

Midlatitude atmospheric OH response to the most recent 11-y solar cycle

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The hydroxyl radical (OH) plays an important role in middle atmospheric photochemistry, particularly in ozone (O₃) chemistry. Because it is mainly produced through photolysis and has a short chemical lifetime, OH is expected to show rapid responses to solar forcing [e.g., the 11-y solar cycle (SC)], resulting in variabilities in related middle atmospheric O₃ chemistry. Here, we present an effort to investigate such OH variability using long-term observations (from space and the surface) and model simulations. Ground-based measurements and data from the Microwave Limb Sounder on the National Aeronautics and Space Administration's Aura satellite suggest an ~7–10% decrease in OH column abundance from solar maximum to solar minimum that is highly correlated with changes in total solar irradiance, solar Mg-II index, and Lyman- α index during SC 23. However, model simulations using a commonly accepted solar UV variability parameterization give much smaller OH variability (~3%). Although this discrepancy could result partially from the limitations in our current understanding of middle atmospheric chemistry, recently published solar spectral irradiance data from the Solar Radiation and Climate Experiment suggest a solar UV variability that is much larger than previously believed. With a solar forcing derived from the Solar Radiation and Climate Experiment data, modeled OH variability (~6–7%) agrees much better with observations. Model simulations reveal the detailed chemical mechanisms, suggesting that such OH variability and the corresponding catalytic chemistry may dominate the O₃ SC signal in the upper stratosphere. Continuing measurements through SC 24 are required to understand this OH variability and its impacts on O₃ further.

decadal variability | odd hydrogen

Quantifying effects of the solar cycle (SC) in Earth's atmosphere helps differentiate relative contributions of natural processes and anthropogenic activities to global climate change (1). From the 11-y SC maximum (max) to minimum (min), the total solar irradiance (TSI) varies only by ~0.1%. However, changes in solar UV fluxes can be much larger (2). Thus, detectable SC impacts on Earth's climate are more likely to be linked to changes in middle (stratosphere and mesosphere, tropopause to ~90 km) and upper (thermosphere and above) atmospheric composition through photochemistry in the UV region.

A number of observational and modeling studies have characterized SC modulations in mesospheric and stratospheric chemistry, especially in ozone (O₃) (3–9). Changes in UV absorption by O₃ at low latitudes over the SC can lead to changes in thermal structures in the middle atmosphere, affecting tropospheric and polar climates, and may lead to changes in global circulations (1). Accurate simulations of the O₃ response to the SC are therefore required for better understanding the sun-climate relationship (10, 11). However, the SC signal in O₃ simulated by different models shows quantitative differences, which may be due to differences in model resolutions, model parameterizations related to dynamical processes, and/or photochemistry that has not yet been critically

examined (12, 13). Diagnostic studies must involve not only O₃ but species that catalytically destroy O₃, such as odd-hydrogen (HO_x) [HO_x = H + OH (hydroxy radical) + HO₂ (hydroperoxyl)] (14–19).

OH, in particular, is a key species in HO_x reaction cycles. It is mainly produced through direct photolysis of water vapor (H₂O) at ~120 and 170–205 nm and photolysis of O₃ at ~200–330 nm, followed by reaction of O(¹D) with H₂O (20). Due to its short chemical lifetime, rapid response of OH to the SC can serve as a good indicator of solar-induced changes in atmospheric composition and chemistry. Unfortunately, very few studies have been performed on the HO_x response to the SC, and little attention has been paid to the impacts of such changes on O₃ (15). Furthermore, recent observations over the declining phase of SC 23 by the Solar Stellar Irradiance Comparison Experiment (SOLSTICE) (21) and the spectral irradiance monitor (SIM) (22) instruments aboard the Solar Radiation and Climate Experiment (SORCE) satellite suggest an unexpectedly large decrease in solar UV irradiance, which has important implications for O₃ and HO_x photochemistry (5). These observations, particularly the solar irradiance data from the SIM, disagree with previous satellite observations and model parameterizations, adding UV variability as another dimension of uncertainty for atmospheric modeling.

The objectives of the present work include the following: (i) providing observational evidence of SC-related changes in OH column abundance (X_{OH}) from 15 y of ground-based measurement, augmented by 5-y satellite OH measurements by the Microwave Limb Sounder (MLS) aboard the National Aeronautics and Space Administration's (NASA) Aura satellite; (ii) quantifying the impacts of using SORCE UV variability on X_{OH} SC variability with a 3D Whole Atmosphere Community Climate Model (WACCM) (2) and a 1D photochemical model (23); and (iii) estimating the sensitivity of stratospheric O₃ to the SC-related OH changes obtained in *ii*. Note that previous studies on the O₃ response to the SC investigate the overall O₃ variability due to chemistry, dynamics, and radiation. Our objective in *iii* is to illustrate the role of OH in the SC modulations of O₃ chemistry.

This study uses long-term OH measurements from space and the surface to investigate the OH response to the SC, providing a basis for simulating long-term variability of HO_x chemistry in the middle atmosphere.

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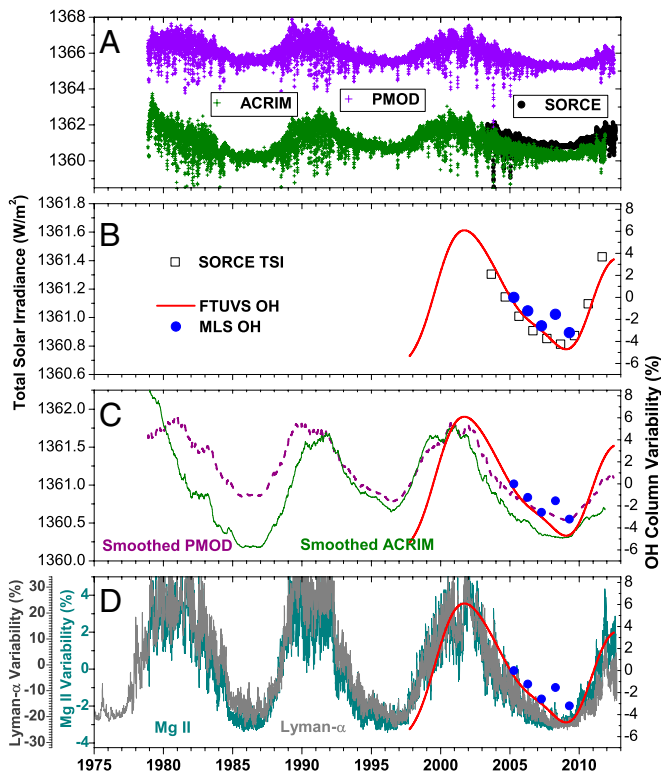


Fig. 2. OH SC variability correlates well with solar parameters. (A) Daily mean TSI from the SORCE (black), PMOD composite (purple), and ACRIM composite (green). (B) FTUVS (red) and MLS (blue) X_{OH} variability (Fig. 1) in comparison to variability in annual mean SORCE TSI (black). (C) Same as in B, but replacing SORCE TSI with smoothed ACRIM and PMOD composites. The PMOD TSI was adjusted by 4.7 W/m^2 . (D) X_{OH} variability in comparison to variabilities in Lyman- α (gray) and Mg-II (cyan) indices.

on multiple satellite measurements), which are proxies for solar UV variations. They both correlate well with the observed X_{OH} variability over SC 23 (Fig. 2D).

Model Results and Discussion

We simulated the SC modulation in X_{OH} with the WACCM, a 3D global atmospheric model extending from the surface to $\sim 140 \text{ km}$ (2). The advantage of using the WACCM is that chemistry, radiation, and dynamics are fully coupled, providing a comprehensive simulation of SC effects on X_{OH} at middle latitudes. Four

50-y-long WACCM runs with different prescriptions of solar UV variability (described below) were carried out.

Most climate models with prescribed solar forcing use a parameterized solar spectral irradiance (SSI) variability developed at the Naval Research Laboratory (NRL), which is primarily based on space-borne UV measurements during 1991–2000 (36). Fig. 3A shows the simulated annual mean X_{OH} from 1964 to 2010 using this NRL solar forcing. The TMF and MLS X_{OH} values are represented by model OH integrated from the upper mesosphere down to 2.3 km and 25 km, respectively. The average SC signal in X_{OH} is only $\sim 3\%$ from max to min, suggesting differences of a factor of ~ 3 between the model and observations (Fig. 3B). Note that another run with the standard WACCM SC setting [parameterized UV variability based on observations in previous SCs (2)] shows similar results.

Although the differences could be partially caused by limitations in our current understanding of middle atmospheric $\text{HO}_x - \text{O}_3$ chemistry, the uncertainty in solar UV variability may be another major source. Haigh et al. (5) reported SORCE (SOLSTICE and SIM) SSI variability from April 2004 through November 2007, which is significantly larger than that of the NRL SSI and can better explain the observed atmospheric O_3 changes (5, 6, 8, 9). However, given the unexpected large discrepancies, whether SORCE SSI should be used in models has been hotly debated since then. Many remain skeptical about SORCE SSI, pending additional validation and future updates on the degradation correction of SORCE instruments (37, 38), whereas others conducted modified solar physics model parameterizations that agree better with SORCE data (39) and provided solar proxy evidence suggesting that the declining phase of SC 23 might be very different from previous SCs (40) (more details are provided in *SI Text*).

Therefore, it is important to investigate the sensitivity of the atmospheric OH SC signal to the large difference between NRL and SORCE SSI data. We repeat the WACCM simulation by replacing NRL SSI with SORCE SSI as the solar forcing. To mimic a full SC, SORCE SSI data are extrapolated back to the max of SC 23 in January 2002 using the Mg-II index as a proxy (*SI Text*). The resultant SSI variability and its comparison with NRL SSI are shown in Fig. 4 (*Inset*, showing an extrapolation scaling factor). The SORCE UV variability is generally larger than that from the NRL model. The relative difference is $\sim 30\%$ with the Lyman- α index (SOLSTICE data) and much larger (a factor of 2–6) at 200–280 nm (mainly SIM data). Considering the difference between SOLSTICE and SIM SSI data at 210–240 nm, we performed two WACCM runs using combined SSI variability from the two instruments with cutoffs at 240 nm and 210 nm, respectively. Fig. 3C shows the annual mean model X_{OH}

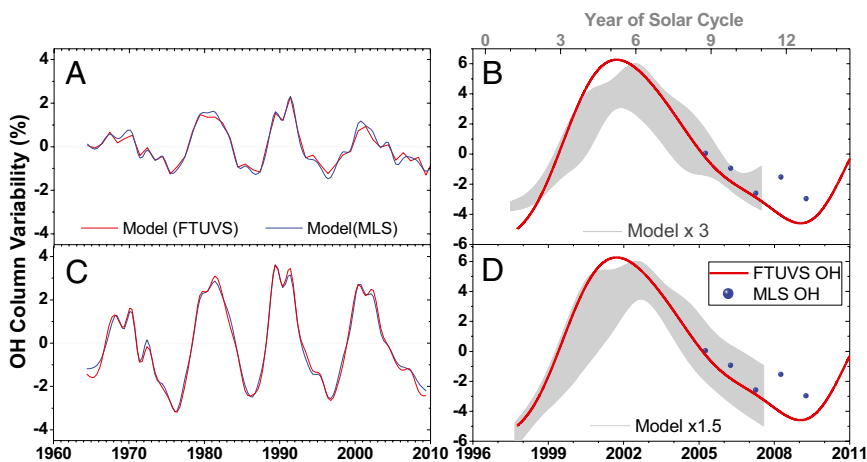


Fig. 3. Comparison of OH SC variabilities from the WACCM and observations. (A) Modeled variability of annual mean X_{OH} (using NRL SSI) integrated over the altitude ranges for FTUVS (red) and MLS (blue) X_{OH} values. (B) Model X_{OH} variability is increased by a factor of 3 (gray) to compare with observed X_{OH} SC signal (red and blue). The gray band indicates the scatter range of model X_{OH} variability over the simulated SCs. (C and D) Equivalent to A and B but for model results using SORCE SSI.

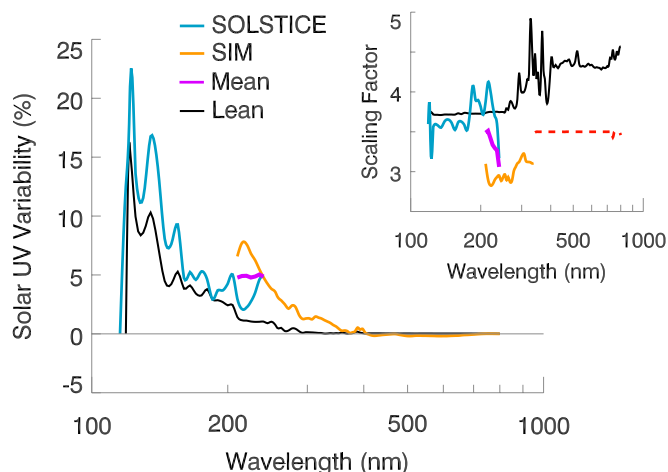


Fig. 4. Solar UV spectral variability derived from SORCE SSI. The blue and orange lines correspond to SSI data from the SOLSTICE and SIM, respectively. The purple line shows the mean of the two at 210–240 nm. The black line is the NRL SSI variation. All spectra have been convolved to the model grid. (Inset) Spectral scaling factors for extrapolating the observed SSI (April 2004–November 2007) to the solar max in January 2002. For values above 340 nm (not important for OH chemistry), an arbitrary factor of 3.5 is applied (dashed line).

using SORCE SSI variability (SOLSTICE, below 240 nm; SIM, above 240 nm). The X_{OH} SC variability is $\sim 6\%$ (twice that in Fig. 3B) and agrees much better with observations ($10 \pm 3\%$ for the TMF, 7–8% for the MLS); the difference between the WACCM and TMF results is reduced to a factor of ~ 1.5 (Fig. 3D). The other WACCM run using 210 nm as the cutoff between SOLSTICE and SIM data gives a slightly larger X_{OH} variability of $\sim 7\%$, closer to FTUVS results and agreeing well with MLS results. Additional SORCE SSI data covering the rising phase of SC 24 are needed before robust conclusions can be made.

To understand the detailed mechanism of the OH response to SC better, we use a 1D photochemical model (24, 25) to study vertical and spectral distribution of OH sensitivity to SSI changes. It has the advantages of much higher computational efficiency and flexibility than the WACCM, allowing for a wide range of sensitivity studies to elucidate the underlying mechanisms responsible for the OH response to SC. The spectral OH response, defined as the ratio of the relative change in model OH to the relative change in solar photon flux at the top of the atmosphere ($\% \Delta[OH] / \% \Delta(\text{photon flux})$), highlights the important processes for OH photochemistry (Fig. 5A) as follows:

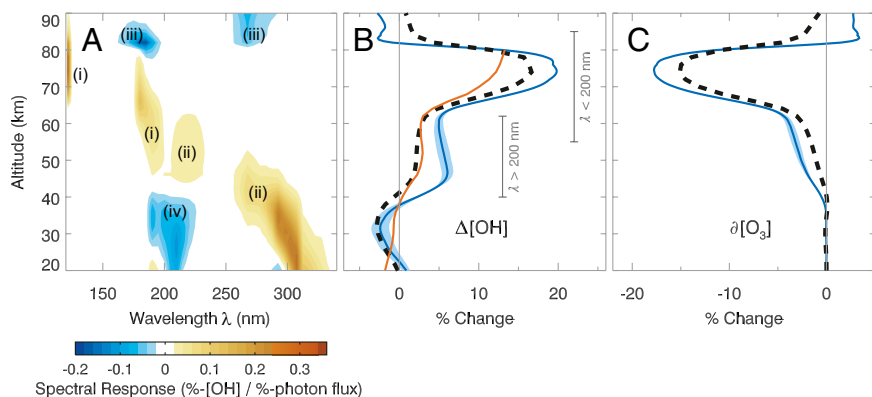


Fig. 5. Vertical profile of OH SC signal and its implications for O_3 . (A) Spectral response of OH to changes in wavelength-resolved solar irradiance (the relative change in OH divided by the relative change in the photon flux) from the 1D model. The reference UV spectrum for perturbation is constructed with SOLSTICE data below 210 nm, SIM data above 240 nm, and the mean of SOLSTICE and SIM data at 210–240 nm when they disagree (Fig. 4). (B) Vertical profiles of OH SC signal from the model run using NRL SSI (black), using SORCE SSI (blue; shade representing the upper and lower limits of results derived using SOLSTICE or SIM data at 210–240 nm), and from Canty and Minschwaner (15) (orange). (C) Corresponding O_3 variability (solely due to the changes in OH in B).

- i) OH enhancements at 65–90 km and 50–80 km occur at the wavelengths of the Lyman- α index and at 170–200 nm, where direct H_2O photolysis is the major OH source.
- ii) Positive OH responses at 210–340 nm correspond to enhanced O_3 photolysis, followed by enhanced OH production through the reaction of $O(^1D)$ (from O_3 photolysis) with H_2O .
- iii) Negative OH responses above 80 km correspond to enhanced photolysis of O_2 (160–200 nm) and O_3 (255–290 nm), which produces atomic oxygen, a sink species for OH. This effect is insignificant in X_{OH} due to the very low OH abundance at these altitudes.
- iv) Negative response at 190–220 nm below 40 km is caused by a shielding effect (17) resulting from UV attenuation by the enhanced overhead O_3 [O_3 at higher altitudes with a positive response to SC (5) absorbs more UV and diminishes the photolysis rates at lower altitudes]. It mostly cancels out effect of ii at these altitudes, leaving a small net negative response.

The vertical profile of model OH response to SC ($\Delta[OH]$) (Fig. 5B) is obtained by convolving the spectral response in Fig. 5A with SSI variability (black, using the NRL; blue, using the SORCE). Earlier modeling work by Canty and Minschwaner (15) (orange) using solar forcing similar to that of the NRL is close to our model result using NRL SSI. Such $\Delta[OH]$ is the overall OH change due to changes in photolysis and OH sources/sinks. The $\Delta[OH]$ derived using SORCE SSI is generally larger than that using NRL SSI, owing to the greater solar UV variability from the SORCE. It is up to 18% at 70–80 km, near 5% at 40–60 km, and slightly negative at 30–40 km. In particular, by using SORCE SSI, OH SC signal increases by at least a factor of 2 at 40–60 km. This region of the atmosphere covers the primary OH density peak at ~ 45 km. Thus, the corresponding differences in SC signal in OH make large contributions to the difference in total OH column SC signal. The integrated X_{OH} response derived using NRL SSI is 3.7%; when SORCE SSI is used, the X_{OH} response increases to 6.4%. These values agree with those from the WACCM.

Implications

Catalytic O_3 loss above ~ 40 km is primarily controlled by HO_x reactions (16, 18, 19). O_3 in this region of the atmosphere is expected to show early signs of O_3 layer recovery (41) and has a strong impact on global stratospheric temperatures and circulation, and thus climate (42). Our findings of the OH response to SC have important implications for O_3 changes associated with HO_x variability. Previous studies of the O_3 response to SC (5, 6, 8, 9) are for the overall O_3 change ($\Delta[O_3]$), including direct changes through photolysis, indirect changes through O_3 -destroying catalysts (e.g., HO_x), and possible indirect changes through thermal structures and circulation [note that our WACCM model $\Delta[O_3]$ is

very similar, if not identical, to $\Delta[\text{O}_3]$ from a previous study using the same model and similar SSI data from both the SORCE and NRL, in which the modeled $\Delta[\text{O}_3]$ using SORCE SSI agrees better with observations (6). It is important to quantify the impact of each individual process. Here, we discuss the component of $\Delta[\text{O}_3]$ that is solely due to $\Delta[\text{OH}]$ (denoted by $\partial[\text{O}_3]$). We made additional 1D model runs by constraining $\Delta[\text{OH}]$ to values from the runs performed above (using NRL and SORCE SSI data) and fixing UV flux (no other components of $\Delta[\text{O}_3]$). All species other than OH are allowed to vary until reaching steady state. The resultant O_3 change represents $\partial[\text{O}_3]$ (Fig. 5C). Above 60 km, $\partial[\text{O}_3] \approx -\Delta[\text{OH}]$ (15). The peak $\partial[\text{O}_3]$ at 75 km is -15% and -18% for the runs using $\Delta[\text{OH}]$ from NRL and SORCE SSI data, respectively. Below 40 km, $\partial[\text{O}_3]$ is negligibly small. At 40–60 km, using $\Delta[\text{OH}]$ from SORCE SSI instead of from NRL SSI leads to nearly doubled $\partial[\text{O}_3]$. Merkel et al. (6) showed that the WACCM modeled $\Delta[\text{O}_3]$ at 40–60 km increases from 0.5% to 1% when NRL SSI is replaced by SORCE SSI. Similar results are also obtained using other models (5, 8). These changes in $\Delta[\text{O}_3]$ at 40–60 km are close to that in $\partial[\text{O}_3]$ alone, suggesting that OH SC variability may be the dominant factor underlying the O_3 response to SC in the upper stratosphere. Although more quantitative diagnostic studies will help confirm this, it is likely that OH and its SC variability play a critical role in the decadal variation in upper stratospheric O_3 , which has to be accurately described before quantitative conclusions on O_3 layer recovery can be made.

Concluding Remarks

Both 1D and WACCM models using NRL SSI produce an X_{OH} response to SC that is much smaller than the observed X_{OH} response at the TMF. Assuming that our current understanding of the $\text{HO}_x - \text{O}_3$ photochemistry system is complete, which may or may not be true, using SORCE SSI gives results much closer to observations. Thus, the uncertainty in SSI variability may be a primary limitation for accurate modeling of OH variability and the corresponding catalytic O_3 change. Although the NRL model could have underestimated the solar forcing in SC 23, several other factors involving the trends in OH sources/sinks could have contributed to the larger observed OH variability.

One candidate is the trend in atmospheric H_2O (43). Satellite and ground-based measurements revealed a decreasing trend of a few percentage points per year in H_2O at 16–26 km during 2000–2005 (43, 44). Remsburg (45) reported an increasing trend in mesospheric H_2O of $\sim 1\%$ per year at 60–80 km. We approximated the H_2O trend at 26–60 km by linear interpolation and simulated the impact of these trends on OH using the 1D model (SI Text). The resulting change in X_{OH} is only -0.2% per year. In addition, after 2005, the H_2O trend switches from negative to positive (44), which does not contribute to the observed X_{OH} decrease during 2005–2009.

Similarly, a non-SC O_3 trend may also contribute to the observed X_{OH} change. A recent study using ground-based LIDAR (light detection and ranging) measurement over the TMF showed a $\sim 2\%$ per decade O_3 trend at 35–45 km since 1997 (46). Trends at other altitudes are not available. Our 1D model sensitivity study suggests that a forced 1% per decade O_3 variability at all altitudes would lead to only a $\sim 0.04\%$ per decade change in X_{OH} . Thus, the potential impact from the long-term non-SC O_3 trend is negligible. Observational evidence suggests that the O_3 SC variability is unlikely to exceed 10% (peak to valley) at all altitudes. Thus, the impact of decadal O_3 variability (SC and non-SC trends) has a minimal impact on OH column variability (within $\sim 0.4\%$ per decade), whereas the OH SC change has a dominant impact on O_3 (see discussions on $\partial[\text{O}_3]$). This clearly indicates the great effectiveness of HO_x catalytic chemistry in controlling upper stratospheric O_3 loss.

Models using SORCE SSI variability produce an X_{OH} response (6–7%) that agrees much better with observed X_{OH} ($\sim 10\%$ from FTUVS, $\sim 7\%$ from MLS). The remaining difference is within the

uncertainty range of TMF X_{OH} , and it could also originate from the aforementioned small impacts of H_2O and O_3 trends. In addition, the extrapolated SORCE SSI variability in this study covers 2002 (max of SC 23) through 2007. The SSI in 2007 is reasonably close but might be slightly larger than the real SC min (2008–2009). This could also lead to a small underestimation in modeled OH SC signal. Updated SORCE SSI data in the future could help to confirm this.

Although models using SORCE SSI over SC 23 agree better with observations than models using NRL SSI, it is too early to conclude that climate models should switch from NRL SSI to SORCE SSI. Questions remain as to why SSI measurements during previous SCs did not show such large variability, whether SORCE SSI variability is applicable to other SCs, whether the difference is at least partially due to possible shortcomings in the NRL model and/or degradation in the SORCE instruments, and whether our current understanding of middle atmospheric $\text{HO}_x - \text{O}_3$ chemistry is complete.

In any case, continuous long-term observations of solar SSI, OH, O_3 , and other related chemical species through SC 24 are crucial for further investigations to solve the above puzzles. Although MLS OH observations were temporarily suspended at the end of 2009 to extend the instrument's lifetime, month-long measurements in each summer over the next few years are planned to cover the peak of SC 24. These extended MLS OH data will be available after careful degradation corrections and validation. This unique dataset, in combination with the continuous ground-based FTUVS measurements, will provide valuable information about the global and vertical distribution of the SC signal in OH. The latter, with an accurately measured SSI variability, can rigorously test the photochemical mechanisms in current models.

Methods

FTUVS OH Data. The ground-based FTUVS at the TMF measures X_{OH} under clear to lightly cloudy conditions. The major systematic error is the uncertainty in the OH line center absorption cross-section (within 10%). The precision uncertainty of the daily max OH is estimated to be 3–5%. The complete diurnal measurement data have been archived at the Aura Validation Data Center (AVDC) of the Goddard Space Flight Center (<http://avdc.gsfc.nasa.gov/>). Any interested users may request an account through the Web site to download the data. The interpolated daily max OH data (after gap filling) used for FFT analysis in this study are provided in Dataset S1. More details about data interpolation and trend analysis are also provided in SI Text.

MLS OH Data. MLS OH data used in this study are from v3.3 retrieval software. We use data at 21.5–0.0032 hPa to calculate the OH column. The systematic uncertainty is within 8% over this pressure range (30). The zonal mean around the TMF (29.5° N, 39.5° N) is used. A similar analysis using data from a $10^\circ \times 25^\circ$ grid box at the TMF was also performed. The results are similar to those presented here.

SORCE Solar Spectral Data. The SOLSTICE measurement (22) has a spectral resolution of 0.1 nm. The SIM measurement (23) has varying spectral resolution (~ 1 nm in the UV setting). The SOLSTICE SSI data used in our models are from v10 retrieval software. A newer v11 version was released during the review process of this paper. A 1D model sensitivity study between v10 and v11 shows no significant impact on OH results. The ongoing degradation correction studies on SIM data are not expected to affect the SSI variability between 2004 and 2007. Details on the data quality and the derivation of the SSI variability for model simulations are included in SI Text.

WACCM Model. The WACCM uses the Model for Ozone and Related Chemical Tracers version 3 (MOZART3) as the chemical mechanism (2). Chemical species are all allowed to vary during model runs. For each UV setting, the model is run from 1960 to 2010. The first 4 y are ignored to allow model spin-up. We use the monthly mean output to derive the OH SC signal. We also generated daily max outputs during the solar max year and solar min year to compare with results using the monthly mean. The difference was found to be very small.

1D Model. The 1D model is a California Institute of Technology/JPL photochemical model that includes over 100 chemical species, over 460 reactions, vertical transport (eddy, molecular, and thermal diffusion), and coupled radiative transfer (23). The chemical kinetics have been updated to JPL06-2 (47). A more recent update of JPL10-6 (48) does not introduce significant differences on reactions related to HO_x chemistry. Sixty-five layers are used to cover from the ground to 130 km. OH fluxes at the surface and the top of the atmosphere are fixed as zero. During model runs, chemical species are not constrained unless otherwise stated. The temperature profile is fixed. The model has been applied to study the diurnal cycle of OH (49). Typical model profiles of OH, O₃, and related species are shown in *SI Text*.

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