

# **1 Production of Odd Hydrogen in the Mesosphere** **2 During the January 2005 Solar Proton Event**

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7 Using measurements from the MLS/Aura and GOMOS/Envisat instru-  
8 ments together with a 1-D ion and neutral chemistry model we study the  
9 changes in odd hydrogen and ozone in the mesosphere during the January  
10 2005 solar proton event. The unique observational data allow us for the first  
11 time to directly test the  $\text{HO}_x$  production theory which involves complex ion  
12 chemistry. MLS measurements from the northern polar region show increases  
13 of OH concentrations by over 100% around the stratopause, and by up to  
14 one order of magnitude in the middle mesosphere after the onset of the SPE.  
15 GOMOS measurements indicate decreases in  $\text{O}_3$  concentration throughout  
16 the lower and middle mesosphere, by up to 90%. The model predictions are  
17 in reasonable agreement with the observations. We point out that models  
18 using the so-called  $P_{\text{HO}_x}/Q$  parameterization to include the effects of ion chem-  
19 istry could underestimate the  $\text{HO}_x$  production and the resulting ozone de-  
20 pletion.

## 1. Introduction

21 Among the most striking phenomena affecting ozone in the middle atmosphere are  
22 solar proton events (SPE). During SPEs, precipitation of energetic protons into the polar  
23 atmosphere results in production of odd hydrogen ( $\text{HO}_x$ ) and odd nitrogen ( $\text{NO}_x$ ) species  
24 [*Porter et al.*, 1976; *Heaps*, 1978; *Solomon et al.*, 1981; *Rusch et al.*, 1981]. Enhancements  
25 of  $\text{HO}_x$  and  $\text{NO}_x$  concentrations lead to depletion of ozone in the mesosphere and upper  
26 stratosphere, respectively, through the well-known catalytic reaction cycles [*e.g. Brasseur*  
27 *and Solomon*, 2005, pp. 401–416].

28 Although the effects of SPEs on atmospheric minor constituents have been studied for  
29 over forty years [see *Verronen*, 2006, for a recent review], there has been a lack of  $\text{HO}_x$   
30 observations. Thus, the theory of  $\text{HO}_x$  production due to SPEs, involving quite complex  
31 hydrate ion chemistry, has so far not been validated by measurements of odd hydrogen.  
32 However, the good agreement in ozone losses between observations and models including  
33 SPE-related  $\text{HO}_x$  production has been an indirect indicator for the “ $\text{HO}_x$  hypothesis” in  
34 the past [*e.g. Jackman et al.*, 2001].

35  $\text{HO}_x$  production due to SPE forcing involves two special features of the ionospheric  
36 D region: water cluster ions and negative ions. The chemical reactions of these species  
37 have to be combined for a full description of the process. The production is dependent not  
38 only on the ionization rate but also on the changes in minor neutral constituents caused by  
39 the proton forcing [*Solomon et al.*, 1981]. Ionization results in a set of initial ions, including  
40  $\text{O}_2^+$ , leading to formation of its hydrate  $\text{O}_2^+(\text{H}_2\text{O})$  via  $\text{O}_4^+$ . There are then a number of  
41 reaction pathways, with increasing degree of hydration and eventual recombination with

42 an electron, as a result of which one water molecule can be converted into two odd  
43 hydrogen species, OH and H. These pathways are effective only at altitudes below 80 km  
44 where water cluster ions can be formed. They can be interrupted by recombination of the  
45 intermediate ions, so that the production of odd hydrogen varies with altitude. Also, at  
46 the lower altitudes where negative ions are more abundant than free electrons, the positive  
47 ions favor negative ions in recombination, resulting in production of HNO<sub>3</sub>. Although a  
48 main part of the produced HNO<sub>3</sub> is photodissociated to produce OH, thus adding to odd  
49 hydrogen production, this pathway is not operative during nighttime and at daytime there  
50 is a delay in the odd hydrogen production due to photolysis lifetime of HNO<sub>3</sub> being of  
51 the order of hours. Similar pathways starting from the NO<sup>+</sup> ion exist. However, these  
52 are considered to be of lesser importance because the primary ion produced by particle  
53 precipitation is O<sub>2</sub><sup>+</sup>.

54 In this paper, we use observations from the MLS/Aura and GOMOS/Envisat instru-  
55 ments to study the production of HO<sub>x</sub> due to the January 2005 SPE and the subsequent  
56 effects on ozone. These unique observational data are compared to the results of a 1-D  
57 model covering an extensive set of ion chemical reactions, including those leading to HO<sub>x</sub>  
58 production during SPEs. We will show that there is a good agreement between the obser-  
59 vations and the model results in the mesosphere, providing first direct confirmation of the  
60 theories of HO<sub>x</sub> production by ion chemistry. We will demonstrate how the  $P_{\text{HO}_x}/Q$  pa-  
61 rameter, which gives the number of odd hydrogen species produced per each SPE-created  
62 ion pair, can lead to an underestimation of HO<sub>x</sub> production and ozone depletion during  
63 sunrise/sunset hours in the mesosphere.

## 2. Modeling

64 The Sodankylä Ion and Neutral Chemistry model, also known as SIC, was originally a  
65 pure ion chemistry model developed for studies of the D-region ionosphere [*Turunen et al.*,  
66 1996]. The current 1-D version, however, includes also neutral chemistry of  $\text{HO}_x$ ,  $\text{NO}_x$ ,  
67 and  $\text{O}_x$  species making it a suitable tool for studies of ionosphere-atmosphere interaction  
68 in the mesosphere and upper stratosphere. A more detailed description of the model is  
69 given by *Verronen et al.* [2005] and *Verronen* [2006, chap. 4].

70 Taking solar flux and background neutral atmosphere from the SOLAR2000 and MSISE-  
71 90 models, respectively, the SIC model was initialized for January conditions at  $70^\circ\text{N}$ ,  
72  $0^\circ\text{E}$ . The model was then run from Jan 15, 0000 UT until Jan 22, 2400 UT twice: first  
73 including solar radiation and galactic cosmic rays as ionization sources, and the second  
74 time including also ionization due to proton precipitation. From here on we identify  
75 these two as CTR and SPE runs, respectively. For the calculation of the ionization rates  
76 due to solar protons, we used the proton flux data from the GOES-11 satellite's particle  
77 detectors. The calculation method is described in detail by *Verronen et al.* [2005].

78 For this study we used  $\text{H}_2\text{O}$  measurements from MLS as input to the model. Selecting  
79 observations made on Jan 15 at latitudes between  $65^\circ\text{N}$  and  $75^\circ\text{N}$ , an average profile was  
80 created and then used in all modeling, including the initialization. We will discuss the  
81 effects of  $\text{H}_2\text{O}$  background selection to the model results in Section 5.

## 3. Observations

82 The Microwave Limb Sounder (MLS) instrument on board the Aura satellite was  
83 launched in July, 2004 [*Pickett et al.*, 2006, and references therein]. In this work we

84 have used the OH measurements made in January, 2005, to study the production of HO<sub>x</sub>  
85 species during the SPE that occurred at the time. MLS is the first satellite instrument  
86 that has been able to monitor the changes in HO<sub>x</sub> concentrations caused by an SPE. The  
87 instrument covers also the mesospheric altitudes, where the SPE-related production of  
88 HO<sub>x</sub> will have an impact on ozone. Version 1.51 data were selected for latitudes between  
89 65°N and 75°N and then screened according to the MLS data quality and description  
90 document [*Livesey et al.*, 2005]. The data above 60 km are not recommended for general  
91 use, because of problems present in many of the daytime retrievals. The next version of  
92 retrieval, currently in final test, fixes these problems. For the present study, we made  
93 comparisons of the two versions for the SPE-induced OH profiles and found no significant  
94 differences. We are therefore confident that the OH data used in this study are reliable  
95 up to 90 km altitude.

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

#### 4. Results

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

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

124 Top panels of Fig. 2 show the OH comparisons for Cases I and II. The model results show  
125 significant increase in OH concentrations when contrasted to values before the onset of the  
126 SPE. In Case I, the concentrations of OH are increased by 100–150% in the stratopause

127 region, from 40 to 65 km. In the middle mesosphere, from 65 to 80, larger increases up to  
128 one order of magnitude are seen, with maximum increase at 73 km. The observed relative  
129 increase agrees well with the model prediction at almost all altitudes. In Case II, the  
130 model concentrations show a 100–200% increase above the quiet-time levels at 40–65 km.  
131 From 65 to 80 km the increase is larger, with a maximum of 500% seen at 70 km. Again,  
132 the observations confirm this increase. In absolute numbers, the model generally shows  
133 10–50% lower concentrations of OH at altitudes above 40 km than the observations for  
134 both Cases I and II as well as for the pre-SPE conditions.

135 Bottom panels of Fig. 2 show the O<sub>3</sub> relative change for Cases I and II. There is clearly  
136 a very good agreement between the model and the measurements. In both cases, the  
137 ozone depletion is seen in the mesosphere with the magnitude depending on the altitude.  
138 The maximum depletions of 90% are seen at 70–80 km. There are also some differences  
139 between model results and the observations. In Case I, the observations, unlike the model,  
140 show an increase of ozone by 30% at 45 km. In Case II, the model underestimates the  
141 depletion between 70 and 80 km, showing 60% decrease, while up to 90% depletion is  
142 observed.

## 5. Discussion

143 Clearly the observations confirm the SPE-induced increase of HO<sub>x</sub> predicted by the  
144 model. Although the HO<sub>x</sub> increase has been indirectly indicated by ozone measurements  
145 before, this is the first SPE study to utilize HO<sub>x</sub> observations. As such it is an important  
146 confirmation of the complex process chains leading from ion pair production to HO<sub>x</sub>

147 increase. Further confidence in the model results is given by the very good agreement  
148 with the observed changes in ozone concentrations.

149 The  $\text{HO}_x$  production is sensitive to the amount of  $\text{H}_2\text{O}$ . In the model, we used MLS  
150 measurements of water vapor from Jan 15 as a fixed input, ignoring the possible day-  
151 to-day variations. However, because the version v1.51 of the MLS  $\text{H}_2\text{O}$  data might be  
152 too strongly influenced by the *a priori* at mesospheric altitudes [Livesey *et al.*, 2005],  
153 we did not pursue to further modify the  $\text{H}_2\text{O}$  background at this point. As a sensitivity  
154 test, we increased the water vapor concentration in the model by 5 to 10% at 40–60 km  
155 and by 5 to 40% between 60 and 80 km, based on the standard deviation of the MLS  
156 Jan 15 average values. The model results (not shown) then overpredicted the absolute  
157 concentration of OH by  $\sim 25\%$  when contrasted to observations. Therefore, some of the  
158 differences between the model and the observations could be explained by uncertainties  
159 in the model background  $\text{H}_2\text{O}$ , including those in the depletion of ozone for Case II at  
160 70–80 km which seem to coincide with larger differences in  $\text{HO}_x$  concentration. The  $\text{H}_2\text{O}$   
161 background is also a potential reason for the general underprediction of OH concentrations  
162 by the model, although other uncertainty factors such as the modeled solar UV flux could  
163 also have an effect.

164 An interesting detail in Case II is the observed 30% increase of ozone around 45 km  
165 altitude. At these altitudes, self-healing effect has been reported to occur [Jackman and  
166 *McPeters*, 1985]. Self-healing affects ozone at high solar zenith angles when the ozone  
167 above is depleted, *e.g.* in the case of an SPE, allowing more UV solar radiation to pass  
168 lower into the atmosphere which then leads to net ozone production. The previously

169 reported increases of ozone due to self-healing have been rather subtle,  $\sim 5\%$ , smaller  
170 than what is seen in Case I. Also in Case II, increase of ozone is seen at 45 km, this time  
171 by 10%. Note that the model predicts no increase, although the optical depth calculation  
172 does take into account the modeled ozone changes during the SPE. This might indicate  
173 that the ozone increase is caused by a process other than the SPE. For example, it could  
174 be due to horizontal transport of ozone which cannot be reproduced by our 1-D model.

175 A useful SPE-related parameter for models that do not include  $\text{HO}_x$  production by  
176 ion chemistry is the so-called  $P_{\text{HO}_x}/Q$  value which defines the number of  $\text{HO}_x$  molecules  
177 produced per each ion pair. Theoretically,  $P_{\text{HO}_x}/Q$  is 2 at maximum but the number varies  
178 significantly with altitude, dropping sharply above 70 km to zero at 80 km and above,  
179 and it is also dependent, *e.g.*, on the magnitude of the ionization rate [*Solomon et al.*,  
180 1981]. At lower altitudes, a part of the  $\text{HO}_x$  production occurs via ion-ion recombination  
181 forming  $\text{HNO}_3$  which is then likely photodissociated to produce OH. When assuming  
182  $P_{\text{HO}_x}/Q$  constant in time, the possible delay in  $\text{HO}_x$  production due to this reaction path  
183 is neglected. This has implications which we here consider, as an example, at 60 km  
184 altitude. Fig. 3 shows the diurnal variation of  $P_{\text{HO}_x}/Q$  on Jan 18 calculated from the  
185 model results in two ways: 1) “directly” by assuming that OH production from  $\text{HNO}_3$   
186 is equal to  $\text{HNO}_3$  production by ion-ion recombination, thus neglecting the delay, and  
187 2) in a “delayed” manner by taking into account that the OH production from  $\text{HNO}_3$   
188 is due to photodissociation at daytime. The direct calculation gives a rather constant  
189  $P_{\text{HO}_x}/Q$  with variation between 1.85 and 2, while the delayed calculation results in larger  
190 variations between 1.15 and 3.65. Although in both calculations the time-integrated  $\text{HO}_x$

191 production is about the same, in the delayed case the  $P_{\text{HO}_x}/Q$  maximum is located around  
192 the noon time when ozone depletion occurs. During an SPE,  $\text{HNO}_3$  is produced by ion-  
193 ion recombination throughout the day. Because there are no significant loss processes  
194 at night, its concentration increases until sunrise after which OH is rapidly released by  
195 photodissociation. Thus,  $\text{HNO}_3$  acts as a night-time reservoir species for  $\text{HO}_x$ . Based  
196 on the model results, on Jan 18 the  $\text{HO}_x$  concentration changes between sunrise and  
197 noon from  $4.3 \times 10^6$  to  $9.2 \times 10^6 \text{ cm}^{-3}$ , with 30% of the total production being by  $\text{HNO}_3$   
198 photodissociation, under high-ionization conditions. In the case that the ionization rate  
199 suddenly decreases after intense proton forcing the proportion can be considerably higher  
200 because the instant production from ion chemical reactions will be lower. Therefore, using  
201 a constant  $P_{\text{HO}_x}/Q$  number throughout the day can lead to an underestimation of the  
202 sunrise/sunset  $\text{HO}_x$  concentrations and the resulting depletion of ozone. At night, the  $\text{HO}_x$   
203 production can be overestimated, *e.g.* in the case of Jan 18 by  $\sim 50\%$  as seen in Fig. 3.  
204 The effects on  $\text{HO}_x$  production should be most important in cases like the present one,  
205 *i.e.* in winter when solar zenith angles are relatively high through the day. In the summer  
206 pole, where solar radiation is present for most of the day,  $\text{HNO}_3$  is photodissociated more  
207 continuously and assuming a constant  $P_{\text{HO}_x}/Q$  is likely to give better results. Separating  
208  $\text{HNO}_3$  production from the total SPE-caused  $\text{HO}_x$  production and using both as input to  
209 models instead of the sole  $P_{\text{HO}_x}/Q$  could improve the parameterization.

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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.

**Figure 2.** Top panels: 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 panels: comparisons of O<sub>3</sub> 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.

**Figure 3.** Number of odd hydrogen molecules per SPE-generated ion pair at 60 km on January 18, assuming that  $\text{HNO}_3$  production by ion-ion recombination leads to instant  $\text{HO}_x$  production (direct) and taking into account the delay due to  $\text{HNO}_3$  photodissociation (delayed). Based on the model results (SPE run).





