

Solar Proton Events as Tests for the Fidelity of Middle Atmosphere Models

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Abstract

Ozone depletions associated with solar proton events have now been observed in nine events: November 1969, January and September 1971, August 1972, June and August 1979, October 1981, and July and December 1982. Since the proton fluxes during these events are fairly well known from satellite observations, modelers have been able to compare model predictions with observations of ozone behavior during these events to test the validity of atmospheric photochemical models. Ozone decreases initially follow approximately their theoretically predicted behavior below about 45 km (where NO_x is thought to cause the ozone decrease), but after about two weeks the observed decrease appears to be larger than the computed decrease. Above 45 km, where HO_x is thought to cause the ozone decrease, the picture of model validity is not as clear. The observed ozone decreases between about 45 and 60 km are substantially more than that predicted by present photochemical models while between about 60 and 85 km the observed ozone decrease is approximately equal to that predicted. Future studies of solar proton events should include observations of both HO_x and NO_x species as well as ozone. These observations could then be compared to model predictions to verify other aspects of photochemical middle atmosphere models.

1. Introduction

Solar proton events (SPEs) offer atmospheric scientists unique opportunities to study the response of the atmosphere to perturbations. Measurements of the proton fluxes impinging the earth's atmosphere during SPEs have taken place over the past thirty or more years. Ozone responses to SPEs have been measured in nine SPEs over the past seventeen years. Both the proton flux and ozone response measurements are fairly reliable. However, since the protons affect ozone in an indirect manner the photochemistry of the interaction is complex.

Changes in ozone caused by the introduction of chlorofluorocarbons are very gradual and difficult to identify. However, the ozone response due to SPEs is generally not a subtle one. If the proton flux from an SPE is strong enough, an ozone decrease is recorded within a couple of hours. Therefore, the atmospheric perturbations caused by the SPEs are ideal cases for tests of atmospheric photochemical models.

SPEs have so far shown two characteristics in causing an ozone decrease. One type of response of the ozone is short term with the ozone decreasing quite rapidly in response to the protons, but then recovering within a couple of hours after the SPE is over. This type of response was observed in all nine SPEs associated with an ozone decrease, occurs at altitudes near the stratopause and above, and is thought to be caused by the HO_x species produced by the protons. The second type of response of ozone is similar to the first in that the ozone decreases rapidly in response to the protons, but then recovers only after several weeks have passed. This type of response, observed only during the giant SPE of August

1972, occurs at middle altitudes in the stratosphere, and is thought to be caused by the NO_x species produced by the protons.

2. Overview of ozone decreases associated with SPEs

Rocket measurements by Weeks *et al.* [1] identified large ozone decreases during the November 1969 solar proton event. These measurements were made at extremely large solar zenith angles (89.8°), show maximum ozone decreases in the mesosphere, and are believed to have been caused by the HO_x species produced during the event. Swider and Keneshea [2], Frederick [3], Swider *et al.* [4], and Solomon *et al.* [5] modeled the behavior of the ozone decrease. Many problems were described when comparing these models with the observations suggesting that ozone decreases of the magnitude implied by the data were extremely difficult to reproduce.

Crutzen *et al.* [6] predicted that the nitric oxide (NO) produced during each of the solar proton events of November 1960, September 1966, and August 1972 might be enough to cause an ozone change. Fortunately, measurements were being made during the August 1972 SPE by the Nimbus IV satellite's BUV instrument launched on April 10, 1970. Heath *et al.* [7] showed that large ozone reductions were apparent in the BUV data up to 19 days after the event between 25 and 47 km. Fabian *et al.* [8] suggested that successful modeling of the ozone behavior during the August 1972 SPE implied a much larger NO production rate by the protons than estimated by Crutzen *et al.* [6], however, Jackman *et al.* [9] concluded that these larger NO production rates were not supported by detailed calculations.

Maeda and Heath [10] pointed out that the ozone response during the August 1972 SPE was different in the southern and northern hemisphere because of the difference in seasons between the two. The southern hemisphere (winter season) showed a larger ozone decrease above 38 km (4 mbar) than did the northern hemisphere (summer season). Reagan *et al.* [11] analyzed and modeled the event in great detail and concluded that the observed temporal behavior of the ozone between 45 and 50 km could not be explained in their model results.

Solomon and Crutzen [12] and Rusch *et al.* [13] examined the August 1972 SPE with a model including chlorine chemistry and temperature feedback. They found generally good agreement between model results and observations at the time of eight days after the event. McPeters *et al.* [14] reanalyzed the BUV data taken during the event, subtracted the direct effect of high energy protons on the BUV instrument, and computed the long-term ozone depletion to be at least a

month when the normal seasonal behavior is taken into account.

As part of the BUV reanalysis, McPeters *et al.* [14] noted substantial short-lived ozone depletions at 50 km (1 mbar) and above during the January and September 1971 SPEs. Detailed photochemical modeling in McPeters *et al.* [14] failed to reproduce the large ozone decreases observed, and it was concluded that the measurements needed to be confirmed by the Nimbus 7 SBUV instrument, which is insensitive to particle contamination during SPEs.

An SPE in July 1982 was the first to provide a reliable check of the observations of ozone depletion noted in the November 1969, and the January and September 1971 SPEs. Two satellites recorded measurements of ozone depletion during the July 1982 SPE. Both the Solar Mesosphere Explorer (SME) [15] satellite and the SBUV instrument on Nimbus 7 [16] showed depletions during this large SPE. The measurements overlapped in the region from 50 to 60 km with the SBUV showing a larger ozone decrease. Solomon *et al.* [17] and Jackman and McPeters [18] offered theoretical explanations of the ozone decrease. Among the observations successfully modeled in these two studies were the large ozone depletions between about 60 and 85 km, the qualitative behavior of larger ozone depletions occurring at larger solar zenith angles, and the possible occurrence of self-healing. The magnitude of the ozone decreases observed by SBUV between 50 and 60 km could not be reproduced by a photochemical model [18].

Observations of ozone depletion by the SME satellite during the July 1982 SPE were quickly followed by measurements of ozone decreases during the December 1982 SPE [19]. These observations were confirmed in the SBUV data [16]. Three other SPEs, namely, those occurring in June and August of 1979 and October 1981 were observed to cause an ozone decrease during the most recent solar maximum [16].

McPeters and Jackman [16] looked at all significant SPEs during the latest solar maximum. The large SPE that occurred on January 31, 1982 might have shown an ozone decrease but the SBUV instrument was turned off on that day. The moderately large SPE of September 1979 showed only a marginal ozone decrease and is not included with those SPEs which have been confirmed to show an ozone decrease.

3. Theory of SPE production of HOx and NOx

A rich array of literature exists on the theory of charged particle production of HOx and NOx species which react with odd oxygen to cause a loss in ozone. We first discuss the SPE production of HOx species and their effects on ozone and second discuss the SPE production of NOx species and their effects on ozone.

All nine events listed previously showed a decrease due to the HOx produced during them. Eight of the SPEs showed decreases only due to the HOx species which means that the decreases were present only during the SPEs or for a couple of hours after them. The NOx species caused a measurable ozone decrease in only one of the SPEs (August 1972). This NOx-produced ozone decrease was maintained at some altitudes (between 35 and 50 km) and latitudes for at least two months past the SPE, however, the HOx-produced ozone decrease above 1 mbar (about 50 km) was reduced drastically by the end of the SPE (Ref. [14], this work).

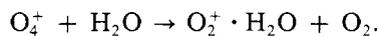
3.1. HOx production by SPEs

The basic theory for HOx production by protons impinging on the earth's atmosphere has been known for several years, however, more recent work has clarified the theory further. Solomon *et al.* [5] offer a clear analysis of the state of knowledge for the HOx production by particles. Other papers which describe the theory of solar proton production of HOx species are Swider and Keneshea [2] and Frederick [3].

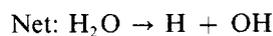
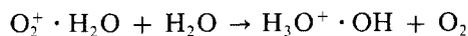
Solar protons and the associated secondary electrons penetrate the atmosphere and expend most of their energy in ionization processes. The production of N_2^+ , O_2^+ , N^+ , and O^+ depends on the efficiency for production by both the protons and the associated electrons (see Ref. [20] and associated references). Since O_2^+ has a smaller ionization potential than N_2^+ , N^+ , or O^+ , most ions rapidly charge exchange to form O_2^+ . Some of the N^+ and O^+ atoms do react with O_2 and N_2 , respectively, to form NO^+ , which is also a potential source of odd hydrogen [5]. Once O_2^+ is formed, it generally follows the path



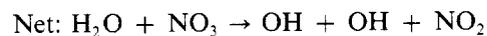
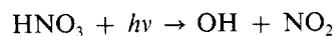
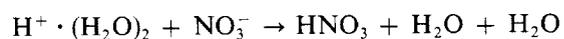
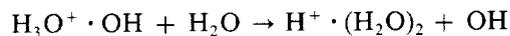
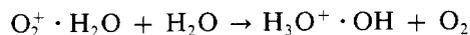
The oxonium ion (O_4^+) then leads to the formation of water cluster ions through



This reaction is followed by further clustering and, ultimately, recombination. The shortest path leading to HOx production is given by:



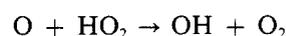
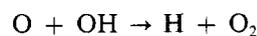
Other paths are possible for $O_2^+ \cdot H_2O$ which lead to HOx production through recombination with free electrons and these are discussed in Solomon *et al.* [5]. At altitudes below about 70 km, the negative ions (especially NO_3^-) become more abundant than the free electrons. A possible path presented is:



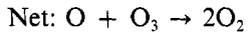
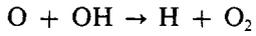
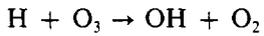
This path or a similar one takes place in the region where negative ions prevail.

Most of the positive ions result in the formation of two HOx species apiece, at least up to 70 km [3, 21]. Above 75 km the HOx species produced per ion pair depend quite strongly on the ionization rate and the duration of the SPE [5].

Below 60 km the following catalytic process leads to the most odd oxygen, and subsequently, ozone destruction



Above 60 km the catalytic process



is the dominant mechanism for ozone destruction. The HOx species react fairly quickly to destroy each other through the reaction

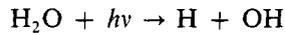


Therefore, the lifetime of HOx is only on the order of hours in the upper stratosphere and mesosphere. This means that a constant source of HOx is necessary to lead to any long term ozone decrease due to HOx species and that an impulse of HOx species into the atmosphere will cause changes in ozone that only last a couple of hours.

Solomon *et al.* [17] derived an analytic formula relating the percent of ozone destruction to the HOx production by the SPE, HOx_{SPE} . This formula is good at altitudes near 70 km and shows clearly the relationship between the change in ambient HOx and the change in ozone. The formula is

$$\% \text{ decrease in } O_x = \left\{ 1 - \left(\frac{2J(H_2O)}{2J(H_2O) + HOx_{SPE}} \right)^{1/2} \right\} 100 \quad (2)$$

At 70 km the ambient HOx level is maintained by production through the photolysis of H_2O



and destruction through reaction (1). Thus sunlight is necessary to maintain the ambient HOx levels. It follows that at the larger solar zenith angles the photolysis rate, J , becomes smaller and the effect of the HOx production by that SPE, which does not depend on sunlight, becomes relatively larger.

At altitudes lower than 70 km the ambient production of HOx also depends on the reaction



Again, the production of $O(^1D)$, a very short-lived species, depends directly on the sunlight because it is produced by the photolysis of O_3 . Thus photochemical models predict a solar zenith angle dependence in the ozone depletion at all altitudes where HOx is being produced by SPEs.

The agreement between the theoretical prediction of ozone change due to an SPE and the observed ozone change is fairly good at altitudes between about 60 and 85 km. This is shown quite well in Fig. 1 (taken from Fig. 3 of Ref. [17]). The model computations are close to the observations during the AM portions of the SME orbit, the AM portion of the orbit being at the very large solar zenith angles. There is less agreement between the model and observations during the PM portions of the SME orbit. Notice that the measurements show larger amounts of ozone depletion at the larger solar zenith angles, consistent with theoretical predictions.

Jackman and McPeters [18] have shown qualitative agreement between theory and SBUV observations at altitudes between about 45 and 60 km during the HOx SPEs. Figure 2 (taken from Fig. 2 of Ref. [18]) shows a comparison between model results and both SME and SBUV data at four altitudes as a function of solar zenith angle. A photochemical equilibrium (PE) model produced the theoretical curve and used the maximum ion pair production rate during the July 1982 SPE

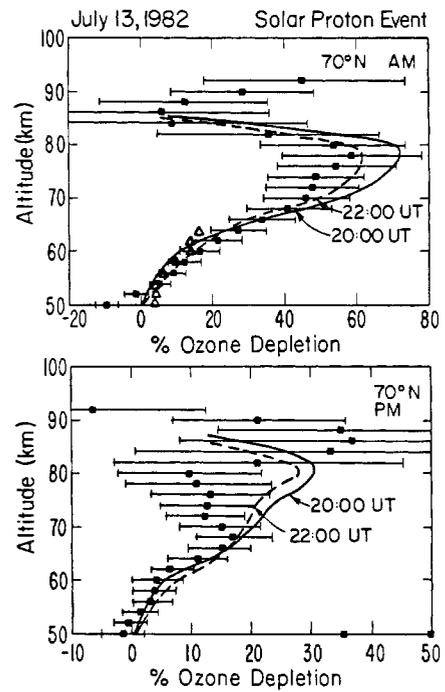


Fig. 1. Taken from Fig. 3 of Solomon *et al.*, Mesospheric ozone depletion during the solar proton event of July 13, 1982 Part II, Comparison between theory and measurements, *Geophys. Res. Lett.*, **10**, 259 (1983), copyright by the American Geophysical Union. Observed ozone depletion on July 13, 1982 at 70° N latitude on the AM and PM portions of the SME orbit (each point represents a mean of three orbits on July 13, 1982 near 1830, 2120, and 2206 UT). Triangles denote data from the UV spectrometer. Model calculated profiles for 2000 and 2200 UT are shown.

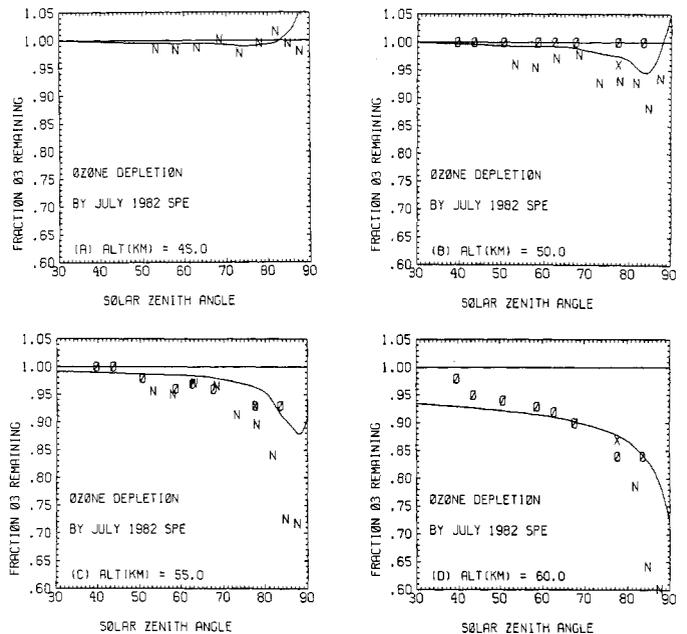


Fig. 2. Taken from Fig. 2 of Jackman and McPeters, the response of ozone to solar proton events during solar cycle 21: a theoretical interpretation, *J. Geophys. Res.*, **90**, 7959 (1985), copyright by the American Geophysical Union. Observations (points) of ozone depletion for the July 13, 1982 SPE and comparison with model results (solid lines) for (a) 45 km, (b) 50 km, (c) 55 km, and (d) 60 km. The N's represent SBUV data, the X's SME ultraviolet spectrometer data, and the O's SME near-infrared spectrometer data. Solid line denotes one-dimensional photochemical equilibrium model-predicted fraction ozone remaining assuming ozone depletion above commensurate with the observations. For clarity, the ordinate value of 1.0 is designated across the figure.

(therefore, the largest HOx production rate possible). The PE model was used in this analysis as the results gave the maximum ozone depletion possible. The PE model also showed clearly the very strong solar zenith angle behavior of the ozone depletion. Since SPEs are time-dependent phenomena it was expected that the PE model results would show a larger amount of ozone depletion than observed in the measurements. Instead, it is clear from Fig. 2(b–d) that the model results underpredict the amount of ozone depletion when compared to the SBUV measurements between 50 and 60 km. Some of these discrepancies may be related to other differences which exist between theory and observations in the upper stratosphere, such as the imbalance between Ox loss and production processes [22–24].

Jackman and McPeters [18] noticed in their model computations for HOx events that most of the ozone decrease at altitudes 55 km and below was the result of decreased ozone above that altitude. When ozone is decreased at a higher altitude, increased ultraviolet radiation penetrates to lower altitudes. Both the ozone and the molecular oxygen absorption cross sections are significant below about 250 nm, thus more ozone dissociating solar flux (decreasing ozone below) and more molecular oxygen dissociating solar flux (increasing ozone below) are associated with the ozone depletion at the higher altitude. At most of the solar zenith angles and altitudes (at and above 45 km) the ozone depletion above leads to ozone depletion below. However, at extremely large solar zenith angles an ozone increase (self-healing) can result at 45 and 50 km in our model computations. Subtle evidence of this self-healing is observed in the SBUV data, see Fig. 2 (a–b) and also Jackman and McPeters [18].

3.2. NOx production by SPEs

Although we have measurements which indicate that only one SPE resulted in a long-term decrease in ozone, this does not minimize the significance of this occurrence. The August 1972 SPE was the largest observed during the last two solar cycles. Several papers have been written on various aspects of this extremely intense SPE. We will deal with its effects on ozone and NOx species.

The NOx family of species (N, NO, NO₂, HNO₃, N₂O₅, HO₂NO₂) have relatively short lifetimes for interchanging from one form of the family to another, but the family as a whole has a long lifetime in the stratosphere, especially at the high latitudes. The destruction of NOx depends on sunlight through



followed by



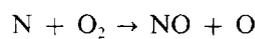
Another way to destroy NOx in the stratosphere is through transport to the troposphere and subsequent rainout as HNO₃ in aqueous solution. These two loss processes are small in the stratosphere and the lifetime of NOx at high latitudes where SPEs are important is on the order of years.

The ozone decrease associated with the August 1972 SPE was concentrated in the polar latitudes, with a smaller amount of ozone decrease at lower latitudes. This can be easily seen in Fig. 3 where the ozone decrease (derived from comparing 1972 with 1971 ozone data) in seven five-degree latitude bands is plotted from 45° up to 80° N latitude. A

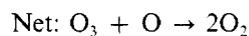
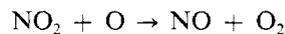
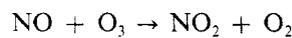
reanalysis of the BUV data was undertaken in this study to produce Fig. 3. The most striking result that can be seen in Fig. 3 is that the ozone depletion at the highest latitudes lasts at least through the end of September. Further analysis has shown that the depletion is prevalent through November. Since the BUV instrument requires sunlight for ozone observations, the ozone at polar latitudes near the winter solstice cannot be measured by BUV. Observations of ozone by BUV in March 1973, however, show that the ozone depletion at high latitudes is no longer apparent. Clearly, the ozone depletion lasts much longer than originally indicated.

Several studies have computed the NOx species resulting from energetic charged particles impinging on the atmosphere. Warneck [25] first suggested that cosmic rays produce NOx. He computed a total yield of 0.33 for each ion pair production by the cosmic ray. Other papers [3, 6, 8, 12, 13, 20, 26, 27] reported numbers from 1.0 up to 2.5 NOx species produced per ion pair. The production rate also varies with the altitude and with the intensity and duration of the SPE [13]. The more NOx is increased, the more the loss of NOx is increased (see eqs. 4 and 5). For the case of the extremely intense August 1972 SPE, the efficiency of NOx production can even become negative during the event [13]. Porter *et al.* [20] in an energy degradation calculation and Frederick [3] and Rusch *et al.* [13] in a computation involving measured dissociation and ionization cross sections for N₂ derived the result that about 1.2–1.3 N atoms are produced per ion pair.

The N atoms produced react very quickly to form NO through



The catalytic cycle that leads to ozone depletion by NOx is given by



We have two pieces of evidence which indicate that SPEs produce NOx. First, a correlation with the production of NOx by the August 1972 SPE is observed in nitrate flux data taken in the Antarctic [28]. A rough calculation of the nitrate flux from the August 1972 SPE using 1.25 N atoms produced per ion pair leads to a maximum possible nitrate flux of about 5 mg/m²/month. This corresponds to a measured peak nitrate value of approximately 0.16 mg/m²/month in the data taken in the Antarctic snowfall for October 1972 [28]. Significant nitrate fluxes in the troposphere are clearly possible from SPEs in the stratosphere.

Second, McPeters [29] has recently shown evidence of an NO increase during the July 1982 SPE. Approximately 6 × 10¹⁴ NO molecules per cm² were observed to be formed in the area above 60° geomagnetic latitude, while we compute a total of about 7 × 10¹⁴ NO molecules produced per cm², again assuming 1.25 NO molecules produced per ion pair. This second comparison is encouraging because it indicates that the number of intermediary particles (the NOx species) which result in the ozone destruction can be predicted fairly well.

Jackman *et al.* [30] showed that the high latitude NOx production can have a substantial year-to-year variability which is related to SPEs. In select years, the stratospheric

production of NO_x due to SPEs can be comparable to the other sources of NO_x above 50° geographic latitude. Recent analysis by Callis and Natarajan [31] has indicated that the spring minimum in the Antarctic ozone may have a solar cycle influence which is related to the NO_x production connected with solar activity. Since SPEs are related to solar activity, with most occurring near or slightly later than solar maximum, NO_x production by SPEs should be included in any detailed analysis of the problem.

The August 1972 SPE has been modeled in several studies. Predictions for ozone depletion due to this SPE have been

presented in Heath *et al.* [7], Fabian *et al.* [8], Reagan *et al.* [11], Solomon and Crutzen [12], and Rusch *et al.* [13]. The studies by Solomon and Crutzen [12] and Rusch *et al.* [13] used chlorine chemistry in their one-dimensional attempts to model the ozone depletion. We plot the ozone depletion from the Solomon and Crutzen [12] paper and compare to the ozone depletion observations of the UV instrument in Fig. 4 at eight days after the event. The theory is taken from case F in Fig. 2 of Solomon and Crutzen [12]. This is not an easy comparison because of the relatively large variation of the observations from day to day and especially from week to

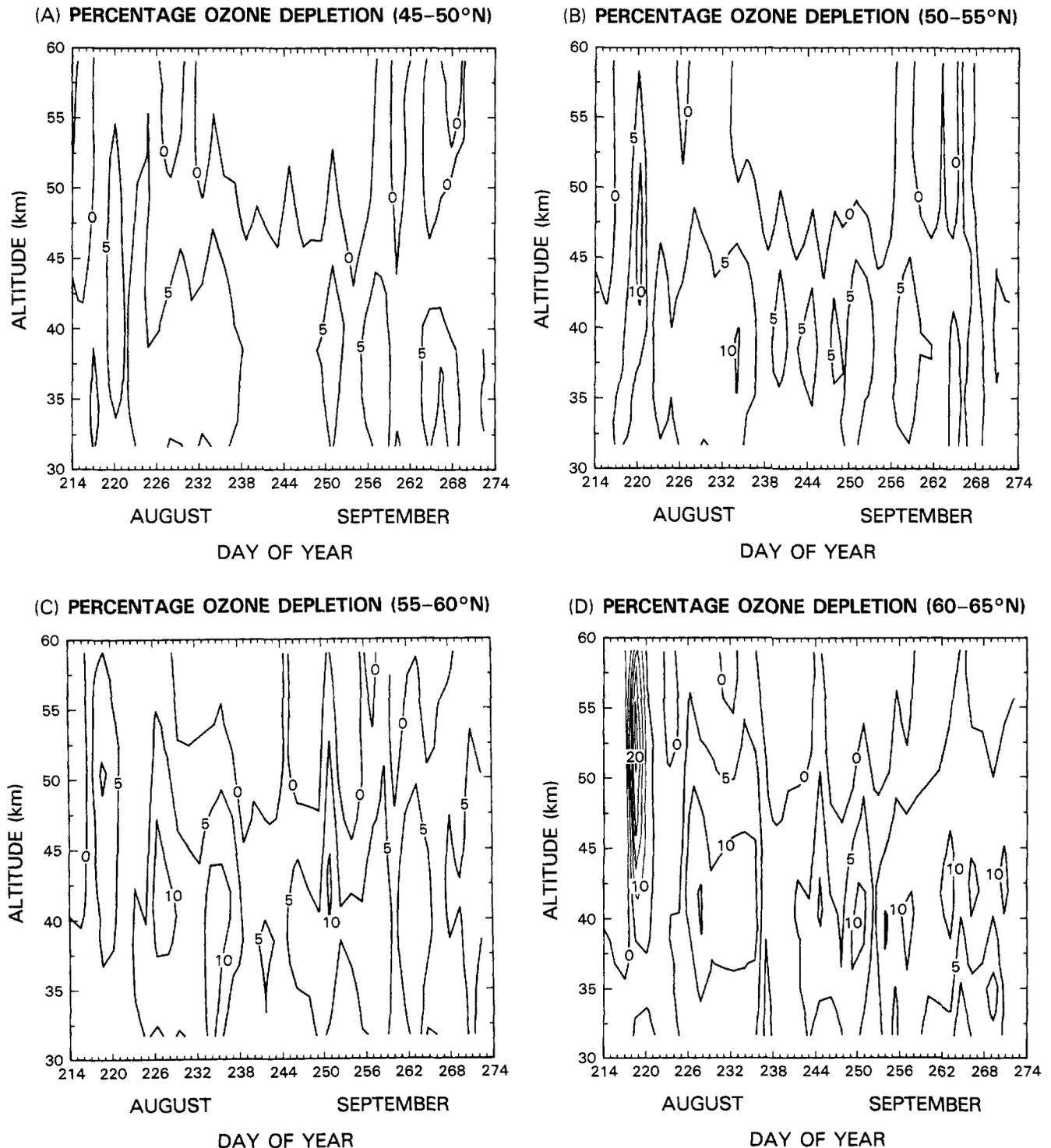


Fig. 3. Ozone depletion in percent during and after the August 1972 SPE in seven latitude bands: (a) 45–50° N, (b) 50–55° N, (c) 55–60° N, (d) 60–65° N, (e) 65–70° N, (f) 70–75° N, and (g) 75–80° N. Contour intervals are 5 percent.

Percentage difference shown computed by comparing 1972 with 1971 ozone data. Abscissa shows month and day of year.

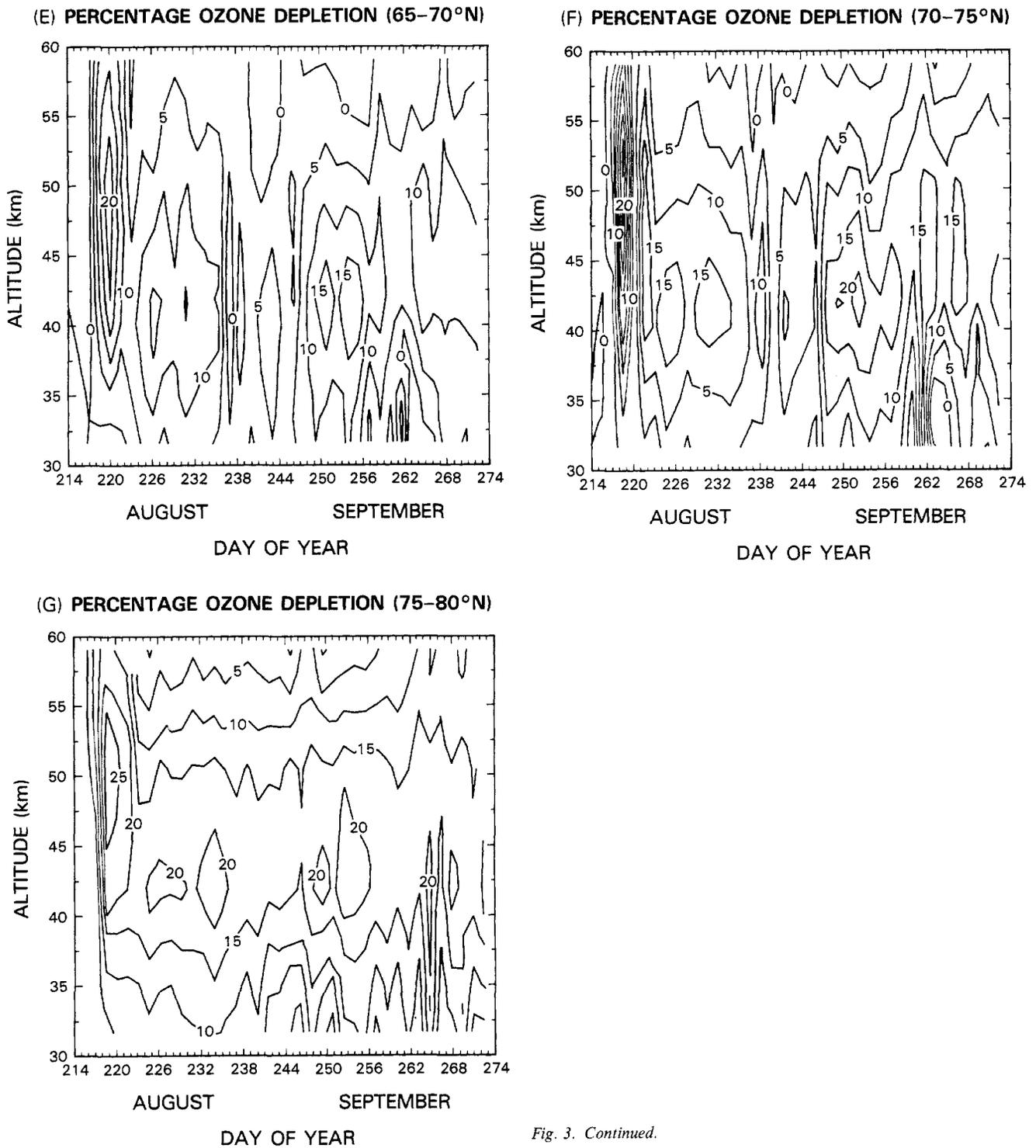


Fig. 3. Continued.

week which are caused by the mixing of air masses from other latitudes. We thus compare ozone measurements in two different longitude bands (-90° to $+90^\circ$ and $+90^\circ$ to $+270^\circ$) in the $75\text{--}80^\circ$ latitude band in Fig. 4. The Fig. 4 ozone depletion values are derived from comparing 1972 with 1971 ozone data. Given the uncertainties in the model and observations, the two agree fairly well. The theoretical computations do, however, show a somewhat larger ozone depletion than that observed between 35 and 50 km.

This 1D model of Solomon and Crutzen [12] does not predict the residual ozone depletion shown continuing through September in Fig. 3. Multidimensional models must be used to investigate these observations.

4. Discussion and conclusions

The study of SPEs on the middle atmosphere requires knowledge of the protons input into the atmosphere as well as ambient concentrations of the species that are affected. We have available good measurements of the proton fluxes as functions of energy from the IMP satellites (given in "Solar Geophysical Data"). From these proton fluxes and energy degradation considerations it is possible to compute the ion pair production and N and N^+ atom production (and subsequently other NO_x species). As discussed earlier, the ions can form water clusters and consequently HO_x species.

Photochemical models predict that both the NO_x and

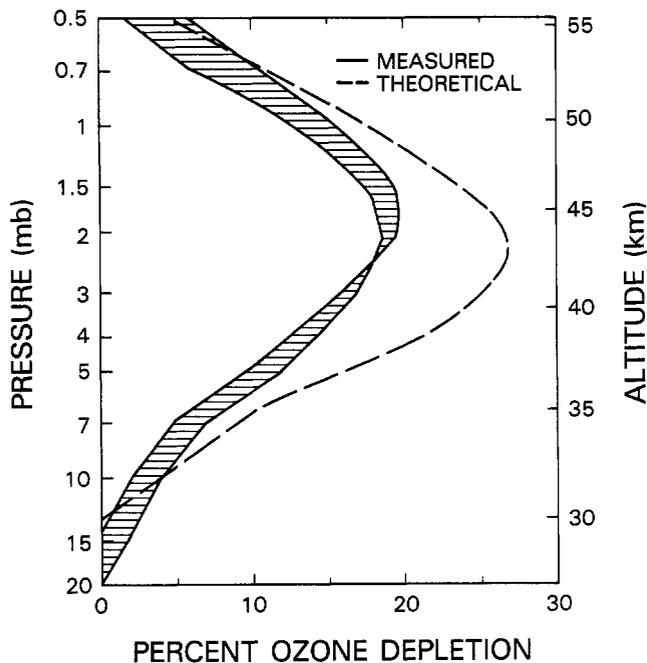


Fig. 4. Ozone depletion (resulting from the August 1972 SPE) in percent from measurements (represented by hatched area connecting the solid lines) and theoretical calculations of Solomon and Crutzen [12] (represented by the dashed line). Both measurements and theory are given at eight days after the event and for the 75–80° N latitude band. The two lines representing the measurements show averages in the two separate longitude bands (-90° to $+90^\circ$ and $+90^\circ$ to $+270^\circ$). Percentage difference shown computed by comparing 1972 with 1971 ozone data.

HOx species lead to catalytic decreases in ozone. Fortunately, we have several measurements of the ozone decrease as a result of the SPEs. We only have a couple of measurements which indicate that other constituents (NOx species) are affected by the protons. In order to verify the middle atmospheric photochemical models it is desirable to have measurements of ion pair production rates, water ion clusters, and HOx species as well as NOx and ozone during SPEs. This is especially true in the upper stratosphere and lower mesosphere where there are substantial differences between the theoretical predictions and the measurements. Measurements of HOx species are badly needed. As far as we know there has only been one measurement of an OH profile above 50 km [32]. Measurements of HO₂ are in a similar state, there having been only column measurements in the stratospheric and lower mesospheric regions [33]. It is desirable to have OH or HO₂ profile measurements during a quiet period and, also, during a proton disturbed period.

We presented recent data from a reanalysis of the BUW measurements during the August 1972 SPE (see Figs. 3 and 4). These data can be compared fairly easily with theoretical analyses using 2D or 3D models. Fabian *et al.* [8] used a 2D model to study the August 1972 SPE with mixed success. Reagan *et al.* [11] did some preliminary analysis of the polar oval cavity which was affected by the SPE. The dynamics are obviously having an effect on the ozone distribution (see Fig. 3) and must be taken into account for any detailed modeling of an SPE in which NOx is produced. A 1D model result for this type of perturbation can be reliably compared with observations for only a week or two after the event. After that, mixing from regions outside the polar cap may start to dramatically affect the ozone distribution.

Since it is well established that the August 1972 SPE [28] affected the nitrate flux in snowfall at the Antarctic, it may be possible to use SPEs as tests of the stratosphere-troposphere exchange in polar regions. Predictions relying on the total NOx production by an SPE in the stratosphere and the mixing between the troposphere and stratosphere should be made and compared to observations.

Other predictions by photochemical models should be made and compared to observations. The launch of the Upper Atmosphere Research Satellite (UARS) at the end of this decade will help in providing measurements of protons, ozone, NO, and NO₂. Unfortunately, no measurements of HOx species are planned for UARS. Models must, therefore, be analyzed quite carefully to see if any other species besides ozone are also affected by the HOx species. It would then be possible to verify these effects in the UARS measurements.

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