



Satellite observations of the global distribution of hydrogen peroxide (H₂O₂) from ACE

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ABSTRACT

A near global distribution of hydrogen peroxide (H₂O₂) in the mid- to upper troposphere and low to mid-stratosphere was obtained by the Atmospheric Chemistry Experiment (ACE) satellite. The data show that hydrogen peroxide exhibits both a seasonal and diurnal cycle with high variability in the upper troposphere. ACE data also show the influence of photochemistry on sunrise and sunset hydrogen peroxide distributions. The tropospheric hydrogen peroxide distribution was compared with output from the three-dimensional chemical transport model GEOS-Chem. The GEOS-Chem model is in good general agreement with ACE for hydrogen peroxide, capturing the main features observed including the diurnal and seasonal variation; however volume mixing ratios (VMRs) for the model are consistently greater than those of ACE.

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1. Introduction

Hydrogen peroxide, H₂O₂, is an important tropospheric oxidising agent [1] and has a strong influence on the atmospheric lifetimes of many anthropogenic and biogenic trace gases [2]. Highly soluble, hydrogen peroxide has a short atmospheric lifetime of a few days [2–5], and has a concentration that is highly variable with location, meteorology and season [5,6]. Understanding the chemistry of hydrogen peroxide is imperative for furthering our knowledge of the oxidising capacity of the atmosphere [1].

The HO_x budget is strongly linked to hydrogen peroxide formation and destruction [7,8]. The reaction of hydroxyl radicals with carbon monoxide (R1) and ozone (R2) leads to

the formation of hydroperoxyl radicals (HO₂) which are hydrogen peroxide precursors [9,10]. Recombination of two hydroperoxyl radicals (R3) leads to the formation of hydrogen peroxide [11].



It has been observed that the rate of hydrogen peroxide formation is dependent on NO_x concentrations [12]. In clean background air hydrogen peroxide formation is independent of NO levels [13], however in polluted air where nitrogen oxide levels are great enough R4 becomes a competing reaction with R3 consuming hydroperoxyl radicals and thus reducing hydrogen peroxide formation. According to Lee et al. [14], the threshold value for NO at

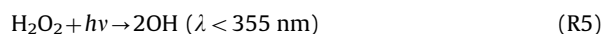
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which hydrogen peroxide formation is substantially reduced is about 100 ppt (parts per trillion).



The main sinks for hydrogen peroxide are dry and wet deposition [15,16] and photolysis [9]. High wind speeds are believed to heighten hydrogen peroxide deposition rates [17]. Hydrogen peroxide photolyses to give two hydroxyl radicals (R5) and thus acts as a significant reservoir for HO_x [2,18]. In the upper troposphere, where the atmosphere is drier, convective injection of peroxides from the boundary layer [7,19], particularly in the tropics, can substantially increase HO_x loadings.



A diurnal cycle is observed for hydrogen peroxide at Mace Head (Republic of Ireland), due to net photochemical production during the daytime and maximum concentrations coincided with peak temperatures and solar irradiation [20]. The amplitude of the diurnal variation is seasonal, predominantly attributed to the solar zenith angle [20]. At high latitudes, in spring organic peroxides have higher volume mixing ratios (VMRs) than hydrogen peroxide, which predominates in the summer [10], and all peroxide concentrations increase from winter to spring. Peroxide concentrations decrease with increasing latitude, and are influenced both by photochemistry and atmospheric dynamics (i.e., the source of air) [21].

Cloud chemistry and physics strongly influence the atmosphere's oxidising capacity, as clouds reduce HO_x and hydrogen peroxide concentrations [22]. Cloud interactions can enhance or deplete hydrogen peroxide more significantly than organic peroxides which are less soluble in water [23]. Due to a large Henry's law constant [24] it can be observed that cloud-water has significantly greater hydrogen peroxide concentrations compared with the surrounding gaseous atmosphere [15].

Hydrogen peroxide is an important molecule in the production of biopolymers in the apoplastic compartment of many plants, however it is particularly toxic to chloroplasts [14,25,26]. Whilst plants have a protective antioxidant system, enhanced levels of hydrogen peroxide have been linked to forest degradation through oxidative stressing of plants due to their inability to scavenge radicals [27]. High concentrations of hydrogen peroxide have been measured in high altitude forest which has been exposed to orographic clouds [28].

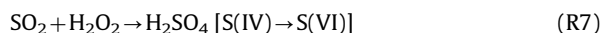
Snow packs have also been suggested as a source of hydrogen peroxide in polar regions [9]. Highly soluble in snow, hydrogen peroxide is released back into the atmosphere as a result of temperature-induced exchange between the atmosphere and the snow pack [10].

In the marine boundary layer higher water concentrations are thought to indirectly enhance hydroperoxyl levels through the reaction with $\text{O}(^1\text{D})$ which leads to a greater concentration of hydroxyl radicals (R6) [2,7]. This also means that greater levels of NO_x are required to curtail hydrogen peroxide formation [13]. Previous studies have also suggested that the presence of water and other species able to

hydrogen bond with hydroperoxyl radicals facilitate hydrogen peroxide production rates [29].



Hydrogen peroxide is a scavenger of sulphur dioxide in the aqueous phase [30,31], converting it into sulphuric acid, thus playing an important role in the oxidation of atmospheric sulphur [32]



Despite the significant number of studies that have been carried out the magnitude of the sources and sinks of hydrogen peroxide are still poorly constrained [4,11]. Large discrepancies between observed hydrogen peroxide values and photochemical models underline this [17]. Determining the concentration of hydrogen peroxide is difficult due to its short lifetime, which is photochemically influenced [21]. Ground-based [16,20,33] and aircraft measurements [4,34,35] for hydrogen peroxide frequently vary by orders of magnitude; for example aircraft campaigns such as INTEX-NA [6], SONEX [8] and TOPSE [21], which were all part of NASA's Global Tropospheric Experiment [36], showed a dramatic variation in the hydrogen peroxide concentrations observed [6].

Most recently, in the 2008 Arctic spring, during NASA's ARCTAS aircraft campaign HO_x distributions were measured in the troposphere of the North American Arctic and the results were interpreted using the GEOS-Chem three-dimensional chemical transport model [37]. It was discovered that the GEOS-Chem model overestimated both the hydroperoxyl radical and hydrogen peroxide concentrations measured during the ARCTAS campaign, and the temperature-dependent aerosol uptake of hydroperoxyl radicals (not *via* hydrogen peroxide formation) was introduced to reduce the discrepancy between the measurements and the model output [37].

The first atmospheric measurements of hydrogen peroxide were carried out by Bufalini et al. [12] studying the role of formaldehyde photooxidation in urban environments. Indirect techniques including fluorescence, colourimetry and chemiluminescence have widely been used to measure hydrogen peroxide [24,33]. Intercomparison of different techniques and a summary of the variety of methods used have previously been detailed in the literature [14].

Remote sensing of hydrogen peroxide could give important insight into the atmospheric HO_x budget and help constrain the tropospheric NO_x budget. To obtain altitude profiles for hydrogen peroxide, accurate spectroscopic data are required including data on pressure-broadening effects, line positions and absolute intensities [5,38]. A number of spectroscopic studies have attempted to determine the absolute line intensities and the integrated intensity for the ν_6 torsion-rotation band ($1170\text{--}1380 \text{ cm}^{-1}$) which is the most suitable one for infrared remote sensing. Data for this band is included in the HITRAN database [5,39].

Thermal emission measurements by the FIRS-2 balloon used a FTS (Fourier transform spectrometer) in the far infrared region to obtain hydroperoxyl concentrations

and hydrogen peroxide profiles using remote sensing techniques [40,41]. The first stratospheric global retrievals of hydrogen peroxide from space were made using the MIPAS instrument [18]. These retrievals showed enhancements in hydrogen peroxide VMRs in the stratosphere over the tropics, as well as observing enrichment of hydrogen peroxide in the Antarctic during spring time in the lower stratosphere. MIPAS observed the diurnal behaviour of hydrogen peroxide with heightened VMRs observed between 32 and 35 km at night [18]. Recently Versick et al. [42] used MIPAS data to produce a stratospheric global distribution between 20 and 60 km.

Using spectra from ACE occultations, Rinsland et al. [43] detected enhanced hydrogen peroxide VMRs in biomass burning plumes originating from the tropics. These findings [43] concur with combustion experiments which suggest that biomass burning is an important source of hydrogen peroxide in agreement with plumes detected during the TRACE-A campaign [35].

2. Observation and retrievals

In August 2003 the Canadian satellite SCISAT-1 was launched into a low highly-inclined circular orbit (altitude 650 km, inclination 74°). The primary remote sensing instrument on board SCISAT-1 is the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS), which provides concentration profiles of the Earth's atmosphere. VMR profiles of trace species from the mid-troposphere through to the lower thermosphere, along with temperature and pressure profiles, are retrieved from transmission spectra [44].

The high-resolution FTS covers the infrared spectral region between 750 and 4400 cm⁻¹. The spectrometer has a 0.02 cm⁻¹ spectral resolution with a maximum optical path difference of ± 25 cm [45]. The ACE-FTS uses solar occultation technique to retrieve over 30 trace species, including multiple isotopologues for some species, with a typical vertical resolution of 3–4 km. The sun tracker locks onto the centre of the sun whilst a set of transmission spectra are taken through the limb of the Earth's atmosphere during sunrise and sunset.

The altitude range for the hydrogen peroxide ACE-FTS version 3.0 retrieval varies as a function of latitude, extending from 5 to 40 km at the equator and 5 to 25 km at the poles. The two microwindows centred about 1231.81 and 1234.5 cm⁻¹, with widths of 1.5 and 1.6 cm⁻¹, respectively, cover the entire altitude range. Smaller (less than 1 cm⁻¹ width) additional microwindows are used to improve retrievals above 15 km (Table 1). Additional microwindows are used to improve the retrieval results for the interferers (Table 2). If we treat the different isotopologues for a given molecule as separate interferers (with each isotopologue having a different VMR profile), there are a total of 15 interferers in the retrieval window for hydrogen peroxide. These interferers include H₂O isotopologues H₂¹⁶O, HDO and HD¹⁸O, CO₂ isotopologues ¹²C¹⁶O¹⁸O and ¹³C¹⁶O¹⁸O, N₂O isotopologues ¹⁴N₂¹⁶O, ¹⁴N ¹⁵N ¹⁶O, ¹⁵N ¹⁴N ¹⁶O, ¹⁴N ¹⁴N ¹⁷O and ¹⁴N ¹⁴N ¹⁸O, CH₄ isotopologues ¹²CH₄, ¹³CH₄ and CH₃D, O₃ and COF₂. All of the line parameters for these interferers

Table 1

Microwindow list for hydrogen peroxide.

Centre frequency (cm ⁻¹)	Microwindow width (cm ⁻¹)	Lower altitude limit (km)	Upper altitude limit (km)
1231.81	1.50	5	25–39
1234.50	1.60	5	25–40
1237.92	0.60	15	25–40
1239.35	0.50	15	25–40
1240.15	0.50	15	25–40
1241.85	0.90	20	25–40
1246.96	0.60	15	25–40
1248.70	0.40	20	25–40
1950.10 ^a	0.35	6–7	15
2624.07 ^b	1.30	5	13
2657.30 ^b	0.35	13	21

Note: The altitude limits for some microwindows vary as a function of latitude.

^a Included to improve results for the interferer H₂O.

^b Included to improve results for the interferer H₂O isotopologue HDO.

Table 2

Interfering molecules for hydrogen peroxide.

Molecule	Molecular formula ^a	Lower altitude limit (km)	Upper altitude limit (km)
H ₂ O	1 (H ₂ O)	5	25–40
H ₂ O	4 (HDO)	5	21
CO ₂	3 (OC ¹⁸ O)	5	25–40
CO ₂	5 (O ¹³ C ¹⁸ O)	5	13
O ₃	0 (O ₃)	5	32
N ₂ O	1 (N ₂ O)	5	25–40
N ₂ O	2 (N ¹⁵ NO)	5	21–28
N ₂ O	3 (¹⁵ NNO)	5	23–32
N ₂ O	4 (N ₂ ¹⁸ O)	5	23–32
N ₂ O	5 (N ₂ ¹⁷ O)	5	21–27
CH ₄	1 (CH ₄)	5	25–40
CH ₄	2 (¹³ CH ₄)	5	25–40
CH ₄	3 (CH ₃ D)	5	21–25
COF ₂	0 (COF ₂)	5	24–32
H ₂ O	5 (HD ¹⁸ O)	5	10

Note: The altitude limits for some microwindows vary as a function of latitude.

^a Numbers indicate the isotopologue abundance (i.e., 1 being the most abundant isotopologue) and zero treats all isotopologues for the species.

in the microwindow, were obtained from the HITRAN 2004 dataset and its subsequent updates [46].

The line list used for the hydrogen peroxide retrieval uses the work of Klee et al. [38] and Perrin et al. [47] for the ν_6 band, as detailed in the HITRAN 2008 database [39]. The systematic retrieval error for the ν_6 band intensity and line list uncertainty is estimated to be 10%.

The statistical errors in the retrieval below 15 km remain low with a typical value of 15%, but these errors can grow to 40–50% as VMRs decline. In the troposphere the major error is the systematic error for the average profiles with minor contributions from the statistical retrieval error. In the stratosphere, the systematic retrieval error is relatively small, but the statistical retrieval error now dominates.

A total of 9176 extravortex occultation measurements recorded by ACE, taken between February 2004 and August

2010, were used in this study and were classified using derived meteorological products [48]. Anomalous data produced in problematic retrievals was filtered. Most of these data can be attributed to the presence of clouds in the limb view of ACE.

2.1. Comparison of ACE with the three-dimensional model GEOS-Chem

The ACE data were compared with the output of the three-dimensional global chemical transport model GEOS-Chem [49]. Due to the high inclination of SCISAT-1 orbit and the solar occultation technique, ACE does not sample the globe uniformly, taking more measurements at high latitudes. To ensure suitable temporal and spatial sampling of the chemical transport model with reference to the ACE data the model output simulations have been sampled at the same location and time as the observations.

2.2. The GEOS-Chem model

The GEOS-Chem global three-dimensional chemical transport model (version v8-02-03 (<http://acmg.seas.harvard.edu/geos/>)) has the ability to simulate trace gases and aerosol distributions in the troposphere [49]. The model is driven by assimilated meteorological products from the Goddard Earth Observing System (GEOS) of the NASA Global Modelling and Assimilation Office (GMAO). We have used here the GMAO GEOS-5 operational meteorology data. The resolution of the meteorological data is degraded for model input to a horizontal resolution of 4° latitude by 5° longitude and with vertical resolution reduced to 47 eta levels by lumping levels above ~80 hPa. GEOS-5 meteorological fields have a temporal resolution of 6 h (3 h for surface variables), a horizontal resolution of 0.5° latitude by 0.667° longitude and a vertical resolution of 72 eta hybrid levels extending from the surface up to 0.01 hPa.

The GEOS-Chem chemical transport model includes over 250 chemical and photochemical reactions to simulate the chemistry occurring in the troposphere. There are eleven chemical pathways included in our run of the GEOS-Chem model which lead to the formation of hydrogen peroxide as detailed in Table 3. The sink mechanisms for hydrogen peroxide are photolysis (R5), hydroxyl attack, leading to the formation of a hydroperoxyl radical and a water molecule, as well as dry and wet deposition. The rate constants used in our run of the GEOS-Chem model for these reactions are those from the Jet Propulsion Laboratory's (JPL's): Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies [50]: A copy of the most recent versions can be obtained at: <http://jpldataeval.jpl.nasa.gov/>.

$k_{\text{GEOS-Chem}}$ (Eq. 1) is the overall rate constant determined for each of the reactions used in our run of the GEOS-Chem model, using A, B and C for constants as defined in Table 3 and where T represents the temperature in kelvin.

$$k_{\text{GEOS-Chem}} = A \times \left(\frac{300}{T} \right)^{B \times \exp(C/T)} \quad (1)$$

The model was spun-up with a three-month run from November 2003 before restarting again in February 2004

Table 3

Summary of the GEOS-Chem reaction rates that contribute to the formation of hydrogen peroxide included in this run of the model.

Reaction	A	B	C
OH + OH + M → H ₂ O ₂ + M	6.9E–31	1.0	0
	2.6E–11	0	0
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂ ^a	2.3E–13	0	600
	1.7E–33	0	1000
C ₃ H ₆ + O ₃ → 0.045H ₂ O ₂ + products	6.5E–15	0	–1900
ISOP + O ₃ → 0.110H ₂ O ₂ + products	1.03E–14	0	–1995
MVK + O ₃ → 0.083H ₂ O ₂ + products	7.51E–16	0	–1521
MACR + O ₃ → 0.124H ₂ O ₂ + products	1.36E–15	0	–2112
IALD + O ₃ → 0.070H ₂ O ₂ + products	2.4E–17	0	0
MVKOH + O ₃ → 0.090H ₂ O ₂ + products	7.51E–16	0	–1521
ACR + O ₃ → 0.090H ₂ O ₂ + products	2.9E–19	0	0
NIALD + O ₃ → 0.076H ₂ O ₂ + products	2.4E–17	0	0
C ₂ H ₄ + O ₃ → 0.139H ₂ O ₂ + products	1.2E–14	0	–2630

Where ACR is acrolein, IALD is a hydroxy carbonyl alkene breakdown product from isoprene (HOCH₂C(CH₃)=CHCHO), ISOP is isoprene, MACR is methacrolein, MVK is methylvinylketone, MVKOH is isoprene plus a hydroxyl radical, NIALD is isoprene plus NO₃. For reactions with more than one rate constant these correspond to the upper and lower pressure limits. A, B and C are described in Eq. (1).

^a Where the overall rate constant $k = (k_1 + k_2) \times (1 + 1.4E^{-21} \times [\text{H}_2\text{O}])^{\exp(2200/T)}$.

to coincide with the first ACE measurements. A total number of 8598 ACE occultations were suitable for comparison with the GEOS-Chem output. The data were subdivided into sunrise (4762) and sunset (3836) occultations to compare the effects of photochemistry upon the hydrogen peroxide distribution.

The GEOS-Chem model output has been co-located to ACE measurements with a temporal accuracy of less than two hours. The GEOS-Chem data have been interpolated to the satellite altitude grid of 1 km resolution. The horizontal resolution used for the GEOS-Chem model was 4° latitude by 5° longitude which is comparable to the path length for limb sounding instruments, such as ACE, that is estimated to be 500 km [51].

2.3. Results and discussion

The ACE near global distribution of hydrogen peroxide (Fig. 1) in the mid- to upper troposphere (5.5–13.5 km) is fairly symmetric about the equator, where average values of up to 700 ppt are observed, with larger values in the northern hemisphere at equatorial and mid-latitudes. Data starting at 80°S and ending at 80°N were separated into equal latitude zones with a width of five degrees. An average profile was calculated for each latitude bin. The ACE data for all of the figures (as an average profile) is provided as supplementary material (Supplementary Tables 1–6). Hydrogen peroxide VMRs decrease rapidly with increasing altitude in the troposphere. ACE measurements are in agreement with the findings of Heikes et al. [34] and Lee et al. [14] that also show greatest hydrogen peroxide VMRs about the equator declining with increasing latitude toward the poles. Very recent research has suggested Arctic haze, polluted air transported northwards from Eurasia, may deplete hydrogen peroxide concentrations by consuming hydroperoxyl radicals [52].

The sunrise and sunset ACE global distributions in Fig. 2 (consisting of 4762 and 3836 occultations, respectively)

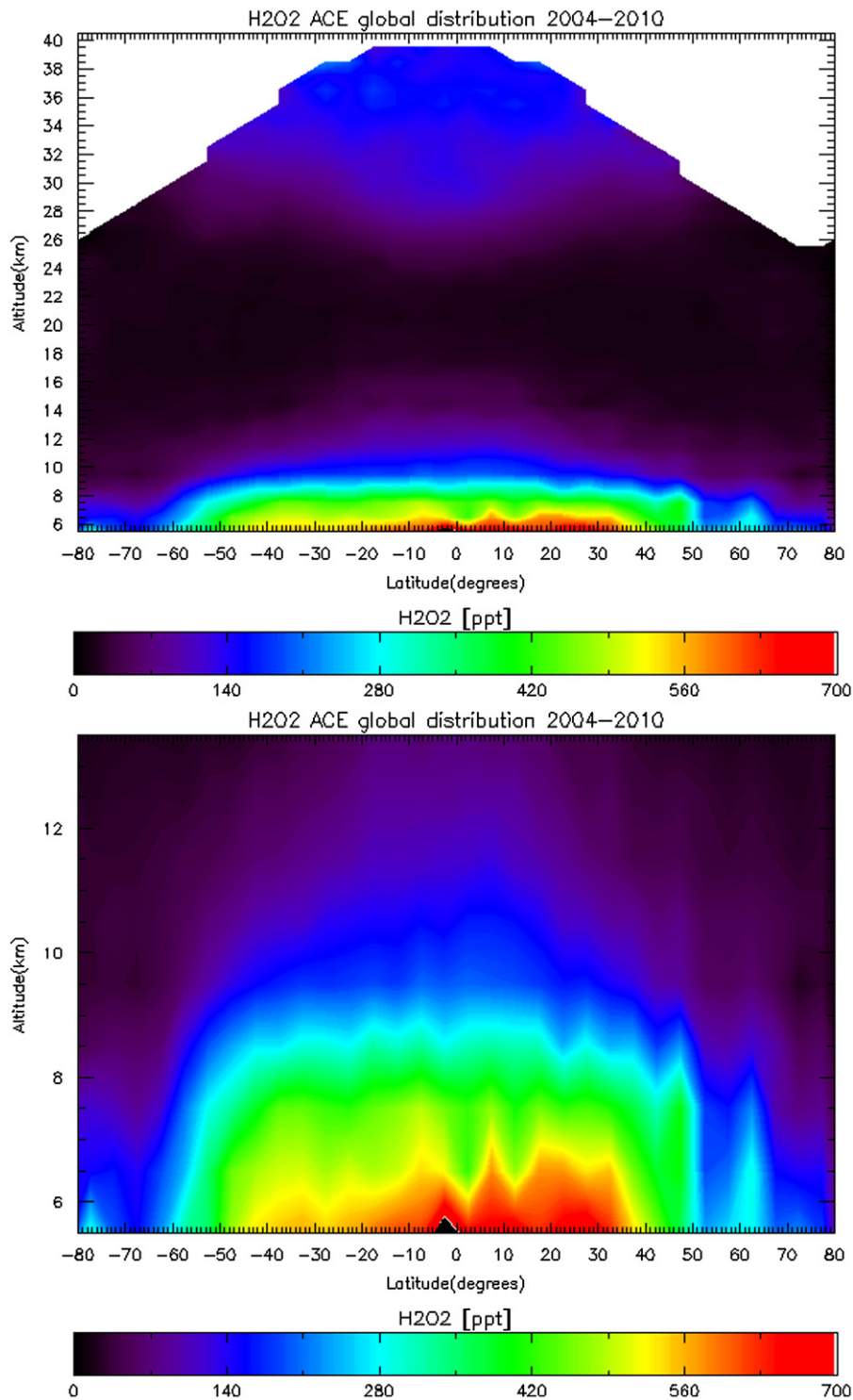


Fig. 1. A near global distribution of the average VMR of hydrogen peroxide (in ppt) as a function of latitude between (a) 5.5 and 40.5 km and (b) 5.5 and 13.5 km altitude obtained from ACE–FTS profiles between February 2004 and June 2010. White patches are where there is no ACE data available. Black shadings in the tropical troposphere correspond to points where hydrogen peroxide exceeds the colour scale limit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

show the diurnal variation of hydrogen peroxide. In the ACE sunrise tropospheric hydrogen peroxide distribution heightened VMRs are localised about the equator with some hot

spots at southern and northern mid-latitudes. The ACE sunset VMRs show stronger enhancements than the sunrise distribution, especially at northern mid-latitudes. In the

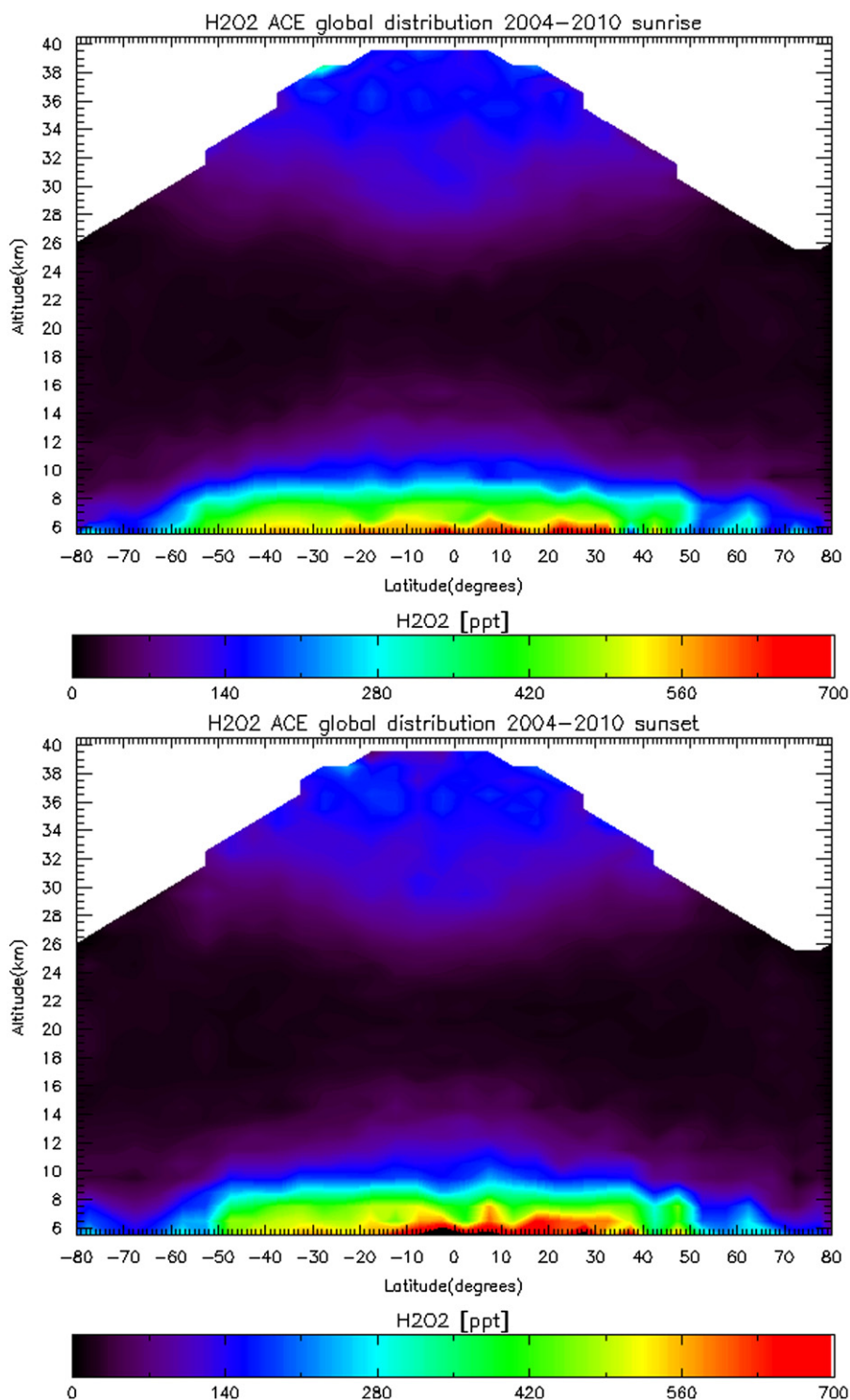


Fig. 2. The (top panel) sunrise (4762 occultations) and (bottom panel) sunset (3836 occultations) near global distribution of the average VMR of hydrogen peroxide (in ppt) as a function of latitude between 5.5 and 40.5 km altitude obtained from ACE-FTS profiles between February 2004 and June 2010. White patches are where there is no ACE data available. Black shadings in the tropics correspond to points where hydrogen peroxide exceeds the colour scale limit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stratosphere between 25 and 40 km hydrogen peroxide VMRs in the ACE sunrise distribution are similar to those observed at sunset.

Focussing solely on the stratosphere and setting the colour scale limit to 350 ppt (Fig. 3) we compare the sunrise and sunset VMRs for hydrogen peroxide. Using the

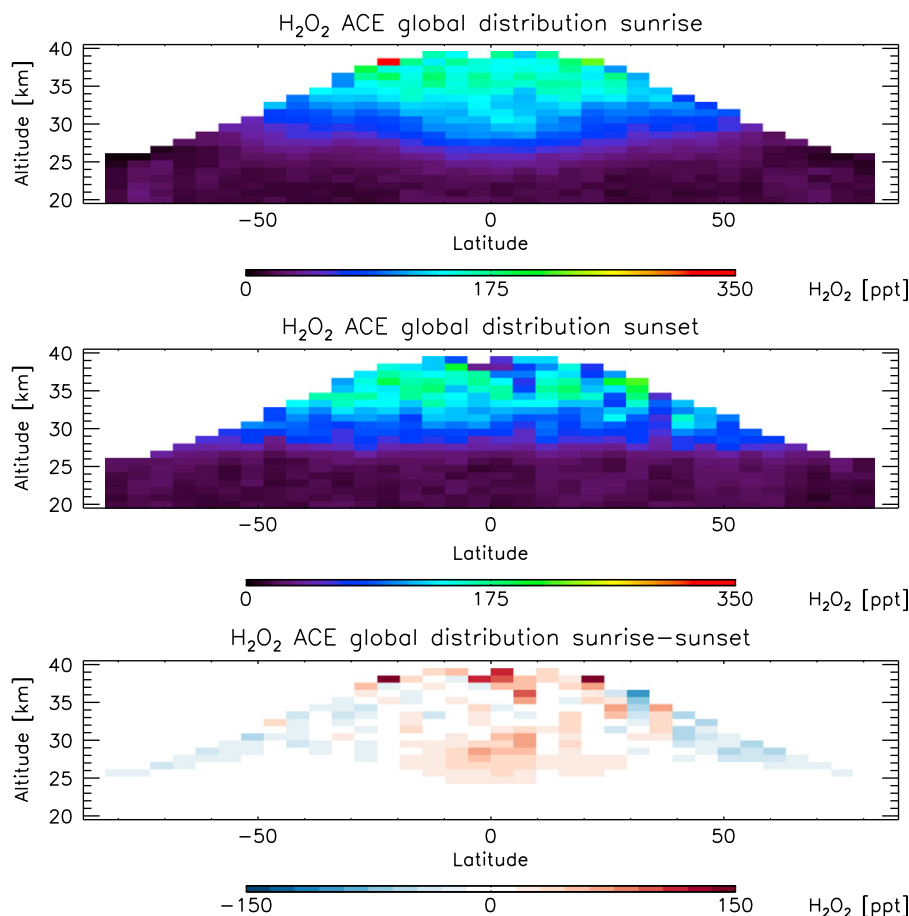


Fig. 3. The stratospheric (top panel) sunrise (4762 occultations) and (middle panel) sunset (3836 occultations) distribution of the average VMR of hydrogen peroxide (in ppt) and (bottom panel) the difference (sunrise–sunset) as a function of latitude between 19.5 and 40.5 km altitude obtained from ACE–FTS profiles between February 2004 and June 2010.

difference plot in Fig. 3 we can observe that sunrise VMRs are greater than sunset VMRs at equatorial latitudes, whereas sunset VMRs are greater than sunrise VMRs at higher northern and southern latitudes. One possible reason for a small mid-stratospheric diurnal variation in hydrogen peroxide was postulated in early work by Connell et al. [53] who suggested that it was due to hydrogen peroxide being in photochemical equilibrium with other HO_x species. Mid-stratospheric hydrogen peroxide may also be sensitive to fluctuations in other trace species concentrations, such as ozone and NO_x [53].

In Fig. 4 the ACE sunrise and sunset global tropospheric distributions were compared with the output of the GEOS-Chem model, which is predominantly a tropospheric model. Whilst the upper scale limit was set to 700 ppt for the ACE sunrise and sunset global distributions, the range had to be increased to 1000 ppt to allow comparison of the ACE model distribution with the GEOS-Chem output, which had higher VMRs.

The GEOS-Chem model was sampled at the same location and local time as the ACE observations. The GEOS-Chem sunrise distribution for hydrogen peroxide has a similar pattern to that of ACE. However, the GEOS-Chem values are elevated relative to those observed by

ACE at similar altitudes. The GEOS-Chem sunset distribution also shows general agreement with the ACE data, although the model predicts a more asymmetric distribution with higher values in the Southern Hemisphere, not observed by ACE. This could be a result of excessive biogenic emission sources being included in the model.

To determine whether the hydrogen peroxide global distribution variations are seasonal, data were divided into four bins: December, January and February (DJF), March, April and May (MAM), June, July and August (JJA) and September, October and November (SON). Each ACE occultation recorded was classified into one of these four bins and each seasonal distribution (Fig. 5) was compared with the corresponding GEOS-Chem output (Fig. 6) for the troposphere. Unfortunately, splitting the data into four categories meant that at some altitudes and latitudes no ACE data was available leaving gaps in the global distribution. Nevertheless the seasonal plots do suggest that there is a noticeable shift in hemispheric hydrogen peroxide VMRs throughout the year.

In DJF hydrogen peroxide VMRs are greatest near the equator, however there is a significant enhancement at southern mid-latitudes (30–50°S) compared with the corresponding northern mid-latitudes. In contrast, during the seasons MAM and JJA the VMRs at northern mid-latitudes

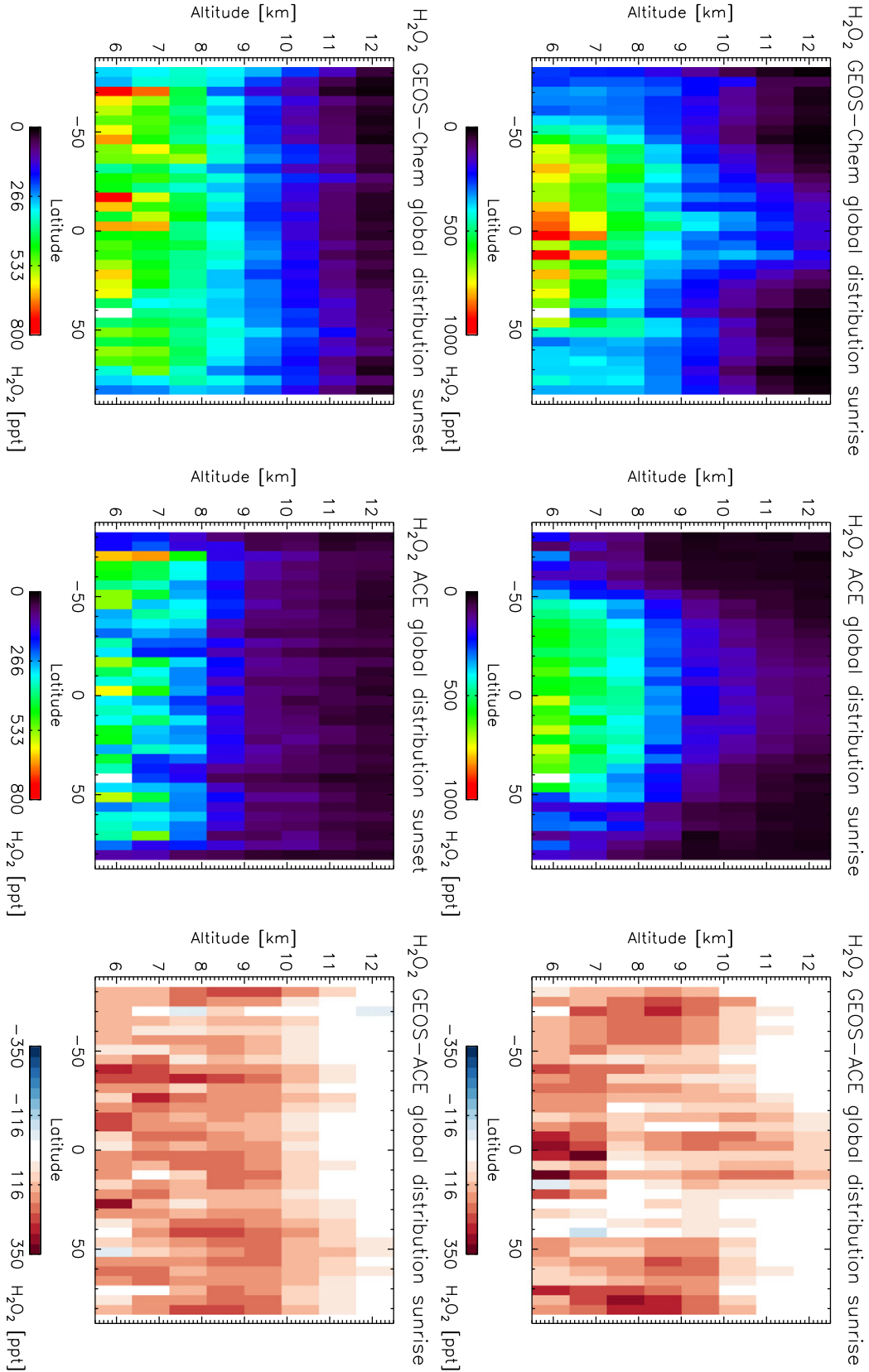


Fig. 4. A comparison of the ACE-FTS (top middle panel) sunrise and (bottom middle panel) sunset distribution of the average VMR of hydrogen peroxide (in ppt) in the troposphere compared with the (top left panel) sunrise and (bottom left panel) sunset, distribution from the GEOS-Chem three-dimensional chemistry transport model. Panels (top right panel) and (bottom right panel) depict the difference between the GEOS-Chem model and the average ACE VMRs for the sunrise and sunset distributions, respectively. Black shadings in the tropics correspond to points where hydrogen peroxide exceeds the colour scale limit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

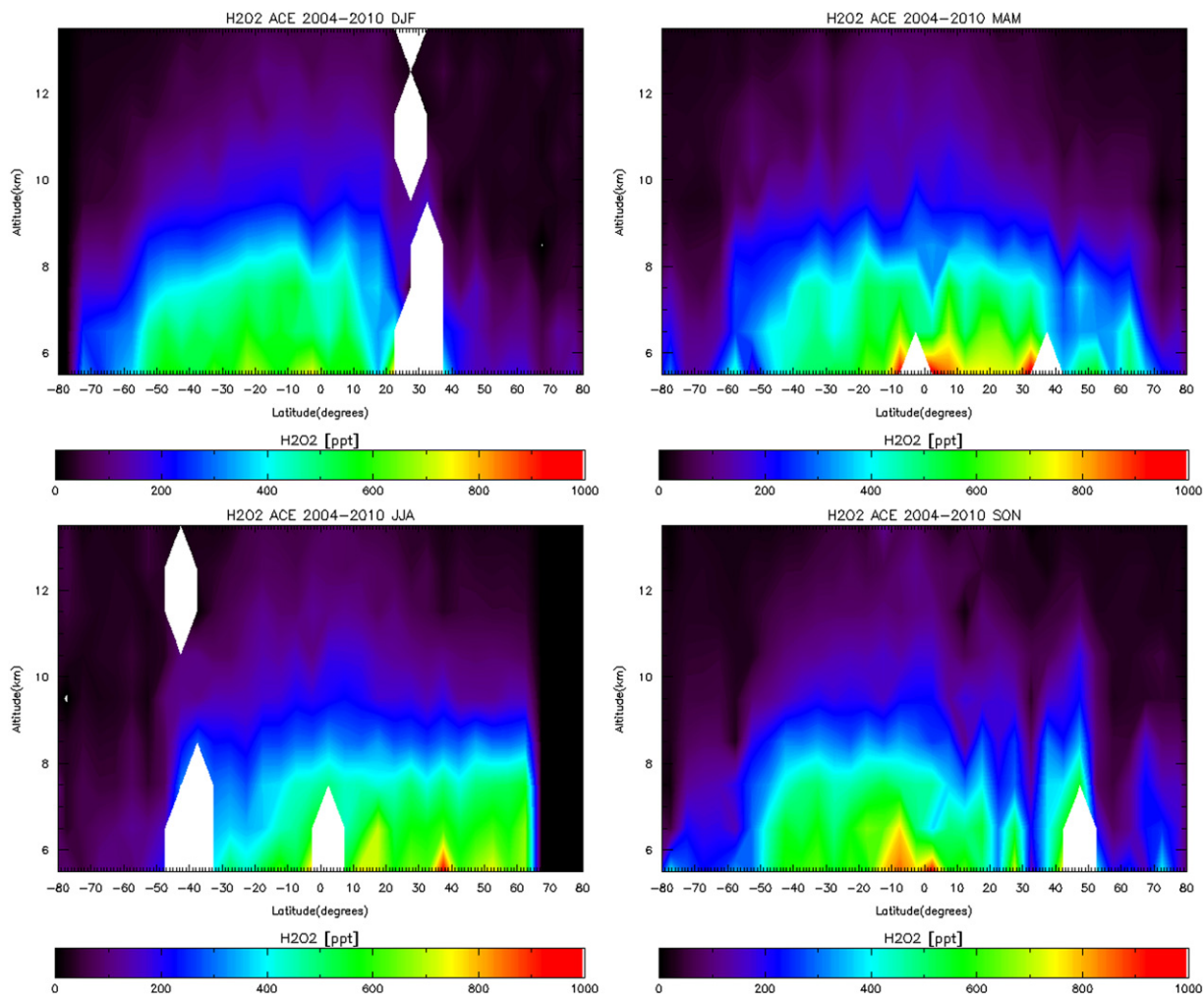


Fig. 5. The ACE-FTS seasonal distribution of the average VMR of hydrogen peroxide (in ppt) in the troposphere is shown. Data was divided into four bins: (top left panel) December, January and February (DJF), (top right panel) March, April and May (MAM), (bottom left panel) June, July and August (JJA) and (bottom right panel) September, October and November (SON). White patches are where there are no ACE data available. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are significantly higher than the equivalent southern mid-latitudes. These enhancements, particularly MAM, are stronger than those observed during the DJF season in the southern hemisphere and extend to latitudes greater than 60°N. In SON there is a southern hemispheric hydrogen peroxide asymmetry, however during this season enhancements can be observed in both hemispheres. Similar trends are observed by ACE and GEOS-Chem for the hydrogen peroxide global distributions despite the higher VMRs consistently assimilated for the GEOS-Chem model compared with the ACE data. Hydrogen peroxide VMRs seem to be highest in both hemispheres' summer months. This would suggest that hydrogen peroxide sources in the summer must be stronger to counteract the increased photolysis rates expected at large solar zenith angles.

Overall while the GEOS-Chem model captures the salient hydrogen peroxide features observed by ACE and has good seasonal agreement, VMRs are significantly higher in the

troposphere. VMRs in the ACE distributions are in the order of 300–700 ppt up to 8 km whereas the GEOS-Chem global distributions are between 500 and 1000 ppt for the same altitudes. In the GEOS-Chem model hydrogen peroxide penetrates significantly further into the upper troposphere compared with the ACE distributions.

Overall, the GEOS-Chem model agrees well with the spatial distributions and trends observed by ACE, although there are noticeable differences. Previous authors [37] have also observed that the GEOS-Chem model overestimates the tropospheric concentration of hydrogen peroxide in the Arctic and an aerosol uptake mechanism of hydroperoxyl radicals (not via hydrogen peroxide formation) was introduced to reduce the difference between the measurements and the GEOS-Chem model. We have chosen not to implement such a mechanism as aerosol uptake is only expected to be high when temperatures are extremely low (such as in the polar spring).

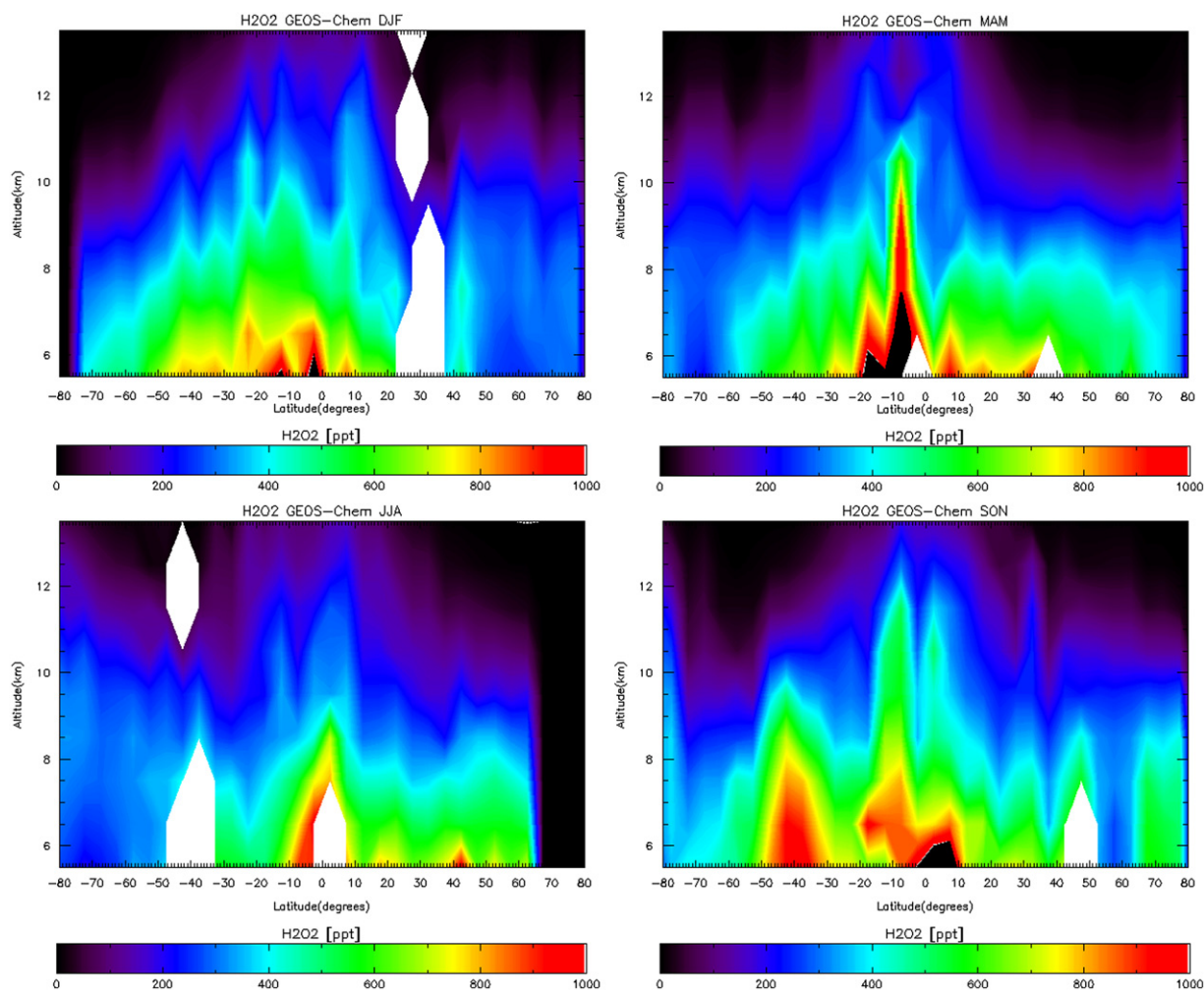


Fig. 6. The GEOS-Chem seasonal distribution of the average VMR of hydrogen peroxide (in ppt) in the troposphere is shown. Data was divided into four bins: (top left panel) December, January and February (DJF), (top right panel) March, April and May (MAM), (bottom left panel) June, July and August (JJA) and (bottom right panel) September, October and November (SON). White patches are where there are no ACE data available. Black shadings in the tropics correspond to points where hydrogen peroxide exceeds the colour scale limit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.4. Sensitivity runs

To explain the trends observed in the ACE and GEOS-Chem data we need to consider the critical factors influencing the hydrogen peroxide budget. The balance in the production and destruction of hydrogen peroxide is governed by HO_x and photochemistry. The rate of hydrogen peroxide production is predominantly a result of hydroperoxyl radical recombination (R3) (association of two hydroxyl radicals in a third body reaction (R8) is a minor source), whereas destruction is dependent on photolysis, as well as dry and wet deposition, to a lesser extent. The reactions of volatile organic compounds lead to the formation of a number of products including hydrogen peroxide.



Organic compounds contribute greatly to the production of hydroperoxyl radicals. The two main sources of

organics are anthropogenic and biogenic emissions. When the VMRs of organics are high hydroperoxyl radical concentrations are greater. At these higher hydroperoxyl concentrations formation occurs more frequently, implying that hydrogen peroxide VMRs increase. The biogenic emissions of organics are highest in the spring and summer growing months.

The counterbalance to this is the rate of photochemical destruction, which is greatest in the summer months, compared to the winter months when it is darker and destruction rates decline. In conjunction with the low winter light levels there is increased anthropogenic emissions, leading overall to higher levels of organic pollution, which heightens the abundance of hydroperoxyl radicals and promotes hydrogen peroxide production.

In order to assess the effects organic emissions have on the production of hydrogen peroxide, compared with other contributions, the GEOS-Chem model has been run several times for a short three-month period omitting one

of the organic sources (anthropogenic, biofuel, biogenic, biomass) each time from the standard model. A control was also run where the chemistry for the GEOS-Chem model was turned off; chemical production and loss in this case was zero.

Removal of the biogenic emission from the GEOS-Chem model had the biggest effect on the hydrogen peroxide production, reducing it by over 20% compared to the standard run. This also impacted the resulting loss, which was smaller, as less hydrogen peroxide had been produced. The removal of the anthropogenic and biomass burning emissions had a minor impact on hydrogen peroxide reducing production compared to the GEOS-Chem standard run by approximately 4 and 5%, respectively. The hydrogen peroxide production is not significantly altered when the biofuel emissions are removed (less than 1%). The removal of biogenic sources from the GEOS-Chem model has the biggest effect on the hydrogen peroxide budget. We can therefore conclude that organic compounds, particularly from biogenic sources, have a strong impact on the production of hydrogen peroxide accounting for about 30% of the modelled concentrations.

Similar three-month sensitivity runs using GEOS-Chem were carried out to assess the importance of dry and wet deposition on the hydrogen peroxide loss mechanism. When dry deposition was turned off in the model the hydrogen peroxide concentrations predicted were 40% greater than the standard model run. Likewise turning off wet deposition increased hydrogen peroxide concentrations by 11%. We can conclude from the GEOS-Chem model that after photochemical destruction, dry deposition is the second most important sink mechanism.

3. Summary and conclusion

The study has described the comparison of the first near global distribution of hydrogen peroxide in the troposphere obtained by ACE with the output of the three-dimensional chemistry transport model GEOS-Chem. Both data sets showed evidence of hydrogen peroxide having a seasonal hemispheric asymmetry with highest VMRs observed in the tropics. Hydrogen peroxide VMRs are greatest about the equator and at mid-latitudes, while decreasing towards the poles. VMRs rapidly decline with increasing altitude in the troposphere. The ACE retrievals in the stratosphere show a small diurnal hydrogen peroxide cycle due to the effects of photochemistry.

The GEOS-Chem model captures the main features of the ACE hydrogen peroxide data, however the model VMRs are significantly higher than those obtained by ACE. The concentration of hydrogen peroxide is highly variable in the troposphere due to the wide variety of sources. Organic compounds, particularly from biogenic sources, and photolysis appear to play key roles in the production and destruction of hydrogen peroxide.

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