

Production of odd hydrogen in the mesosphere during the January 2005 solar proton event

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[1] Using measurements from the MLS/Aura and GOMOS/Envisat instruments together with a 1-D ion and neutral chemistry model we study the changes in odd hydrogen and ozone in the mesosphere during the January 2005 solar proton event. The unique observational data allow us for the first time to directly test the HO_x production theory which involves complex ion chemistry. MLS measurements from the northern polar region show increases of OH concentrations by over 100% around the stratopause, and by up to one order of magnitude in the middle mesosphere after the onset of the SPE. GOMOS measurements indicate decreases in O₃ concentration throughout the lower and middle mesosphere, by up to 90%. The model predictions are in reasonable agreement with the observations. We point out that models using the so-called P_{HO_x}/Q parameterization to include the effects of ion chemistry could underestimate the HO_x production and the resulting ozone depletion. **Citation:** Verronen, P. T., A. Seppälä, E. Kyrölä, J. Tamminen, H. M. Pickett, and E. Turunen (2006), Production of odd hydrogen in the mesosphere during the January 2005 solar proton event, *Geophys. Res. Lett.*, 33, L24811, doi:10.1029/2006GL028115.

1. Introduction

[2] Among the most striking phenomena affecting ozone in the middle atmosphere are solar proton events (SPE). During SPEs, precipitation of energetic protons into the polar atmosphere results in production of odd hydrogen (HO_x) and odd nitrogen (NO_x) species [Porter *et al.*, 1976; Heaps, 1978; Solomon *et al.*, 1981; Rusch *et al.*, 1981]. Enhancements of HO_x and NO_x concentrations lead to depletion of ozone in the mesosphere and upper stratosphere, respectively, through the well-known catalytic reaction cycles [e.g., Brasseur and Solomon, 2005, pp. 401–416].

[3] Although the effects of SPEs on atmospheric minor constituents have been studied for over forty years (see Verronen [2006], for a recent review), there has been a lack of HO_x observations. Thus, the theory of HO_x production due to SPEs, involving quite complex hydrate ion chemistry, has so far not been validated by measurements of odd hydrogen. However, the good agreement in ozone losses between observations and models including SPE-related

HO_x production has been an indirect indicator for the “HO_x hypothesis” in the past [e.g., Jackman *et al.*, 2001].

[4] HO_x production due to SPE forcing involves two special features of the ionospheric D region: water cluster ions and negative ions. The chemical reactions of these species have to be combined for a full description of the process. The production is dependent not only on the ionization rate but also on the changes in minor neutral constituents caused by the proton forcing [Solomon *et al.*, 1981]. Ionization results in a set of initial ions, including O₂⁺, leading to formation of its hydrate O₂⁺(H₂O) via O₄⁺. There are then a number of reaction pathways, with increasing degree of hydration and eventual recombination with an electron, as a result of which one water molecule can be converted into two odd hydrogen species, OH and H. These pathways are effective only at altitudes below 80 km where water cluster ions can be formed. They can be interrupted by recombination of the intermediate ions, so that the production of odd hydrogen varies with altitude. Also, at the lower altitudes where negative ions are more abundant than free electrons, the positive ions favor negative ions in recombination, resulting in production of HNO₃. Although a main part of the produced HNO₃ is photodissociated to produce OH, thus adding to odd hydrogen production, this pathway is not operative during nighttime and at daytime there is a delay in the odd hydrogen production due to photolysis lifetime of HNO₃ being of the order of hours. Similar pathways starting from the NO⁺ ion exist. However, these are considered to be of lesser importance because the primary ion produced by particle precipitation is O₂⁺.

[5] In this paper, we use observations from the MLS/Aura and GOMOS/Envisat instruments to study the production of HO_x due to the January 2005 SPE and the subsequent effects on ozone. These unique observational data are compared to the results of a 1-D model covering an extensive set of ion chemical reactions, including those leading to HO_x production during SPEs. We will show that there is a good agreement between the observations and the model results in the mesosphere, providing first direct confirmation of the theories of HO_x production by ion chemistry. We will demonstrate how the P_{HO_x}/Q parameter, which gives the number of odd hydrogen species produced per each SPE-created ion pair, can lead to an underestimation of HO_x production and ozone depletion during sunrise/sunset hours in the mesosphere.

2. Modeling

[6] The Sodankylä Ion and Neutral Chemistry model, also known as SIC, was originally a pure ion chemistry

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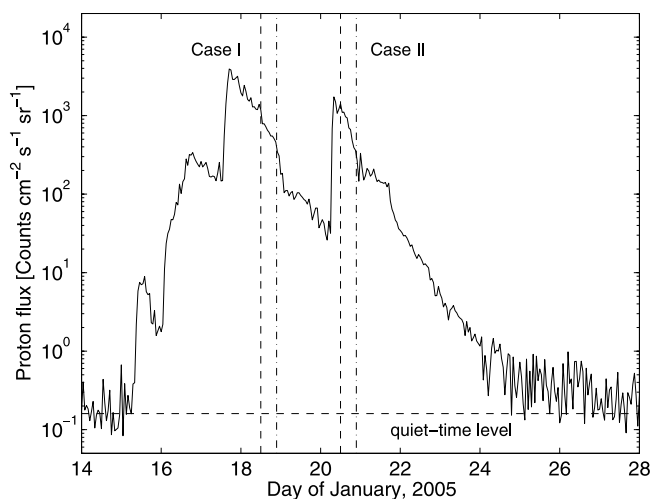


Figure 1. GOES-11 proton flux measurements in January 2005. Channel for energies larger than 10 MeV. Horizontal dashed line marks the quiet-time flux level. The vertical dash and dash-dot lines mark the times of OH and ozone comparisons, respectively.

model developed for studies of the D-region ionosphere [Turunen *et al.*, 1996]. The current 1-D version, however, includes also neutral chemistry of HO_x , NO_x , and O_x species making it a suitable tool for studies of ionosphere-atmosphere interaction in the mesosphere and upper stratosphere. A more detailed description of the model is given by Verronen *et al.* [2005] and Verronen [2006, chap. 4].

[7] Taking solar flux and background neutral atmosphere from the SOLAR2000 and MSISE-90 models, respectively, the SIC model was initialized for January conditions at 70°N , 0°E . The model was then run from Jan 15, 0000 UT until Jan 22, 2400 UT twice: first including solar radiation and galactic cosmic rays as ionization sources, and the second time including also ionization due to proton precipitation. From here on we identify these two as CTR and SPE runs, respectively. For the calculation of the ionization rates due to solar protons, we used the proton flux data from the GOES-11 satellite's particle detectors. The calculation method is described in detail by Verronen *et al.* [2005].

[8] For this study we used H_2O measurements from MLS as input to the model. Selecting observations made on Jan 15 at latitudes between 65°N and 75°N , an average profile was created and then used in all modeling, including the initialization. We will discuss the effects of H_2O background selection to the model results in Section 5.

3. Observations

[9] The Microwave Limb Sounder (MLS) instrument on board the Aura satellite was launched in July, 2004 [Pickett *et al.*, 2006, and references therein]. In this work we have used the OH measurements made in January, 2005, to study the production of HO_x species during the SPE that occurred at the time. MLS is the first satellite instrument that has been able to monitor the changes in HO_x concen-

trations caused by an SPE. The instrument covers also the mesospheric altitudes, where the SPE-related production of HO_x will have an impact on ozone. Version 1.51 data were selected for latitudes between 65°N and 75°N and then screened according to the MLS data quality and description document [Livesey *et al.*, 2005]. The data above 60 km are not recommended for general use, because of problems present in many of the daytime retrievals. The next version of retrieval, currently in final test, fixes these problems. For the present study, we made comparisons of the two versions for the SPE-induced OH profiles and found no significant differences. We are therefore confident that the OH data used in this study are reliable up to 90 km altitude.

[10] The Global Ozone Monitoring by Occultation of Stars (GOMOS) instrument on board the Envisat satellite was launched in March, 2002 [Kyrölä *et al.*, 2004, and references therein]. GOMOS is able to measure ozone concentrations throughout the middle atmosphere and in the lower thermosphere up to 100 km, making it a powerful instrument for mesospheric studies. We have used the night-time measurements made in January, 2005, at latitudes between 65°N and 75°N . Data version 6.0c were further restricted by requiring the solar zenith angle at the measurement point to be larger than 110° , and the target star temperature to be larger than 7000 K. These requirements assure a good accuracy of the observations.

4. Results

[11] Figure 1 shows the observed proton flux from the GOES-11 satellite at the geostationary orbit. The SPE begins on Jan 15 and the fluxes are highest on Jan 17–18 and Jan 20–21. Although the elevated values exceed the quiet-time flux by several orders of magnitude, the mesospheric effects of the January 2005 SPE were moderate compared to the extraordinary large events, e.g., in October 2003 [Verronen *et al.*, 2005]. However, model studies show significant increases of mesospheric HO_x concentrations especially during the peaks of proton forcing for this event [Seppälä *et al.*, 2006].

[12] An SPE has its strongest influence on HO_x concentrations during sunset, night, and sunrise because of the relatively small background production at those times [Solomon *et al.*, 1981]. On the other hand, the largest decreases of ozone will occur during sunrise and sunset times because the availability of atomic oxygen is required for the HO_x catalytic cycles to function. The minimum solar zenith angle is about 90° at the considered geolocation in January, so that in this case noon actually means twilight conditions during which ozone is depleted. Therefore, we have chosen noon time for comparisons between the model and the OH measurements from MLS. The resulting decrease of ozone can then be monitored in the following night by GOMOS observations because without solar radiation ozone recovery is very slow. Two cases were considered: Case I on Jan 18 and Case II on Jan 20. For both cases high proton fluxes were observed at noon, as seen in Figure 1, so that relatively large changes are expected in HO_x and ozone concentrations.

[13] Figure 2 (top) shows the OH comparisons for Cases I and II. The model results show significant increase in OH

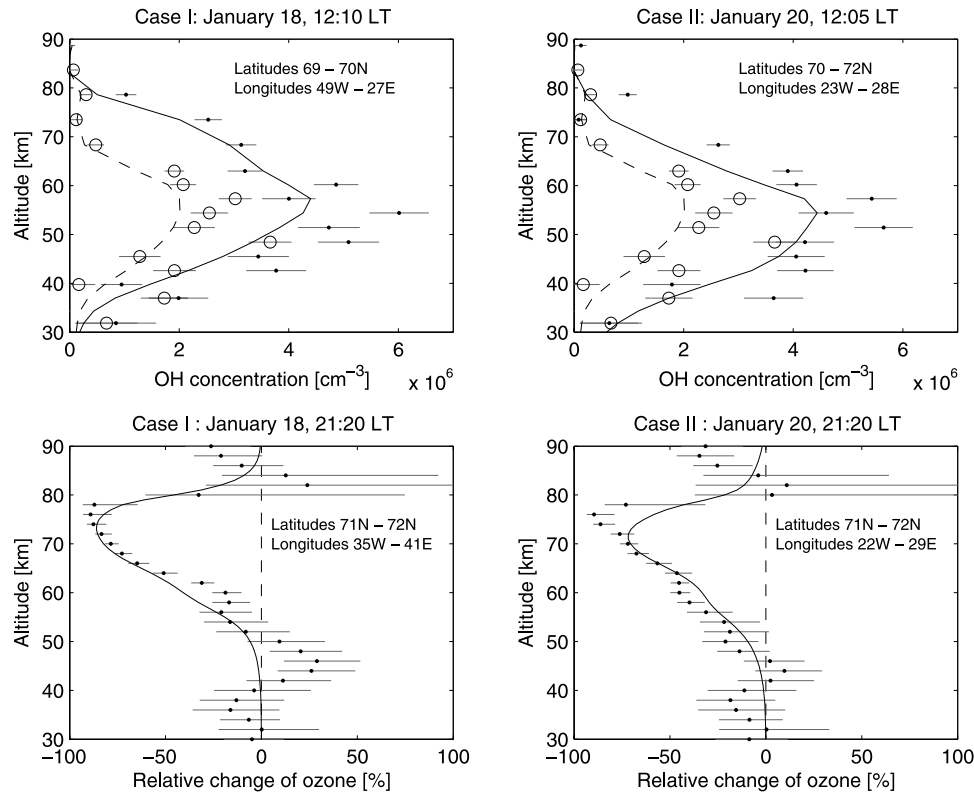


Figure 2. (top) Comparisons of OH concentrations. MLS values, which are error weighted averages for the latitude and longitude regions indicated in the panels, are marked by dots, with the statistical error estimates shown with horizontal lines. The solid lines mark the model results from the SPE run. The dashed lines and the circles present reference values, i.e., the modeled and observed OH concentrations for Jan 15 before the onset of the SPE, respectively. (bottom) Comparisons of O₃ relative change. GOMOS values are calculated relative to the average of concentrations measured on Jan 12–15, and are marked by dots. The uncertainty limits, shown with the horizontal lines, are calculated by combining the statistical error estimates of Jan 18 and Jan 20 observations with the standard deviations of the reference values from Jan 12–15. The model values, marked by the solid lines, show the relative difference between SPE and CTR run results.

concentrations when contrasted to values before the onset of the SPE. In Case I, the concentrations of OH are increased by 100–150% in the stratopause region, from 40 to 65 km. In the middle mesosphere, from 65 to 80, larger increases up to one order of magnitude are seen, with maximum increase at 73 km. The observed relative increase agrees well with the model prediction at almost all altitudes. In Case II, the model concentrations show a 100–200% increase above the quiet-time levels at 40–65 km. From 65 to 80 km the increase is larger, with a maximum of 500% seen at 70 km. Again, the observations confirm this increase. In absolute numbers, the model generally shows 10–50% lower concentrations of OH at altitudes above 40 km than the observations for both Cases I and II as well as for the pre-SPE conditions.

[14] Figure 2 (bottom) shows the O₃ relative change for Cases I and II. There is clearly a very good agreement between the model and the measurements. In both cases, the ozone depletion is seen in the mesosphere with the magnitude depending on the altitude. The maximum depletions of 90% are seen at 70–80 km. There are also some differences between model results and the observations. In Case I, the observations, unlike the model, show an increase of ozone by 30% at 45 km. In Case II, the model underestimates the

depletion between 70 and 80 km, showing 60% decrease, while up to 90% depletion is observed.

5. Discussion

[15] Clearly the observations confirm the SPE-induced increase of HO_x predicted by the model. Although the HO_x increase has been indirectly indicated by ozone measurements before, this is the first SPE study to utilize HO_x observations. As such it is an important confirmation of the complex process chains leading from ion pair production to HO_x increase. Further confidence in the model results is given by the very good agreement with the observed changes in ozone concentrations.

[16] The HO_x production is sensitive to the amount of H₂O. In the model, we used MLS measurements of water vapor from Jan 15 as a fixed input, ignoring the possible day-to-day variations. However, because the version v1.51 of the MLS H₂O data might be too strongly influenced by the a priori at mesospheric altitudes [Livesey *et al.*, 2005], we did not pursue to further modify the H₂O background at this point. As a sensitivity test, we increased the water vapor concentration in the model by 5 to 10% at 40–60 km and by 5 to 40% between 60 and 80 km, based on the standard

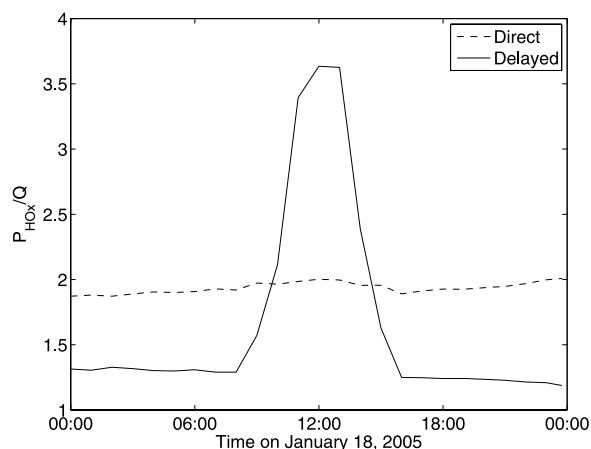


Figure 3. Number of odd hydrogen molecules per SPE-generated ion pair at 60 km on January 18, assuming that HNO_3 production by ion-ion recombination leads to instant HO_x production (direct) and taking into account the delay due to HNO_3 photodissociation (delayed). Based on the model results (SPE run).

deviation of the MLS Jan 15 average values. The model results (not shown) then overpredicted the absolute concentration of OH by $\sim 25\%$ when contrasted to observations. Therefore, some of the differences between the model and the observations could be explained by uncertainties in the model background H_2O , including those in the depletion of ozone for Case II at 70–80 km which seem to coincide with larger differences in HO_x concentration. The H_2O background is also a potential reason for the general underprediction of OH concentrations by the model, although other uncertainty factors such as the modeled solar UV flux could also have an effect.

[17] An interesting detail in Case II is the observed 30% increase of ozone around 45 km altitude. At these altitudes, self-healing effect has been reported to occur [Jackman and McPeters, 1985]. Self-healing affects ozone at high solar zenith angles when the ozone above is depleted, e.g., in the case of an SPE, allowing more UV solar radiation to pass lower into the atmosphere which then leads to net ozone production. The previously reported increases of ozone due to self-healing have been rather subtle, $\sim 5\%$, smaller than what is seen in Case I. Also in Case II, increase of ozone is seen at 45 km, this time by 10%. Note that the model predicts no increase, although the optical depth calculation does take into account the modeled ozone changes during the SPE. This might indicate that the ozone increase is caused by a process other than the SPE. For example, it could be due to horizontal transport of ozone which cannot be reproduced by our 1-D model.

[18] A useful SPE-related parameter for models that do not include HO_x production by ion chemistry is the so-called P_{HO_x}/Q value which defines the number of HO_x molecules produced per each ion pair. Theoretically, P_{HO_x}/Q is 2 at maximum but the number varies significantly with altitude, dropping sharply above 70 km to zero at 80 km and above, and it is also dependent, e.g., on the magnitude of the ionization rate [Solomon et al., 1981]. At lower altitudes, a part of the HO_x production occurs via ion-ion recombination forming HNO_3 which is then likely photodissociated to

produce OH. When assuming P_{HO_x}/Q constant in time, the possible delay in HO_x production due to this reaction path is neglected. This has implications which we here consider, as an example, at 60 km altitude. Figure 3 shows the diurnal variation of P_{HO_x}/Q on Jan 18 calculated from the model results in two ways: 1) “directly” by assuming that OH production from HNO_3 is equal to HNO_3 production by ion-ion recombination, thus neglecting the delay, and 2) in a “delayed” manner by taking into account that the OH production from HNO_3 is due to photodissociation at daytime. The direct calculation gives a rather constant P_{HO_x}/Q with variation between 1.85 and 2, while the delayed calculation results in larger variations between 1.15 and 3.65. Although in both calculations the time-integrated HO_x production is about the same, in the delayed case the P_{HO_x}/Q maximum is located around the noon time when ozone depletion occurs. During an SPE, HNO_3 is produced by ion-ion recombination throughout the day. Because there are no significant loss processes at night, its concentration increases until sunrise after which OH is rapidly released by photodissociation. Thus, HNO_3 acts as a night-time reservoir species for HO_x . Based on the model results, on Jan 18 the HO_x concentration changes between sunrise and noon from 4.3×10^6 to $9.2 \times 10^6 \text{ cm}^{-3}$, with 30% of the total production being by HNO_3 photodissociation, under high-ionization conditions. In the case that the ionization rate suddenly decreases after intense proton forcing the proportion can be considerably higher because the instant production from ion chemical reactions will be lower. Therefore, using a constant P_{HO_x}/Q number throughout the day can lead to an underestimation of the sunrise/sunset HO_x concentrations and the resulting depletion of ozone. At night, the HO_x production can be overestimated, e.g., in the case of Jan 18 by $\sim 50\%$ as seen in Figure 3. The effects on HO_x production should be most important in cases like the present one, i.e., in winter when solar zenith angles are relatively high through the day. In the summer pole, where solar radiation is present for most of the day, HNO_3 is photodissociated more continuously and assuming a constant P_{HO_x}/Q is likely to give better results. Separating HNO_3 production from the total SPE-caused HO_x production and using both as input to models instead of the sole P_{HO_x}/Q could improve the parameterization.

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