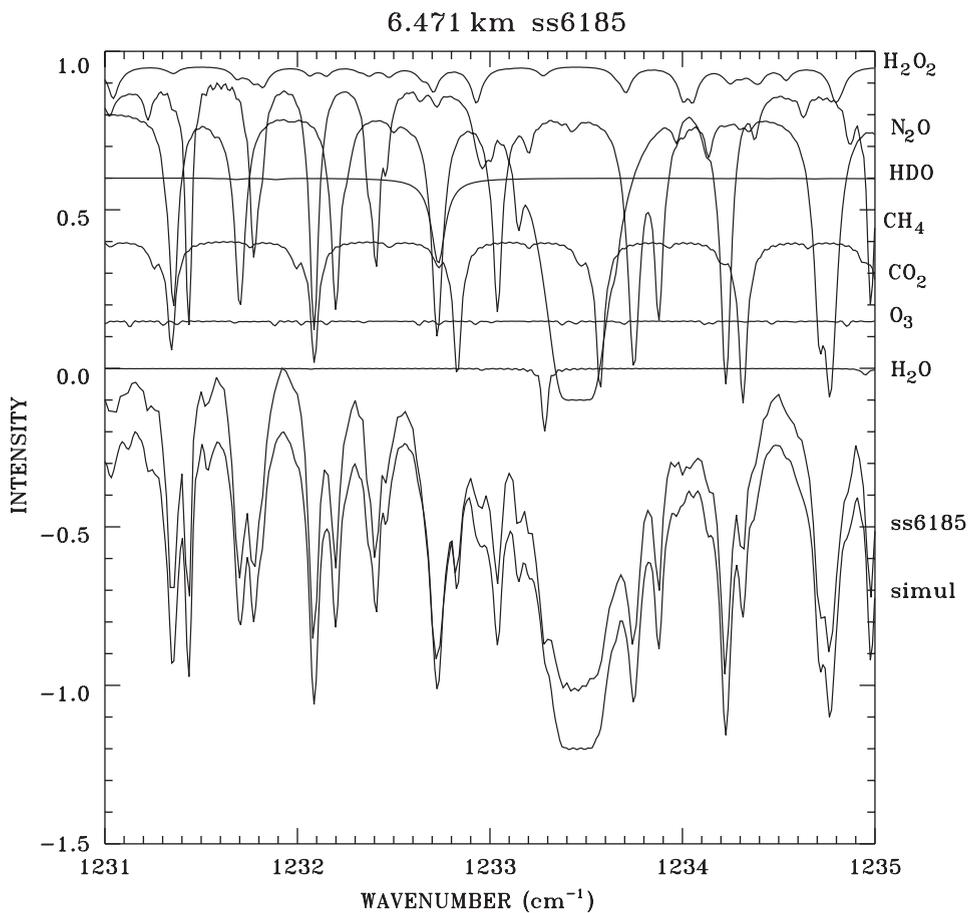
Fig. 2. Comparison of measured and simulated spectra for ss6185. Measured and simulated spectra are offset vertically for clarity with only the stronger absorbers simulated.

H_2O_2 absorption to depths similar to those observed in the ACE spectrum. A set of reference profiles was used in the simulation for the other molecular species. An approximate match between the measured and simulated depths has been achieved. The simulations assume the version 2.2 tangent heights and the temperature profile retrieved for the occultation. The maximum optical path difference of the ACE instrument (25 cm) and 1.25 mrad diameter field of view were adopted. However, the simulations do not account for instrument self-apodization, which increases with wavenumber, slightly decreasing the effective spectral resolution [11,18].

Fig. 3 shows a comparison of normalized measured and calculated spectra for ss6185 in the mid-troposphere. Two panel plots compare results obtained by retrieving the H_2O_2 profile and those obtained assuming a H_2O_2 mixing ratio of zero at all altitudes. The upper panels show the residual (measured minus calculated) on an expanded vertical scale. Asterisks for the residual plot assume a H_2O_2 mixing ratio of zero
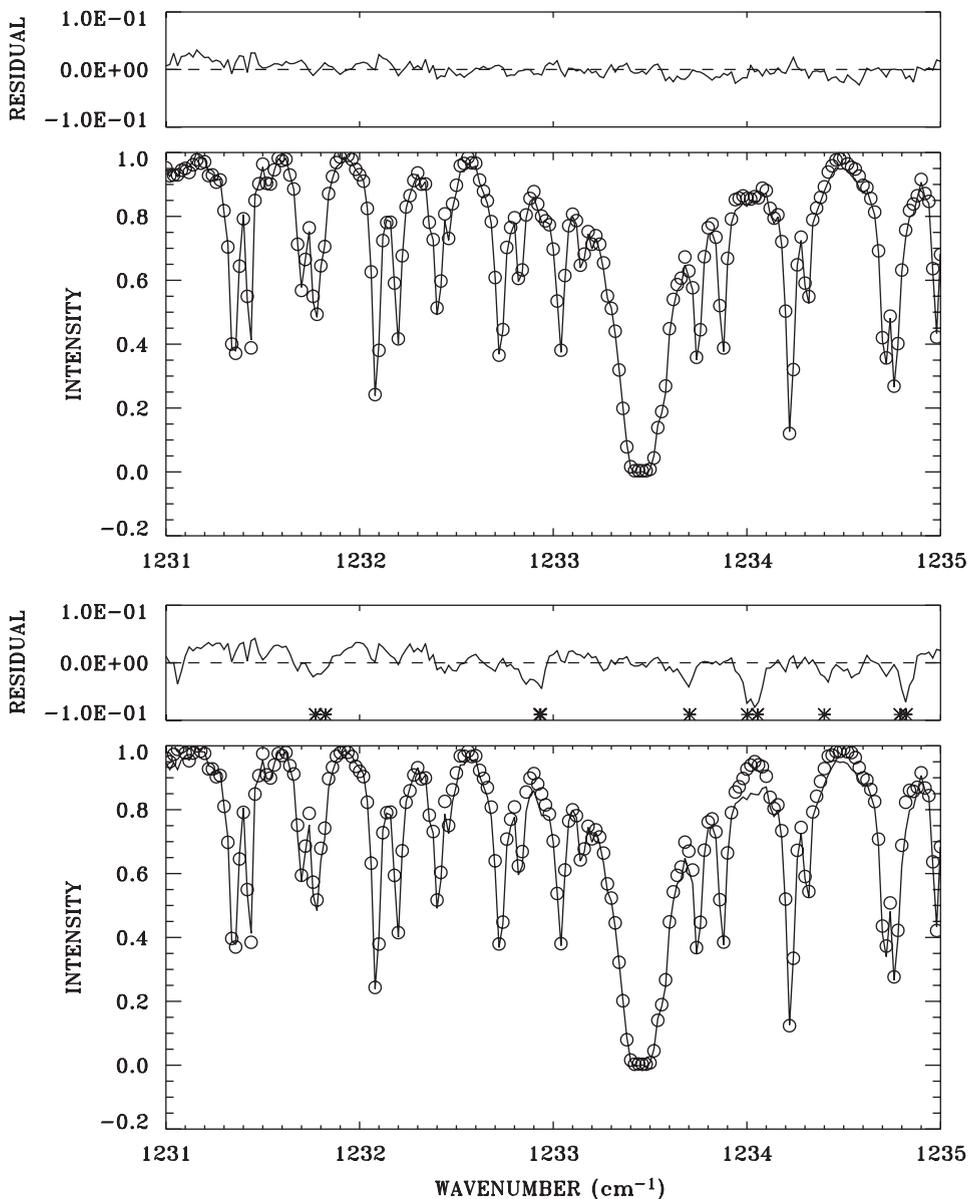

Fig. 3. Normalized spectrum and fit for ss6185 at a tangent altitude of 9.19 km. Residuals (measured minus calculated) are plotted on an expanded vertical scale. Upper panel plots show results from the best-fit profile for H_2O_2 and the lower panel plots show results obtained with the mixing ratio of H_2O_2 set to zero at all altitudes. Asterisks mark the location of stronger H_2O_2 lines.

with the location of the strongest H_2O_2 lines marked. Fig. 4 presents a comparison of retrievals for ss6185 from version 2.2 and the NASA Langley algorithm. Molecules fitted in the NASA Langley analysis were H_2O_2, N_2O, CO_2, CH_4, O_3, HDO, and H_2O. The ACE retrieval for H_2O_2 covers 5–12 km altitude and is based on sequential fitting of interferences in a window spanning 1230.8–1235.4 cm^{-1}. The lower altitudes are likely impacted by the limitations of this procedure, which will be updated in version 3 ACE retrievals. Both profiles show elevated H_2O_2 mixing ratios with close agreement between the mixing ratio and the altitude of the peak. Error bars from both do not include possible systematic error in the assumed spectroscopic parameters of H_2O_2. The H_2O_2 v_6 band integrated intensity determined from the simultaneous measurement of that band and the far infrared [15] is consistent with the HITRAN 2004 value [12].

We present in Fig. 5 ss6185 version 2.2 volume mixing ratio versus altitude profiles for HCOOH, CO, C_2H_6, and HCN. All are well-documented relatively long-lived biomass-burning products. Similar distributions are measured with maxima about 10 km. The maxima occur higher in altitude than the mixing ratio peak retrieved for H_2O_2.

Fig. 6 presents MODIS fire pixel counts [19] and kinematic back trajectories calculated for altitudes of 5, 7 and 9 km for ss6185 (plus symbol). The back trajectories were generated with the HYSPLIT4 (Single-Particle Lagrangian Integrated Trajectory Model) [20]. The back trajectories indicate the emissions originated near the east coast of South America. As the austral spring time period (September–October) is a well-known dry period in the tropics, when seasonally high accumulation of pollutants occurs, particularly over the South Atlantic Ocean between Brazil and southern Africa when widespread vegetative fires are common [21]. Our analysis suggests that such emissions were the likely source of the elevated H_2O_2 mixing ratios measured in ss6185. As the location is over the Atlantic and the lifetime of H_2O_2 is short, the measurement and back trajectories indicate ACE sampled a young biomass-burning plume. Previous studies of ACE measurements have documented elevated tropical–subtropical mixing ratios from such Austral spring middle–upper tropospheric scenes during 2004 and 2005 [22,23]. Ground-based high spectral resolution FTS measurements
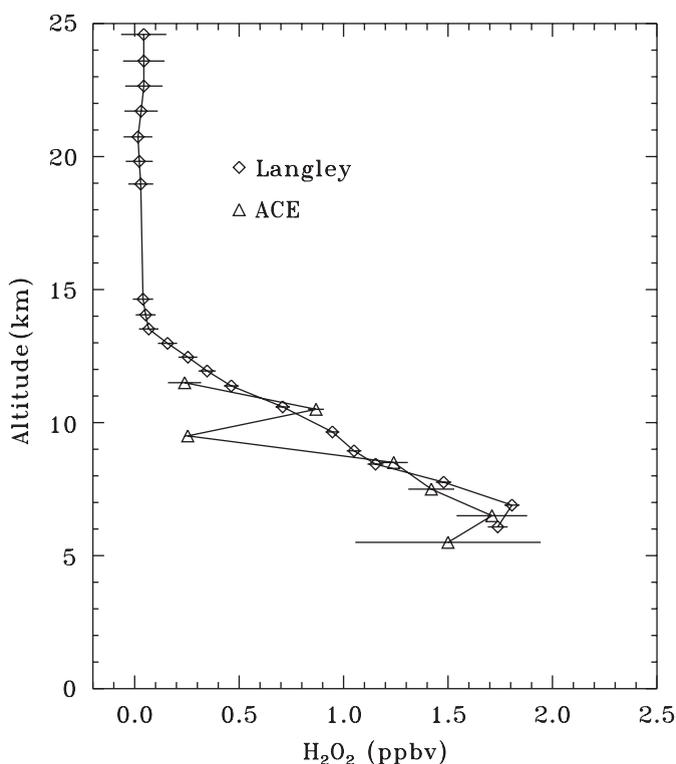

Fig. 4. Comparison of H_2O_2 ss6185 volume mixing ratio profiles from ACE version 2.2 and those retrieved with the algorithm at NASA Langley. Error bars indicate 1-σ statistical uncertainties.
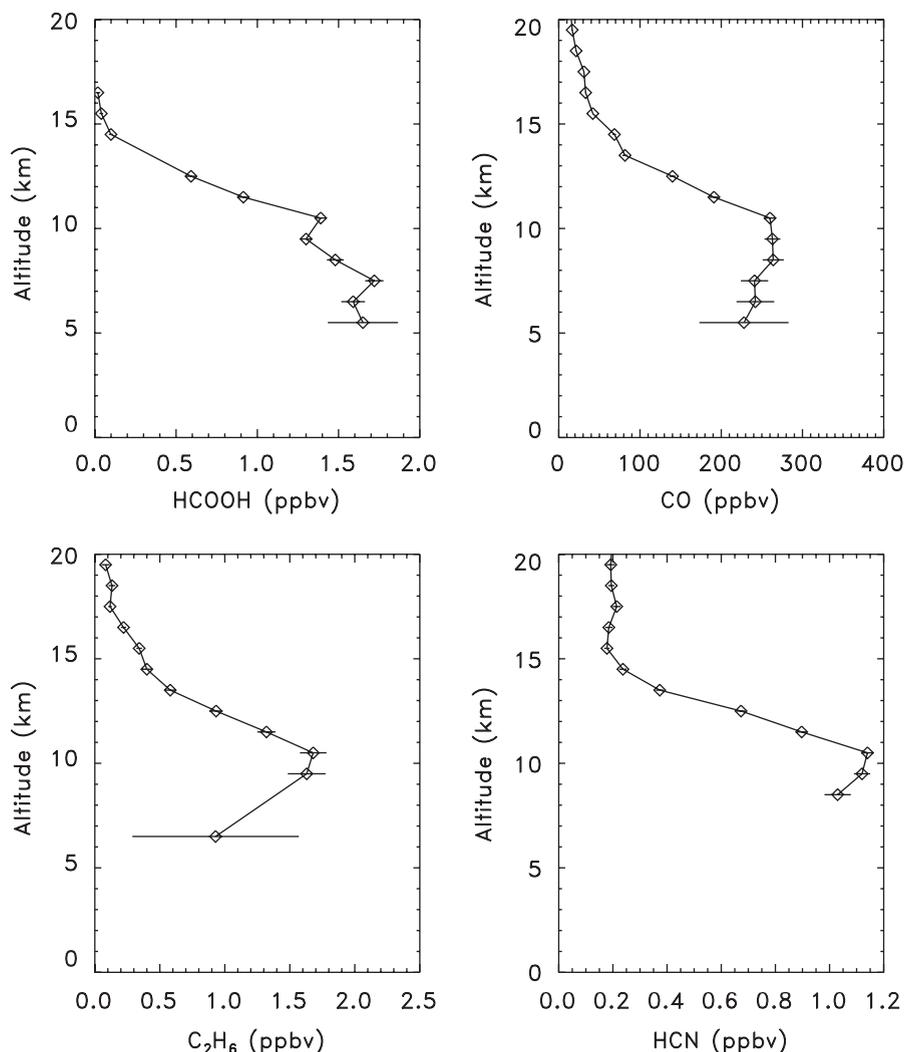
Fig. 5. Version 2.2 volume mixing ratio versus altitude profiles for HCOOH, CO, C_2H_6, and HCN from ss6185. Error bars indicate 1-σ statistical uncertainties.

have also documented transport of tropical fire emissions of longer-lived species to southern hemisphere lower mid-latitude sites at Lauder, New Zealand (45°S latitude) [24,25] Wollongong, Australia (34°S latitude) [26].

5. Summary and conclusions

Several occultations measured by the ACE Fourier transform spectrometer show elevated tropospheric H_2O_2 mixing ratios. Back trajectories and fire count statistics for the occultation with the highest measured mixing ratios support the hypothesis that the elevated mixing ratios likely resulted from the transport of surface emissions to the middle and upper troposphere shortly after a deep tropical convective event [3]. The measurement of elevated H_2O_2 in the ACE version 2.2 database is supported by an analysis of the same occultation with an independently developed retrieval algorithm [17]. Analysis of ACE FTS measurements based on HITRAN 2004 [12] supplemented with a cross-section database [27] has also resulted in detections of C_2H_4 (ethene), C_3H_4 (propyne), C_3H_6O, $CH_3COO_2NO_2$ (PAN), and H_2CO (formaldehyde) in a young biomass-burning plume [28]. This study, previous analyses [22,23], and the detection of fire emission species in biomass-burning plumes [28] highlight the potential of the high spectral resolution/high signal-to-noise ACE
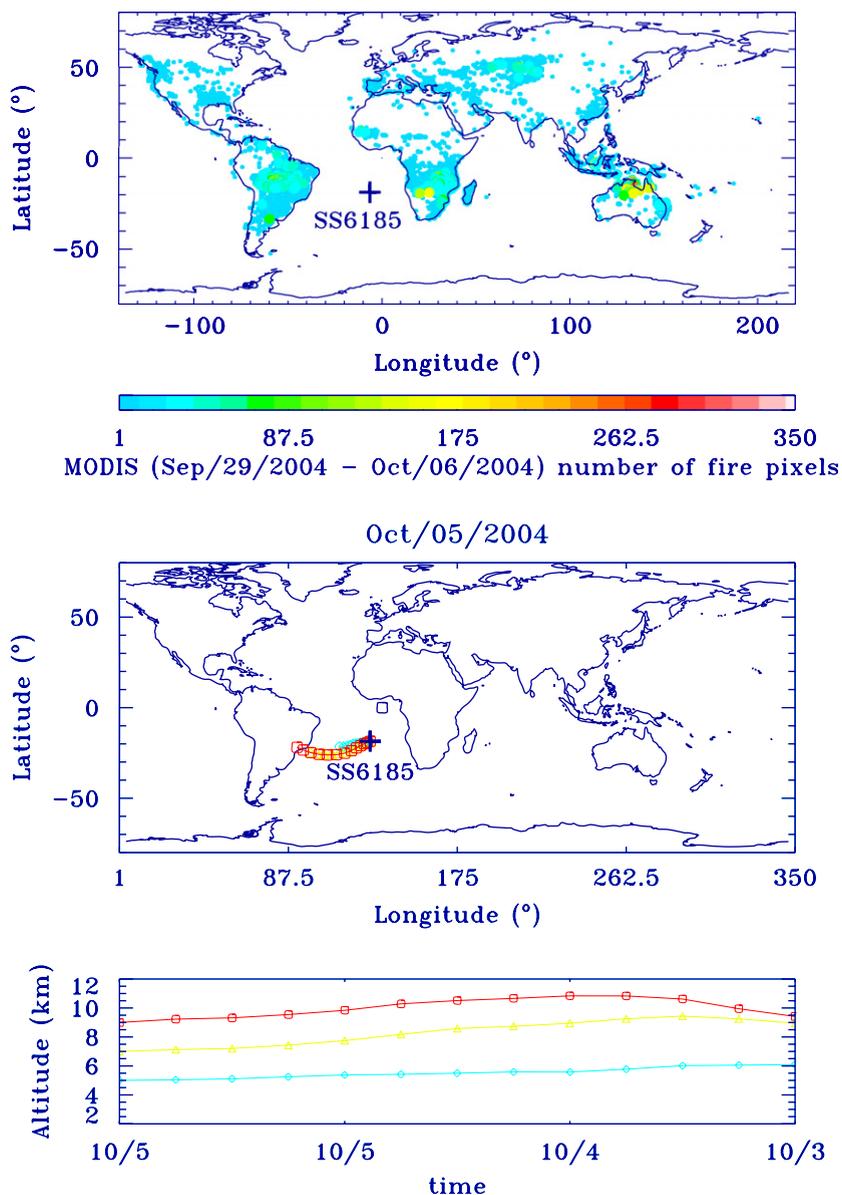
Fig. 6. MODIS fire counts and kinematic back trajectory calculations for ss6185. A plus symbol indicates the location of the measurement. Back trajectories were calculated for starting altitudes of 5, 7, and 9 km.

measurements to detect and quantify the vertical profiles of previously unidentified tropospheric species despite the limited spatial and temporal sampling of the ACE observations.

Acknowledgments

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