Seasonal and solar cycle variability of OH in the middle atmosphere

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[1] The photochemistry of the hydroxyl radical (OH) in the middle atmosphere involves the action of solar ultraviolet radiation in many respects. The production of stratospheric OH is initiated through the photodissociation of ozone, and in the mesosphere, OH is produced directly from the photolysis of water vapor. We present an analysis of measurements of the vertical column abundance of OH from Fritz Peak Observatory, Colorado, for seasonal and solar cycle variability. The OH column data span over two 11year solar cycles and include a wide range of diurnal and seasonal conditions. Hydroxyl abundances show distinct annual and semiannual cycles, with amplitudes of 4.4% and 2.5%, respectively. About half of the seasonal variation in OH can be explained by the annual cycle of ultraviolet intensity, and by annual and semiannual cycles in ozone and water vapor in the middle atmosphere. On longer time scales, a positive correlation with the NOAA MgII solar index is observed. The amplitude of 11-year solar cycle variations in OH is $4.2 \pm 2.4\%$, which is consistent with photochemical model calculations that consider changes in ozone and water vapor photodissociation rates. Changes in the vertical distribution of ozone over the solar cycle are found to have a smaller effect on the OH column. INDEX TERMS: 0340 Atmospheric Composition and Structure: Middle atmospherecomposition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 1650 Global Change: Solar variability; KEYWORDS: Hydroxyl, stratosphere, atmospheric chemistry

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1. Introduction

[2] Hydroxyl (OH) plays an important role in the photochemistry of the middle atmosphere through its ability to regulate ozone (O_3) , and through reactions between stable and active forms of other ozone-destroying compounds. Current understanding of the chemistry of OH and the odd-hydrogen family of radicals ($HO_x = H + OH + HO_2$) appears incomplete, as there are clear discrepancies between satellite, balloon, and ground based measurements and models [e.g., Summers and Conway, 2000; Canty et al., 2000]. Model calculations predict that maximum OH concentrations are in the range of 2 to 3×10^7 cm⁻³ between 40 to 50 km, and that the amount of OH at all altitudes is a function of the intensity of solar ultraviolet radiation. A primary cause for this radiative dependence arises from the production of OH from the reaction of water (H2O) with metastable atomic oxygen $(O(^{1}D))$

$$H_2O + O(^1D) \rightarrow 2OH.$$
(1)

Although this reaction rate constant is not a function of temperature and is independent of altitude and time, the abundance of $O(^{1}D)$ is controlled through its production via

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the photolysis of ozone, (mainly in the O_3 Hartley and Huggins bands between 200 and 330 nm)

$$O_3 + h\nu \rightarrow O_2 + O(^1D). \tag{2}$$

[3] An additional mechanism for hydroxyl production occurs in the mesosphere through the photodissociation of water vapor (in the Schumann–Runge band region at 175–205 nm, and Lyman α near 121 nm)

$$H_2O + h\nu \rightarrow OH + H.$$
(3)

Throughout much of the middle atmosphere, the destruction of OH occurs primarily through the HO_x recombination reaction

$$OH + HO_2 \rightarrow H_2O + O_2. \tag{4}$$

[4] Odd-hydrogen is in photochemical steady state throughout much of the stratosphere and mesosphere [*Allen et al.*, 1984] such that

$$k_1[H_2O][O(^1D)] + J_{H2O}[H_2O] = k_4[OH][HO_2]$$
(5)

where k_1 and k_4 are the rate constants for reactions (1) and (4), respectively, and J_{H2O} is the photolysis frequency for

H₂O (reaction (3)). The ratio [HO₂]/[OH] is determined largely by HO_x partitioning reactions and is very nearly constant above 40 km [*Brasseur and Solomon*, 1986], thus we substitute [HO₂] = Const × [OH] into equation (5) to obtain a simple proportionality expression for [OH]

$$[OH] \propto \sqrt{k_1 [H_2 O] [O(^1 D)] + J_{H2O} [H_2 O]}. \eqno(6)$$

It should be clear that the square root dependence arises from the destruction of OH through reaction (4), leading to a quadratic loss term in the steady state continuity equation for HO_{x} .

[5] A further relation exists between $O(^{1}D)$ and ozone,

$$\left[O(^{1}D)\right] \propto J_{O3}[O_{3}] \tag{7}$$

where J_{O3} is the photolysis frequency for O_3 (reaction (2)). Both J_{O3} and J_{H2O} are functions of the local actinic flux, and can be expected to vary according to variations in solar intensity and slant path absorption by the atmospheric overburden.

[6] Relative changes in OH in the upper stratosphere can be approximated by taking the logarithmic derivative of relations (6) and (7), neglecting reaction (3)

$$\frac{d[OH]}{[OH]} \propto \frac{1}{2} \left(\frac{d[H_2O]}{[H_2O]} + \frac{dJ_{O3}}{J_{O3}} + \frac{d[O_3]}{[O_3]} \right)$$
(8)

In a similar manner, changes in mesospheric OH can be approximated by neglecting reaction (2) in relation (6)

$$\frac{\mathrm{d[OH]}}{\mathrm{[OH]}} \propto \frac{1}{2} \left(\frac{\mathrm{d[H_2O]}}{\mathrm{[H_2O]}} + \frac{\mathrm{dJ_{H2O}}}{\mathrm{J_{H2O}}} \right)$$
(9)

[7] With these relationships in mind, we expect that the amplitude of variations in OH should be half as large as changes in O_3 , H_2O , and solar intensity. In general, the latter is spectrally dependent as are the magnitudes of relevant J-values; nevertheless, this simple framework provides a foundation for interpreting the OH response at selected altitudes to ultraviolet variations within certain wavelength regions.

2. OH Measurements and Seasonal Behavior

[8] The database of atmospheric hydroxyl from Fritz Peak Observatory (40°N, 105°W), Colorado, extends back to 1977 and is one of the most extensive records of a trace species affecting O₃ [*Burnett and Minschwaner*, 1998]. These are high resolution, differential absorption measurements obtained using a system of four Fabry–Perot interferometers and double-grating monochromator. The complete spectrophotometer system precisely quantifies OH absorption of solar ultraviolet in a single rovibronic transition at 308.1 nm [*Burnett and Burnett*, 1983].

[9] Hydroxyl column measurements from 1977 to 2000 are presented in Figure 1 as a function of solar zenith angle. Each point represents an integration of four to six spectral scans obtained over a time scale of about 20 minutes. The data show a large diurnal variation with peak values occurring at small solar zenith angles (SZA), decreasing to



Figure 1. Hydroxyl vertical column abundances from Fritz Peak Observatory, 1977–2000, consisting of 19,322 measurements (dots). A polynomial fit to the mean diurnal variation is derived from these data and used to normalize the OH measurements (dashed curve).

smaller OH abundances at larger SZA. This behavior with respect to SZA is expected based on slant path absorption by ozone and oxygen, which modulates the actinic flux and consequently the photodissociation rates for ozone and water vapor. The diurnal variation of the OH column, however, is larger than predicted by photochemical models [*Canty et al.*, 2000]. Maximum discrepancies occur at the smallest SZA ($\sim 20^{\circ}$) where the model column OH is 25% smaller than observed.

[10] The focus of the present study is on seasonal and long term OH variations about the mean. These are most apparent by normalizing with respect to relatively larger changes observed over a diurnal time scale. Normalized OH abundances are calculated by dividing all measurements by appropriate mean values at each SZA [*Burnett et al.*, 1988]. The mean SZA dependence of OH column abundances, indicated in Figure 1, is obtained from a fourth-order polynomial fit to the measurements. Henceforth, we will refer exclusively to the normalized OH abundance.

[11] Monthly mean values of column OH indicate a clear seasonal pattern shown in Figure 2. Note these are means taken over all solar zenith angles and years for a given month. The seasonal OH variation is well represented by a harmonic function with annual and semiannual cycles [Burnett et al., 1989], also indicated in Figure 2. The annual component peaks in February with an amplitude of 4.4%, while the semiannual cycle peaks in December and June with an amplitude of 2.5%. It should be recognized that, due to seasonal changes in solar declination, summer data contain the full diurnal range of solar zenith angles shown in Figure 1, while winter data are restricted to angles greater than 63°. We tested our results for sampling biases by computing means for $63-70^{\circ}$ SZA, and for morning and afternoon separately, and found little difference in monthly means.

[12] Part of the seasonal OH variation can be related to annual and semiannual variations in ozone and water vapor, and to the annual variation in solar intensity due to the eccentricity of the Earth's orbit. As an example of these



Figure 2. Monthly mean OH measurements from 1977–2000 (crosses with dotted curve). Error bars indicate standard deviation of the mean. A two-component harmonic function (solid curve) is fit to the annual and semiannual OH variations.

effects, Figure 3 shows seasonal variations in O_3 and H_2O at 2 mb, near the maximum in OH concentration predicted by our model (see below). Also indicated in Figure 3 are changes in the exoatmospheric solar flux arising from the Earth's orbital eccentricity. The solar intensity variation is about $\pm 3\%$, with maximum in January. These variations are independent of wavelength and may impact all photolytic rate constants, including J_{O3} and J_{H2O} discussed above.

[13] The ozone seasonal variation shown in Figure 3 is derived from observations by the Solar Backscatter Ultraviolet (SBUV) instrument on board the NIMBUS 7 satellite [*McPeters et al.*, 1984]. We computed monthly means within a 20° latitude by 20° longitude region centered on Fritz Peak Observatory, using data between November 1978 and June 1990. Annual and semiannual changes in ozone were derived from a Fourier analysis of SBUV measurements at pressure levels between 30 and 0.5 mb. The phases and amplitudes of these components are functions of altitude and will have varying impacts on the total OH column. For the present analysis, the effect appears to be dominated by the strong annual cycle indicated in Figure 3, with maximum in December and amplitude of about 14%.

[14] A similar analysis was used to quantify 12- and 6month variations in water vapor using zonally averaged observations from the Halogen Occultation Experiment (HALOE) and Microwave Limb Sounder (MLS) on board the Upper Atmosphere Research Satellite [e.g., *Randel et al.*, 1998]. The water vapor data cover the time period 1991–1997, and show higher interannual variability and generally smaller seasonal amplitudes than for ozone. At 2.2 mb, the H₂O seasonal variation is dominated by a semiannual cycle with maxima in January and June. The amplitude is about 2%. Analysis of HALOE ozone observations over the 1991–1997 period indicate seasonal variations consistent with the SBUV results shown in Figure 3.

[15] A one-dimensional photochemical model was used to calculate the effects of variations in solar irradiance, ozone, and water vapor on OH. The model is adapted from the ROSE 3-D middle atmospheric model [*Rose and Bras*-



Figure 3. Annual percent variation in irradiance due to the eccentricity of the Earth's orbit (dotted curve). Also shown are normalized seasonal H_2O (dashed curve) and O_3 (dash-dotted curve) at 2.2 mb and 2 mb respectively. Normalized monthly mean OH (solid curve) is shown for comparison.

seur, 1989], and the baseline case is constrained by mean profiles of water vapor, ozone, and methane from HALOE observations [*Russell et al.*, 1993] at 40°N latitude. This allows the base model to accurately represent observations of the main species that affect OH [*Canty et al.*, 2000]. Water vapor and ozone concentrations between 30 and 0.5 mb were further modified using annual and semiannual Fourier components, as discussed above, to represent seasonal changes in these species. All photolytic rates were modulated according to the seasonal changes in exoatmospheric irradiance shown in Figure 3, and included effects of changing atmospheric absorption by the ozone overburden.

[16] As seen in Figure 4, these changes can partially explain the observed seasonal changes in OH. The model



Figure 4. Modeled seasonal variation in OH (dotted curve) obtained by considering changes in irradiance, H_2O , and O_3 , along with observed variation in monthly mean OH (solid curve). Model results are for a constant SZA of 60° .



Figure 5. Monthly means of the NOAA MgII index (solid curve) and normalized monthly mean OH (dotted curve). Error bar indicates the average magnitude of standard deviation in the monthly OH data.

seasonal behavior is dominated by annual cycles in solar irradiance and ozone, and accounts for about 50% of the observed OH seasonality. Causes for the remaining 50% hydroxyl variation not captured by the model have not been identified. A small effect in modeled OH due to changes in water is seen in July, but it is not significant enough to reproduce the secondary maximum in the hydroxyl column measurements.

3. Solar Cycle OH Variations

[17] To further investigate longer term changes in hydroxyl, we normalize by the seasonal mean cycles discussed above to produce monthly mean, deseasonalized OH abundances. Resulting data from 1977 to 2000 are displayed in Figure 5. Also shown are monthly means of the NOAA MgII index from 1978 to 2000, normalized by the average value over the entire data series. This index is a compilation of spacecraft measurements of the chromospheric MgII absorption line core-to-wing ratio at 280 nm [*Viereck and Puga*, 1999], which began with Nimbus 7 SBUV in late 1978 and continue to the present with SBUV2 supplemented by results of the SUSIM, SOLSTICE and GOME experiments. The MgII index has been shown to be a good proxy for solar ultraviolet irradiance changes over the eleven-year solar oscillation [*Deland and Cebula*, 1998].

[18] The OH and MgII time series in Figure 5 both contain solar cycle variations. Harmonic fits to the elevenyear cycle show amplitudes of $4.2 \pm 2.4\%$ and $3.2 \pm 0.4\%$ for OH and MgII index, respectively. The variations are most closely matched over solar cycle 22, from 1985 to 1996. The correlation coefficient (covariance divided by the standard deviations of both data sets) is 0.50 over this time period, indicating that half of the observed variance in OH may be related to solar cycle effects.

[19] Model calculations show that the observed variations in OH are consistent with solar cycle changes in ultraviolet intensity. As discussed previously, we expect relative changes in OH concentrations to be half as large as changes in photodissociation rates for ozone and water vapor. The linkage to variations in MgII index involves scale factors that relate changes in monochromatic irradiances to changes in the MgII index. These scale factors range from about nine at Lyman α , to nearly one over the O₃ Hartley band [*Chandra et al.*, 1995]. We applied these factors to modify the exoatmospheric solar spectrum used for our photochemical model calculations, producing subsequent variations in spectral actinic fluxes and photolysis rates.

[20] Calculated changes in OH between solar maximum and solar minimum are shown in Figure 6 for a representative solar zenith angle of 25°. In fact, the model OH changes from solar maximum to minimum were nearly independent of solar zenith angle. The largest fractional difference is seen in the mesosphere as a result of changes in the photodissociation rate for water vapor. At 70 km, about two-thirds of water photolysis occurs in the Lyman α region near 121 nm, and one-third is due to photodissociation in the Schumann-Runge region between 180 and 200 nm. MgII scale factors [Chandra et al., 1995] give rise to solar flux variations of about $\pm 30\%$ and $\pm 5\%$ for Lyman α and Schumann-Runge spectral regions, respectively, producing a net effect on water photolysis of about $\pm 22\%$ near 70 km. Consistent with equation (9), the amplitude of OH variation at this altitude is half as great, from 10 to 12%.

[21] Below about 50 km, ozone photodissociation is the governing mechanism for OH production. In the ozone Hartley spectral region, MgII scale factors imply a solar cycle amplitude of about $\pm 2\%$, which leads to an expected OH variation, based on equation (8), of $\pm 1\%$ from 20 to 50 km. Results shown in Figure 6 are consistent with this view.

[22] The modeled change in total column OH is $\pm 3.3\%$, which is somewhat smaller than the observed solar cycle amplitude but within the uncertainty limits. It should also be recognized that possible variations in other species may contribute to the observed OH changes. Measurements of ozone from the SBUV instrument show ozone variations in phase with solar activity, with amplitudes between 2 and 5%



Figure 6. Modeled amplitude of OH variations from solar maximum to solar minimum, considering changes in the ultraviolet irradiance alone (dotted curve) and in combination with solar cycle changes in ozone (solid curve). The change in total column OH for the latter case is 3.5%.



Figure 7. Monthly mean normalized OH data (dotted curve), along with a combined MgII-MEI data set (solid curve) which represents the combined effects of solar cycle variability and El Niño.

depending on altitude [Hood, 1997]. Figure 6 shows the impact on modeled OH that results from including solarcycle changes in ozone along with the above changes in photodissociation rates. Between 40 and 60 km, the OH solar-cycle amplitude increases by an additional 1.5%. This is about half of the ozone amplitude and consistent with equation (8). At lower altitudes, changes in ozone cause a reduction in the OH solar amplitude below 40 km, which is related to a shift in HO_x partitioning (toward HO₂ due to the reaction $OH + O_3 \rightarrow HO_2 + O_2$), and to a shielding effect from changes in the ozone overburden in the upper stratosphere and mesosphere. The net effect on the total OH column, therefore, is small compared to changes in photodissociation rates. The modeled solar-cycle amplitude in the total OH column increases to 3.5% when changes in ozone and photodissociation are considered together.

4. Discussion

[23] The correspondence between observations and model results for seasonal and solar cycle variability confirms the important role thought to be played by ultraviolet radiation, O_3 , and H_2O in regulating the abundance of OH. It is interesting to note that the semiannual variation in H_2O between about 5 and 1 mb is very similar to the OH column behavior (compare Figure 2). However, the amplitude of H₂O changes are too small to produce a significant effect in the model. This close correlation in seasonal behavior between H₂O and column OH suggests that hydroxyl concentrations may be more sensitive to water vapor abundances at these altitudes (35-50 km) than predicted by the square-root proportionality of relation 6. This finding may also be related to the model OH deficit observed in comparison to OH measurements between 40 and 50 km by the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) [Summer and Conway, 2000], although it should be noted that the August 1997 MAHRSI mission occurred near a time of OH column minimum in seasonal as well as solar cycle variations.

[24] The solar cycle behavior in modeled hydroxyl is in better agreement with observations. The model OH solar cycle amplitude (3.5%) is within the range of observed amplitudes (1.8% to 6.6%) and the calculations indicate a more dominant impact due to changes in solar ultraviolet irradiance in comparison to changes in O₃. Unfortunately, there are no long-term measurements of middle atmospheric H₂O in sufficient quantity and quality to extract solar cycle effects. Our results suggest that H₂O solar cycle variations are not needed to explain the OH column data, and that the amplitude of any solar cycle changes in water vapor are likely to be small in the middle atmosphere ($\leq 6\%$). Interestingly, the model predicts that solar-cycle variations in ozone lead to a negative OH amplitude of up to 2% in the lowermost stratosphere (Figure 6), i.e., maximum OH concentrations during periods of minimum solar activity. The impact of this reversal on the model OH column, however, is not significant as the model predicts a small contribution from the lower stratosphere (<10%) to the total column of OH.

[25] The Fritz Peak OH column data also indicate interannual changes that are not related to source gas variations in any obvious way. During a relatively stable period of OH abundances between 1980 and 1996, interannual changes accounted for about 25% of the variance (the other 75% resulted from seasonal and solar cycle effects discussed above). We examined deseasonalized O_3 means from SBUV for comparison with interannual OH column variations and found no statistically significant covariances, regardless of altitude. The lack of long-term, sufficiently accurate H₂O measurements above 30 km impedes a further analysis of interannual OH variations.

[26] Three prominent features in the OH time series, involving smaller abundances by 20-30% compared with the long-term mean, occurred during 1977-1978, 1983, and in 1997 [Burnett and Minschwaner, 1998]. Interestingly, two of these features coincide with strong El Niño events. A sense of the correlation between OH column means and a combined, MgII-ENSO index is given in Figure 7. For this comparison, we use the Multivariate El Niño Southern Oscillation (ENSO) Index (MEI) [Wolter and Timlin, 1993] which measures changes in ENSO based on observations of sea-level pressure, zonal and meridional components of surface wind, sea and air surface temperatures, and total sky cloud fraction. As displayed in Figure 7, increases in the MEI in 1983 and 1997 coincide with large observed decreases in OH. For the part of solar cycle 23 covered here (May 1996 to November 2001), the OH and MEI time series are anticorrelated with a correlation coefficient of -0.59.

[27] A combined MgII-MEI index, defined as MgII(1– $0.06 \times$ MEI), shows surprising similarities with the hydroxyl data, yet it is unclear how El Niño could cause nearly concurrent changes in column OH. One might expect a time lag between changes in the MEI and changes in the composition and photochemistry of the middle atmosphere. On the other hand, it has been established that El Niño exerts an influence on tropospheric ozone and water vapor [*Chandra et al.*, 1998] as well as the physics and chemistry of the tropical tropopause region [*Gettleman et al.*, 2001]. If tropospheric OH is affected by El Niño and this signal is being transferred to the midlatitude OH column data, then the changes would need to be quite large and the contribu-

tion of tropospheric OH to the total column must be much larger than predicted in the model.

5. Conclusion

[28] The twenty-four year record of OH column abundances presented here contains seasonal and solar cycle variations that are related to variations in ultraviolet intensity and the distributions of longer lived source gases in the stratosphere and mesosphere. About half of the OH seasonal behavior can be explained by combined effects of the annual cycle in solar irradiance intensity, along with seasonal cycles of O₃ and H₂O. Observed seasonal amplitudes are larger than can be simulated using a photochemical model, and the phase is offset by 1-2months. A seasonal pattern observed in H₂O near 2 mb bears a striking resemblance to the OH column seasonal behavior, although the sensitivity of model hydroxyl to changes in water vapor is not sufficiently large to reproduce the strong semiannual component in the OH column observations.

[29] There is a strong positive correlation between OH and the MgII index, particularly during solar cycle 22. The amplitude of OH solar-cycle variations is $4.2 \pm 2.4\%$. Photochemical calculations that incorporate changes in ultraviolet irradiance and ozone in the stratosphere and lower mesosphere predict a solar cycle variation of 3.5%in column OH, which is in good agreement with the measurements. The largest fractional changes in modeled OH (>10%) are found to occur in the upper mesosphere as a result of solar cycle variations in Lyman α and Schumann– Runge photodissociation of water vapor. An apparent anticorrelation may exist between column OH and ENSO during periods of large OH excursions from the mean; however a mechanism that might link the two data sets has not yet been identified.

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